Nutrient recovery from bio-digestion waste: From field experimentation to model-based optimization

Thèse en cotutelle
Doctorat en génie des eaux

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Résumé

La prise de conscience croissante de l'épuisement des ressources naturelles, la demande croissante de nutriments et d'énergie pour la production alimentaire et les normes de plus en plus strictes de décharge des nutriments et de fertilisation, ont donné lieu à une attention accrue pour la récupération des nutriments à partir des déchets municipaux et agricoles. Cette thèse de doctorat vise à stimuler la transition vers une bio-économie en fournissant des (moyens à développer des) stratégies durables pour la récupération des nutriments à partir des déchets organiques après la production de bio-énergie par la digestion anaérobie. Une attention particulière est accordée à la valorisation des produits récupérés comme substituts renouvelables aux engrais chimiques et/ou comme engrais organo-minéraux durables dans l'agriculture. Trois phases de recherche complémentaires ont été exécutées: 1) l'inventaire des technologies et la classification des produits, 2) l'évaluation de la valeur des produits, 3) la modélisation et l'optimisation des procédés.

Dans la première phase, une revue systématique des technologies et une classification des produits ont été réalisées. Dans la seconde phase, la caractérisation des produits et des analyses de bilan de masse dans des stations de récupération des ressources de l'eau et des déchets (StaRRED) à grande échelle ont été exécutées. Une évaluation économique et écologique de différents scénarios de bio-fertilisation a été menée et les scénarios les plus durables ont été sélectionnés pour une évaluation agronomique réalisée ultérieurement sur le terrain et à l'échelle de la serre. Dans la troisième phase, une librairie générique de modèles pour la récupération des nutriments a été élaborée visant à modéliser la quantité et la qualité d'engrais. Une meilleure compréhension de la performance et des interactions des processus unitaires a été obtenue par des analyses de sensibilité globale. Les modèles ont été utilisés avec succès comme un outil pour la configuration et l'optimisation des chaînes de traitement. Sur la base de toutes les connaissances acquises, une feuille de route générique pour la mise en place des stratégies de récupération des nutriments en fonction des marchés et des législations des engrais, et de la caractérisation des déchets a été développée.

En tant que telle, la présente thèse développe les concepts de fermeture maximale des cycles des nutriments dans une approche du berceau-au-berceau. Le travail apporte des preuves importantes de l'impact positif des produits récupérés sur l'économie, l'agronomie et l'écologie de la production végétale intensive. En outre, cette thèse offre des informations et des outils fondamentaux pour faciliter la mise en œuvre et l'optimisation des stratégies durables de récupération des nutriments. Ces résultats ouvrent de nouvelles possibilités pour une croissance économique durable axée sur les ressources biologiques et créent ainsi une situation gagnant-gagnant pour l'environnement, la société et l'économie en Belgique, au Canada, et au-delà.

Summary

The increasing awareness of natural resource depletion, the increasing demand of nutrients and energy for food production, and the more and more stringent nutrient discharge and fertilization levels, have resulted in an increased attention for nutrient recovery from municipal and agricultural wastes. This PhD dissertation aims at stimulating the transition to a bio-based economy by providing (tools to develop) sustainable strategies for nutrient recovery from organic wastes following bio-energy production through anaerobic digestion (= bio-digestion waste). Particular attention is paid to the valorization of the recovered products as renewable substitutes for chemical fertilizers and/or as sustainable organo-mineral fertilizers in agriculture. Three complementary research phases were conducted: 1) technology inventory and product classification, 2) product value evaluation, 3) process modelling and optimization.

In the first phase, a systematic technology review and product classification was performed. In phase 2, product characterizations and mass balance analyses at full-scale waste(water) resource recovery facilities (WRRFs) were executed. An economic and ecological evaluation of different bio-based fertilization scenarios was conducted and the most sustainable scenarios were selected for subsequent agronomic evaluation at field and greenhouse scale. In phase 3, a generic nutrient recovery model library was developed aiming at fertilizer quantity and quality as model outputs. Increased insights in unit process performance and interactions were obtained through global sensitivity analyses. The models were successfully used as a tool for treatment train configuration and optimization. Based on all acquired knowledge, a generic roadmap for setting up nutrient recovery strategies as function of fertilizer markets, legislations, and waste characterization was established.

As such, the present dissertation further develops the concepts of maximally closing nutrient cycles in a cradle-to-cradle approach. The work reveals important evidence of the positive impact of recovered products on the economy, agronomy, and ecology of intensive plant production. Moreover, it provides the fundamental information and tools to facilitate the implementation and optimization of sustainable nutrient recovery strategies. All of this may open up new opportunities for sustainable and more bio-based economic growth and thus create a win-win situation for the environment, the society, and the economy in Belgium, Canada, and beyond.

Samenvatting

Het toenemende bewustzijn omtrent de uitputting van natuurlijke hulpbronnen, de groeiende vraag naar nutriënten en energie voor de voedselproductie en de steeds strengere lozings- en bemestingsnormen voor nutriënten, hebben geresulteerd in een verhoogde aandacht voor nutriëntrecuperatie uit gemeentelijk en landbouwafval. Dit proefschrift beoogt de overgang naar een bio-gebaseerde economie te stimuleren door het verstrekken van (instrumenten voor de ontwikkeling van) duurzame strategieën voor nutriëntrecuperatie uit organisch afval na bio-energie productie via anaerobe vergisting. Bijzondere aandacht wordt besteed aan de valorisatie van de gerecupereerde producten als hernieuwbare kunstmestvervangers en/of als duurzame organo-minerale meststoffen in de landbouw. Drie complementaire onderzoeksfasen werden uitgevoerd: 1) technologie-inventarisatie en product-classificatie, 2) evaluatie van de productwaarde, 3) modellering en procesoptimalisatie.

In de eerste fase werd een systematisch technologisch overzicht gemaakt en werd een product-classificatie opgesteld. In fase 2 werden de producten gekarakteriseerd en werden massabalansen in afval(water)grondstofrecuperatie-installaties (AGRI's) op volle schaal berekend. Een economische en ecologische evaluatie van verschillende bio-gebaseerde bemestingsscenario's werd verricht en de meest duurzame scenario's werden geselecteerd voor daarop volgende agronomische evaluatie op het veld en in de serre. In fase 3 werd een generieke modellenbank voor nutriëntrecuperatie ontwikkeld, gericht op het modelleren van meststof-kwantiteit en -kwaliteit. Beter inzicht in de prestaties van de eenheidsprocessen en interacties werd verkregen via globale gevoeligheidsanalyses. De modellen werden met succes gebruikt als instrument voor configuratie en optimalisatie van de behandelingstrein. Op basis van alle verworven kennis werd een generiek stappenplan ontwikkeld voor het opstellen van nutriëntrecuperatie strategieën als functie van meststofmarkten, wetgevingen en de karakterisering van de afvalstroom.

Als zodanig ontwikkelt dit proefschrift verder de concepten van het maximaal sluiten van nutriëntenkringlopen in een cradle-to-cradle benadering. Het werk onthult significant bewijs van de positieve impact van gerecupereerde producten op de economie, agronomie en ecologie van de intensieve gewasproductie. Bovendien biedt het de fundamentele informatie en instrumenten om de implementatie en optimalisatie van duurzame strategieën voor nutriëntrecuperatie te bevorderen. Dit alles kan leiden tot nieuwe kansen voor een duurzame en meer bio-gebaseerde economische groei en kan dus een win-win situatie creëren voor het milieu, de maatschappij en de economie in België, Canada en daarbuiten.

Mots-clés / Keywords / Trefwoorden

Mots-clés: agriculture durable, berceau au berceau, bio-économie, digestion anaérobie, engrais renouvelables, gestion durable des ressources, librairie des modèles de récupération des nutriments, recyclage des nutriments, stratégies agricoles alternatives, traitement du digestat, valorization des déchets organiques.

Keywords: alternative farming strategies, anaerobic digestion, bio-based economy, cradle to cradle, digestate treatment, nutrient recovery model library, nutrient recycling, renewable fertilizers, sustainable agriculture, sustainable resource management, organic waste valorization.

Trefwoorden: alternatieve landbouwstrategieën, anaerobe vergisting, bio-economie, cradle to cradle, digestaatbehandeling, duurzaam beheer van grondstoffen, duurzame landbouw, hernieuwbare meststoffen, modellenbank voor nutriëntrecuperatie, recyclage van nutriënten, valorisatie van organisch afval.

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List of abbreviations

Ac	Acetate
AD	Anaerobic digestion
ADM1	Anaerobic digestion model No. 1
AE	Algebraic equation
AM	Animal manure
AmS	Ammonium sulfate
API	Application programming interface
ASM	Activated sludge model
AS	Activated sludge
AT	Australia
BCR	Bubble column reactor
BE	Belgium
Bu	Butyrate
CA	Canada
CAPDET	Computer assisted procedure for the design and evaluation of wastewater treatment systems
CAPEX	Capital expenditures
CaUE	Calcium use efficiency
CF	Chemical fertilizer
CFT	Cut-off threshold
CH	Switzerland
CHP	Combined heat and power generation
COD	Chemical oxygen demand
CRH	Critical relative humidity
CSD	Crystal size distribution
CSR	Controlled- and slow-release
CSTR	Continuously stirred tank reactor
CUI	Command-line user interface
DAE	Differential algebraic equation
DD	Digestate derivatives
DE	Germany
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DTB	Draft tube baffled type crystallizer
DW	Dry weight
EBPR	Enhanced biological phosphorus removal
EC	Electrical conductivity
ED	Electrodialysis
EU	European Union
FAO	Food and Agricultural Organisation of the United Nations
FBR	Fluidized bed reactor
FI	Finland
FO	Forward osmosis
FW	Fresh weight
G	Gas phase component
GHG	Greenhouse gas
GISCOD	General integrated solid waste co-digestion modelling tool
GN_Direct	DIviding RECTangles algorithm for global optimization
GSA	Global sensitivity analysis
GUI	Graphical user interface
HRT	Hydraulic residence time
HSD	Honestly significant difference
ICBM	Introductory Soil Carbon Balance Model
ICP-OES	Inductively coupled plasma optical emission spectrometry
IRR	Internal rate of return
IWA	International Water Association
JP	Japan

LCA	Life cycle assessment
LCFA	Long chain fatty acid
LF	Liquid fraction
LHS	Latin hypercube sampling
K	Kelvin
KUE	Potassium use efficiency
MA	Mineral acid
MANNER-NPK	MANure Nitrogen Evaluation Routine modelling tool
MAP	Magnesium ammonium phosphate = N-struvite
MC	Monte Carlo
MDDEFP	Ministère du Développement Durable, de l'Environnement, de la Faune et des Parcs
MF	Microfiltration
MgUE	Magnesium use efficiency
MKP	Magnesium potassium phosphate = K-struvite
MSL	Model specification language
MW	Molecular weight
NAC	Neutral ammonium citrate
ND	Not determined
NDICEA	Nitrogen dynamics in crop rotations in ecological agriculture
NINV	Net investment
NIST	National Institute of Standards and Technology
NL	The Netherlands
NPV	Net present value
NRT	Nutrient recovery technology
NRM	Nutrient recovery model
NRM-AD	Nutrient recovery model: Anaerobic digester
NRM-Chem	Nutrient recovery model: Chemical dosing unit
NRM-Heat	Nutrient recovery model: Heating unit
NRM-Prec	Nutrient recovery model: Precipitation/crystallization unit
NRM-Scrub	Nutrient recovery model: Scrubbing unit
NRM-Settle	Nutrient recovery model: Settling unit
NRM-Store	Nutrient recovery model: Storage tank
NRM-Strip	Nutrient recovery model: Stripping unit
NRM-UO	Nutrient recovery model user objective
NUE	Nitrogen use efficiency
N/A	Not applicable
ND	Not determined
No.	Number
OC	Organic carbon
ODE	Ordinary differential equation
OPEX	Operational expenditures
p	Partial pressure
P	Precipitated component
PAE	Plant available elements
PAEV	Plan agro-environnemental de valorisation
P-PAE	Phosphorus extractable with $CaCl_2$
PAl	Ammonium lactate extractable phosphorus
PAO	Phosphorus accumulating organism
PE	Person equivalent
PHA	Poly-hydroxy-alkanoate
PHREEQC	PH REdox EQuilibrium (in C language)
PP	Poly-phosphate
Prhizon	Phosphorus extractable with rhizon soil moisture samplers
Pro	Propionate
PSD	Particle size distribution
PUE	Phosphorus use efficiency
Pw	Water extractable phosphorus
RK4ASC	Runge Kutta 4 Adaptive Step size Control integration algorithm
RO	Reversed osmosis

S	Soluble component
SAR	Sodium adsorption ratio
Sc	Scenario
SI	Saturation index
SMS	Soil moisture sampler
SOC	Soil organic carbon
SRB	Sulfate reducing bacteria
SRC	Standardized regression coefficient
SRT	Solids retention time
SS	Suspended solids
SUE	Sulfurous use efficiency
TDS	Total dissolved solids
TF	Thick fraction
TMCS	Transmembrane chemosorption
TS	Total solids
TSP	Triple superphosphate
TSS	Total suspended solids
UF	Ultrafiltration
USA	United States of America
Va	Valerate
VFA	Volatile fatty acid
VIF	Variance inflation factor
VODE	Variable-coefficient ordinary differential equation solver
VSEP	Vibratory shear enhanced processing
VSS	Volatile suspended solids
WAS	Waste activated sludge
WRRF	Water resource recovery facility
WSA	Water-sparged aerocyclone
WWTP	Wastewater treatment plant
X	Biological particulate component

List of symbols

Symbol	Description	Unit
a	Specific surface of the gas bubbles per reactor volume	$[\mathrm{L}^{-1}]$
α	Collision efficiency factor	-
a_{seed}	Specific area of surface per gram of seed material before the seed crystals start to grow in the crystallizing solution	$[\mathrm{L}^2\ \mathrm{M}^{-1}]$
C_i	Carbon content of component i	$[\mathrm{M}\ \mathrm{M}^{-1}]$
°C	Degree Celcius	-
d	Average gas bubble diameter	$[L]$
D_l	Liquid phase diffusion coefficient	$[\mathrm{L}^2\ \mathrm{T}^{-1}]$
D_g	Gas phase diffusion coefficient	$[\mathrm{L}^2\ \mathrm{T}^{-1}]$
d_p	Particle diameter	$[L]$
D°H	German degrees of hardness	-
δ	Turbulence constant	-
$f_{product,substrate}$	Yield (catabolism only) of product on substrate	$[\mathrm{M}\ \mathrm{M}^{-1}]$
f_ns_P	Fraction of non-settleable precipitates	-
f_ns_X	Fraction of non-settleable solids	-
$\bar{G}$	Root mean square velocity gradient	$[\mathrm{T}^{-1}]$
$H_{T,i}$	Temperature dependent Henry coefficient of component i	$[\mathrm{M}\ \mathrm{L}^{-3}\ \mathrm{atm}^{-1}]$
i	Discount rate	-
$I_{H_2,substrate}$	Hydrogen inhibition for substrate degradation	-
$I_{H_2S,substrate}$	Hydrogen sulfide inhibition for substrate degradation	-
$I_{NH,limit}$	Inhibition of biomass growth due to lack of inorganic nitrogen	-
$I_{pH,bac}$	pH inhibition of acetogens and acidogens	-
$I_{pH,i}$	pH inhibition of component i	-
K_a	Aggregation constant	-
K_{ad}	Acid dissociation constant	-
K_b	Floc break-up constant	$[\mathrm{T}^{\delta-1}\mathrm{L}^{-3}]$
$k_{B,T}$	Temperature dependent nucleation rate coefficient	$[\mathrm{M}\ \mathrm{L}^{-2}\ \mathrm{T}^{-1}]$
$k_{dec,i}$	First order decay rate for biomass death of component i	$[\mathrm{T}^{-1}]$
$k_{dis,i}$	Complex particulate first order disintegration rate of component i	$[\mathrm{T}^{-1}]$
$k_{D,T}$	Temperature dependent dissolution rate coefficient	$[\mathrm{M}\ \mathrm{L}^{-2}\ \mathrm{T}^{-1}]$
$k_{G,i}$	Individual gaseous mass transfer coefficient of component i	$[\mathrm{L}\ \mathrm{T}^{-1}]$
$K_{G,i}$	Overall gaseous mass transfer coefficient of component i	$[\mathrm{L}\ \mathrm{T}^{-1}]$
$k_{G,T}$	Temperature dependent growth rate coefficient	$[\mathrm{M}\ \mathrm{L}^{-2}\ \mathrm{T}^{-1}]$
$k_{hyd,i}$	First order hydrolysis rate of component i	$[\mathrm{T}^{-1}]$
K_{ip}	Ion pairing equilibrium constant	-
$k_{L,i}$	Individual liquid mass transfer coefficient of component i	$[\mathrm{L}\ \mathrm{T}^{-1}]$
$K_{L,i}$	Overall liquid mass transfer coefficient of component i	$[\mathrm{T}^{-1}]$
$K_{L/G,i}$	Overall liquid-gas mass transfer coefficient of component i	$[\mathrm{L}\ \mathrm{T}^{-1}]$
$k_{m,i}$	Specific Monod maximum uptake rate of component i	$[\mathrm{T}^{-1}]$
K_s	Solubility product	$[\mathrm{M}\ \mathrm{L}^{-3}]$
Ks_i	Monod half saturation constant of component i	$[\mathrm{M}\ \mathrm{L}^{-3}]$
k_T	Temperature dependent liquid-solid transfer coefficient	$[\mathrm{M}\ \mathrm{L}^{-3}\ \mathrm{T}^{-1}]$
K_w	Water dissociation constant	-

Symbol	Description	Unit
K_i	Potassium content of component i	$[\mathrm{M\ M^{-1}}]$
$[L]$	Length (dimension)	-
$M_{fertilizer}$	Total mass / moles of fertilizer	$[M]$
M_{seed}	Mass of seed material in the reactor	$[M]$
MW	Molecular weight	$[\mathrm{M\ M^{-1}}]$
$[M]$	Mass / Moles (dimension)	-
n	Liquid-solid transfer reaction order	-
N	Total number of periods	$[T]$
N_A	Avogadro constant (6.022E23 mol^{-1})	$[\mathrm{M^{-1}}]$
n_B	Reaction order for nucleation	-
n_D	Reaction order for dissolution	-
n_G	Reaction order for growth	-
N_{part}	Number of particles	-
N_i	Nitrogen content of component i	$[\mathrm{M\ M^{-1}}]$
$p_{i,gas}$	Partial pressure of component i in the gas phase	atm
P_i	Phosphorus content of component i	$[\mathrm{M\ M^{-1}}]$
Q_{gas}	Gas flow rate	$[\mathrm{L^3\ T^{-1}}]$
Q_{in}/Q_{out}	In- and outgoing flow rates	$[\mathrm{L^3\ T^{-1}}]$
Q_{liq}	Liquid flow rate	$[\mathrm{L^3\ T^{-1}}]$
Q_{prec}	Precipitate extraction rate (for NRM-Prec)	$[\mathrm{L^3\ T^{-1}}]$
$Q_{recycle}$	Recycle flow rate (for NRM-Scrub)	$[\mathrm{L^3\ T^{-1}}]$
r	Regression coefficient	-
R	Universal gas law constant (0.082)	L atm mol^{-1} K^{-1}
R_T	Net cash flow at time t	$
S	Saturation ratio	-
$S_i^{in}/\ S_i^{out}$	In- and outgoing activities of component i	$[\mathrm{M\ L^{-3}}]$
S_i	Sulfur content of component i	$[\mathrm{M\ M^{-1}}]$
t	Time	$[T]$
T	Temperature	K
$[T]$	Time (dimension)	-
u	Average rise velocity of gas bubbles	$[\mathrm{L\ T^{-1}}]$
υ	$= \upsilon^+ + \upsilon^-$ = sum of the number of positive and negative species = stoichiometric liquid-solid transfer coefficient	-
$V_{fertilizer}$	Total fertilizer volume	$[\mathrm{L^3}]$
V_{gas}	Head space volume / gas volume	$[\mathrm{L^3}]$
$\upsilon_{i,j}$	Stoichiometric coefficient for component i on process j	$[\mathrm{M\ M^{-1}}]$
V_{liq}	Liquid volume	$[\mathrm{L^3}]$
$Y_{substrate}$	Biomass substrate yield	$[\mathrm{M\ M^{-1}}]$
ρ	Density of the flow	$[\mathrm{M\ L^{-3}}]$
ρ_{aggl}	Net rate of floc (agglomerate) appearance	$[\mathrm{L^{-3}\ T^{-1}}]$
ρ_j	Specific kinetic rate for process j	$[\mathrm{M\ L^{-3}T^{-1}}]$
θ_{gas}	Mean residence time of gas bubble in the reactor	[T]
φ	Volume fraction	-

Dedicated to the future in the sincere hope for
a more sustainable resource management

Dédié à l'avenir dans l'espoir sincère pour
une gestion plus durable des ressources

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"Intelligence leads to respect, passion persuades, but character is destiny."

Céline Vaneeckhaute

Les Éboulements, February 27 2015

Foreword

This dissertation consists of three complementary phases: 1) technology inventory and product classification, 2) product value evaluation, 3) process modelling and optimization. The first two phases were conducted at Ghent University (Belgium, PhD supervisors: Prof. F.M.G. Tack and Prof. E. Meers) during May 2011 - April 2013, whereas the third phase was conducted at Université Laval (model*EAU,* supervisor: Prof. P.A. Vanrolleghem) during May 2013 - April 2015 in collaboration with the enterprise Primodal Inc. (industrial co-supervisor: Dr. E. Belia). The first and second phase of the PhD were financed by i) Ghent University under the appointment of assisting academic staff, ii) the European Commission under the Interreg IVb Project *Arbor (Accelerating Renewable Energies through valorization of Biogenic Organic Raw Material)*, and iii) the Environmental & Energy Technology Innovation Platform (MIP) under the project *Nutricycle*. The third phase of the PhD was funded by i) the Natural Sciences and Engineering Research Council of Canada (NSERC), ii) the Fonds de Recherche de Québec sur la Nature et les Technologies (FRQNT), and iii) Primodal Inc. through an Industrial Innovation Scholarship (Bourse en Milieu de Pratique, BMP Innovation doctorat), awarded to Céline Vaneeckhaute in May 2013.

The dissertation is presented in a paper format. All papers were redrafted in order to logically fit in the dissertation and avoid unnecessary repetition. Nevertheless, attempts were made to provide adequate information in the introduction section of each chapter so as to make it fully accessible as a stand-alone article. Material for illustration was also added. The following peer-reviewed papers were included in the dissertation:

1. Chapter 2: Vaneeckhaute, C.[a,c], Lebuf, V.[b], Michels, E.[c], Belia, E.[d], Tack, F.M.G.[c], Vanrollegem, P.A.[a], Meers, E.[c], revisions submitted. Nutrient recovery from bio-digestion waste: Systematic technology review and product classification.
2. Chapter 3: Vaneeckhaute, C.[a,c], Meers, E.[c], Michels, E.[c], Christiaens, P.[e], Tack, F.M.G.[c], 2012. Fate of macronutrients in water treatment of digestate using vibrating reversed osmosis. Water Air Soil Pollut. 223(4), 1593-1603.
3. Chapter 4: Vaneeckhaute, C.[a,c], Meers, E.[c], Michels, E.[c], Buysse, J.[f], Tack, F.M.G.[c], 2013b. Ecological and economic benefits of the application of bio-based mineral fertilizers in modern agriculture. Biomass Bioenerg. 49, 239-248.
4. Chapter 5: Vaneeckhaute, C.[a,c], Meers, E.[c], Ghekiere, G.[g], Accoe, F.[b], Tack, F.M.G.[c], 2013c. Closing the nutrient cycle by using bio-digestion waste derivatives as chemical fertilizer substitutes: A field experiment. Biomass Bioenerg. 55, 175-189.
5. Chapter 5: Vaneeckhaute, C.[a,c], Ghekiere, G.[g], Michels, E.[c], Vanrolleghem, P.A.[a], Tack, F.M.G.[c], Meers, E.[c], 2014. Assessing nutrient use efficiency and environmental pressure of macro-nutrients in bio-based mineral fertilizers: A review of recent advances and best practices at field scale. Adv. Agron. 128, 137-180.
6. Chapter 6: Vaneeckhaute, C.[a,c], Janda, J.[c], Meers, E.[c], Tack, F.M.G.[c], 2015a. Efficiency of soil and fertilizer phosphorus use in time: A comparison between

recovered struvite, $FePO_4$-sludge, digestate, animal manure, and synthetic fertilizer, in: Rackshit, A., Singh, H.B., Sen, A. (Eds.), Nutrient Use Efficiency: From Basics to Advances. Springer, New Dehli, India.

7. Chapter 6: Vaneeckhaute, C.[a,c], Janda, J.[c], Vanrolleghem, P.A.[a], Meers, E.[c], Tack, F.M.G.[c], 2015b. Phosphorus use efficiency in bio-based fertilizers: A bio-availability and fractionation study. Pedosphere, accepted.
8. Chapter 7: Vaneeckhaute, C. [a,c], Zeleke, A. [c], Meers, E. [c], Tack, F.M.G.[c], submitted. Comparative evaluation of pre-treatment methods to enhance phosphorus release from digestate.
9. Chapter 8: Vaneeckhaute, C.[a,c], Meers, E.[c], Tack, F.M.G.[c], Belia, E.[d], Vanrolleghem, P.A.[a], 2015c. Modelling of nutrient recovery systems: Advances and limitations, in: Meers, E., Velthof, G. (Eds.), The Recovery and Use of Mineral Nutrients from Organic Residues. Wiley, West Sussex, UK.
10. Chapter 9: Vaneeckhaute, C.[a,c], Claeys, F.H.A.[h], Tack, F.M.G.[c], Meers, E.[c], Belia, E.[d], Vanrolleghem, P.A.[a], submitted. Development, implementation and validation of a generic nutrient recovery model (NRM) library.
11. Chapter 10: Vaneeckhaute, C.[a,c], Claeys, F.H.A.[h], Belia, E.[d], Tack, F.M.G.[c], Meers, E.[c], Vanrolleghem, P.A.[a], submitted. Global sensitivity analysis in nutrient recovery model (NRM) applications: Factor prioritization, treatment train configuration and optimization.
12. Chapter 11: Vaneeckhaute, C.[a,c], Belia, E.[d], Tack, F.M.G.[c], Meers, E.[c], Vanrolleghem, P.A.[a], in preparation. Roadmap for setting up nutrient recovery strategies.

The institutions of the co-authors are given below:

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The first author, Céline Vaneeckhaute, wrote all above-mentioned papers. All papers were reviewed and commented by the associated co-authors. The first author developed the concept of each paper and also undertook all experimental work at lab, field, and greenhouse scale, all modelling work, as well as the data processing and statistical analyses. For papers 4-5 (field-scale assessments), Inagro vzw (Beitem, Belgium) helped in setting up the fertilization scenarios. The firm Bocotrans (Tielt, Belgium) conducted the manure application to the field using pc-controlled injection, while Inagro vzw provided machinery for the harvest at the field. Both practices were performed under assistance and coordination of Céline Vaneeckhaute. For papers 4, 6, 7, and 8 MSc thesis students (under supervision of Céline Vaneeckhaute) provided assistance in conducting the physicochemical lab work and collecting samples at the field. For paper 10 (model development), DHI (Merelbeke, Belgium) helped in the establishment of the PHREEQC-Tornado software coupling.

It should be noted that next to these peer-reviewed papers, multiple reports, national papers, conference papers, and presentations have been published. An overview of all publications is given at the end of this dissertation.

Finally, the obtained data were used for holistic life cycle assessments (LCA) by the Luxembourg Institute of Science and Technology (LIST) (Esch-sur-Alzette, Luxembourg), the University of Bath (Bath, UK), and Bangor University (Gwynedd, UK). A summary of the main findings to date is provided in Chapter 12, based on the following papers:

1. Vázquez-Rowe, I.[a,b,c], Golkowska, K.[a], Lebuf, V.[d], Vaneeckhaute, C.[e,f], Michels, E.[e], Meers, E.[e], Benetto, E.[a], Koster, D.[a], submitted. Environmental assessment of digestate treatment technologies using LCA methodology.
2. Vaneeckhaute, C.[e,f], Adams, P.[g], Rodhe, L.[h], Thelin, G.[i], Styles, D.[j], Prade, T.[k], D'Hertefeldt, T.[l], in preparation. Wide-scale use of recycled nutrients: Bottlenecks or opportunities?
3. Adams, P.[g], Vaneeckhaute, C.[e,g], in preparation. Life cycle assessment of on-farm anaerobic digestion and digestate reuse: A case-study.

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In this work, Céline Vaneeckhaute provided the data for the LCAs, undertook meetings with the associated institutes to develop the concept of the assessments, and helped interpreting the results, writing and reviewing the papers (on-going).

CHAPTER 1:

GENERAL INTRODUCTION

Need for a sustainable resource management

(Pictures: Sutton et al., 2013)

As introduction to this dissertation, the present chapter provides the rationale of the research (Section 1.1), the specific problem statements and research objectives (Section 1.2.1), the overall objectives and expected impact (Section 1.2.2), and the originality of the PhD (Section 1.3). The structure of the dissertation and interrelationships between the chapters are described in Section 1.4.

1.1 Rationale

In the transition from a fossil reserve-based to a bio-based economy, it has become a critical challenge to maximally close nutrient cycles and migrate to a more effective and sustainable resource management, both from an economical and an ecological perspective. Estimates of nutrient reserves are highly uncertain, but based on population growth and future demand for nutrients, it is expected that depletion will occur within 93 to 291 years for phosphorus (P), 235 to 510 years for potassium (K), and 20 years for zinc (Zn) (Elser and Bennett, 2011; Neset and Cordell, 2012; Scholz and Wellmer, 2013). Geopolitical moves can, however, shift this date forward, making nutrient scarcity an imminent threat. Moreover, the quality of the remaining natural resources is declining, there is no substitute available, and to date these nutrients cannot be manufactured. At the same time, the agricultural demand for bio-available mineral fertilizers is continuously increasing, mainly due to the rising world population, the increasing meat consumption, and the cultivation of energy crops (Godfray *et al.*, 2010; Syers *et al.*, 2008). This imbalance between availability and demand will continue to considerably push up the prices for nutrient resources in the near future. The increasing cost for fossil energy is another important price influencing factor, as a strong positive correlation between energy prices and fertilizer costs has been observed (Oskam *et al.*, 2011). Next to these economic consequences, the current use of chemical fertilizers also results in an important environmental impact. The production and transport of these mineral fertilizers requires significant amounts of fossil energy (Gellings and Parmenter, 2004). For example, the production of reactive ammonium (NH_4) through the extraction of unreactive atmospheric nitrogen gas (N_2) via the Haber Bosch process amounts to a fossil energy consumption of 35.2-40.5 GJ ton^{-1} NH_4 (EFMA, 2014). The total energy consumption is equivalent to ± 2 % of world energy use (EFMA, 2004; Sutton *et al.*, 2013). Hence, the dependency of agriculture on fossil reserve-based mineral fertilizers (especially N, P, and K) must be regarded as a very serious threat to future human food security (Sutton *et al.*, 2013; van Vuuren *et al.*, 2010).

Despite these unfavourable prospects, a large amount of minerals is again dispersed in the environment through processing or disposal of waste streams, often in difficult to extract, non-bio-available form such as sewage sludge, industrial sludge, manure, household waste, incineration ashes, etc. (Hou *et al.*, 2012). In addition, the observed intensification of animal production and the resulting manure excesses, combined with a limited availability of arable land for the disposal of waste (manure, sludge, etc.) and the excessive use of chemical mineral fertilizers, has led to surplus fertilization and nutrient accumulation in many soils worldwide. These phenomena have caused environmental pollution. Leaching of nitrates and phosphates or runoff to water bodies has led to eutrophication of surface waters, atmospheric emissions, as well as soil erosion (Sutton *et al.*, 2013). In turn, these sources of pollution have stimulated the introduction of increasingly stringent regulations for the application of nutrients to agricultural fields, and have led to more strict requirements for the quality of discharge/emission from waste(water) treatment facilities (Kang *et al.*, 2011; Ranatunga *et al.*, 2013; WERF, 2010). A new global effort is needed to address 'The Nutrient Nexus', where reduced nutrient losses and improved nutrient use efficiency across all sectors simultaneously provide the foundation for a greener economy to produce more food and energy while reducing environmental pollution (Sutton *et al.*, 2013; WERF, 2010). Indeed, **nutrient cycles represent a key nexus point between global economic, social, and environmental challenges** (Mo and Zhang, 2013; Sutton *et al.*, 2013).

In the case of P, for example, a recent global scenario analysis (Fig. 1.1) indicated that meeting the increasing long-term P demand would likely require demand management measures to reduce business-as-usual demand by two-thirds, and the remaining third could be met through a high recovery of P from human excreta, manure, food waste, and mining waste. However, achieving such a high recovery and reuse scenario will undoubtedly require substantial changes to physical infrastructure, new partnerships, and strategic policies to guide P recovery and reuse in an integrated way (Cordell and White, 2011).

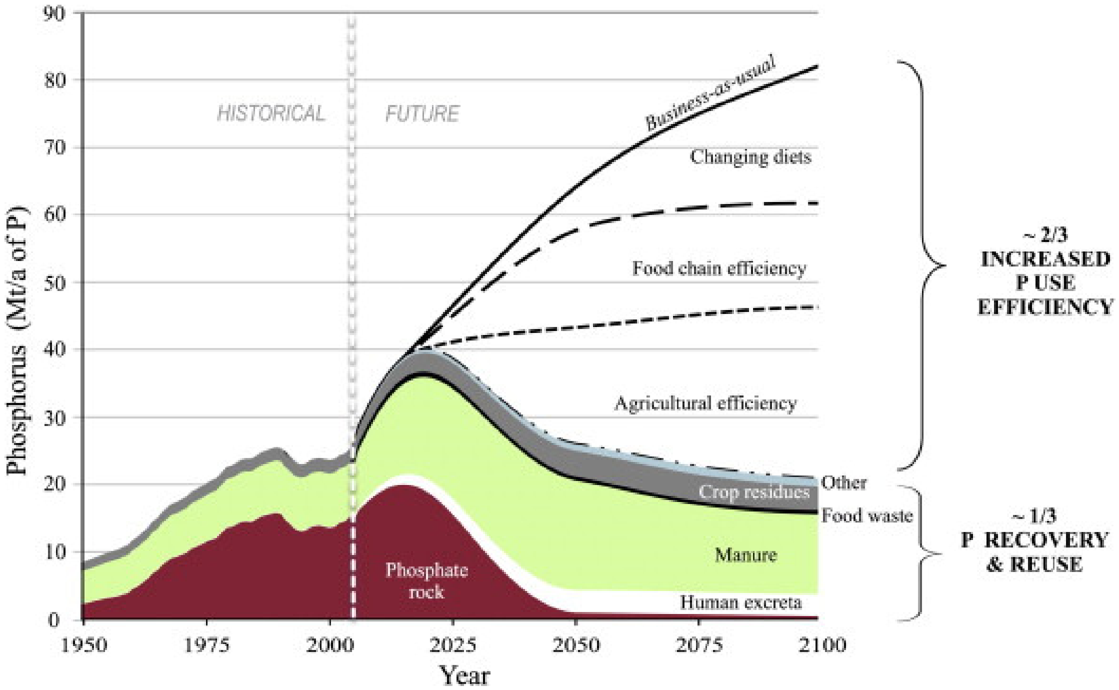


Figure 1.1 A sustainable scenario for meeting long-term future phosphorus demand (million ton y^{-1}) through increased phosphorus use efficiency and recovery (Cordell and White, 2011).

Medium (2020) and long-term (2050) strategic environmental policy objectives are being or have been set across the world in order to support the growth of a more innovative, resource-efficient economy, based on the sustainable production of bio-based products (bio-energy and bio-materials) from renewable biomass sources (Bio-Economy Network Canada, 2015; EuropaBio, 2014; Novotny, 2013; UNEP, 2013). In the framework of these objectives, the anaerobic (co-)digestion of sewage sludge, organic biological waste (crop residues and other food waste), and animal manure has been evaluated as one of the most energy-efficient and environmentally friendly technologies for bio-energy production, organic biodegradable waste valorization, and potential recovery of valuable nutrient resources, which are concentrated in the remaining (mineralized) digestate (EC, 2011; Fehrenbach *et al.*, 2008; UNEP, 2013). Despite its great potential, further sustainable development of this technology is currently hindered, because these digestates can often not or only sparingly be returned to agricultural land in their crude unprocessed form. This is especially the case in high-nutrient regions, such as (parts of) Western Europe (e.g. Flanders (Belgium), the Netherlands, Nord-Rein Westfalen (Germany), Bretagne (France), Denmark, etc.), the Eastern and Midwestern United States of America (USA) and Canada (e.g. Quebec, Alberta, Ontario, Pennsylvania, California, etc.), and areas of East and South Asia, due to strict legislative constraints related to the overproduction of animal manure in comparison to the available arable land to spread it on (see above; FAO, 2004a; Lemmens *et al.*, 2007; WCC, 2015). As such, for example, in Flanders (Belgium), digestates produced as a by-product from the (co-)digestion of animal manure are currently still categorized as ‘waste’ and ‘animal manure’ in environmental and fertilizer legislations and are penalised accordingly. Moreover, in most countries, periods when spreading fertilizer on agricultural land is allowed, are regulated in order to minimize nutrient leaching. Therefore storage capacity for digestate becomes expensive due to its high volume, and transportation problems may occur during application periods. Hence, further processing of digestate into transportable/exportable end products, concentrated mineral fertilizers (cfr. chemical fertilizers), and/or environmentally neutral components is required to overcome practical and potential environmental problems, and legislative bottlenecks related to the direct application of digestate.

So far, the technical approach for digestate processing was similar to the approach for the treatment of manure and wastewater. This means that the focus was on little cost-effective, energy-intensive, and non-sustainable nutrient removal practices through destruction or emission, e.g. biological nitrification/denitrification (Lemmens *et al.*, 2007). Hence, again clearly a paradox exists: N is extracted as N_2 from the atmosphere in large quantities for the chemical production of mineral fertilizers (see above: Haber Bosch process), whereas it is forced to transform again into N_2 during digestate, manure, and wastewater processing. **The challenge for anaerobic digestion plants now is to achieve optimal recovery and recycling of nutrients from the digestate in a sustainable way.** As such, regulatory drivers can be met and an internal revenue source can be produced, i.e. the present ‘waste’ problem can be turned into an economic opportunity.

Although to date many technologies for the recovery of nutrients from wastewater, manure, and digestate have been proposed and implemented to varying degrees, there is no common strategy to promote the use of these sources of nutrients by farmers (USEPA, 2012; WERF, 2010). As a consequence, the details of their application and potential benefits are not well established in the farming community (Novotny, 2012; WERF, 2010). Also, the price of recovered fertilizers is generally still higher than the price of chemical fertilizers, resulting in a persistent uncertainty of fertilizer sales (EC, 2011; Seymour, 2009; USEPA, 2013). Moreover, a high inconsistency in marketing prices has been observed in regions where commercialization has been possible (Seymour, 2009). Challenges remain with regard to the recovery of nutrients as pure marketable commodities with stable composition and added value for the agricultural sector, such as controlled- or slow-release granular fertilizer products or concentrated solutions with high nutrient use efficiency (Guest, 2015; Rahman *et al.*, 2014; WERF, 2010). Much more could also be done in terms of identifying markets for recovered nutrients and bringing down barriers to their increased use, and implementing and optimizing the technologies that are already available (Guest, 2015; Khunjar and Fisher, 2014; Novotny, 2013; Seymour, 2009; USEPA, 2012; WERF, 2010).

1.2 Problem statement, objectives, and impact

1.2.1 Problem statement and specific research objectives

This PhD dissertation aims at stimulating the transition to a bio-based economy by providing (tools to develop) sustainable strategies for nutrient (and energy) recovery from digested biodegradable waste (hereafter referred to as bio-digestion waste or digestate) with economic valorization of the recovered products as: i) renewable bio-based substitutes for chemical fertilizers (= inorganic recovered products) and/or ii) sustainable bio-based organo-mineral fertilizers (= organic products containing recycled nutrients) in agriculture. Specifically, this research strives to optimize and foster the implementation of best available technologies for nutrient recovery (= technology push) with focus on demand-driven agricultural valorization of the recovered products (= market pull). The specific objectives of this multidisciplinary PhD are pursued through three complementary research phases:

PHASE I:* *Technology inventory and product classification

- **Problem statement I.1:** The choice of the best set of nutrient recovery technologies (NRTs) depends on the characteristics of the input waste stream and has a strong influence on the composition and properties of the resulting fertilizer end and by-products. Understanding the fundamentals of the existing processes is thus of paramount importance to sustainably create new high-quality fertilizers. Contemporary knowledge on NRTs is spread over a handful of academic and industrial experts, but an overall comprehensive overview is lacking. Moreover, a classification of recovered products on the basis of their fertilizer properties is missing. Consequently, the use of bio-based fertilizers is hindered, as these products are mostly classified as waste in environmental legislation, despite the fact that some of them have similar properties as conventional fossil reserve-based chemical fertilizers.

- **Objective I.1:** To create a **systematic overview** of technologies for nutrient recovery from bio-digestion waste and a **classification** of the resulting end products. Hereby, it is also aimed to investigate the technical and economic state-of-the-art of the existing technologies and those under development, and to gather available information on product quality.

PHASE II: Product value evaluation

- **Problem statement II.1:** During anaerobic digestion and digestate processing, multiple derivatives are produced, some of them having potential for reuse as chemical fertilizer substitutes. In-depth research on the composition and properties of these products compared to conventional fertilizers is scarce, and studies on the fate of nutrients in digestate processing are lacking, though very relevant.
- **Objective II.1:** To characterize the physicochemical properties of digestate and its various (recovered) derivatives on different points in time and for different full-scale installations in order to conduct complete **mass balance analyses**. Special attention should be given to general conditions, electrical conductivity and pH, macronutrients and their speciation, essential and non-essential trace elements, organic carbon, and nutrient ratios. Potential bottlenecks for reuse should be identified.

- **Problem statement II.2:** In general, the production cost of recovered fertilizers is still higher than the price of chemical mineral fertilizers. Even when producers reduce their marketing cost, agricultural use will remain limited because there is no common strategy to promote the use of these nutrient sources by farmers. Existing economic studies on technology evaluation do not take the whole-chain-benefits of nutrient recovery into account, although overall costs for the agricultural and waste processing sector may significantly reduce when nutrient recovery strategies would be applied.
- **Objective II.2:** To perform an **economic and ecological evaluation** of different bio-based fertilization scenarios in a concept of cradle-to-cradle agricultural reuse of valuable macro- and micronutrients, and to explore the whole-chain marketing value of the recovered products as compared to chemical mineral fertilizers.

- **Problem statement II.3:** An important issue in resource recovery is social perception and agricultural acceptance. Currently, the agricultural use of recovered products is marginal, because its availability is still limited to farmers and as such, the details of its application and potential benefits are not well established in the farming community. Long-term field experiments are required to prove and validate the fertilizer potential of these products. This will help to better classify bio-based products in legislation concerning environment and fertilizers, and serve as a support to stimulate their use.
- **Objective II.3:** To experimentally assess the fertilizer potential and impact on soil quality and crop production by field and greenhouse application of renewable fertilizers as compared to traditional agricultural practices using chemical fertilizers and animal manure (= **agronomic evaluation**).

PHASE III: Process modelling and optimization

- **Problem statement III.1:** Mathematical models are becoming important tools to aid technology development, process operation, and optimization. However, current models used for conventional treatment plant design, process optimization, and control do not allow the integration of nutrient recovery practices. This flaw is related to the omission of key fundamental physicochemical components and reactions that are essential to mathematically describe nutrient recovery. Thus, to date, no generic models for nutrient recovery systems based on adequate chemical speciation and reaction kinetics are available and implemented. Consequently, the potential to adequately put together a treatment train of unit processes and their operating conditions to maximize resource recovery and fertilizer quality is missing.
- **Objective III.1:** To develop **generic integrated biological-physicochemical process models** for the best available nutrient recovery systems based on in-depth chemical speciation and reaction kinetics, aiming at fertilizer quality and quantity as model outputs.

- **Problem statement III.2:** Although many industrial technologies for nutrient recovery are already proposed and used to varying degrees, challenges remain in improving their operational performance, decreasing the economic costs, and recovering the nutrients as marketable products with added value for the agricultural sector. Finding the appropriate combination of technologies for a particular waste flow and the optimal process conditions for the overall treatment train is a key concern.
- **Objective III.2:** To apply the developed models as a **tool for process optimization** of single nutrient recovery systems, as well as for determining optimal combinations of unit processes in order to maximize resource recovery (nutrients, energy) from a particular waste stream and minimize energy and chemical requirements.

1.2.2 Overall objectives and expected impact

Overall, this research aims to support the transition from a fossil reserve-based to a bio-based economy by facilitating sustainable resource management through nutrient and energy recovery via anaerobic digestion of biodegradable wastes and valorization of the resulting digestate in a cross-sectorial approach (Fig. 1.2).

At the scale of waste(water) (including manure, sludge, digestate, etc.) treatment, the aim is to promote the transition from treatment or disposal plants to waste(water) resource recovery facilities (WRRFs). Nowadays, significant amounts of energy are wasted through the production (via Haber Bosch and mining; see above) and associated transport of bio-available nutrients (e.g. NH_4-N) from sources that are not bio-available (e.g. atmospheric N_2) (Fig. 1.3: upper red arrows). However, ultimately these bio-available nutrients end up in waste(water) treatment plants (WWTPs), where they are generally transformed again into a non-bioavailable form

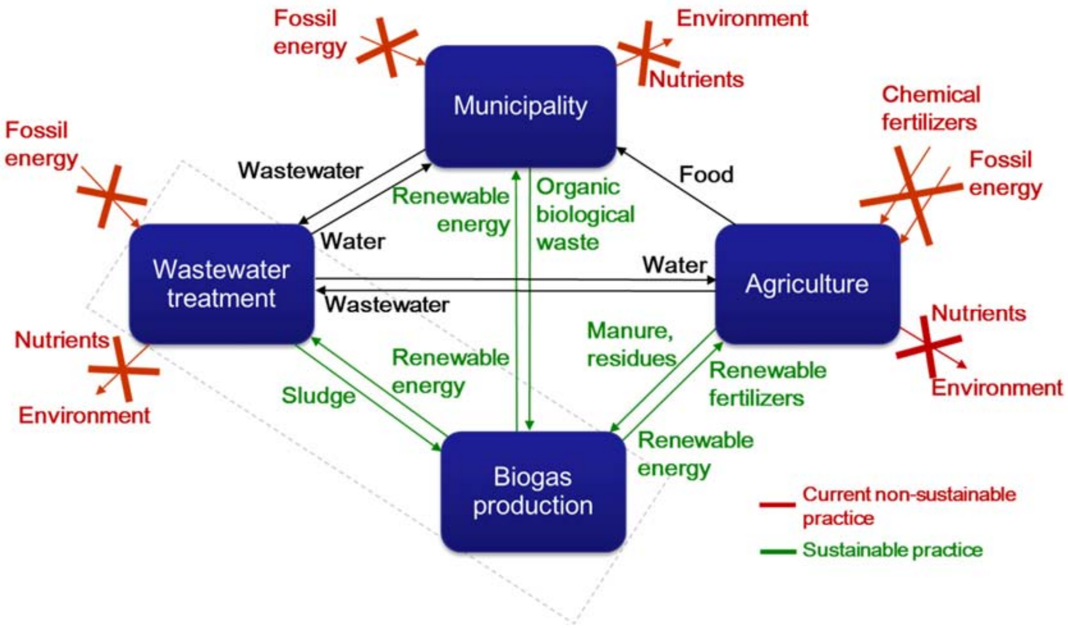


Figure 1.2 Cross-sectorial approach to sustainable resource management. Red arrows: current non-sustainable approach. Green arrows: targeted sustainable approach. Note that energy and nutrient recovery are often integrated in the water recovery facility.

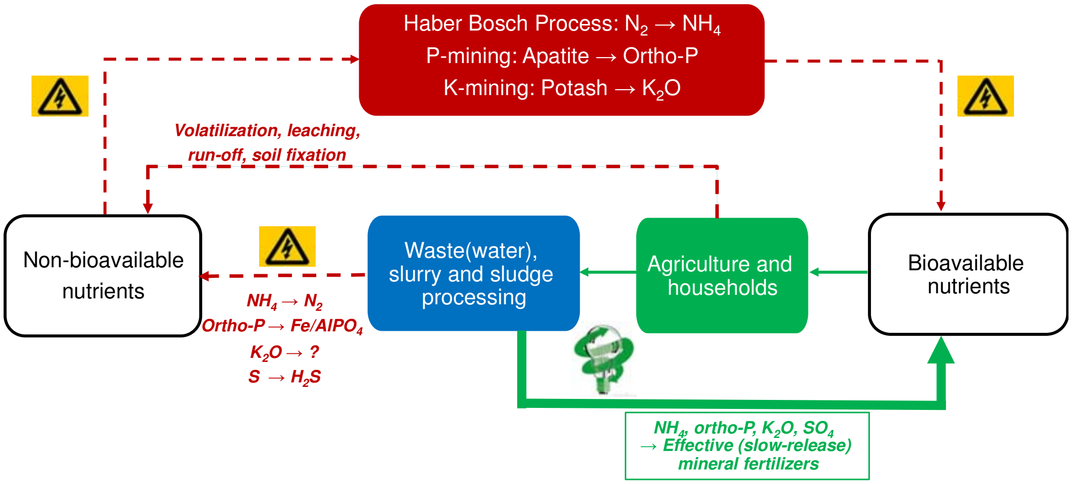


Figure 1.3 Cross-sectorial transition from nutrient removal to recovery. Red arrows: non-sustainable nutrient flows that should be minimized. Green arrows: targeted sustainable closed nutrient cycle.

using energy intensive processes, e.g. biological nitrification-denitrification (Fig. 1.3: lower red arrows). This research targets the sustainable extraction of bio-available nutrients from waste(water) systems and subsequent reuse as concentrated bio-based fertilizers with high nutrient use efficiency (Fig. 1.3: green arrows). Hence, overall, at the scale of waste(water) treatment, it is aimed to stimulate the paradigm shift from non-sustainable practices of nutrient removal into sustainable approaches of cradle-to-cradle nutrient recovery.

As such, this PhD research clearly addresses 'the Nutrient Nexus' and is therefore very important to the three pillars of sustainable development: environment, society, and economics (Fig. 1.4).

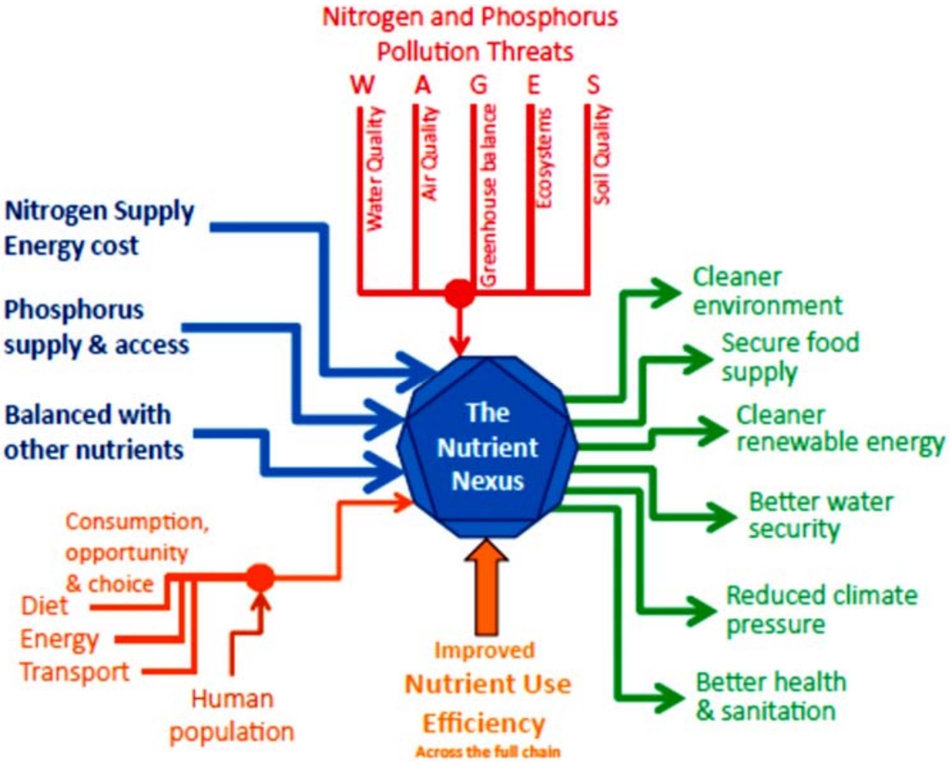


Figure 1.4 'The Nutrient Nexus': nutrient cycles represent a key nexus point between global economic, social, and environmental challenges; improving full-chain Nutrient Use Efficiency becomes the shared key to delivering multiple benefits (Sutton *et al.*, 2013).

The current imbalance between nutrient availability in waste(water) treatment systems and the demand for high-efficiency fertilizers in agricultural systems will lead to continuously increasing costs of nutrient resources in the near future. By providing strategies for nutrient recovery, treatment plants may reduce their environmental impact, while at the same time allowing to market recovered nutrients for high-quality reuse and increase their profitability. On the other hand, by converting to the use of sustainable and effective fertilizers, such as slow-release granules or concentrated solutions with high nutrient use efficiency, the agricultural sector can reduce its environmental impact caused by nutrients, can become less dependent of the use of chemical fertilizers, and improve its social acceptance, while developing a sustainable and profitable agriculture. This PhD dissertation further develops the concepts of closing nutrient cycles (= waste to feed/food), thereby stimulating the decoupling of economic growth from the use of natural resources, addressing food security for future generations, and mitigating the environmental impact of traditional waste stream processing or disposal. Ultimately, this research may help reducing the waste of finite resources and environmental pollution, while residues may acquire economic value. This would open up new opportunities for sustainable and more bio-based economic growth and thus create a win-win situation for both the environment, society, and the economy in Belgium, Canada, and beyond.

1.3 Originality

The originality of the present work can be considered from different points of view (Fig. 1.5).

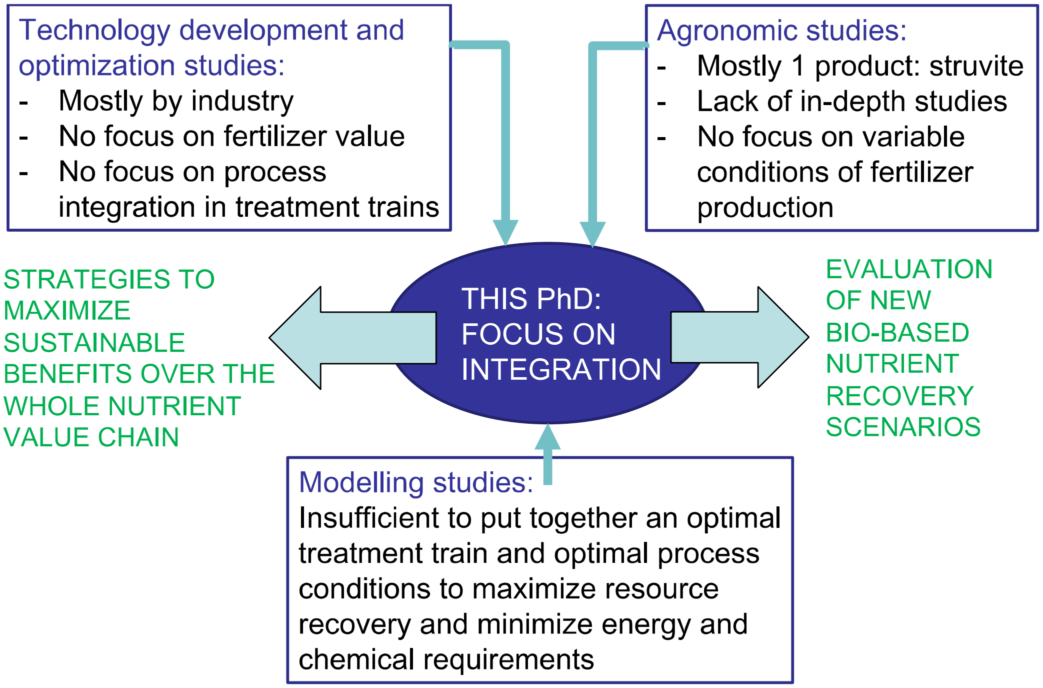


Figure 1.5 Schema indicating the originality of the PhD dissertation.
Boxes refer to current available research studies.
Arrows indicate the focus of this PhD.

Current available studies focusing on nutrient recovery technology development and optimization (mainly conducted by industry) do mostly not consider the fertilizer value and demand of the resulting products, nor the integration of the technology in treatment trains for nutrient recovery. On the other hand, studies concerning the evaluation of recovered fertilizer quality (mainly on struvite, produced at lab-scale, mostly performed by universities or research groups) do not account for the variable conditions under which these fertilizers have to be produced. Furthermore, although mathematical models are useful tools for technology development, process operation, and optimization, current models are incapable to adequately put together a treatment train of unit processes and to evaluate the operating conditions that maximize nutrient recovery and fertilizer quality at minimal cost.

The originality of the present work resides in its focus on bridging the gap between industrial technology development (= technology push) and demand-driven nutrient valorization (= market pull) following a multidisciplinary cross-sectorial approach. The research integrates a technology inventory and product classification, economic and ecological scenario analyses, experimental data assessments (focusing on technology AND product quality), modelling and treatment train optimization, to select and optimize whole-chain sustainable nutrient recovery strategies. For the first time, the available knowledge on nutrient recovery technologies (state-of-the-art, process conditions, economics, commercial processes available, etc.) is compiled in a comprehensive overview, while the resulting end products are classified according to their fertilizer characteristics. Moreover, new (best available) products, such as ammonium sulfate from acidic air scrubbers, are used as sustainable substitute for conventional chemical fertilizers (next to other digestate derivatives) in different original bio-based fertilization scenarios at the field-scale. Also highly innovative is the development of three-phase dynamic process models for nutrient recovery systems based on adequate chemical speciation and their application for treatment train optimization. As such, unit process interactions (input characteristics, chemical dosage, fertilizer production, etc.) can be considered, and strategies that maximize sustainable benefits can be determined.

1.4 Dissertation plan and interrelationships

Multidisciplinary in nature, this dissertation consists of three complementary phases (see Section 1.2): 1) technology inventory and product classification, 2) product value evaluation, 3) process modelling and optimization. The first two phases were conducted at Ghent University (Belgium, PhD supervisors: Prof. F.M.G. Tack and Prof. E. Meers), whereas the third phase was conducted at Université Laval (Quebec, Canada, supervisor: Prof. P.A. Vanrolleghem) in collaboration with the enterprise Primodal Inc. (Quebec, Canada, supervisor: Dr. E. Belia). The dissertation is presented in a paper format. The principal objective of each chapter and how it interconnects with other chapters of the dissertation is detailed in Figure 1.6 and further described below. An overview of the peer-reviewed papers used per chapter, with indication of the state of publication and the co-authors is provided in Table 1.1.

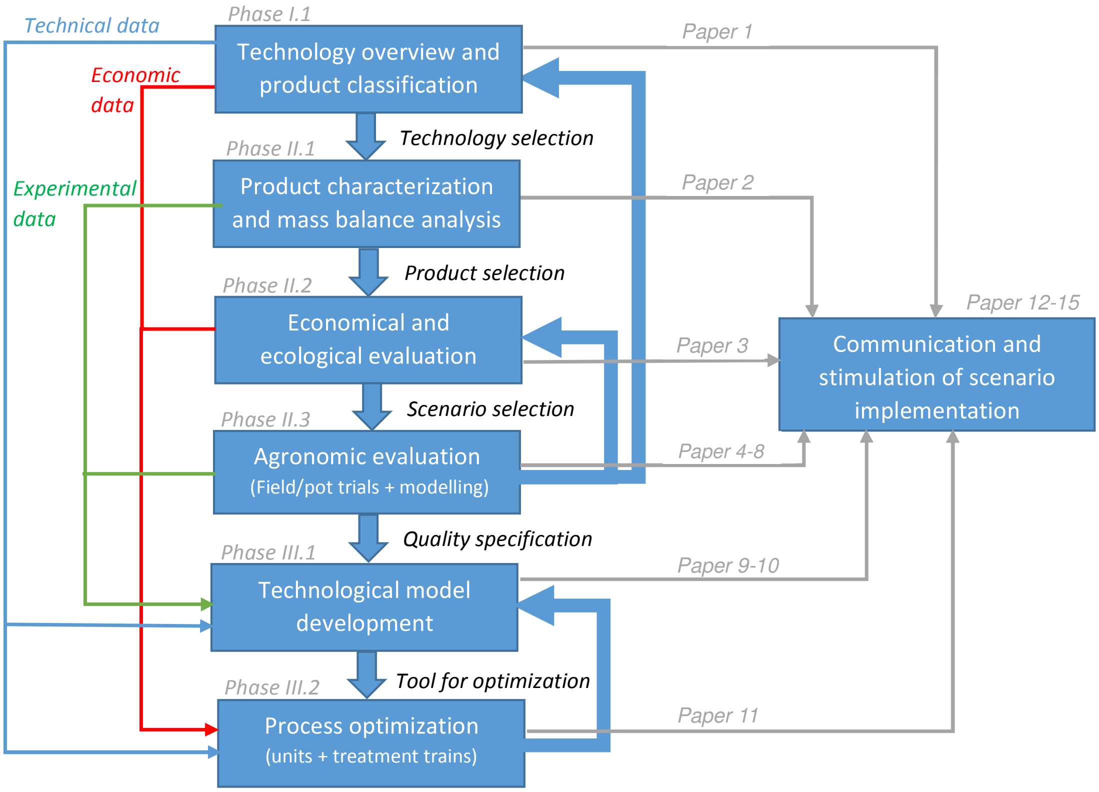


Figure 1.6 Overview of the PhD research strategy and interrelationships.
Phase I: technology inventory and product classification;
Phase II: product value evaluation; Phase III: process modelling and optimization.
Blocks and phase numbers correspond to the objectives defined in Section 1.2.1.

Table 1.1 Overview of peer-reviewed papers per chapter, state of publication, and co-authors. Note: other publications (national papers, scientific reports, proceedings, etc.) are given at the end of this dissertation.

Chapter	Paper	State of publication	Co-authors[a]
2	1	Revisions submitted	EB, EM, EM2, FT, PV, VL
3	2	Published (2012)	EM, EM2, PC, TF
4	3	Published (2013)	EM, EM2, FT, JB
5	4-5	Published (2013)/Published (2014)	EM, EM2, FA, FT, GG, PV
6	6-7	Published (2015)/Accepted (2015)	EM, FT, JJ, PV
7	8	Submitted	AZ, EM, FT
8	9	Accepted (2015)	EB, EM, FT, PV
9	10	Submitted	EB, EM, FC, FT, PV
10	11	Submitted	EB, EM, FC, FT, PV
11	12	In preparation	EB, EM, FT, PV
12	13-15	Submitted/In preparation	DK, DS, EB2, EM, EM2, GT, IV, KG, LR, PA, TP, VL

[a] AZ = Aga Zeleke; DK = Daniel Koster; DS = David Styles; EB = Evangelina Belia; EB2 = Enrico Benetto; EM = Erik Meers; EM2 = Evi Michels; FA = Frederik Accoe; FC = Filip Claeys; FT = Filip Tack; GG = Greet Ghekiere; GT = Gunar Thelin; IV = Ian Vázquez-Rowe; JB = Jeroen Buysse; JJ = Joery Janda; KG = Katarzyna Golkowska; LR = Lena Rodhe; PA = Paul Adams; PC = Patrick Christiaens; PV = Peter Vanrolleghem; TD = Tina D'hertefeldt; TP = Thomas Prade; VL = Viooltje Lebuf.

The work begins with a **systematic overview** and critical comparison of available and developing technologies for nutrient recovery from bio-digestion waste, as well as a **classification** of the resulting end products in Chapter 2 (= Phase I, Paper 1; Vaneeckhaute *et al.*, 2013a). Note that this chapter was continuously updated and completed by inclusion of the findings obtained throughout this PhD research.

Chapters 3 to 7 cover the experimental content of the dissertation aiming at product value evaluation (= Phase II). In Chapter 3, the fate of macronutrients in digestate processing is investigated through detailed **physicochemical and mass balance analyses** of a full-scale recovery facility (Paper 2; Vaneeckhaute *et al.*, 2012). Based on further in-depth product characterizations, an **economic and ecological evaluation** of different agricultural reuse scenarios is presented in Chapter 4 (Paper 3; Vaneeckhaute *et al.*, 2013b). The most interesting scenarios are selected for field-scale implementation. The fertilizer potential and the impact on soil and crop production of these bio-based fertilization scenarios as substitutes for conventional practices, using animal manure and chemical fertilizers, in agriculture is then explored by means of **field and greenhouse experiments** in Chapters 5-6 (Papers 4-7; Vaneeckhaute *et al.*, 2013c, 2014, 2015a, 2015b). Chapter 5 provides the proof-of-concept of closing nutrient cycles in a cradle-to-cradle approach by means of two-year field-trial results, using high-level performance indicators for measuring farming's pressure on the environment and how that pressure is changing over time. Recommendations for good management practices for the implementation of bio-based fertilization scenarios are also provided.

It should be noted that, in line with (European) legislative constraints, Chapters 4 and 5 mainly focus on the (simultaneous) replacement of conventional fertilization, i.e. animal manure additionally supplied with chemical N and K fertilizers, by bio-based alternative scenarios. Nevertheless, in light of P depletion and the increasingly strict regulations for P fertilizer application to agricultural soils (especially in P saturated regions), the effective use of (fixed) soil P and the recovery of products with high P use efficiency evidently also deserves increased attention. The field-scale assessment above revealed interesting observations in terms of soil P extraction when applying bio-based products. In order to confirm and further study these findings, a detailed greenhouse experiment evaluating the P release and use efficiency of various bio-based P fertilizers as compared to their fossil reserve-based counterparts is elaborated in Chapter 6.

Given the beneficial agronomic value of struvite as concentrated P fertilizer in Chapter 6, a brief **lab-scale experiment** is presented in Chapter 7 (Paper 8) showing the potential of various pre-treatments to improve the release of P in the liquid fraction of digestate during solid-liquid separation. This is especially relevant in P saturated regions to increase the local valorization of the remaining (P-poor) organic thick fraction, meanwhile increasing the struvite (or Ca/Mg-P precipitate or concentrated P-solution) recovery potential from the liquid fraction and its purity. Indeed, the current potential for struvite production is often limited as traditional digestate processing practices mostly involve the (non-sustainable) elimination of P and organic carbon from the local agricultural cycle through export of the separated thick fraction.

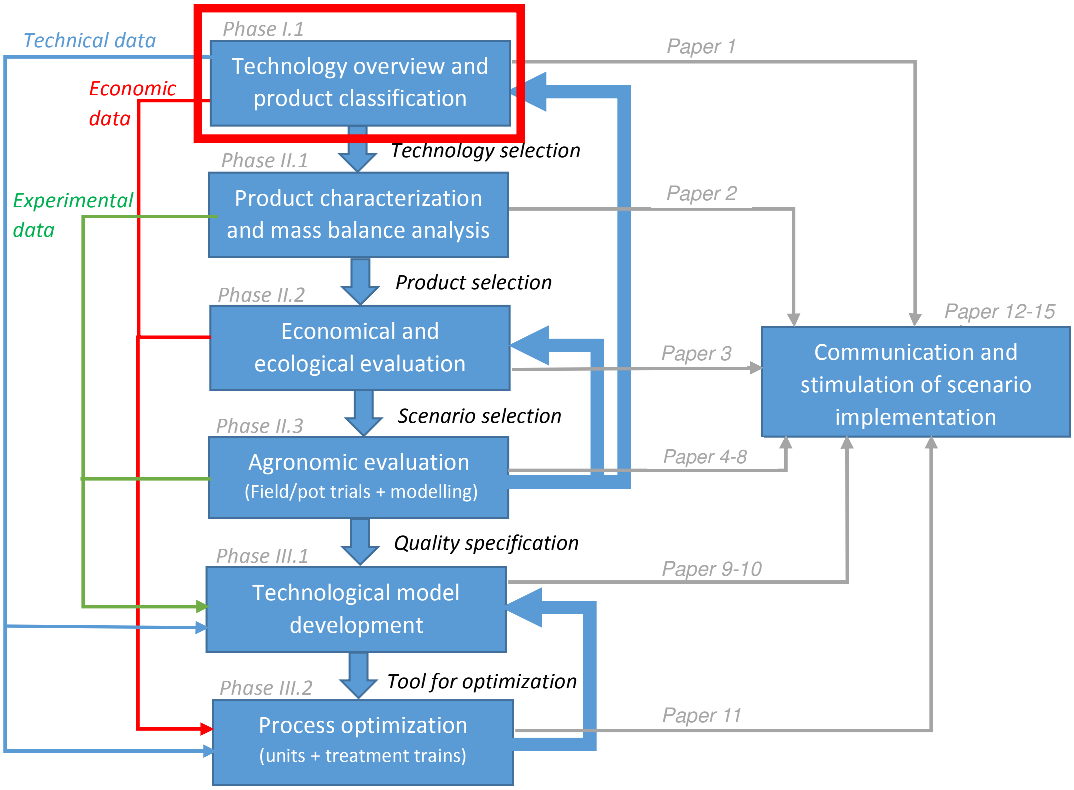
Chapters 8 to 10 cover the modelling content of the dissertation (= Phase III). Indeed, although the above chapters provide evidence of the agronomic, economic, and ecological value of bio-based products, a prerequisite for marketing is that they can compete with conventional fertilizer quality specifications. The findings illustrate that mathematical models can be very valuable tools for optimization of both process/treatment train performance and fertilizer quality.

First, important fertilizer quality specifications (based on the previous chapters), as well as advances and limitations in modelling of nutrient recovery systems are reviewed in Chapter 8 (Paper 9; Vaneeckhaute *et al.*, 2015c). This is necessary to clearly define and justify the specific modelling objectives and approach. In Chapter 9 (Paper 10), the development, implementation, and validation of a **generic nutrient recovery model (NRM) library** with focus on the sustainable production of marketable fertilizers is elaborated. Chapter 10 (Paper 11) presents **global sensitivity analyses,** performed to identify the factors (input characteristics, operational conditions, and kinetic parameters) with the highest impact on the model outputs of interest. Increased insights in the interactions between unit process inputs and outputs are reported and recommendations for future monitoring and research are provided. Based on the results, the valuable use of the NRM library as a **tool for configuration and optimization** of nutrient recovery treatment trains that maximize resource recovery and minimize energy and chemical requirements is demonstrated.

Finally, in order to facilitate communication and nutrient recovery scenario implementation, a generic **roadmap for setting up nutrient recovery strategies** from digestate is presented in Chapter 11 (Paper 12). This chapter should provide useful guidance for waste(water) processing utilities aiming at implementing nutrient recovery strategies.

In addition, the data obtained in this dissertation were and are being used by various research institutions (Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg, University of Bath, Bath, United Kingdom, UK, and Bangor University, Gwynedd, UK) for **holistic life cycle assessments** (LCA) of digestate processing and nutrient recovery strategies. A summary of the main findings obtained to date is provided in Chapter 12 (Papers 13-15). These LCA studies provide quantitative estimations of the overall improvements in process sustainability and can therefore greatly help in global policy making, communication, and stimulation of recovery scenario implementation.

Finally, based on all results, observations, and experiences acquired during the PhD research, **general conclusions and recommendations** towards the different stakeholders in the field of nutrient recovery are compiled in Chapter 13.



PHASE I

TECHNOLOGY INVENTORY & PRODUCT CLASSIFICATION

CHAPTER 2:

NUTRIENT RECOVERY FROM BIO-DIGESTION WASTE: SYSTEMATIC TECHNOLOGY REVIEW AND PRODUCT CLASSIFICATION

Digestate production through anaerobic digestion: bottleneck or opportunity?
(Picture: Roese Energietechnik GmbH, Breitungen, Germany)

Redrafted from:

Vaneeckhaute, C., Lebuf, V., Michels, E., Belia, E., Tack, F.M.G., Vanrollegem P.A., Meers, E., revisions submitted. Nutrient recovery from bio-digestion waste: Systematic technology review and product classification.

Abstract

Nutrient recovery from digested biodegradable waste as marketable products has become an important task for anaerobic digestion plants to meet both regulatory drivers and market demands, while producing an internal revenue source. As such, the present waste problem could be turned into an economic opportunity. The aim of this chapter was to provide a comprehensive overview and critical comparison of the available and emerging technologies for nutrient recovery from digestate and a classification of the resulting end products according to their fertilizer characteristics. Based on the stage of implementation, the technical performance, as well as financial aspects, struvite precipitation/crystallization, ammonia stripping and (subsequent) absorption using an acidic air scrubber were selected as best available technologies to be applied at full-scale for nutrient recovery as marketable fertilizer commodities. The resulting end products can and should be classified as renewable N/P-precipitates and N/S-solutions, respectively, in fertilizer and environmental legislations. This would stimulate their use and foster nutrient recovery technology implementation. A promising technology also exists in vibratory membrane filtration for the recovery of both N/K-concentrates and reusable water. However, the technical and economic performance of this technology for the treatment of digestate is to be studied at pilot- and full-scale. Further research on the physicochemical characteristics of recovered products, as well as on the agronomic, environmental, and economic impact of substituting conventional (chemical) fertilizers by bio-based alternatives is indispensable for effective marketing and application of these commodities as renewable fertilizers in agriculture.

Keywords: *anaerobic digestion; bio-based fertilizers; digestate; residuals valorization; sustainable agriculture; sustainable resource management.*

Résumé

La récupération de nutriments à partir de déchets biodégradables digérés et la confection de produits commercialisables sont devenues des tâches importantes des installations de digestion anaérobie afin de répondre aux exigences réglementaires et celles du marché, tout en produisant une source de revenus interne. Ainsi, le problème des déchets pourrait être transformé en une opportunité économique. L'objectif de ce chapitre était de fournir une vue d'ensemble et une comparaison critique des technologies disponibles et émergentes pour la récupération des nutriments présents dans le digestat et une classification des produits finaux en fonction de leurs propriétés fertilisantes. Basé sur l'état de la mise en œuvre, la performance technique ainsi que les aspects financiers, la précipitation/cristallisation de struvite, le stripage et l'absorption (ultérieure) d'ammoniac en utilisant un laveur à air acide ont été sélectionnés à titre des meilleures technologies disponibles applicables à grande échelle pour la récupération des nutriments comme produits fertilisants commercialisables. Les produits finaux résultants peuvent et devraient être classées comme N/P-précipités et N/S-solutions renouvelables, respectivement, dans les législations sur les engrais et celles sur l'environnement. Cela stimulerait leur utilisation et favoriserait la mise en œuvre des technologies pour la récupération des nutriments. Une technologie prometteuse supplémentaire, la filtration membranaire vibrante, permet également la production de N/K-concentrats et d'eau réutilisable en même temps. Cependant, la performance technique et économique de cette technologie devrait être étudiée davantage à l'échelle du pilote et à grande échelle. De plus amples recherches sur les caractéristiques physicochimiques des produits récupérés, ainsi que sur l'impact agronomique, environnemental et économique de la substitution des engrais conventionnels (chimiques) par des alternatives biologiques sont indispensables pour la commercialisation et l'application efficace de ces produits comme engrais renouvelables dans le secteur agricole.

Mots-clés: *agriculture durable; bio-engrais; digestat; digestion anaérobie; gestion durable des ressources; valorisation des résidus.*

2.1 Introduction

The focus of waste management has shifted from disposal and destruction to minimization, recovery, and recycling. Anaerobic (co-)digestion is an established, environmentally friendly, and efficient technology to convert animal manure, sewage sludge, organic biological food/industrial wastes, and/or energy crops into renewable energy and digestates rich in bio-available (macro)nutrients (Batstone and Jensen, 2011; Fehrenbach *et al.*, 2008; Mata-Alvarez *et al.*, 2014; Wilkinson, 2011). Despite its high potential, the further sustainable development of this technology is currently hindered, especially in high-nutrient regions, because the digestate cannot or only sparingly be returned to agricultural land in its crude form. This technical barrier is mainly posed by legislative constraints (strict nitrogen (N) and phosphorus (P) fertilization levels in the frame of environmental legislations), as well as practical (large volumes) and economic (high transportation and storage costs) complications (Chapter 1; Lemmens *et al.*, 2007). Further processing is required in order to concentrate and recover the nutrients as high-quality end products, thereby overcoming the obstacles related to the direct application of digestate.

The selection of the nutrient recovery technology (NRT) depends on the input waste stream characteristics and has a strong influence on the composition and properties of the resulting fertilizer end and by-products. Understanding the fundamentals of the existing processes is thus of paramount importance to sustainably create new high-quality fertilizers. Contemporary knowledge on NRTs and product quality is spread over a handful of academic and industrial experts. Reviews on the potential of particular technologies, e.g. struvite crystallization (Le Corre *et al.*, 2009), microalgae production (Fenton and Uallachain, 2012), membranes (Masse *et al.*, 2007), and on P recovery only (Desmidt *et al.*, 2015; Morse *et al.*, 1998), have been published, but an overall comprehensive overview is lacking. Moreover, a shortcoming of many research articles and reviews on nutrient recovery is the lack of attention given to the quality, value, and demand for the final nutrient product. Because of these flaws, the use of recovered bio-based fertilizers is currently not or not sufficiently encouraged in environmental legislations (mostly these products are classified as waste), although some of them have similar properties as conventional fossil reserve-based chemical fertilizers (see Chapters 3-6; Vaneeckhaute *et al.*, 2012, 2013a,b,c, 2014, 2015a, 2015b). In turn, these legislative bottlenecks hinder the marketing and efficient use of bio-based products.

The aim of this chapter is to provide a systematic overview and critical comparison of technologies for the recovery of macronutrients from digestate, as well as a classification of the resulting end products based on their fertilizer characteristics. The focus is on the recovery of N, P, and potassium (K), but parallel attention is given to sulfur (S), calcium (Ca), and magnesium (Mg). First, the general composition of digestate is briefly discussed (Section 2.2). In the core of this chapter, the technical and economic state-of-the-art of the existing technologies and those under development is explored (Section 2.3) and available information on product quality and value is compiled (Section 2.4.1-2.4.2). Qualitative and legislative requirements for effective fertilizer marketing, as well was market trends and prices are also discussed (Section 2.4.3-2.4.4). To this end, an intensive discussion platform was established involving existing international academic experts, administrations, and companies active in the field of nutrient recovery. A detailed literature review was also conducted. Financial and technical aspects for the most established technologies at full-scale were further investigated by requesting budget proposals using a predefined questionnaire to key technology suppliers in the field. The survey involved capital and operational costs, use of consumables, recovered product quality, and potential revenues, among other technical items. As such, this review chapter can provide the fundamental basis to classify and categorize recycled products in environmental and fertilizer legislations, thereby stimulating their economic valorization as marketable commodities. This, in turn, may foster the development and implementation of innovative nutrient recovery technologies.

2.2 Digestate characteristics

Digestate is the remaining product after biogas production in an anaerobic digester. It contains the non-digested recalcitrant organic fraction, water, micro- and macronutrients (Möller and Müller, 2012; Vaneeckhaute *et al.*, 2012, 2013b,c, 2014). The composition of digestate varies strongly according to the composition of the feedstock (biodegradable waste) that is digested. Hence, giving a standard composition of digestate is not possible. Because of this constraint, 213 digestates from different (co-)digestion plants in Flanders (Northern part of Belgium confronted with high nutrient pressure) were sampled and analyzed during four years (2008-2011; Vlaco, 2012). Product quality ranges are compiled in Table 2.1. Based on the results, a short overview of how physicochemical characteristics change during the digestion process and how the feedstock influences the digestate composition is given below.

Table 2.1 Composition (10th percentile, median, 90th percentile; No. of observations: 213) of unprocessed digestate (VLACO, 2012). w% = % on fresh weight.

Parameter	Unit	Unprocessed digestate		
		10-perc	median	90-perc
Dry weight	w%	4.98	8.70	12.0
Organic matter	w%	2.8	5.3	7.6
pH(H_2O)	-	8.1	8.3	8.6
Electrical conductivity	mS cm^{-1}	20	32	45
Total N	w%	0.17	0.42	0.75
NH_4-N	g L^{-1}	0.52	2.15	3.41
NO_3-N	mg L^{-1}	3.10	5.85	10.0
C:N-ratio	-	3.89	6.58	13.7
Total P_2O_5	w%	0.14	0.39	0.65
Total K_2O	w%	0.20	0.35	0.50
Total CaO	w%	0.16	0.30	0.55
Total MgO	w%	0.03	0.09	0.20

During anaerobic digestion, easily degradable organic matter is converted into methane (CH_4) and carbon dioxide (CO_2), while complex organic matter, such as lignin, remains in the digestate, thereby increasing its amount of effective organic carbon (OC). This is the OC that remains in the soil after one year and thus contributes to the humus built-up (average: 33.7 kg ton^{-1} in digestate vs. 20.0 kg ton^{-1} in pig manure on fresh weight (FW); Vlaco, 2012). As such, the digestate contains important soil-improving qualities (WPA, 2007). The percentage of organic dry matter can vary between 30 and 80 %, with lower values for increasing slurry fractions and higher values for increasing fractions of kitchen and garden waste (KGW). The average dry matter content of 100 % KGW was estimated at 21 % (WPA, 2007), whereas the median dry matter content of the 213 studied digestates amounted to 8.7 % (Table 2.1).

Due to the degradation of 70-90 % of volatile fatty acids (VFAs) during digestion, the pH is increased and odor emissions are significantly lower during the application of digestate on agricultural fields as compared to pig slurry (Bond *et al.*, 2012). The pH of slurry is on average 7.1 (WPA, 2007), whereas the median digestate pH amounts to 8.3 (Table 2.1). However, the higher pH causes an increased risk for NH_3 volatilisation. This is why injecting the digestate is strongly advised (WPA, 2007).

Next, during the digestion process, organically bound N is released as ammonium (NH_4^+), which is directly available for crop uptake. The higher the share of NH_4-N, the higher the efficiency of the digestate as a N fertilizer. An input stream with a high N level is pig slurry (average: 6.78 kg N ton^{-1} FW), in comparison to cattle slurry (3.75 kg N ton^{-1} FW) and maize (4.00 kg N ton^{-1} FW) (WPA, 2007). The Vlaco (2012) data showed a median total N content of 4.2 kg N ton^{-1} FW (Table 2.1). When digesting raw pig slurry, more than 80 % of the N becomes available as NH_4^+. However, for digestates produced from organic waste such as KGW, the share of NH_4^+ is often not higher than 44-47 %, which is even lower than the value for raw pig slurry (± 60 %). Digestates with a low NH_4-N content are mostly originating from organic food/industrial wastes, including KGW (WPA, 2007).

Furthermore, the total P content of the input streams is not changed during the digestion process, but the organically bound P becomes available for the plant during digestion. Pig slurry has a high P_2O_5 content of roughly 5 kg ton^{-1} FW. By adding co-products to pig slurry the P_2O_5 content of the digestate is somewhat lowered. The 213 studied digestates showed a median total P_2O_5 content of 3.9 kg ton^{-1} FW (Table 2.1).

Also the total contents of K, Ca, Mg, and heavy metals are not altered during anaerobic digestion. K, Ca, and Mg become soluble. Zinc (Zn) and copper (Cu) contents in the digestate can become critically high, especially during the digestion of 100 % pig slurry, since the dry matter content decreases. This can hinder the beneficial reuse of recovered products, although both elements are essential micronutrients for healthy plant growth (Hillel, 2008).

Finally, impurities such as weed seeds and pathogens can be killed off during the digestion process (Bond *et al.*, 2012). The extent to which this inactivation is sufficient depends entirely on the temperature and residence time in the digester and on the type of organism.

2.3 Technology overview

2.3.1 Three-step framework for nutrient recovery

Before going into the details of the nutrient recovery technologies for digestate treatment, one should be aware that anaerobic digestion itself usually constitutes an intermediate step, among other potential technologies, in the processing treatment train. Indeed, from a technological perspective, nutrient recovery from biodegradable waste for reuse as concentrated fertilizer products can be represented by a three-step framework (Fig. 2.1). Note that not all recovery systems require all three components.

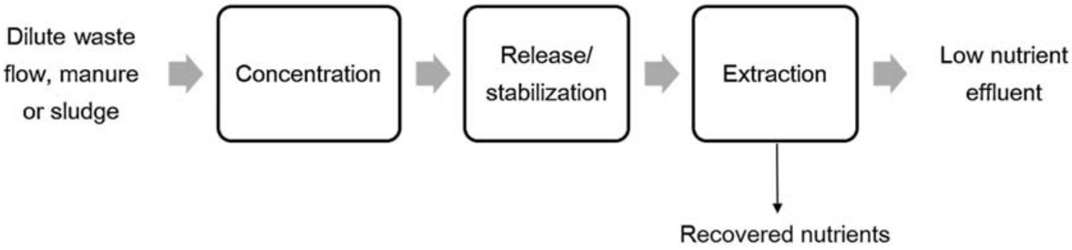


Figure 2.1 Three-step framework for nutrient recovery as concentrated fertilizer products.

First, a concentration step can be applied to increase the nutrient content (N → 1000 mg L^{-1} and P → 100 mg L^{-1}) of the waste stream. Established technologies for this purpose are enhanced biological P removal (EBPR) (Lesjean *et al*., 2003; Pastor *et al*., 2008), adsorption/ion exchange (Jorgensen and Weatherley, 2003), the use of biomass such as algae, duckweed, and purple non-sulfur bacteria (Gonzalez-Fernandez *et al*., 2011; Xu and Chen, 2011), chemical precipitation (De Haas *et al*., 2000; Pratt *et al*., 2012), and nanofiltration/reversed osmosis (Masse *et al*., 2007). Next, a nutrient release/stabilization step may be used to generate a low flow stream with high nutrient availability. Based on the digestate characteristics presented above (Section 2.2), anaerobic digestion can be categorized as a nutrient release/stabilization step. Other potential technologies for this purpose are aerobic digestion (Liu *et al*., 2010), thermolysis (Azuara *et al*., 2013), sonication (Castrillon *et al*., 2011), microwave treatment (Tyagi and Lo, 2013), or chemical extraction (Carrere *et al*., 2010).

Finally, the nutrient extraction or recovery step may take place. To date, there is no straightforward definition of a nutrient recovery technology (NRT). **In this review we consider an NRT as a process that: 1) creates an end product with higher nutrient concentrations than the crude digestate (= concentrated product that contains both minerals and organics), or 2) separates the envisaged nutrients from organic compounds, with the aim to produce an end product that is fit for use in the chemical or fertilizer industry or as a chemical fertilizer substitute.** The breakthrough of such technologies would make it possible to reuse reactive nutrients locally and close nutrient cycles in a cross-sectorial cradle-to-cradle approach (Chapter 1: Fig. 1.2). The existing and developing NRTs for digestate processing are further reviewed and discussed in the sections below. The preceding concentration and alternative nutrient release/stabilization steps are out of scope of the present review, and will thus not be studied. Reference is made to Mehta *et al.* (2015) for a technology description of such processes.

2.3.2 Digestate processing technologies

In the past decade, a diverse range of technologies that can be applied for digestate processing has been developed. However, certainly not all of them can be considered as an NRT. An overview of existing digestate processing technologies is presented in Figure 2.2. The technologies delineated as NRT are indicated in shaded boxes. It must be noted that these technologies could also be applied on undigested manure, sludge, and wastewater. However, as indicated above, implementing anaerobic digestion as an intermediate step can highly improve the overall process efficiency.

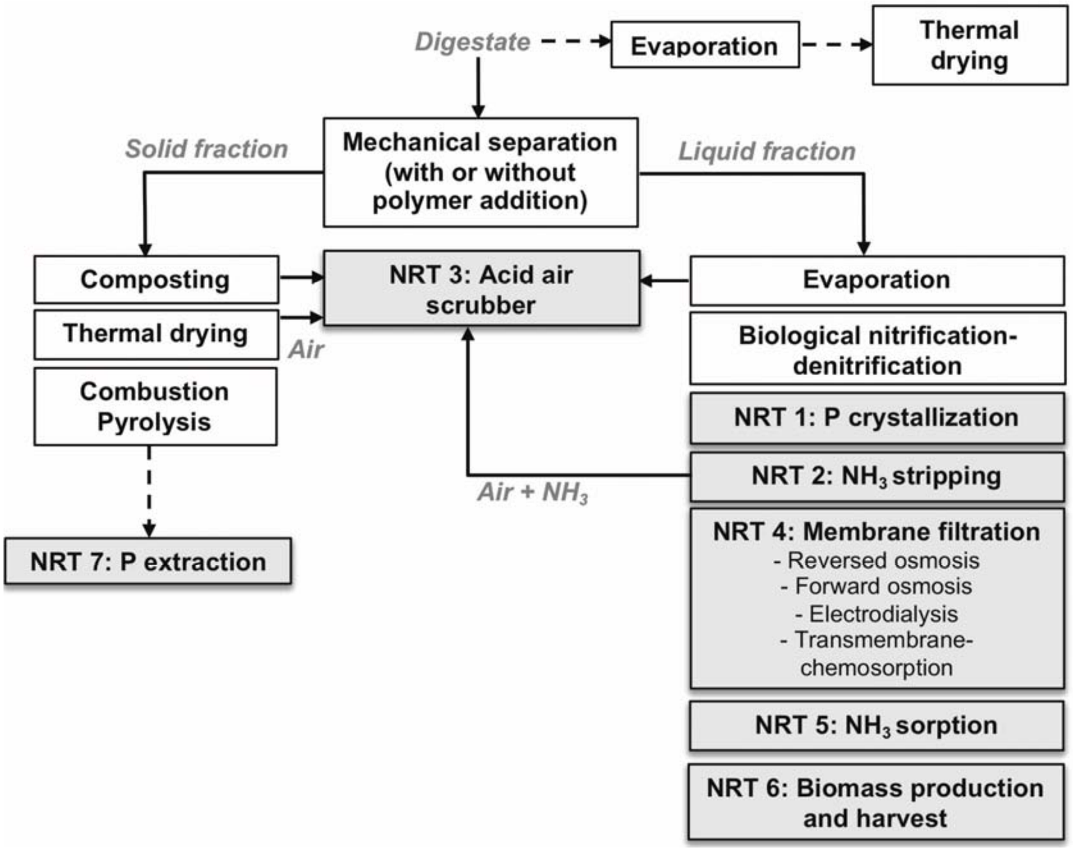


Figure 2.2 Schematic overview of digestate processing technologies.
Shaded boxes: nutrient recovery technology (NRT).

In general, digestate processing starts with a mechanical separation into a liquid fraction and solid or thick fraction (Hjorth *et al.*, 2010). Most of the N and K end up in the liquid fraction, while most of the recalcitrant organic matter, P, Ca, and Mg is recovered in the thick fraction (Chapter 3; Vaneeckhaute *et al.*, 2012). From literature, the technologies for nutrient recovery from the liquid fraction available or under development today are: 1) chemical crystallization (Le Corre *et al.*, 2009; Uludag-Demirer *et al.*, 2005), 2) gas stripping and absorption (Bonmati and Flotats, 2003; Gustin and Marinsek-Logar, 2011; Liao *et al.*, 1995), 3) acidic air scrubbing (Bonmati and

Flotats, 2003; Melse and Ogink, 2005; Melse *et al.*, 2009), 4) membrane separation (Kertesz *et al.*, 2010; Ledda *et al.*, 2013; Waeger *et al.*, 2010), 5) ammonia sorption (Guo *et al.*, 2013; Pelin *et al.*, 2013; WRAP, 2012), and 6) biomass production and harvest (Gonzalez-Fernandez *et al.*, 2011; Xu and Shen, 2011). For the thick fraction, only P extraction from ashes produced by combustion or pyrolysis can be considered a potential NRT (Adam *et al.*, 2009; Schoumans *et al.*, 2010). However, as it is critically questioned whether incineration is a sustainable technology, the interest is growing to maximally extract nutrients from the crude digestate, thereby eliminating the solid-liquid separation step or producing an organic, P-poor thick fraction. For extractive nutrient recovery to become a viable option, the process must have an equivalent treatment efficiency as conventional treatment, the process must be cost-effective, the process must be simple to operate and maintain, and most importantly, **there must be a market for the recovered nutrient products**. The technical and economic state-of-the-art of the above-mentioned NRTs is discussed below. Product quality and fertilizer markets are discussed in section 2.4. All costs are expressed in euros (€) and *Canadian dollar (CAD)* (€ 1 ≈ *1.415 CAD*; November 2014).

2.3.3 Phosphorus precipitation and crystallization (NRT 1)

2.3.3.1 Chemical struvite recovery

Nutrient recovery through P precipitation and crystallization is a mature technology, mostly involving the addition of Mg ($MgO/MgCl_2$) to a solution containing soluble PO_4-P (ortho-P) and ammonium, thereby increasing the pH to 8.3-10 and inducing the precipitation of struvite, $MgNH_4PO_4{:}6H_2O$ (Le Corre *et al.*, 2009). The process has been implemented at full-scale installations for wastewater, (digested) sludge and manure treatment, as well as at pilot-scale for the treatment of crude digestate. The most established processes commercially available today are: i) *AIRPREX*, Berliner Wasserbetriebe (Germany, DE), ii) *ANPHOS,* Colsen (the Netherlands, NL), iii) *CAFR,* NALVA (DE), iv) *Ceres*, Ceres Milieutechniek (Belgium, BE), v) *NuReSys*, Akwadok (BE) (Desmidt *et al.*, 2012), vi) *Nutritec*, Sustec (NL), vii) *Pearl,* Ostara (Canada, CA), viii) *Phosnix*, Unitika (Japan, JP), ix) *PHOSPAQ,* Paques (NL) (Abma *et al.*, 2010), and x) *PRISA*, Aachen University (DE) (Montag *et al.*, 2007). Moreover, in Gelderland (NL) four installations are available for the production of K-struvite ($KMgPO_4{:}6H_2O$) from calf manure (Graeser *et al.*, 2008). These processes have the ability to remove and recover over 80-90 % of the soluble P in the waste(water) flow, yet only 10-40 % of the NH_4-N can be captured (Le Corre *et al.*, 2009). Crystal/pellet sizes range from 0.5 mm to 5 mm and above, depending on the final end-use. The design involves fluidized bed reactors and continuously stirred tank reactors.

At present, struvite recovery can be economical on side streams from wastewater treatment with a P load of more than 20 % by weight, as it has the potential to reduce operational costs related to energy and chemical (iron (Fe) / aluminium (Al)) consumption and nuisance struvite formation in piping/equipment. Meanwhile, a high-quality, slow-release granular fertilizer with agricultural reuse perspectives is produced (Latifian *et al.*, 2012; Ryu *et al.*, 2012; Shu *et al.*, 2006; WERF, 2010). Assuming that a treatment plant can recover 1 kg of struvite from 100 m^3 of wastewater (Münch and Barr, 2001), Shu *et al.* (2006) estimated chemical savings for P recovery from digester supernatants at € 0.19 *(0.27 CAD)* d^{-1} (compared to alum), savings from reduced sludge handling at € 0.002 *(0.003 CAD)* d^{-1}, from reduced sludge disposal at € 0.023 *(0.033 CAD)* d^{-1}, from reduced cleaning of struvite deposits at € 3.8-19.2 *(5.4-27.1 CAD)* d^{-1}, and savings from reduced landfilling at € 0.002 *(0.003 CAD)* d^{-1}. As such, the loss of producing struvite could amount to € 0.05 *(0.07 CAD)* d^{-1}, while the gain for the treatment plant can be € 0.52 *(0.74 CAD)* d^{-1} (Shu *et al.*, 2006). Hence, assuming a struvite plant would cost € 1.4 *(2.0 CAD)* million, the payback period of a plant processing ± 55,000 m^3 d^{-1} of waste could be less than five years according to this study (Shu *et al.*, 2006).

However, operational costs and payback times are highly dependent on the input composition (e.g. available P, Mg, and pH) as it determines the chemical (NaOH, Mg) and energy costs, which can range between € 200-75,000 *(282-106,000 CAD)* y^{-1} (Jaffer *et al.*, 2002). Dockhorn (2009) estimated operating and maintenance costs for a plant treating 350,000 person equivalents (PE) at € 2,800 *(3,960 CAD)* ton^{-1} struvite if the PO_4-P concentration is 50 mg L^{-1}, and € 520 *(735 CAD)* ton^{-1} if the PO_4-P concentration is 800 mg L^{-1}. Battistoni *et al.* (2005a,b) estimated operating costs at € 0.19-0.28 *(0.27-0.40 CAD)* m^{-3} digestate. Based on budget proposals provided by the above-mentioned suppliers in the context of the present review, capital costs may range from € 2,300-24,500 *(3,250-34,600 CAD)* kg^{-1} P d^{-1}, while revenues from struvite valorization in agriculture range from ± € 45 *(64 CAD)* ton^{-1} struvite in Belgium (NuReSys, Waregem, BE, personal communication 2013) to ± € 109-314 *(154-444 CAD)* ton^{-1} in Australia (Doyle and Parsons, 2002), and ± € 250 *(353 CAD)* ton^{-1} in Japan (Kohler, 2004). Values of € 736 *(1,041 CAD)* and € 1,393 *(1,970 CAD)* ton^{-1} have also been reported (Dockhorn, 2009). As such, overall profits of struvite production may range from € -7,800 *(-11,030 CAD)* y^{-1} (loss) to € 89,400 *(126,400 CAD)* y^{-1} (gain) (Münch and Barr, 2001).

Although worldwide some utilities have installed these systems, the uptake of this technology has not been widespread due to market, regulatory, and site-specific conditions. Also, important technical challenges remain in the further reduction of chemical requirements, the guarantee of a pure product, as well as the stable and controlled production of struvite. If struvite would be recovered only from municipal wastewater treatment plants worldwide, 0.63 million tons of P (as P_2O_5) could be harvested annually (Shu *et al.*, 2006).

However, an important constraint is that in conventional digestate treatment anno 2014 (Fig. 2.2) most of the P is lost in the thick fraction after solid-liquid separation. Hence, the overall P recovery potential from digestate as struvite is limited to the remaining soluble P in the liquid fraction. In recent years, methods to improve the release of P in the liquid fraction, e.g. microwave treatment and/or acid extraction, are therefore gaining increased attention (see Chapter 7). This is especially interesting in P saturated regions so as to recover more P as struvite from the (acidified) liquid fraction, while improving the local valorization potential of the (P-poor) organic thick fraction.

2.3.3.2 Electrochemical struvite recovery

Researchers at the Fraunhofer Institute for Interfacial Engineering and Biotechnology in Germany have patented an electrochemical process to precipitate struvite without chemical addition and with low energy consumption (70 Wh m^{-3}) (IGB, 2012). A mobile pilot plant using an electrolytic cell consisting of an inert cathode and a sacrificial Mg anode is currently in the test phase. The electrolytic process splits the water molecules into hydroxide (OH^-) ions and hydrogen gas (H_2) at the cathode. Oxidation takes place at the anode: Mg^{2+} ions are released into the solution and react with P and N to form struvite. At lab-scale, P removal efficiencies above 99 % were achieved. No further economic or technical information is available to date.

2.3.3.3 Bio-electrochemical struvite recovery

An energy-efficient method of concurrent H_2 and struvite production was investigated at Pennsylvania State University (USA), based on bio-electrochemically driven struvite crystallization at the cathode of a single chamber microbial electrolysis struvite precipitation cell (Cusick and Logan, 2012). In a microbial electrolysis cell, microorganisms convert organic and inorganic matter into electrical current at a significantly lower potential (minimum of 0.2 V when bacteria are used) than that needed for splitting water in electrochemical struvite precipitation (Section 2.3.3.2). At lab-scale, P removal efficiencies ranged from 20 to 40 %, with higher removals obtained using mesh cathodes than with flat plates. Overall energy efficiencies based on substrate and electricity inputs were high (73±4 %) and not dependent on the applied voltage. However, the technical and economic feasibility of scaling up this technology is challenging. To date, neither pilot nor full-scale installations have been implemented and tested.

2.3.3.4 Calcium phosphate recovery

Next to Mg, calcium hydroxide ($Ca(OH)_2$) can also be added to the liquid fraction in order to increase the pH (> 10.0) and temperature (70 ℃), thereby inducing P precipitation as $Ca_5(PO_4)_3OH$ (hydroxyapatite) or $CaHPO_4{:}2H_2O$ (brushite). The reaction is fast (5 min), but often preceding CO_2 stripping must be applied to avoid unwanted calcium carbonate ($CaCO_3$) precipitation. Examples of commercial calcium phosphate precipitation processes are: i) *Crystalactor*, DHV Water (NL) (Eggers *et al.*, 1991), ii) *FIX-Phos,* TU DA (DE), iii) *Kurita*, Kurita Water Industries (JP), iv) *Phostrip*, Tetra Technologies inc. (USA) (Szpyrkowicz and Ziliograndi, 1995), and v) *P-Roc*, Kit-CMM (DE) (Berg *et al.*, 2007). Removal efficiencies of 80-100 % P have been achieved, but 50-60 % is more typical. Based on a market demand in the framework of this study to the suppliers mentioned above, capital costs may range between € 2,300-2,900 kg^{-1} P d^{-1}. Operational costs are mainly determined by the amount of $Ca(OH)_2$ required, which on its turn highly depends on the input waste characteristics. Finally, Quan *et al.* (2010) reported on the ability to couple $CaNH_4PO_4{:}4H_2O$ precipitation and ammonia stripping in a water sparged aerocyclone (WSA) in order to recover both P and N. To date, this path has only been examined at lab-scale, but further research on this methodology seems interesting.

2.3.4 Ammonia stripping and absorption (NRT 2)

Stripping of ammonia (NH_3) involves the physical transfer of NH_3 from the aqueous phase (waste stream) to a gas phase, mostly in a packed bed tower. The gas is then transferred to an air scrubber (Section 2.3.5), where mass transfer and absorption of the NH_3 from the gas to a liquid phase, mostly sulfuric acid (H_2SO_4), takes place in order to form and recover a concentrated solution of ammonium sulfate ($(NH_4)_2SO_4$; AmS) as an end product (Liao *et al.*, 1995; USEPA, 2010). AmS is an inorganic salt, which could be reused as a marketable fertilizer rich in direct available macronutrients, N and S, thereby providing a valuable substitute for chemical fertilizers based on fossil resources (Chapters 4-5; Vaneeckhaute *et al.*, 2013b,c, 2014). Alternatively, ammonium nitrate (NH_4NO_3) fertilizer (by addition of HNO_3; Udert *et al.*, 2014), a concentrated ammonia solution (by addition of liquid NH_3), or other ammonia salts can be produced, depending on local legislations and options for land application. Ammonia stripping is developed at full-scale and sometimes implemented for wastewater treatment. The implementation of this technology for the treatment of N-rich digestate and manure is on the rise.

Commercially available stripping technologies for (digested) sludge and manure treatment are: i) *AMFER*, Colsen (NL), ii) *ANAStrip*, GNS (DE), and the (untitled) stripping processes developed by the manufacturers: iii) Anaergia (Canada, CA), iv) Branch Environmental Corp (USA), v) Europe Environnement (France, FR), and vi) RVT Process Equipment (DE). Theoretically, these systems may achieve NH_3 recovery efficiencies up to 98 %, but they are generally operated to reach 80-90 % recovery in order to reduce the operating costs. At present, most stripping units implemented at full-scale focus on the production of AmS fertilizer. The AmS content in the recovered solution ranges from ± 25 % AmS (*ANAStrip*, GNS) and 30 % AmS (Branch Environmental Corp) to 38 % AmS (Anaergia; RVT Process Equipment) and 40 % AmS (*AMFER*, Colsen; Europe Environnement).

Capital costs of stripping are relatively low compared to biological activated sludge (AS) systems for nutrient removal and depend on the method used for pH-increment. This can occur i) chemically by use of base, mostly sodium hydroxide (NaOH) (Branch Environmental Corp; Europe Environnement; RVT Process Equipment), or ii) physically by simultaneous stripping of CO_2 (Anaergia; Colsen), optionally in combination with the addition of low-quality gypsum ($CaSO_4$) for parallel recovery of $CaCO_3$ (GNS). Operational costs depend a lot on the operational temperature, pH, and liquid flow rate. For a 90 % NH_3 recovery efficiency from leachate at a temperature of 70 ºC, a pH of 11, and a flow rate of 70 m^3 h^{-1}, overall costs are estimated at ± € 8.1 *(11.5 CAD)* m^{-3}, while at a temperature of 30 ºC this would be ± four times less, i.e. € 2.0 *(2.8 CAD)* m^{-3} (Collivignarelli *et al.*, 1998).

A comparison of budget proposals provided by the above suppliers for NH_3 stripping and absorption systems treating a digestate flow of 800 m^3 d^{-1} at 2,400 mg NH_4-N L^{-1} (90 % recovery) resulted in a capex ranging from ± € 500,000 *(710,000 CAD)* to € 1.58 *(2.23 CAD)* million if the pH-increase is conducted chemically, and from € 3.5 *(5.0 CAD)* million to € 11-15

(16-21 CAD) million if the pH-increase is established physically. Electricity consumption for this case was estimated by the suppliers at 127-400 kWh_{el} h^{-1} (1.54-12 kWh_{el} m^{-3}), heat consumption at 2,115-2,333 kWh_{th} h^{-1} (62-69 kWh_{th} m^{-3}; note: ± 50 % could be recovered within the process), and H_2SO_4 (concentrated at 95-97 %) consumption at 5.5-6.8 ton d^{-1} or 7.0-10 kg m^{-3} digestate. If NaOH is used for pH-increase, it consumption would amount to 6.0-6.5 kg m^{-3}. As such, operational costs range between € 1.4 and € 2.5 *(2.0-3.5 CAD)* million y^{-1} depending on the system, equivalent to € 4.5-8.6 *(6.4-12.2 CAD)* m^{-3} of digestate.

Currently, advanced processes for biological removal of NH_3, such as deammonification via Anammox (Magri *et al.*, 2013), are often still cheaper (depending on the technology provider). However, as stripping could (partially) replace a nitrification-denitrification step, additionally remove odorous compounds and dust particles, and produce a marketable end product, it is expected that this technology can be competitive, especially in regions where N demand is high (WERF, 2010). Where commercialization of the AmS-solution is possible, revenues currently range from € 90 to 120 *(130-170 CAD)* ton^{-1} FW, which under optimal process conditions should largely compensate the operational costs. Moreover, the higher process stability (e.g. to input variation, freezing conditions, etc.), lower surface requirements (for the above case: ± 1,500 m^2), higher ability for treatment of high N flows, immediate start-up, and ease of automation are all drivers for implementation of stripping units instead of conventional biological systems.

The major technical bottlenecks observed to date in NH_3 stripping are scaling and fouling of the packing material, and the consequent high energy and chemical requirements (Bonmati and Flotats, 2003; Lemmens *et al.*, 2007; Quan *et al.*, 2010). To avoid scaling, one can install a lime-softening step before stripping, which removes a large part of the Ca, Mg, carbonic acids and carbonates, and increases the pH. In case of high buffering capacity, a preceding CO_2 stripper might also be economical. To avoid fouling, it is important that during preceding solid-liquid separation as many suspended solids as possible are retained in the solid fraction. Nonetheless, it is unavoidable that the packing material will have to be cleaned periodically. Because of these constraints, some of the above manufacturers have developed a stripping process without internal packing (Anaergia; Colsen). As such, the process developed by Anaergia would be capable of handling waste flows containing up to 8-9 % total suspended solids (TSS). Note that both technologies also operate without any chemical addition. Hence, although capital costs are higher (see above), in terms of sustainability and operational costs, these processes are probably the best available options to date.

Furthermore, a combination of the NH_3 stripping technology and struvite precipitation was studied by Quan *et al.* (2010). Both processes were taking place simultaneously in a WSA reactor at lab-scale. The wastewater containing NH_3 is pumped into the water jacket and then sparged towards the centerline of the WSA through the porous section of the inner tube wall, thus forming a large gas-liquid contact area. The transfer of NH_3 from liquid to air is high (> 97 %) due to the very small amount of liquid. The authors claim that the WSA, in comparison to the traditionally used packed towers, is characterized by a good mass transfer performance and self-cleaning function. The technology would therefore be suitable for air stripping of wastewaters containing suspended particles at a temperature of 30 °C and a pH > 11. However, to date, no pilot nor full-scale application is available.

Finally, the Dutch company Dorset developed a low-energy (< 1 kW m^{-3}) NH_3 stripping system for manure and digestate treatment without air recirculation or ventilation. The system consists of rotating disks that are partly submerged in either the liquid manure or the receiving H_2SO_4-solution. The NH_3 coming from the gas phase at the first disk is absorbed in H_2SO_4 at the other disk. Recoveries of ± 80 % NH_3 are obtained at pilot-scale (Dorset, 2014).

2.3.5 Acidic air scrubbing (NRT 3)

Acidic air scrubbing mostly concerns a packed tower in which sulphuric acid (H_2SO_4) is sprayed with nozzles over the packing material and treatment air is blown into the tower in counter-current (Melse and Ogink, 2005; USEPA, 2000). As is the case for NH_3 stripping and absorption (Section 2.3.4), mostly ammonium sulfate ($(NH_4)_2SO_4$; AmS) is produced and the wash water is recycled until it is saturated and the removal efficiency of NH_3 cannot be guaranteed anymore. At that point, the AmS-solution should be removed and fresh H_2SO_4 added.

The technology is used at full-scale at anaerobic digestion and sludge/manure processing plants. Examples of well-established technology developers are Dorset Farm Systems (NL/USA), Envitech (CA), and Inno+ (NL). Average NH_3 recovery efficiencies of 91-99 % are found in literature (Manuzon *et al.*, 2007; Melse and Ogink, 2005; USEPA, 2000). Investment costs (in case of a new installation for air treatment of one stable) are estimated at € 18 *(25 CAD)* kg^{-1} NH_3 recovery, whereas exploitation costs (including variable and fixed costs) of an acidic air scrubber are estimated at € 6-7 *(8.5-10 CAD)* kg^{-1} NH_3 recovery (Arends *et al.*, 2008; Melse and Willers, 2004). As these costs are expected to reduce with 50 % (investment) and 14-25 % (exploitation) for large-scale projects (Melse and Willers, 2004; Melse and Ogink, 2005), the installation is economically viable at many waste-processing plants.

The main operational costs can be attributed to the energy (0.057 kWh 1,000 m^{-3} air) and acid (minimum 1.5 L H_2SO_4 at 98 % kg^{-1} NH_3 recovery; note: depends on AmS concentration) requirements (Melse and Willers, 2004). However, power inputs depend a lot on the reactor type, ranging from 3.8 atm cm^3 air s^{-1} for spray-chambers to 260 atm cm^3 air s^{-1} for venturi scrubbers (Cooper and Alley, 2011). An interesting advantage of an acidic air scrubber is that odors, dust particles, and water vapour can also be removed. Technical bottlenecks are mainly related to corrosion problems. The reject AmS-solution is already recognised in Flanders and the Netherlands as a mineral fertilizer in environmental and fertilizer legislations. Requirements for recognition in Quebec are discussed in Section 2.4.4. Nevertheless, marketing is still hindered due to its variable N and S content (30-100 kg N ton^{-1}; 61-100 kg S ton^{-1}), acidic and corrosive features (pH 2.5-7; high salt content: 100-150 mS cm^{-1}), as well as social perception and farmers' distrust in its fertilizer properties (Chapters 4-5; Vaneeckhaute *et al.*, 2013b,c, 2014). It should be noted that the product properties are highly dependent on the technology provider, not only in terms of AmS content (see above), but also in terms of pH. Manufacturers delivering a fertilizer product at relatively high pH, suitable for direct application in agriculture, are Anaergia (pH 5.5) and RVT Process Equipment (pH 6-7).

2.3.6 Membrane filtration (NRT 4)

2.3.6.1 Pressure-driven membrane filtration

Pressure-driven membrane filtration, involving microfiltration (MF), ultrafiltration (UF), and/or reversed osmosis (RO), is an established technology in wastewater treatment. It has, however, not yet proven to be a valuable option for the treatment of digestate, manure, and sludge. Only a few commercial pilots have been installed at full-scale manure and digestate processing facilities, mostly on a short-term basis because of excessive operational costs. Nevertheless, the produced membrane filtration concentrates are an interesting nutrient source, which could potentially be reused as chemical fertilizer substitutes rich in N and K (Chapter 3; De Hoop *et al.*, 2011; Ledda *et al.*, 2013; Vaneeckhaute *et al.*, 2012; Velthof, 2011). Examples of manufacturers for slurry filtration systems are: i) A3 Watersolutions (DE), ii) AquaPurga International (NL), iii) New Logic (CA), iv) VP Systems (NL), and v) Wehrle Umwelt GmbH (DE). Operating temperatures range from 10-40 °C, while the pH is usually between 6 and 8. RO has also been applied at full-scale in combination with NH_3 stripping of liquid digestate (*Biorek Process*, BIOSCAN (Denmark, DK); Norddahl and Rohold, 1998).

In reality, the cost of an RO filtration system for manure and digestate treatment is difficult to determine because it depends on the frequency of membrane cleaning and replacement, as well as the permeate and concentrate end-use, which on its turn are site and region specific (Masse *et al.*, 2007). Gerard (2002) estimated the cost of manure treatment using two RO cycles at € 12 *(17 CAD)* m^{-3} for a 2 m^3 d^{-1} flow at a pilot-scale installation in France. At a pig farm in Canada, the company Purin Pur estimated the costs of an UF-RO treatment train at € 4.22 *(5.97 CAD)* m^{-3} in 2000 (Charlebois, 2000). In 2009-2010, a large pilot project was established in the Netherlands, in which, with authorization of the European Commission, the RO concentrate of eight different manure/digestate processing facilities was applied to agricultural fields. The costs of the installations plus the costs of transporting the final products amounted to € 9-13 *(13-18 CAD)* ton^{-1} manure/digestate, which was economically feasible for seven of the eight installations as the price received for treating the manure at that time amounted to € 11-13 *(7.8-9.2 CAD)* ton^{-1} waste (De Hoop *et al.*, 2011; Velthof, 2011). The economic value of the RO concentrates is estimated at € 6.1±1.1 *(8.6±1.6 CAD)* ton^{-1} FW (Chapter 3; Vaneeckhaute *et al.*, 2012), while the average price paid by farmers during the pilot project was € 1.25 *(1.77 CAD)* ton^{-1} in 2009 and € 1.19 *(1.68 CAD)* ton^{-1} in 2010. Yet, the standard deviation was high (Velthof, 2011). No other prices for membrane concentrate marketing have been reported to date.

The biggest technical problem stated in membrane filtration is clogging and fouling of the membrane, resulting in significant chemical and energy requirements (Kertesz *et al.*, 2010;

Waeger *et al.*, 2010). The equivalent energy requirement for an RO system is estimated at 4-6 kWh m^{-3} (Moon and Lee, 2012; Semiat, 2008). To reduce cleaning requirements, vibrating (60-90 Hz) shear enhanced processing (VSEP) has been used for manure purification at pilot-scale (Johnson *et al.*, 2004; New Logic, 2008). Although this technology may provide an interesting solution, little data are available on the system performance in relation with the energy consumption and treatment costs. The energy consumption per vibration is estimated at 8.83 kW (Johnson G., New Logic Inc., Ontario, CA, personal communication 2011), while the energy consumed by the recirculation pump is estimated at 9.4 kWh m^{-3} of permeate in a 154 m^2 membrane area unit (VSEP series i-10; Akoum *et al.*, 2005). This could be reduced to 6 kWh m^{-3} if plane ceramic membranes are used. Energetic calculations based on these data indicate that large VSEP units will consume significantly less energy per m^3 of permeate than traditional cross-flow filtration. Nevertheless, energy consumption and economic performance remain critical points of attention in the evaluation of membrane technologies for nutrient recovery. As information on the technical performance of this technology for the treatment of digestate is lacking, the use of a VSEP filtration unit in a full-scale digestate treatment train will be further studied in Chapter 3 (Vaneeckhaute *et al.*, 2012).

Different alternative technologies to improve the performance of membrane filtration in terms of chemical and energy requirements, as well as operational costs are currently under development. The most studied examples are forward osmosis (Section 2.3.6.2; Chen *et al.*, 2012b; Li *et al.*, 2013; Sant'Anna *et al.*, 2012; Zhao *et al.*, 2012), electrodialysis (Section 2.3.6.3; Ippersiel *et al.*, 2012; Mondor *et al.*, 2008), and transmembrane chemosorption (Section 2.3.6.4; Sustec, 2014).

2.3.6.2 Forward osmosis (FO)

During the last couple of years, there has been a global increase in interest in forward osmosis (FO) as opposed to RO (Zhao *et al.*, 2012). Similar as in RO, a semi-permeable membrane is used in FO, but no external pressure is required. The permeate flow is obtained by creating a difference in osmotic pressure between the liquid waste stream and a draw solution such as sodium chloride (NaCl) on the other side of the membrane. Through water extraction, the liquid waste stream is concentrated and the draw solution diluted. The draw solution should then again be concentrated through water removal.

FO is still under development and could be an interesting technology for use in domestic wastewater treatment (Chen *et al.*, 2012b), food processing (Sant'Anna *et al.*, 2012), and seawater desalination (Li *et al.*, 2013), but also for the concentration of digestate. The potential advantages of FO are its low energy consumption, low fouling propensity, reduced or easy cleaning, low costs, high salt rejection, and high water flux (Sant'Anna *et al.*, 2012). However, to date, the equivalent energy requirement ranges from 3 to 8 kWh m^{-3} (Moon and Lee, 2012). Hence, it is too early to say that the FO technique is capable enough to compete with or displace the prevalent membrane filtration techniques, primarily RO. The biggest technical challenge is to find a reliable and economic way to concentrate the draw solution. Researchers expect that the further development of FO to a reliable system, applicable at full-scale for manure and digestate treatment, will take another five to ten years (Zhao *et al.*, 2012).

2.3.6.3 Transmembrane chemosorption (TMCS)

Transmembrane chemosorption (TMCS) is a hybrid membrane process, which was developed in pig slurry treatment systems in the Netherlands in order to recover N from liquid waste streams as a concentrated $(NH_4)_2SO_4$ solution (several 100 g NH_4^+ L^{-1}; Sustec, 2014). By increasing the pH, NH_3 is brought into the gas phase, diffuses through a hollow-fibre membrane with gas-filled pores, and is captured at the other side of the membrane in a sulphuric acid solution (Rulkens *et al.*, 1998). Compared to stripping, TMCS requires a very small amount of energy, less than 1 kWh m^{-3} (Sustec, Wageningen, NL, personal communication 2013). The company Sustec works on the further development of this technology. Pilot tests are carried out at Varkens Innovatie Centrum in Sterksel (NL) and at the pig farm Kempfarm (Leunen, NL). In these installations recovery efficiencies of 99 % NH_3 are achieved. Norddahl *et al.* (2006) obtained NH_3 recovery efficiencies of 70 % when using similar membrane contactors for the treatment of digestate.

2.3.6.4 Electrodialysis (ED)

During electrodialysis (ED), NH_3 in the diluate solution is transferred by electromigration to an adjacent solution by an ion-exchange membrane under the driving force of an electrical potential. This means that the main ionic compounds in the liquid digestate (= the diluate cells), i.e. NH_4^+, K^+, and bicarbonate (HCO_3^-), are transferred and concentrated. Mondor *et al.* (2008) suggested that the combined use of ED and RO membranes to recover and concentrate NH_4^+ is potentially interesting (83 % NH_3 recovery at lab-scale), but the process must include a mechanism to trap volatilized NH_3 (17 %). Ippersiel *et al.* (2012) used ED as a pre-treatment to NH_3 stripping without pH modification for the treatment of swine manure. The maximum achievable total NH_4-N concentration in the concentrate solution (seven times the input concentration) was limited by water transport from the manure to the concentrate compartment. This was attributed to the transfer of solvated ions and osmosis. To date, ED has only limited application at full-scale and it mostly concerns small installations. Extensive testing is required to gain further insights into the process operation, certainly for the treatment of complex waste matrices as manure and digestates. At present, especially the high energy consumption, i.e. 3.25-3.60 kWh kg^{-1} NH_4-N (Mondor *et al.*, 2008, 2009; Ippersiel *et al.*, 2012) and 1.2-1.5 kWh kg^{-1} K (Decloux *et al.*, 2002), and strongly variable costs for membranes, electrodes, and casings are important bottlenecks for implementation (Verliefde A., Ghent University, Belgium, personal communication 2013).

2.3.7 Ammonia sorption (NRT 5)

A number of materials may be used to selectively adsorb ammonium (NH_4^+) from waste flows. These materials include zeolites, clays, and resins. Adsorption is carried out in a packed column. Once the adsorption media is saturated, the column is taken offline and is regenerated to recover the NH_4^+. Regeneration can be achieved by a number of techniques, including nitric acid (HNO_3) washing, sodium chloride (NaCl) washing, or biologically. The technique to be used depends on the adsorption material and the desired end product. Adsorption can therefore either be operated as a batch process using a single column, or a series of multiple columns can be sequenced to provide continuous operation (Ganrot, 2012; WRAP, 2012).

In the context of wastewater treatment, especially natural zeolites have been succesfully used as adsorption agent for final NH_4-N removal (Çelik *et al.*, 2001; Du *et al.*, 2005; Jorgensen *et al.*, 1976; Jorgensen and Weatherley, 2003; Koon and Kaufman, 1975; Wang *et al.*, 2011; Weatherley and Miladinovic, 2004; Wei *et al.*, 2011; Zhang *et al.*, 2011). Mainly the use of clinoptilolite, $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}:12(H_2O)$, has been studied because of its low-cost availability (Pelin *et al.*, 2013). However, full-scale wastewater treatment plants that employ the NH_4^+ ion exchange technique are scarce, and few applications have been developed to recover NH_4-N, for example, for agricultural purposes (Hedström, 2001; Pelin *et al.*, 2013). Nevertheless, because the zeolite is porous, the ammonium can leak out of the zeolite at a much slower rate than it was adsorbed. This makes the ammonium-filled clinoptilolite itself a potential slow-release fertilizer (Ganrot, 2012). An important remark is that the initial N concentration in the above-mentioned applications was only a few 10 mg L^{-1}. Over the past decade, there has been increasing interest of using natural zeolite for NH_4-N removal from waste streams with relatively high N concentration or high ionic strength (Hankins *et al.*, 2004; Liu and Lo, 2001; Milan *et al.*, 1997; Wang *et al.*, 2006). However, its applicability in practice for the treatment of the liquid fraction of digestate (containing both high N and ionic concentrations) still remains to be demonstrated, as does the use of the nutrient-enriched clinoptilolite or other regenerated N-solutions as a fertilizer (Guo *et al.*, 2013; Lemmens *et al.*, 2007; Pelin *et al.*, 2013).

To date, removal efficiencies of 18 % P (probably due to adsorption) and 15-60 % N (due to ion exchange) have been reported for the treatment of human urine using clinoptilolite at lab-scale (Ganrot, 2012). This means that the technology would currently not be feasible as stand-alone NRT for digestate processing, though it may be used as an intermediate step in the digestate treatment train. As such, some research has been performed towards the combined use of zeolite and struvite precipitation to obtain a slow-release fertilizer with both high N and P concentrations. Overall recovery efficiencies of 100 % P and 83 % N have been obtained at lab-scale, and the fertilizer potential of the resulting product has been demonstrated at greenhouse scale (Ganrot, 2012). Moreover, Liberti *et al.* (1982) investigated a system where NH_4^+ ions were concentrated by the NH_4^+ ion exchange technique, followed by air stripping of NH_3 gas, which was subsequently absorbed in sulfuric acid. Zeolites may also be used to further treat the effluent produced by membrane filtration of the liquid fraction of digestate (Guo *et al.*, 2013). Hence, although there is potential to use zeolites as a technology for nutrient recovery, to date the use of this process for digestate treatment can rather be considered as an intermediate or final concentration step in the three-step framework (Fig. 2.1).

An important challenge for implementation of zeolites for digestate treatment is fouling of the adsorbent bed, as well as maintaining the bed capacity after multiple recovery/regeneration cycles (WRAP, 2012). Moreover, to date, experiments on the operational performance, process optimization, and recovery/regeneration methodologies are mostly carried out at lab-scale. Hence, further investigation into the process efficiency at pilot-scale is required (Hedström, 2001).

Finally, costs of this technology are expected to be low, but will depend on the nearby availability of the zeolites used, the required pre-treatment of the packing column to obtain NH_4^+ selectivity, the recovery/regeneration method (if applicable), and the required frequency of regeneration. No cost-benefit analyses for nutrient recovery from digestate using zeolites have been reported on in literature to date.

2.3.8 Biomass production and harvest (NRT 6)

Both macrophytes (mostly duckweeds and water hyacinths) and microalgae have been examined for biological nutrient recovery (Fenton and Uallachain, 2012; Hasan and Chakrabarti, 2009; Shilton *et al.*, 2012). Duckweed (*L. minor*, *L. punctate*, *S. polyrrhiza*, *S. oligorrhiza*) ponds have been successfully used as an efficient and potentially low-cost option in (anaerobically digested) agricultural waste polishing, generating a biomass with high protein content. A detailed overview of the nutrient and heavy metal content of duckweed as function of water quality has been reported (Leng, 1999; Ramjeed-Samad, 2010). Based on its mineral composition, the plant appears to have the ability to recover 600, 56-140, 400, 100, 60, 32, and 24 kg ha^{-1} y^{-1} of N, P, K, Ca, Mg, Na, and Fe, respectively, at a production of 10 ton dry weight (DW) ha^{-1} (Leng, 1999). Xu and Shen (2011) found removal efficiencies of 83.7 and 89.4 % for total N and P from pig wastewater, respectively, using *S. oligorrhiza* in eight weeks at a harvest frequency of two times a week. Mohedano *et al.* (2012) found an average of 98.0 % total N and 98.8 % total P recovery at full-scale, resulting in an average biomass (*L. punctate*) protein content of 28-35 %. However, above 60 mg N L^{-1} a toxic effect was noticed perhaps due to high levels of free ammonia in the water. Hence, levels below this value should be maintained in order to obtain a consistently high protein content (15-45 % by DW, depending on the N supply; Hasan and Chakrabarti, 2009).

Skillicorn *et al.* (1993) estimated the capital costs for a 0.5 ha large duckweed system at ± € 2,600 *(3,700 CAD)*. However, capital costs are significantly influenced by land area requirements, next to the costs associated with pond inoculation, harvesting, and disposal of biomass. As such, Mburu *et al.* (2013) evaluated the capital expenditures (CAPEX) for a full-scale waste stabilization pond at € ± 705,000 *(1 million CAD)* (based on 2,700 person equivalents (PE) at 8.3 m^2 PE^{-1}), and at € ± 276,000 *(390,000 CAD)* (for 2,700 PE at 3.4 m^2 PE^{-1}) for a pilot-scale horizontal subsurface flow constructed wetland. Maintenance costs for the first design are, however, significantly lower: € 283 *(400 CAD)* compared to € 23,300 *(33,000 CAD)* for 2,700 PE. As such, the total cost of these 'green' nutrient recovery systems can be evaluated at € 12-33 *(17-47 CAD)* PE^{-1} y^{-1}, with an average of € 14.4 *(20.4 CAD)* PE^{-1} y^{-1}, whereas the cost for a traditional activated sludge system is at least three times higher. However, without water reuse, associated gray-water sales, and duckweed valorization, currently the economic viability of duckweed systems remains questionable (Hasan and Chakrabarti, 2009).

Furthermore, the ability of microalgae to assimilate excess nutrients from the environment has been thoroughly studied (Cai *et al.*, 2013). However, to date, tests of growing algae in waste(water) are mostly at laboratory scale. Pilot-scale algae cultivation continues to face many problematic issues, including contamination, inconsistency in waste(water) components, and unstable biomass production. The major challenge associated with culturing algae in nutrient-rich natural water and slurry comes from the design of the cultivation system. The addition of polymer that precipitates suspended solids, thereby allowing light penetration, would improve the technical feasibility of growing algae on the liquid fraction of (digested) slurry. Nevertheless, Muylaert and Sanders (2010) predict that breakthrough of algae in the bio-based economy will last another 5-15 years, as currently costs of algae production are too high as compared to other types of biomass. Estimates of the algal production cost range from € 3.2-240 *(4.5-340 CAD)* kg^{-1} dry biomass (Benemann, 2008; Couteau and Sorgeloos, 1992; Lavens and Sorgeloos, 1996). Prior economic-engineering feasibility analyses have concluded that even the simplest open pond systems, including harvesting and algal biomass processing equipment, would cost at least € 78,000 *(113,000 CAD)* ha^{-1} and possibly significantly more (Benemann, 2008). To this, the operating costs will need to be added.

The harvested algae/macrophytes can serve as a feedstock for the chemical and biofuel industry, can be used as animal feed (provided that the necessary amendments in legislation are made), or spread out as a fertilizer (Demirbas, 2011; Lundquist *et al.*, 2010). As such, El-Shafai et al. (2007) estimated a biomass value of € 5,300 *(7,450 CAD)* y^{-1} (by comparison with other feed sources) for a protein yield of approximately 11 ton ha^{-1} y^{-1} (*L. gibba*). Next to the large footprint required, biomass harvesting remains an important technical bottleneck, which requires further research.

2.3.9 Phosphorus extraction from ashes/biochar (NRT 7)

The remaining ashes after combustion of biodegradable waste (manure, sludge, digestate) contain P, K, Al, and silicium (Si) compounds and possibly heavy metals such as Cu, Zn, and cadmium (Cd). Several companies have designed different processes to extract P from such combustion ashes (Schoumans *et al.*, 2010). These processes can be subdivided into thermochemical and wet-chemical technologies. The Finnish company Outotec, for example, adds $MgCl_2$ and heats the ashes up to 1,000 °C in order to gasify the heavy metals. Phosphorus is bound as $CaHPO_4$ and sold as chemical mineral fertilizer substitute. The Belgian company EcoPhos developed and tested, at lab-scale, a chemical P extraction process by addition of hydrogen chloride (HCl) to combustion ashes (Bolland, 1996). Also the Swedish company EasyMining developed a process (*Cleanmap Technology*) that involves the use of HCl, which is suitable for ashes from incinerated manure. Other P recovery processes from ash are: *ICI Amfert* (NL), *Mephrec* (DE), *PAsH* (DE), *RecoPhos* (Austria (AT), BE, DE, FR, Switzerland (CH)), *sephos* (DE), and *susAN/AsH DEC* (AT, DE, Finland (FI), NL). P recoveries up to 78 % are found in literature (Petzet *et al.*, 2012; Schoumans *et al.*, 2010). Operational costs for wet extraction itself can be lower than € 1 *(1.4 CAD)* m^{-3} fresh slurry, whereas net costs for combustion (including revenues from energy and P recovery) range from € 0-10 *(0-14 CAD)* ton^{-1} FW slurry, depending on the water content. However, a thorough flue gas cleaning system is indispensable and post-processing to remove heavy metals is often required. Hence, few full-scale installations currently exist.

Experiments with pyrolysis of manure cakes have also been conducted. The fraction of nutrients recovered in the resulting biochar is larger than in incineration ashes and the plant-availability of the nutrients tends to be higher, especially for P. It was estimated that the value of P in bio-char is about five times higher than the value of P in ash: < € 1 *(1.4 CAD)* m^{-3} vs. € 4.25 *(6.01 CAD)* m^{-3} (Schoumans *et al.*, 2010).

Nevertheless, as digestate is classified as a waste stream that is eligible for recycling as soil conditioner, it is in a lot of countries not authorised to convert the product into energy by combustion/pyrolysis according to environmental legislations. Alternatively, P could be extracted from dried or dewatered digestate, but to date such tests are absent in literature. Some processes attempting to recover P from dried or dewatered sludge are: *lEACHPOs* (CH), *Mephrec* (DE), *PHOXNAN/10PROX* (DE), and *Seaborne* (DE).

2.3.10 Critical comparison

Based on the above compiled information, a critical comparative technology overview is given in Table 2.2. At present, only struvite precipitation/crystallization, NH_3 stripping and absorption in a tower (with or without packing), acidic air scrubbing, and pressure-driven membrane filtration have been applied at **full-scale** for nutrient recovery from digestate. Of these technologies, only the first three have shown potential to be economically viable for implementation at digestate processing facilities.

Traditional membrane filtration systems often suffer technical problems in wastewater treatment, making them economically not yet viable for digestate treatment. An interesting solution may exist in vibrating membrane filtration (VSEP) using RO membranes. However, further research is required in order to evaluate the technical and economic performance of this process (see Chapter 3). Nevertheless, it should be pointed out that membrane filtration is the most established technology to date for the simultaneous **recovery of both N and K**.

Further, Table 2.2 shows that the NRT that currently achieves the highest simultaneous nutrient **recovery efficiency of both N and P** would be biomass production and harvest. However, the overall cost of this treatment is still high and large surface areas are required, making its potential implementation very region-specific. Further research to improve the economic and technical feasibility of this technology is recommended.

Table 2.2 Technology overview: technology, mechanism, feed, % recovery, main technical bottlenecks, economic and ecological evaluation, stage of development, and references. ↑ = relatively high; ↓ = relatively low; CAPEX = capital expenditures; OPEX = operational expenditures; PE = person equivalent; RO = reversed osmosis; R&D = research and development. Note: in order to reduce table complexity, costs are only expressed in € (€ 1 ≈ 1.415 CAD; November 2014).

Technology	Mechanism	Feed	% recovery	Main technical bottlenecks	Economic evaluation	Ecological Evaluation	Stage of development	References
Struvite precipitation	Physicochemical	Liquid	80-90 % P 10-40 % N	Precipitation in piping/equipment; Pollution with organic compounds; Stable and controlled production	Can be profitable; CAPEX: € 2,300-24,500 kg^{-1} P d^{-1}; OPEX: € -520-2,800 ton^{-1} struvite or € -200-75,000 y^{-1} Overall: € -7,800-89,400 y^{1}	Chemical use (NaOH, Mg) ↑; Fe/Al use ↓; Landfill ↓; Sludge handling and disposal ↓; Cleaning of struvite deposits ↓	Full-scale	Jaffer *et al.* (2002); Le Corre *et al.* (2009); Shu *et al.* (2006); Technology providers
	Electrochemical	Liquid	> 99 % P	R&D Needed	R&D needed	Chemical use ↓; Energy use ↓: < 70 Wh m^{-3}	Lab Pilot: test phase	IGB (2012)
	Bio-electrochemical	Liquid	20-40 % P	R&D Needed	R&D needed	Energy efficiency ↑: 73±4 %; H_2 production	Lab	Cusick and Logan (2012)
Calcium phosphate precipitation	Physicochemical	Liquid	50-100 % P	Co-precipitation of $CaCO_3$; Preceding CO_2 stripping often required	Can be profitable; CAPEX: € 2,300-2,900 kg^{-1} P d^{-1}; OPEX: depends on $Ca(OH)_2$ use	Chemical use ($Ca(OH)_2$) ↑; Fe/Al use ↓	Full-scale: manure & wastewater; Lab: digestate	Berg *et al.* (2007); Eggers *et al.* (1991); Technology providers
NH_3 stripping & absorption	Physicochemical: tower (packed bed or no packing)	Liquid	Up to 98 % N; Typical: 80-90 % N	Fouling and corrosion of packing material	CAPEX: € 0.5-15 million, OPEX: € 4.5-8.6 m^{-3}, both for 800 $m^3 d^{-1}$ at 2.4 g N m^{-3} (90 % recovery); Overall: € 2.0-8.1 m^{-3} for 70 $m^3 h^{-1}$; Depends on pH and temperature; Can (partially) replace activated sludge system; Interest in S ↑	Odors ↓; Energy use (air/ heat) ↑: 1.54-12 kWh_{el} m^{-3} and 62-69 kWh_{th} m^{-3}; Acid use ↑: 7-10 kg H_2SO_4 m^{-3}; Base use (↑): 0-6.5 kg NaOH m^{-3}, all for 800 m^{-3} d^{-1} at 2.4 g N m^{-3} (90 % recovery); Chemical use for cleaning ↑	Full-scale	Bonmati and Flotats (2003); Collivignarelli *et al.* (1998); Lemmens *et al.* (2007); Technology providers
	Physicochemical: water-sparged aerocyclone	Liquid	> 97 % NH_3	R&D needed; Scale-up?!	Interest in S ↑; Potential for simultaneous P recovery	Self-cleaning; Energy use ↓; Acid use ↑; Chemical use ↓	Lab	Quan *et al.* (2010)
	Physicochemical: rotating disks	Liquid	± 80 % NH_3	R&D needed; Scale-up?!	Interest in S ↑; No air scrubber required	Energy use ↓: < 1 kW; Acid use ↑; Chemical use ↓	Pilot	Dorset (2014)
Acidic air scrubbing	Physicochemical	Gas	91-99 % N	Fouling/corrosion of packing material; Performance under freezing conditions?!	Can be profitable; CAPEX: € 13 kg^{-1} NH_3 removal; OPEX: € 6-7 kg^{-1} NH_3 removal; Interest in S ↑	Odor ↓; Energy use (air) ↑: min. 0.057 kWh kg^{-1} NH_3; Acid use ↑: min. 1.5 L H_2SO_4 kg^{-1} NH_3	Full-scale	Manuzon *et al.* (2007); Melse and Ogink (2005); Melse and Willers (2004); USEPA (2000)
Membrane filtration	Physical: pressure-driven membrane filtration	Liquid	N and K; % depends on pre-treatment	Membrane blocking & scaling; High maintenance and power requirements	High CAPEX & OPEX: € 4-13 m^{-3}	Energy use ↑: 4-6 kWh m^{-3} (RO); Chemical use (cleaning) ↑	Full-scale	Charlebois (2000); De Hoop *et al.* (2011); Gerard (2002); Kertesz *et al.* (2010); Moon and Lee (2012); Semiat (2008); Velthof (2011); Waeger *et al.* (2010)

Technology *(Continuation)*	**Mechanism**	**Feed**	**% recovery**	**Main technical bottlenecks**	**Economic evaluation**	**Ecological Evaluation**	**Stage of development**	**References**
	Physical: forward osmosis	Liquid	R&D needed	Reverse solute diffusion; Need for new membrane development and draw solute design	Costs ↓ (no data available)	Energy use ↓ (to be confirmed): 3-8 kWh m^{-3}; Chemical use ↓: less cleaning	Full-scale: desalination, food processing; Full-scale digestate/ manure: in 5-10 y	Moon and Lee (2012); Sant'Anna *et al.* (2012); Zhao *et al.* (2012)
	Physicochemical: transmembrane chemosorption	Liquid	70-99 % NH_3	Membrane clogging	Depends on mass transfer; Similar costs as stripping	Energy use ↓: < 1 kWh m^{-3}; Chemical use (acid) ↑	Pilot	Norddahl *et al.* (2006); Rulkens *et al.* (1998); Sustec (2014)
	Electrochemical: electrodialysis	Liquid	80-83 % NH_3	High energy consumption; Variable costs for membranes, electrodes, cases; Acid NH_3 trap required; Post-treatment (RO/stripping) required	High costs (no data available)	Energy use ↑: 3.25-3.60 kWh kg^{-1} NH_4-N or 1.2-1.5 kWh kg^{-1} K; NH_3 volatilization	Full-scale: limited; Lab: digestate/manure	Decloux *et al.* (2002); Ippersiel *et al.* (2012); Mondor *et al.* (2008, 2009)
NH_3 sorption	Physicochemical	Liquid	18 % P 15-60 % NH_3	Fouling of the packing column; Regeneration and maintenance; Post- and/or pre-treatment required	Potentially low costs relative to other technologies (depending on availability, pre-treatment, and regeneration); Further research needed for digestate treatment	Energy use ↓; Chemical use ↑	Full-scale: limited for wastewater; Lab: digestate	Ganrot (2012); Guo *et al.* (2013); Lemmens *et al.* (2007); Pelin *et al.* (2013); WRAP (2012)
Biomass production and harvest	Biological	Liquid	84-98 % N 90-99 % P	Harvest method; Reduced light penetration; Dilution often required; Large surface area; Toxic if N > 60 mg L^{-1}	Capex: > € 80,000 ha^{-1}; Overall (macrophytes): € 12-33 PE^{-1} y^{-1} Overall (algae): € 4-300 kg^{-1} dry weight	Surface ↑: 3.4-8.3 m^2 PE^{-1}; Energy use ↑ (CO_2 addition); Polymer use ↑	Pilot/Full-scale: duckweed; Mostly lab: algae	Benemann, (2008); Couteau and Sorgeloos, (1992); Lavens and Sorgeloos, (1996); Mburu *et al.* (2013); Mohedano *et al.* (2012); Skillicorn *et al.* (1993); Xu and Shen (2011)
P extraction from ashes/ bio-char	Thermochemical / Wet-chemical	Solid	Up to 78 % P	Often heating, flue gas cleaning, and heavy metal removal required; pH, temperature, and chemical choice are critical	< € 1 m^{-3} slurry (wet extraction); € 3 ton^{-1} slurry (pyrolysis); € 0-10 m^{-3} slurry (combustion)	Combustion = sustainable?!; Energy use ↑: temperature-dependent; Chemical use ↑: process-dependent	Full-scale: incinerated sludge; Lab: incinerated digestate, but often not authorized!	Bolland (1996); Petzet *et al.* (2012); Schoumans *et al.* (2010)

In terms of **costs**, NH_3 sorption and recovery of N-enriched (natural) zeolites is probably the lowest-cost option available to date (depending on the nearby availability of the adsorbent). However, recovery efficiencies are relatively low and further testing is required on the implementation of this technology for digestate treatment. Moreover, the marketing value of the recovered N-zeolites remains to be explored. The use of this technology in combination with struvite or stripping (depending on the purpose) may be interesting, in order to maximize the overall nutrient recovery potential at minimal costs.

Further, from an **ecological point of view** (chemical and energy use), transmembrane chemosorption, forward osmoses, (bio)electrochemical struvite recovery, and NH_3 sorption appear as the most interesting NRTs. However, none of these technologies is currently applied at full-scale for the treatment of digestate. Yet, after sufficient testing and optimization, these systems have the potential to become part of commonly used digestate processing technologies. The extraction of P from ashes or biochars seems the least promising technology, because it can be questionned whether combustion/pyrolysis of digestate is a sustainable treatment option and if this should be encouraged.

Finally, from a **technical perspective**, it can be stated that further fine-tuning is still required for all technologies in order to minimize operational costs, especially in terms of energy and chemical consumption, produce high-quality, pure fertilizers, and economically valorize the recovered nutrients. The best available and most established technologies for nutrient recovery from digestate in terms of technical performance and fertilizer marketing potential are struvite precipitation, ammonia stripping and absorption using a stripping column with or without packing, and acidic air scrubbing. It is not surprising that these are the only technologies to date that have been successfully implemented at full-scale digestate processing facilities.

2.4 Fertilizer quality, markets, and regulations for reuse

2.4.1 Fertilizer quality specifications

For efficient use in the agricultural sector, recovered nutrient products must have the following characteristics:

a) Consistent chemical nutrient composition and uniform distribution compatible with fossil reserve-based chemical fertilizers:

The three principal macronutrients in fertilizer mixes, so called because they are required in the largest quantities, are nitrogen (N), phosphorus (P), and potassium (K). The most common fertilizers in current use are mixtures of compounds containing the three components, conventionally expressed in terms of the relative percentages of N, P_2O_5, and K_2O by weight (Hillel, 2008). The nutrient ratio to be used in mixed fertilizers depends on crop requirements and soil characteristics, e.g. a 1:1:1 ($N:P_2O_5:K_2O$) ratio is the base fertilizer for grain crops, sugar beets, potatoes, and vegetables on soddy podzols, gray forests, and chernozems, while a 1:1.5:1 ratio is applied at planting time for grains, vegetables, and industrial crops.

Nitrogen promotes healthy leaf, stem, and branch growth. Most plant forms can't metabolize N in its natural state (N_2), so fertilizers must incorporate N compounds that plants can use, such as ammonium nitrate and ammonium sulfate (Hillel, 2008). The high solubility of these forms, however, makes them especially vulnerable to leaching by percolating water. Phosphorus provides the materials needed for seed germination and healthy root system development, while K materials promote healthy flowering and fruit production. To be available as nutrient to plants, P must be present in the soil solution as the anions $H_2PO_4^-$ or HPO_4^{2-}. This element is frequently deficient and chemical mineral fertilizers must be added. The added P, however, may not remain in available form for long, because it tends to be converted to less soluble or insoluble forms, either by reaction with Ca or with Fe and Al oxides in the soil, or by strong adsorption onto the edges of clay crystals. The interest in slow-release granulated P fertilizers is therefore growing (Palmer and Kay, 2005). Potassium nutrients tend to cling to clay and organic matter, thereby causing the immobilization or fixation of K ions. For this reason, soils often require the careful addition of K in the form of fertilizer around plant root system structures to ensure this nutrient's availability (Barber, 1995).

Other important macronutrients include sulfur (S), calcium (Ca) and magnesium (Mg), hydrogen (H), oxygen (O), as well as carbon (C). Nine additional elements are essential nutrients for many plants, albeit in small quantities. Hence, they are called micronutrients or trace elements. These include boron (B), chlorine (Cl), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) (Hillel, 2008). They can be applied separately as micronutrient fertilizer, but are often incorporated in mixed fertilizers (ratios depend on crop and soil conditions).

b) A low salinity, sodicity, and a pH close to neutral:

The term **soil salinity** refers to the presence of electrolytic mineral solutes, most commonly Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, and CO_3^{2-}, in concentrations that are harmful to many plants in the soil and in the aqueous solution within it. Overall salinity is usually expressed in terms of total dissolved solids (TDS) or electrical conductivity (EC). **Soil sodicity** generally refers to the dispersion of clay resulting in deterioration of soil structure by clogging of large pores in the soil. This occurs when the sodium (Na) ion predominates in the exchange complex of the soil. Hence, the **sodium adsorption ratio** (SAR), i.e. the ratio of monovalent Na over divalent Ca and Mg, is an important parameter to evaluate. Fertilizers can also affect a soil's **pH**, which is a measure of the soil's acidity. When acidity levels are too high (hence the pH too low), essential minerals and nutrients may be prevented from reaching a plant's root system, the concentration of potentially toxic metal ions may increase, and the activity of soil microorganisms may be inhibited (Hillel, 2008). Moreover, strongly acidic or basic fertilizers may cause plant burning, while basic fertilizers may also favour NH_3 volatilization.

c) Desirable physical characteristics:

The important physical properties of **liquid fertilizers** are density and viscosity. The strength of the gelling agent (i.e. the thickener) is also critical. It should be strong enough to keep the solids in suspension, but not so strong that the liquid is too thick to be pumped and poured. Important physical characteristics of **solid fertilizers** are particle size, density, granule hardness, and moisture content (Barnes and Fortune, 2006; Dombalov *et al.*, 1999; Fittmar, 2009; Haby *et al.*, 2003; McCauley *et al.*, 2009; Sahoy, 2013). The effect of these parameters and typical values for conventional chemical mineral fertilizers are presented in Table 2.3.

Table 2.3 Desirable physical characteristics of solid fertilizers: parameter, process affected, impact, and typical values; compiled from Barnes and Fortune (2006), Dambolav *et al.* (1999), Fittmar (2009), Haby *et al.* (2003), McCauley *et al.* (2009), and Sahoy (2013).

Parameter	Process affected	Impact	Typical values
Particle size and distribution	Fertilizer effectiveness	➢ size ↓ → dissolution in H_2O ↑ → rate of nutrient release ↑ → nutrient leaching ↑	1-4 mm
	Further processing	➢ size ↑ → ease of washing ↑, filtering ↑, transportation ↑ and storing ↑	
	Purity	➢ size ↑ → surface area to volume ratio ↓ → purity ↑ ➢ uniformity ↑ → purity ↑	
	Occupational health and safety	➢ granulation ↑ → distribution of fertilizer powder ↓	
	Environmental aspects	➢ granulation ↑ → dust formation ↓ → nutrient leaching ↓	
Density	Storing	➢ density ↑ → packing volume ↓	700-1,570 kg m^{-3}
	Calibrating machinery		
Hardness	Handling and storing	➢ hardness ↑ → resistance to crushing forces, abrasion, and impacts ↑ ➢ hardness ↑ → thermal stability ↑	crushing strength: 0.5-7.5 kg cm^{-2}
	Environmental aspects	➢ hardness ↑ → fertilizer dustiness ↓	
Moisture content	Handling and storing	➢ CRH[a] ↑ → ease of handling and storing in wet environments ↑ ➢ CRH[a] ↓ → clump formation ↑, ease of spreading ↓, ease of storing ↓ (should be prevented from getting wet) ➢ surface area ↑ → water absorption ↑	CRH[a]: 72-92 %

[a] CRH = critical relative humidity = relative humidity of the surrounding atmosphere (at a certain temperature) at which the material begins to absorb moisture from the atmosphere and below which it will not absorb atmospheric moisture.

It should be noted that granule hardness also depends on the chemical composition of the fertilizer, the shape of the particles, and how much moisture it contains. On its turn, moisture absorption depends on the chemical composition of the fertilizer, environmental conditions, and the shape and size of the particles.

d) No/minimal pathogen content: Depending on the temperature of the process, anaerobic digestion as a pre-treatment step to nutrient recovery can provide partial or complete pasteurization of the waste material (Bond *et al.*, 2012; Tchobanoglous *et al.*, 2003). In European legislation, a product is considered pasteurized if it was subjected to 1 h heating at 70 ℃ or an equivalent treatment (regulation EG 1069/2009 or former 1774/2002; EC, 2002, 2009), whereas in the USA the requirement to obtain class A biosolids (= potential use at home gardens, lawns, etc.) is at least 30 min heating at 70 ℃ or an equivalent of that (Tchobanoglous *et al.*, 2003). In Canada, currently the USA requirements for class A biosolids are used to classify a product as P1 (= free of fecal pathogens) in the regulatory framework for recycling of fertilizer residuals (MDDEFP, 2012).

e) No/minimal odor: Anaerobic (co-)digestion of organic wastes results in odor reduction (Bond *et al.*, 2012; Tchobanoglous *et al.*, 2003). However, to meet regulatory standards for odor and greenhouse gas emissions, air scrubbers are required at most waste processing facilities.

f) Be authorized for registration and application in accordance with regulatory standards: see Section 2.4.4.

2.4.2 Classification of recovered products

A classification of products that can be recovered from digestate is provided in Table 2.4. Comparative information on their fertilizer characteristics and marketing value is also presented. Based on their fertilizer composition, the current available recovered products can be classified as N/P-, K/P-, or P-precipitates, P-extracts, N/S-solutions, N/K-concentrates, N-zeolites, and biomass. The two recovered bio-based products that are currently supplied in the largest quantities and offer the highest potential for agricultural valorization are struvite from chemical precipitation and AmS from stripping and acidic air scrubbing. These products can be classified as N/P-precipitate and N/S-solution, respectively. N/K-concentrates could become an important recovered fertilizer in the future, if a technical and economic membrane filtration option would become available, for example, the VSEP technology (Chapter 3).

In-depth product characterization in time and long-term field trials aiming at the evaluation of the environmental impact of bio-based products are rare in literature, but highly important in the development of a market for recovered nutrients. Several researchers have investigated the fertilizer properties of struvite and the product has been evaluated as an eco-friendly fertilizer for agricultural production (Rahman *et al.*, 2011; 2014). However, the findings reported are mainly based on greenhouse studies, whereas long-term field trials using recovered struvite from (digested) bio-waste produced at full-scale are limited (Thompson, 2013). Moreover, to reduce costs, these field trials are focussed on plant yield and P uptake in particular, but do not investigate the release and mobility of (other) nutrients and heavy metals.

Next, no reference has been found in literature on the beneficial value of recovered AmS fertilizer, except for the two-year field trial conducted in the context of this dissertation (Chapter 5; Vaneeckhaute *et al.*, 2013b,c, 2014). For membrane filtration concentrates, the only study that has been reported on to date is the pilot plant project in the Netherlands, in which the product has been applied during a two-year field experiment (De Hoop *et al.*, 2011; Velthof, 2011). In order to establish the use of bio-based products in the agricultural community and to hasten the integration of these products in environmental and fertilizer legislations, more in-depth field trials focusing on the environmental impact of these products, next to their agronomic potential, should be conducted. Best management practices should also be established. All of this may help to better estimate the economic value of these amendments compared to the conventional used chemical fertilizers. Indeed, to be economically profitable, the price allocated to the recovered nutrients should be in accordance with the market price of N, P, K, and S in traditional mineral fertilizers.

Table 2.4 Classification of recovered end products: class, technology, feedstock, product, composition/quality, current marketing value, and references.

Class	Technology	Feedstock	Product	Composition/quality	Marketing value	References
N/P-precipitates	Struvite precipitation (chemical)	Liquid fractions, (acidified) raw digestate	$MgNH_4PO_4{:}6H_2O$	Pure struvite: 6 % N, 29 % P_2O_5, 10 % Mg; Ostara: 5 % N, 28 % P_2O_5, 10 % Mg; Crystalactor: 9 % N, 46 % P_2O_5, 16 % Mg; Crystals (0.5-5 mm); Slow-release; Purity?!	€ 45-1,393 ton^{-1} *(64-1,970 CAD ton^{-1})*	Dockhorn (2009); Doyle and Parsons (2002); Kohler (2004); Technology providers
	Struvite precipitation (electrochemical)	Liquid fractions	$MgNH_4PO_4{:}6H_2O$	R&D needed	R&D needed	IGB (2012)
	Struvite precipitation (bio-electrochemical)	Liquid fractions	$MgNH_4PO_4{:}6H_2O$	R&D needed (40 % soluble P removal)	R&D needed	Cusick and Logan (2012)
K/P-precipitates	Struvite precipitation (chemical)	Liquid fractions, (acidified) raw digestate	$KMgPO_4{:}6H_2O$	R&D needed	R&D needed	Graeser *et al.* (2008)
P-precipitates	Calcium phosphate precipitation	Liquid fractions, (acidified) raw digestate	$Ca_5(PO_4)_3OH$ $CaHPO_4{:}2H_2O$	P_{tot}: 10-11 %; Crystals; Purity?!	R&D needed	Berg *et al.* (2007); Eggers *et al.* (1991)
P-extracts	P extraction	Ashes/biochar	Acid P-extract, $CaHPO_4$, struvite, Fe/Al-PO_4	P_2O_5: 15-35 %; High P bio-availability; Purity?!	€ 0.89-4.25 m^{-3} *(1.4-6.01 CAD m^{-3})*	Petzet *et al.* (2012); Schoumans *et al.* (2010)
N/S-solutions	Stripping & absorption	(Decarbonated) liquid flows	$(NH_4)_2SO_4$-solution	AmS: 25-38 %; N: 30-100 kg m^{-3}; S: 61-100 kg m^{-3}; pH: 3-7; High salt content: 30-150 mS cm^{-1}	€ 90-120 ton^{-1} *(130-170 CAD ton^{-1})*	Liao *et al.* (1995); USEPA (2000); Vaneeckhaute *et al.* (2013a,b,c, 2014); Technology providers
	Acidic air scrubbing	Strip gas, air	$(NH_4)_2SO_4$-solution	N_{tot}: 30-70 kg m^{-3}; S: 61-100 kg m^{-3}; pH: 3-7; High salt content: 30-150 mS cm^{-1}	€ 90-120 ton^{-1} *(130-170 CAD ton^{-1})*	Vaneeckhaute *et al.* (2013a,b,c, 2014); Technology providers
	Transmembrane chemosorption	Tested on urine; Potential for liquid fractions of manure/digestate	$(NH_4)_2SO_4$-solution	Several 100 g NH_4^+ L^{-1}	R&D needed	Sustec (2014)
N/K-concentrates	Reversed osmosis	Permeate from ultrafiltration, microfiltration or dissolved air flotation	N/K-concentrates	N_{tot}: 3-11 kg ton^{-1}: 92 % NH_4-N, 8 % organic N; K_2O_{tot}: 5.0-13.6 kg ton^{-1}; P_2O_{5tot}: 0-1.4 kg ton^{-1}; Purity?!	€ 1.19-1.25 ton^{-1} *(1.68-1.77 CAD ton^{-1})*	De Hoop *et al.* (2011); Vaneeckhaute *et al.* (2012); Velthof (2011)
	Forward osmosis	Liquid fractions	N/K-concentrates	R&D needed; Potential for high-quality product through high rejection	R&D needed	Moon and Lee (2012); Sant'Anna *et al.* (2012); Zhao *et al.* (2012)
	Electrodialysis	(Filtrated) liquid fractions	N/K-concentrates	R&D needed; 7 x the input concentration	R&D needed	Decloux *et al.* (2002); Ippersiel *et al.* (2012); Mondor *et al.* (2008, 2009)
N-zeolites	NH_3 sorption	(Filtrated) liquid fractions (to be confirmed for digestate)	N-enriched Clinoptilolite	Slow-release fertilizer; Potential contamination (metals, etc.); R&D needed	R&D needed	Ganrot (2012); Guo *et al.* (2013); Lemmens *et al.* (2007); Pelin *et al.* (2013)
Biomass	Biomass production & harvest	Diluted liquid fractions	Biomass (algae, macrophytes)	Duckweed: 30 % P on dry weight; High content of proteins, N, P, K, C; Potential for biofuel and chemical industry, or as animal feed	€ 5,300 *(7,450 CAD)* y^{-1} for a protein yield of ± 11.1 ton ha^{-1} y^{-1}	Demirbas (2011); El-Shafai *et al.* (2007); Leng (1999); Hasan and Chakrabarti (2009); Lundquist *et al.* (2010)

2.4.3 Fertilizer market trends and prices

As in the case of fuel, fertilizers are internationally traded commodities and their prices are determined by global supply and demand factors. The world demand for agricultural commodities is rising, driven by growing populations, increased demand for meat, and strong government biofuel initiatives. This rising demand has resulted in increased agricultural commodity prices, which, in turn, has led to higher profit margins for farmers. The latter has enabled farmers to increase fertilizer usage to boost yields as a means of increasing production (Oskam *et al.*, 2011). World fertilizer nutrient (N + P_2O_5 + K_2O) consumption reached 180.1 million tons in 2012, up by 1.9 % over 2011, and the demand is estimated to grow at 1.95 % per year from 2012 to 2016. During this period, the demand for N, P, and K is forecast to grow annually by 1.3 %, 2.0 %, and 3.7 %, respectively (FAO, 2012).

On the other hand, several minerals, such as P and K, which are nowadays being extracted through mining, are becoming scarce at rapid pace (Fixen and Johnston, 2012). If agriculture would continue to be dependent on high rates of P application, a depletion of more than 50 % of the total resource base by 2100 and a complete depletion during the 22^{nd} century in the worst case is predicted (van Vuuren *et al.*, 2010). The resulting imbalance between the increased demand and depleting supply for nutrients has substantially driven up fertilizer prices in recent years. As an example, every one-cent per kg increase in the fertilizer price adds about 61 million CAD *(€ 43 million)* to the Canadian farmers' annual fertilizer bill (AAFC, 2012). Agriculture and Agri-Food Canada (AAFC, 2012) estimates that the average prices paid for fertilizers in Canada increased by about 29 % in 2011, which could be translated into about a 969 million CAD *(€ 685 million)* increase in the Canadian farmers' 2011 fertilizer bill.

Besides production cost, the price of fertilizers at the retail level is also affected by prices for gasoline and diesel, because transportation costs represent an important part of the cost of marketing fertilizers. In Canada, the correlation (R^2) between the price of natural gas and the price of N fertilizer was estimated at 0.74, based on monthly data over 1991-2010 (AAFC, 2012). The effective use of nutrients, as well as the cradle-to-cradle recycling of these valuable resources from waste flows, is therefore essential in order to guarantee a sustainable nutrient supply for future food production.

From the technology review above, the two recovered bio-based products that currently offer the highest potential for agricultural valorization are struvite and ammonium sulfate (AmS). As a fertilizer, **AmS** supplies two fundamental nutrients: N and S. Of the total worldwide amount of N fertilizers, only 4 % is AmS (Sutton *et al.*, 2013), mainly due to its relatively low N content as compared to that of, for instance, urea (21 % and 45 %, respectively). Recently, however, the worldwide supply of AmS has increased, in part due to the production of AmS by direct reaction crystallization from (spent) sulfuric acid and NH_3. This additional AmS supply has been absorbed quickly in the marketplace because of a general increase in fertilizer demand and an increased need for S nutrition in particular. Deficiency of S became a problem for more than 75 countries according to United Nations statistics (UN, 2014) and supply of this nutrient could be efficient by using new (recovered) fertilizers containing sulfate (Till, 2010). The current additional production capacity of AmS from waste streams has not even been sufficient to fulfill the market requirements, however, and naturally, this gap in the supply-demand relationship has led to a rise in AmS prices. As one might expect, the price of AmS varies with the various types of product quality available. The largest disparity is related to particle size, where reported prices of granular (2-3 mm) crystals are up to three times higher than these of < 1 mm crystals (Gea-Messo, 2013). This price differential can be a strong incentive to produce large crystals. Hence, the trend of the market is toward the production of the so-called 'granular' AmS quality, with a coarse fraction of 80 % > 1.8 mm, which has a higher sales return compared to standard quality, but requires an improvement of the production process (Gea-Messo, 2013).

Next, the demand for controlled- and slow-release (CSR) fertilizers, such as struvite, will continue to grow as they prove to be an efficient alternative to conventional fertilizers because of their environmentally friendly, resource-saving, and labor-saving (mainly due to the decreased application frequency) characteristics (Glauser at al., 2013; Palmer and Kay, 2005). However, because of the high price of these products relative to conventional fertilizers, their use is still limited primarily to ornamental, horticultural, and turf applications. As larger production scales for these materials are achieved, costs will continue to decline, making them more attractive for commodity/open-field/broad-acre crops, such as maize, wheat, and potatoes. Coated fertilizers, particularly polymer-coated products, have been the fastest-growing segment of the CSR fertilizer market and will continue to grow at a faster rate than other CSR fertilizer types. Overall, global demand for these products will continue to increase at about 2 % annually during 2012-2017 for horticultural and turf applications, including agricultural crop applications (Glauser *et al.*, 2013).

Considering the full nutrient chain, at present on average over 80 % of N and 25-75 % of P consumed end up lost in the environment, wasting the energy used to prepare them and causing emissions of greenhouse gases and nutrient compounds to water (Sutton *et al.*, 2013). Hence, if the production price of recovered AmS and struvite from organic wastes would be competitive with that of chemical fertilizers and if their application proves not harmful for crop production and soil quality, these products may and should be used to fulfill future fertilizer market demands, thereby meeting the challenge to produce more food and energy with less pollution.

2.4.4 Regulations for reuse in the European Union and Canada (Quebec)

2.4.4.1 Towards a revised fertilizer regulation in the European Union

In the European Union (EU), new fertilizers should obtain an EC (European Commission) conformity certificate (= conform to the revised European Fertilizer Regulation criteria) in order to be sold throughout Europe. The revision of the EU Fertilizer Regulation 2003/2003 (EC, 2003), currently under discussion, will widen the scope of the Regulation to include inorganic, organo-mineral, and organic fertilizers, organic soil improvers, liming products, growing media, as well as plant bio-stimulant and agronomic fertilizer additives. This will considerably facilitate the placing on the market both of organic products containing recycled nutrients (e.g. processed biosolids, digestates, composts, biochars) and inorganic recovered products (e.g. struvite, phosphates recovered from sewage sludge, incineration ash, etc.). Fertilizing materials which are certified to comply with the new essential requirements outlined in the EU Fertilizer Regulation (minimum nutrient content, quality, and safety criteria) will be authorised to be placed on the Internal Market (transported and sold across the European Union), whereas at present such products registered as 'fertilizers' in one Member State cannot be exported or require a new registration dossier for sale in another Member State (except in cases where there has been mutually recognition by the authorities of the importing Member State).

Despite these favourable prospects, harmonization of the Fertilizer Regulation with other regulations will be required before effective marketing of bio-based products in the EU will be possible. As such, clarification is needed regarding the application of REACH (2007) (European chemical regulation) for substances (digestates, recovered products) leaving the waste status. There is also a need for coherence with the Animal By-Products Directive (EG 1069/2009 or former 1774/2002; EC, 2002, 2009) and the Nitrates Directive (91/676/EEC; EC, 1991). In particular, fertilizer products recovered from manures are currently penalised by the limitations for spreading 'processed manure' as defined in the Nitrates Directive. This could be resolved if the criteria defining 'mineral fertilizers' under the revised Fertilizers Directive were considered to also define a product as no longer being regarded as 'processed manure' under the Nitrates Directive. Finally, digestates and recovered products are also still subject to end-of-waste criteria under the Waste Framework Directive (2008/98/EC; EC, 2008), but it is likely that the associated obligations (e.g. traceability) will not be adopted. Instead, each Member State will have to put in place national end-of-waste criteria.

2.4.4.2 Fertilizer regulations in Canada and Quebec

At the Canadian level, the Canadian Food Inspection Agency regulates agricultural fertilizers through the Fertilizers Act (Minister of Justice, 2006) and Fertilizer Regulations (Minister of Justice, 2013). At provincial level, regulations on the beneficial use of fertilizing residuals are provided by the 'Ministère du Développement Durable, Environnement, Faune et Parcs' (MDDEFP, 2012). An important incentive for reuse is that incineration of biodegradable organic material, such as manure, municipal solid waste, and sewage sludge, will be prohibited from 2020 on by the MDDEFP. Currently, ± one million tons of fertilizer residuals are used annually on agricultural soils, however, mostly in hard-extractable form. Hence, the MDDEFP promotes the valorization of reusable resources, including nutrients, organic matter, and energy from bio-waste through its 'Plan Agro-Environnemental de Valorisation' (PAEV). Valorization must rely on good management practices:

i. Strategies to reduce the risks for the environment and human health to a minimum;
ii. Strategies to reduce greenhouse gas emissions to a minimum;
iii. **Practices that take in account the effectiveness and value of the resources (=**

product efficiency).

As a consequence, multiple municipalities in Quebec (Ville de Saint-Hyacinthe, Ville de Repentigny, Ville de Montréal, Ville de Québec, etc.) are intensively looking for more sustainable practices of sludge and municipal solid waste collection and treatment, involving anaerobic digestion and valorization of the resulting digestate, e.g. Centre de Biométhanisation de l'Agglomération de Québec (CBAQ): https://www.ville.quebec.qc.ca/grandsprojetsverts/matieresresiduelles/matieres_organiques/index.aspx. This transition emphasizes the importance of this PhD research.

According to the federal Fertilizers Regulation, the ammonium salt of sulfuric acid containing at least 20 % N can be recognized as a mineral fertilizer (class 1.2; Minister of Justice, 2013). Recovered AmS should therefore be upgraded or the recovery process should be optimized to produce fertilizers acceptable for agricultural use according to current standards. At present, there exists no particular category for magnesium-ammonium-phosphate fertilizers, but struvite may be classified either as ammonia phosphate (class 2.2; Minister of Justice, 2013) or precipitated phosphate (class 2.11; Minister of Justice, 2013). When one would like to register and apply a novel product, detailed information, including product identification, characterization, test data, and all other information relevant to identifying the risk to the environment, is required in order to obtain the authorization of the Minister of Justice (2013). **Hence, field and pot experiments are indispensable to prove the fertilizer effectiveness of these novel products.**

2.5 Need for further research

Most NRTs described above are derived from the wastewater treatment sector where they are well developed or under development. Application of these technologies for digestate, sludge, and manure treatment, however, causes new technical bottlenecks. Moreover, adjusting the process in a way that the characteristics of the end products can be made client-specific and more predictable is an important concern. A lot of efforts by several companies and research institutes are being put into solving these technical issues. However, lab, pilot, and/or full-scale tests are expensive and time-consuming. Hence, the development of a process and treatment train optimization tool for resource recovery that allows to predict fertilizer quantity and quality under variable conditions (operation, input characteristics, etc.) may be a highly valuable contribution to overcome the above bottlenecks (see Chapters 8-10).

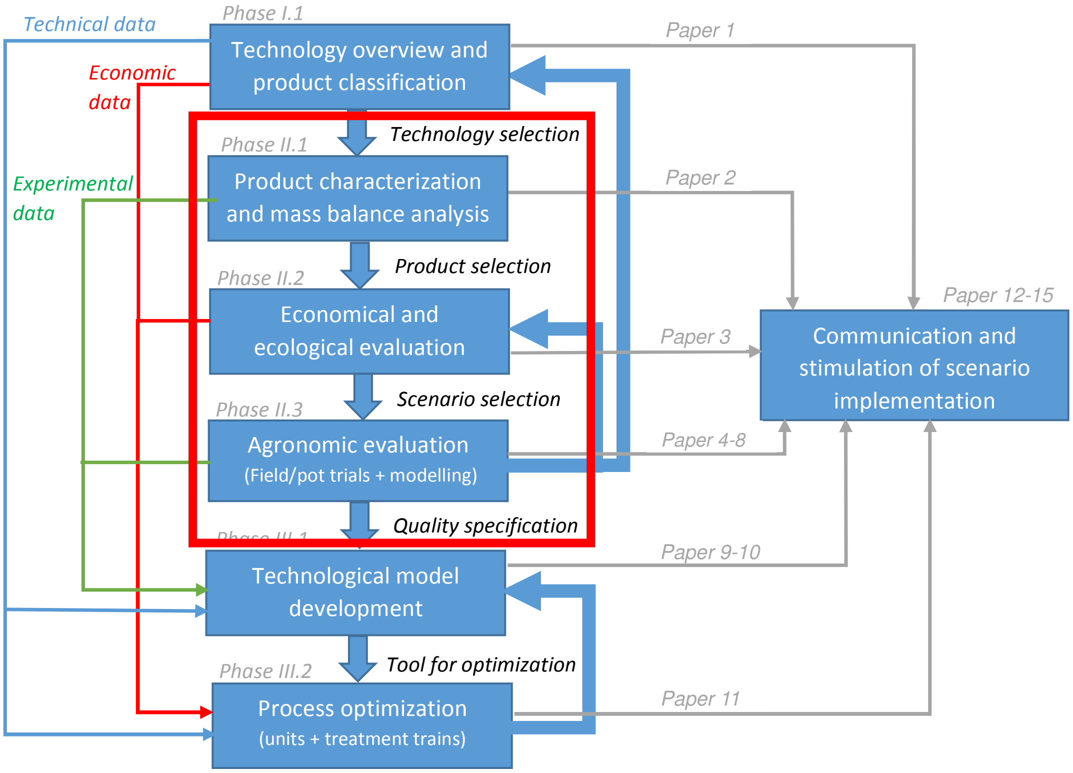
Next, a research area that deserves more attention is the valorization of end products and the economic evaluation of implementing NRTs in a centralised or decentralised approach. Both aspects are interlinked, because the added value of the end products will affect the profitability of implementing such technologies. The end products could either be used as mineral fertilizer substitute, sustainable organo-mineral fertilizer (replacement for manure), or as raw material for industrial processes. When farmers are the end-users, it is essential that the fertilizer value of the end product is demonstrated by incubation studies or field trials to assess plant availability of the present nutrients and the applicability of these products for several cropping systems (see Chapter 5; Vaneeckhaute *et al.* 2013c, 2014). Industrial end-users also have both technical and regulatory requirements for the input streams of their production processes, which have to be taken into account.

Furthermore, a clearly defined and homogenized legislative framework is indispensable for future developments in the area of nutrient recovery. Clearly, certain end products have similar characteristics as fossil reserve-based mineral fertilizers. If these products would achieve the regulatory status of 'renewable' mineral fertilizer according to fertilizer regulations, it would be possible to apply them as substitute for chemical mineral fertilizers in addition to animal manure (or raw digestate). Such a legislative transition would greatly help to overcome the present 'barriers-to-change' in the area of nutrient management and to achieve successful marketing of recovered products for agricultural use.

Finally, one of the most important topics in global policy making is the overall improvement of process sustainability. This leads to the proposition to further investigate the environmental impact of NRTs, see, e.g. Chapter 4 (Vaneeckhaute *et al.*, 2013b). Indeed, these technologies may also have some adverse effects on the environment, related to the consumption of fossil fuels, use of chemicals, possible NH_3 emissions, transport, etc. However, if their implementation could reduce the production and use of chemical mineral fertilizers in the farming community, (partially) replace non-sustainable nutrient removal practices in the waste(water) processing sector, produce renewable energy (anaerobic digestion), and thereby avoid the emissions posed by untreated animal manure and other biodegradable wastes, overall a serious decrease in primary energy consumption and greenhouse gas emissions could be achieved. Sutton *et al.* (2013) reported that a global improvement in full-chain nutrient use efficiency of 20 % in 2020 relative to 2013 would deliver an estimated saving of 20 million tons of reactive N. This would equate to a global improvement in human health, climate, and biodiversity in the order of € 143 (40-319) billion per year *(202 (57-197) billion CAD per year)*. A thorough investigation and evaluation of nutrient recovery strategies and treatment trains by means of life cycle assessments could provide an objective basis for further policy making (see Chapter 12).

2.6 Conclusions

Struvite precipitation/crystallization, NH_3 stripping and absorption, and acidic air scrubbing can be selected as best available technologies for nutrient recovery from digestate. These technologies have already been implemented at full-scale and have the ability to produce marketable end products. Vibrating membrane filtration (VSEP) also shows potential to become part of the commonly used nutrient recovery technologies, but its technical and economic performance at full-scale remains to be demonstrated. All technologies require further technical fine-tuning in order to minimize operational costs, especially related to energy and chemical use, and to improve the quality and predictability of the produced fertilizers. To date, recovered bio-based fertilizers can be classified as renewable N/P-, K/P-, or P-precipitates, P-extracts, N/S-solutions, N/K-concentrates, N-zeolites, and biomass. Future research should further explore, verify, and improve the fertilizer characteristics and marketing value of these products towards industrial and agricultural end-users.



PHASE II

PRODUCT VALUE EVALUATION

CHAPTER 3:

FATE OF MACRONUTRIENTS IN WATER TREATMENT OF DIGESTATE USING VIBRATING REVERSED OSMOSIS

Air picture of the case study site: Goemaere Eneco Energy, Diksmuide, Belgium
(Picture: Reynen J.)

Redrafted from:

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Abstract

In the transition from a fossil reserve-based to a bio-based economy, it has become an important challenge to maximally recover and recycle valuable nutrients from digestate processing. Membrane filtration is a suitable technology to separate nutrients in easily transportable concentrates, which could potentially be reused as renewable fertilizers, in the meantime producing high-quality water. However, traditional membrane filtration systems often suffer technical problems in waste stream treatment. The aim of this study was to evaluate the performance of vibratory shear enhanced processing (VSEP) in the removal of macronutrients (N, P, K, Ca, Mg) and salts (Na) from the liquid fraction of digestates, reducing their concentrations down to dischargeable/reusable water. In addition, the reuse potential of VSEP-concentrates as sustainable substitutes for fossil reserve-based mineral fertilizers was evaluated. Removal efficiencies for N and P by two VSEP filtration steps were high, though not sufficient to continuously reach the Flemish legislation criteria for discharge into surface waters (15 mg N L^{-1} and 2 mg P L^{-1}). Additional purification can occur in a subsequent lagoon, yet further optimization of the VSEP filtration system is advised. Furthermore, concentrates produced by one membrane filtration step showed potential as N/K fertilizer with an economic value of € 6.3±1.1 *(8.9±1.5 CAD)* ton^{-1} fresh weight. Further research is required to evaluate the impact on crop production and soil quality by application of these new potential renewable fertilizers, and the associated economic and ecological impact.

***Keywords**: anaerobic digestion; bio-based fertilizers; digestate processing; nutrient recycling; vibrating membrane filtration; water quality.*

Résumé

Pour permettre le passage d'une économie axée sur les ressources fossiles à une économie axée sur les ressources biologiques, la récupération et le recyclage optimal des nutriments provenant du digestat constituent un défi important. La filtration membranaire est une technologie adaptée à la concentration des nutriments dans des concentrés facilement transportables et utilisables en tant qu'engrais renouvelables et à la production d'une eau de haute qualité. Cependant, les systèmes traditionnels de filtration membranaire souffrent souvent de problèmes techniques dans le traitement des flux de déchets. L'objectif de cette étude était d'évaluer la performance de la filtration membranaire vibrante (VSEP) dans l'enlèvement des macronutriments (N, P, K, Ca, Mg) et du sel (Na) de la fraction liquide du digestat afin d'obtenir de l'eau déchargeable ou réutilisable. En outre, le potentiel de réutilisation des concentrés de VSEP comme substituts durables aux engrais minéraux fossiles a été évalué. La performance d'enlèvement de N et P en deux étapes de filtration était élevée, mais pas suffisante pour atteindre en permanence les critères de la législation flamande pour déversement dans les eaux de surface (15 mg N L^{-1} et 2 mg P L^{-1}). Une purification supplémentaire peut être réalisée dans une lagune, mais une optimisation plus poussée du système de filtration VSEP est conseillée. En outre, les concentrés produits par une étape de filtration membranaire ont révélé un engrais N-K potentiel d'une valeur économique de € 6.3±1.1 *(8.9±1.5 CAD)* $tonne^{-1}$ poids frais. Des recherches supplémentaires sont nécessaires pour évaluer l'impact de l'application de ces engrais potentiels sur la production agricole et la qualité des sols, et l'impact économique et écologique associé.

Mots-clés: *bio-engrais; digestion anaérobie; filtration membranaire vibrante; qualité de l'eau; recyclage des nutriments; traitement du digestat.*

3.1 Introduction

The European 2001/77/EG guideline states that, by 2020, 13 % of the generated electricity in Belgium should be based on renewable resources. Strikingly, the current renewable contribution comprises only 4.7 % in relative renewable share of the overall national energy production (Mira-T, 2010). In this respect, the Flemish Energy Agency (2010) estimates that based on the production potential of various renewable technologies (solar, wind, hydro, biomass, and other), 72 % of the renewable objectives in Flanders need to be derived from bio-energy (FEA, 2010). Hereby the production of biogas through anaerobic (co-)digestion of energy crops, organic residues, and animal wastes has been evaluated as one of the most energy-efficient and environmentally beneficial technologies for bio-energy production (Fehrenbach *et al.*, 2008).

In spite of its high potential, it was not until 2007 that, following adaptations in the Manure Decree, anaerobic digestion effectively launched as a budding market in Belgium. However, an important issue complicating the development of bio-digestion in Flanders and other high-nutrient regions is that the produced digestate may not, or only sparingly, be returned to arable land as a fertilizer in its crude unprocessed form (Chapter 1; Lemmens *et al.* 2007). The underlying reason for this technical prerequisite is that, due to the intensive industrial animal production, the northern part of Belgium (Flanders) is confronted with an overproduction of animal manure in comparison to the available arable land to spread it on. As a consequence, overfertilization has led to eutrophication of water bodies. This resulted in the condemnation of Belgium in respect with the EU Nitrate Directive (91/676/EEC; EC, 1991), forcing local administrators and governments to enforce more stringent regulations regarding manure and digestates.

Previous chapters have shown the relevance and importance of recovering and recycling valuable nutrients from the digestate in a sustainable and environmentally friendly manner. Initial steps of digestate processing generally involve the use of separation and/or dewatering technologies, using emulsion or powder based polymers for flocculation (Hjorth *et al.*, 2010). The resulting thick fractions are commonly pasteurized and stabilized turning them into exportable organic soil conditioners, rich in phosphorus (P). The liquid fraction still contains most of the digestate's potassium (K) and inorganic nitrogen (N), next to the remaining soluble P. Chapter 2 has revealed the potential to extract and recover these valuable nutrients from the liquid digestate for reuse as concentrated fertilizer products, thereby providing sustainable substitutes for fossil reserve-based mineral fertilizers.

To date, the best available technologies for nutrient recovery from the liquid fraction are struvite precipitation/crystallization, ammonia stripping, and (subsequent) acidic air scrubbing, in order to produce N/P and N/S fertilizers, respectively (Chapter 2). In addition, membrane filtration technologies are of increasing interest in order to recover N/K fertilizers. Indeed, membrane filtration may potentially be used to separate nutrients from the liquid digestate in easily transportable and usable N/K-concentrates that can be applied when and where needed, according to plant requirements for optimum growth and contamination vulnerability of the agricultural site (Kertesz *et al.*, 2010; Masse *et al.*, 2007). Moreover, selective reversed osmosis (RO) membranes (1 nm pore size) can also produce water of relatively high quality that could be discharged or reused (Gagliardo *et al.*, 1998; Roeper *et al.*, 2007).

In spite of all their benefits, traditional membrane technologies often experience technical problems for waste stream treatment, mainly caused by membrane fouling and clogging (Masse *et al.* 2007). Membrane fouling is characterized by a decline in flux, due to the deposition and accumulation of materials on the membrane surface or within the pore structure (Cheryan, 1998). In its strictest sense, fouling causes an irreversible flux decline, which can only be restored by thermo-chemical cleaning, if it can be recovered at all. In short-term studies, clean water flux could always be recovered following intensive acidic and alkaline cleaning (Bilstad *et al.*, 1992), which, however, still leads to high operational costs. Because of these technical bottlenecks, to date membrane filtration has not yet proven to be a viable option for the treatment of digestate.

Atkinson (2005) and Johnson *et al.* (2004), from New Logic Research (Emeryville, Ontario, Canada), reported on the use of vibrating shear enhanced processing (VSEP) for manure purification. The system uses vibrating (60-90 Hz) RO-membranes to minimize flux reduction due to concentration polarization and membrane fouling (Kertesz *et al.*, 2010). As such, the VSEP technology has the potential to make it technically feasible to convert nutrient-rich waste flows into dischargeable water according to the Flemish legislation criteria for discharge into surface waters (15 mg N L^{-1}, 2 mg P L^{-1}, and 125 mg COD L^{-1}, i.e. chemical oxygen demand). Meanwhile, operational costs may be reduced. Nevertheless, studies evaluating the performance of the VSEP technology in a pilot/full-scale digestate treatment train aiming at the production of dischargeable/reusable water and N/K-concentrates are absent in literature.

This chapter aims to study the fate of macronutrients (N, P, K, calcium (Ca), magnesium (Mg)) and sodium (Na ~ salt content) in the treatment process of the liquid fraction of digestate produced by co-digestion of animal manure, energy maize, and residues from the food industry, using vibrating reversed osmosis to reduce their concentrations down to dischargeable/reusable water. To this end, process streams have been characterized and mass balances throughout the treatment train were set up. First, the potential of the VSEP technology to transform the liquid fraction of digestate into dischargeable/reusable water is assessed. Next, the prospects for reusing nutrient-rich VSEP-concentrates in a sustainable cradle-to-cradle concept are explored and evaluated.

3.2 Material and methods

3.2.1 Site description and experimental set-up

The test site is a full-scale biogas plant (378 kW_{el}) located in Diksmuide, Belgium (Goemaere Eneco Energy). It concerns an anaerobic digester with an input feed consisting of animal manure (30 %), energy maize (30 %), and residues from the food industry (40 %), with a total capacity of 12,000 tons y^{-1} of fresh weight (FW). The digestate treatment process, operational since October 2007, is schematically represented in Figure 3.1.

The digestate (10±0 % dry weight, DW) is first separated into a liquid and thick fraction (19±3 % DW) using a rotating drum, after adding polymer solution. The resulting thick fraction is then guided to a screw press for further dewatering, followed by a dryer, in order to obtain an exportable end product at 76±1 % DW. The liquid fraction is filtrated twice by a VSEP using RO-membranes (Fig. 3.2; VSEP Series i-84, ± 140 m^2 membrane area, New Logic, Emeryville, Ontario, Canada). Each filtration step results in a concentrate and permeate flow. The permeate produced by the second filtration should meet the Flemish legislation criteria for discharge into surface waters.

Figure 3.2 Pilot installation of the vibratory shear enhanced processing (VSEP) technology at Goemaere Eneco Energy, Diksmuide, Belgium. Picture: Vaneeckhaute C.

Total daily incoming feed volume to the VSEP for the first (1st) filtration is 50 m^3 (Fig. 3.1). At an operational time of 12 h d^{-1}, this results in a feed flow of 4.2 m^3 h^{-1}. The feed includes liquid fraction produced by the rotating drum (2.3 m^3 h^{-1}), recycled concentrate from the second (2nd) membrane filtration step (0.50 m^3 h^{-1}), washing water from the rotating drum (0.50 m^3 h^{-1}), and cleaning water for the VSEP (0.80 m^3 h^{-1}). The membrane recovery rate is 80 %, thus resulting in a permeate flow of 40 m^3 d^{-1} and a concentrate flow of 10 m^3 d^{-1} produced by the 1st filtration. The permeate (40 m^3 d^{-1}) is then forwarded towards the VSEP for the 2nd filtration. At an operational time of 6 h d^{-1}, this results in a feed flow of 6.7 m^3 h^{-1}. The 2nd filtration, with membrane recovery rate of 85 %, produces a permeate flow of 34 m^3 d^{-1} and a concentrate flow of 6.0 m^3 d^{-1}.

Because the VSEP-permeate is warm (45 °C) and biologically inactive, it cannot be discharged in surface waters as such. It is guided to a lagoon for cooling, biological reactivation, and further water polishing (Fig. 3.3). The lagoon consists of two compartments (width: 12 m, length: 21 m).

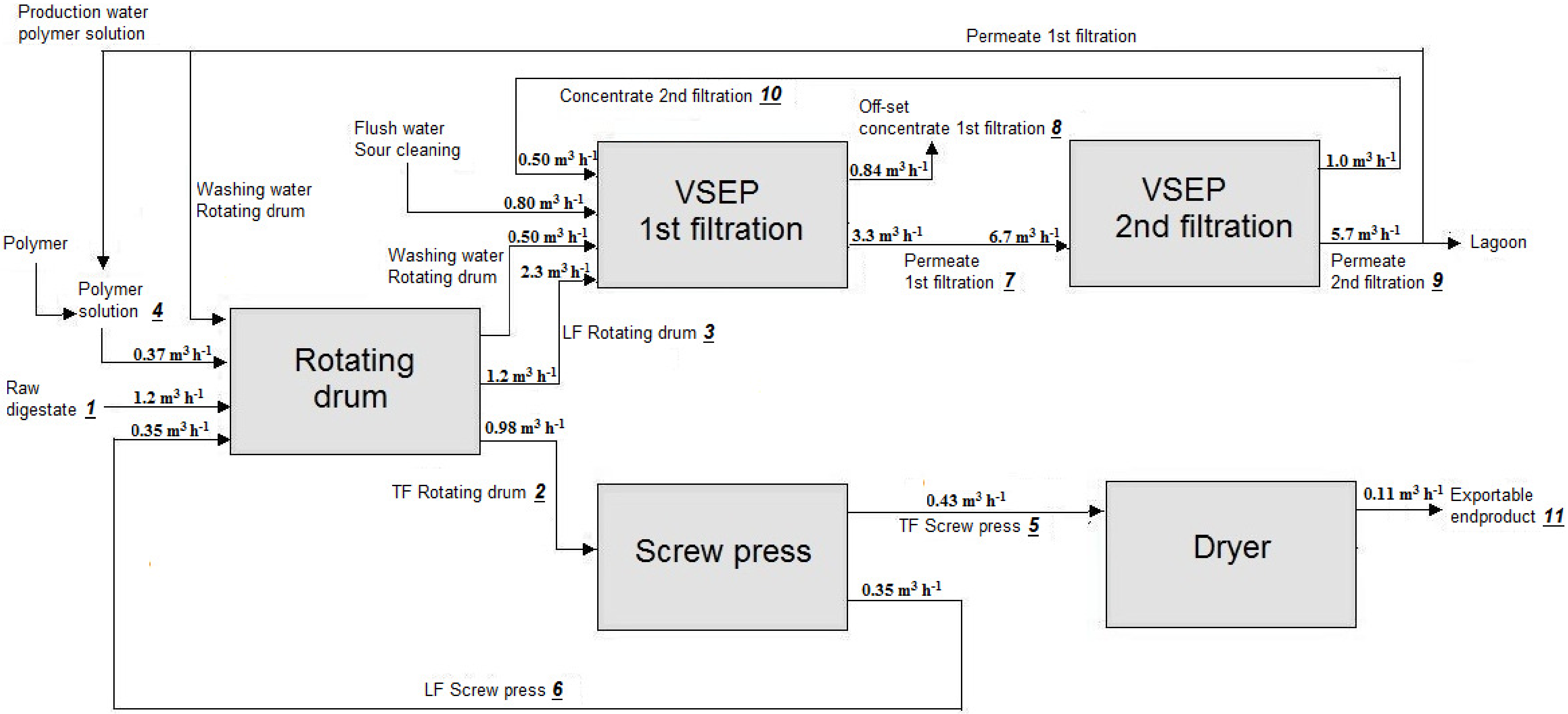

Figure 3.1 Schematic representation of the digestate treatment process. Numbers *1-11* mark the sample locations. The volumetric flow rates of streams 3, 7, and 10 change during the process. LF = liquid fraction; TF = thick fraction; VSEP = vibratory shear enhanced processing.

The first compartment (depth: 2.5 m) is mechanically aerated in order to cool down the water and to provide oxygen for biological processes. In this compartment NH_4-N is converted into NO_3-N (nitrification). The second compartment (depth: 1 m) is half-filled with porous lava stones and has a low water flow velocity. This allows the rooting of different macrophyte species, such as the marsh marigold *(Caltha palustris)*, which take up nutrients for growth. Also, in this compartment NO_3-N is converted into N_2 (denitrification), while organic matter is microbiologically degraded. The lagoon thus serves as a buffer zone where further biological purification, as well as natural purification by dilution with rainwater, of the VSEP-permeate occurs.

Figure 3.3 Lagoon for final effluent treatment at Goemaere Eneco Energy, Diksmuide, Belgium. Pictures: Vaneeckhaute C.

Samples for physicochemical analysis of the process streams were taken during two sampling campaigns spread over two months time. During each sampling event, two homogenized samples (ten liters each) were taken of the different process streams on a different time of the day (= total of four samples per stream). The samples were collected in polyethylene sampling buckets and transported within 1 h from the test site to the laboratory, carried in cooler boxes filled with ice. In the laboratory, the four replicate samples were stored cool (1-5 °C) and kept separate for replicate analysis. Each sample was analyzed twice in order to detect the precision of the analytical method. The following process flows were sampled (Fig. 3.1): raw digestate (1), thick (2) and liquid (3) fraction produced by the rotating drum, polymer solution (4), thick (5) and liquid (6) fraction produced by the screw press, permeate (7) and concentrate (8) produced by the 1st filtration step, permeate (9) and concentrate (10) produced by the 2nd filtration step, and finally the exportable end product (11). Moreover, the contents of N and P, as well as the COD in the second compartment of the lagoon following membrane filtration were daily monitored at the test site during the experimental period (two months).

3.2.2 Liquid sample analysis

Electrical conductivity (EC) and pH were determined potentiometrically using a WTW F537 conductivity electrode (Wissenschaftlich Technischen Werkstäten, Weilcheim, DE) and an Orion 520A pH meter (Orion Research, Boston, USA), respectively. The salt content was estimated as total dissolved solids (TDS) from the EC using the following approximation: TDS (mg L^{-1}) = EC ($\mu S\ cm^{-1}$) x 0.64 (Ali *et al.*, 2012; Van Ranst *et al.*, 1999). Total N content was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest, Köningswinter, DE) after digestion of the sample in a sulphuric-salicylic acid mixture. Finally, the captured ammonia in the distillate was titrated with 0.01 mol L^{-1} hydrogen chloride (HCl) in the presence of a methyl red bromocresol green mixed indicator (Van Ranst *et al.*, 1999). Total P content was determined using the colorimetric method of Scheel (1936; Van Ranst *et al.*, 1999) after wet digestion of the liquid samples (2.5 g sample + 2 mL nitric acid, HNO_3, + 1 mL hydrogen peroxide, H_2O_2). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, UK). Ca and Mg were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Vista MPX, Palo Alto, CA, USA) after wet digestion (as described above). The total hardness (D°H, German degrees of hardness) was computed from the Ca and Mg contents, using the formulations in CSA (2015). Na and K in the digested samples (see above) were analyzed using a flame photometer (Eppendorf ELEX6361, Hamburg, DE). The COD was determined photometrically using Dr. Lange standardized cuvette-tests (Dr. Bruno Lange GmbH & Co, KG Düsseldorf, DE).

3.2.3 Thick sample analysis

The dry weight (DW) content was determined as residual weight after 48 h drying at 100 °C in an oven (EU 170, Jouan s.a, Saint Herblain, FR). The EC and pH were measured using a WTW F537 conductivity electrode (Wissenschaftlich Technischen Werkstäten, Weilcheim, DE) and an Orion 520A pH meter (Orion Research, Boston, USA), respectively, after equilibration for 1 h in deionized water at a 5:1 liquid:dry sample ratio and subsequent filtering (white ribbon, MN 640 m, Macherey-Nagel, Düren, DE). The salt content was derived from the EC as described in Section 3.2.2. Total N was determined using the Kjeldahl procedure (Section 3.2.2; Van Ranst *et al.*, 1999). For the determination of P, dry samples were incinerated at 450 °C during 4 h in a muffle furnace (Nabertherm, Lilientahl, DE). The P content was then determined by the colorimetric method of Scheel (1936; Van Ranst *et al.*, 1999) after digestion of the residual ash (1 g ash + 5 mL of 3 mol L^{-1} HNO_3 + 5 mL of 6 mol L^{-1} HNO_3). Ca and Mg in the digested samples were analyzed by means of ICP-OES, while Na and K in the digested samples were determined using a flame photometer (Section 3.2.2).

3.2.4 Mass balance calculations

Process flow rates were monitored by means of flow meters at inlet and outlet points of each process step (rotating drum, screw press, VSEP 1st filtration, VSEP 2nd filtration, dryer). Nutrient mass flow rates were assessed by multiplying the volumetric flow rate and nutrient concentrations for each individual flow. This allowed calculating removal/recovery efficiencies of macronutrients in the liquid fraction of the digestate for each process step.

3.3 Results

3.3.1 Physicochemical characterization of process flows

Average macronutrient contents (+ standard deviations of the replicates) in the different process flows were analyzed (Table 3.1). It is clear that the permeate produced by one filtration step did not meet the Flemish discharge legislation criteria of 15 mg N L^{-1} and 2 mg P L^{-1}. N and P contents in the VSEP-permeate produced by the 2nd filtration were low, although average concentrations were also not below the discharge criteria. Nevertheless, in the subsequent lagoon, the average concentrations for N and P based on daily monitoring during the experimental period were 12±6 mg N L^{-1} and 1.6±1.0 mg P L^{-1}, respectively, and thus met the discharge levels. Furthermore, it was observed that the COD in the VSEP-permeates can reach high peaks related to the addition of citric acid ($C_6H_8O_7$) during acidic cleaning events. Nevertheless, the COD in the lagoon (26±10 mg COD L^{-1}) was constantly below the Flemish discharge level of 125 mg COD L^{-1} due to microbial breakdown of the organic matter and dilution with rainwater. Finally, it was observed that average concentrations of Ca, Mg, and Na in the permeate produced by the 2nd filtration step were very low, in agreement with the low salt content (0.56 g salt kg^{-1} FW or 0.88 mS cm^{-1}) and total hardness (0.19±0.12 D°H) of this process flow.

3.3.2 Mass balances

Figures 3.4, 3.5, and 3.6 exhibit mass balances of the process for N and P, K and Na, and Ca and Mg, respectively. The volumetric flow rates (m^3 h^{-1}) can be found in Figure 3.1. It should be remarked that the flow rate of some streams (3, 7, and 10) change in the digestate treatment process (output one unit vs. input subsequent unit). As a first step in the process, the incoming mass flow to the rotating drum is determined mainly by the raw digestate produced by the anaerobic digester. Also the liquid fraction produced by the subsequent screw press is recycled to the rotating drum. Polyelectrolyte was used to improve the separation efficiency. The resulting thick fraction is further dewatered by the screw press and dried to an exportable end product. The separated liquid mass flow contained more N, K, and Na than the corresponding thick flow. Reversely, the thick mass flow was richer in P, Ca, and Mg. The liquid fraction produced by the rotating drum enters the VSEP filtration system. As expected, most of the macronutrients after the 1st filtration step ended up in the concentrate. The permeate produced by the 1st VSEP filtration step is submitted to a 2nd filtration. The concentrate produced by this 2nd filtration is recycled to the VSEP for the 1st filtration step. During the sampling period, the permeate produced by the 2nd filtration did not continuously meet the Flemish legislation criteria for discharge into surface waters. It was guided to a lagoon for further biological and natural purification, as well as for cooling.

Table 3.1 Concentrations (g kg^{-1} FW) of N, P, K, Na, Ca, Mg, dry weight (DW, %), density (g L^{-1}), electrical conductivity (EC, mS cm^{-1}), salt content (g kg^{-1} FW), total hardness (D°H), and chemical oxygen demand (COD, mg L^{-1}) in the characterized process flows (mean ± standard deviation; n = 4). Numbers 1-11 correspond with the sample locations in Figure 3.1. FW = fresh weight; LF = liquid fraction; TF = thick fraction.

Process flow	**N (g kg^{-1} FW)**	**P (g kg^{-1} FW)**	**K (g kg^{-1} FW)**	**Na (g kg^{-1} FW)**	**Ca (g kg^{-1} FW)**	**Mg (g kg^{-1} FW)**
1. Digestate	4.6 ± 0.4	2.2 ± 0.8	3.5 ± 0.9	1.4 ± 0.6	2.3 ± 0.1	1.1 ± 0.1
2. TF Rotating drum	4.4 ± 0.0	4.4 ± 1.9	2.1 ± 0.2	1.1 ± 0.1	4.3 ± 0.1	2.2 ± 0.2
3. LF Rotating drum	2.6 ± 0.3	0.23 ± 0.11	1.5 ± 0.1	0.76 ± 0.13	0.054 ± 0.002	0.064 ± 0.024
4. Polymer solution	0.32 ± 0.03	0.46 ± 0.29	0.077 ± 0.022	0.045 ± 0.011	0.0046 ± 0.0023	0.00055 ± 0.00033
5. TF Screw press	5.7 ± 0.1	6.0 ± 2.3	2.1 ± 0.5	1.1 ± 0.3	6.3 ± 0.4	2.7 ± 0.2
6. LF Screw press	3.2 ± 1.9	1.8 ± 0.8	1.7 ± 0.1	0.90 ± 0.08	2.1 ± 0.1	1.4 ± 0.3
7. VSEP-permeate 1st filtration	0.13 ± 0.02	0.11 ± 0.00	0.18 ± 0.13	0.080 ± 0.089	0.00056 ± 0.00013	0.00028 ± 0.00007
8. VSEP-concentrate 1st filtration	7.3 ± 1.6	0.42 ± 0.08	2.9 ± 1.0	1.0 ± 0.6	0.19 ± 0.11	0.13 ± 0.16
9. VSEP-permeate 2nd filtration	0.094 ± 0.040	0.11 ± 0.00	0.11 ± 0.02	0.041 ± 0.019	0.00095 ± 0.00084	0.00023 ± 0.00001
10. VSEP-concentrate 2nd filtration	0.98 ± 0.20	0.12 ± 0.01	0.69 ± 0.25	0.28 ± 0.21	0.018 ± 0.007	0.014 ± 0.013
11. Dry end product	18 ± 1	14 ± 0	7.8 ± 0.3	2.4 ± 1.7	19 ± 2	8.0 ± 0.9

Process flow	**DW (%)**	**Density (g L^{-1})**	**EC (mS cm^{-1})**	**Salt content (g kg^{-1} FW)**	**Total hardness (D°H)**	**COD (mg L^{-1})**
1. Digestate	10 ± 0	-	57	187	574 ± 14	-
2. TF Rotating drum	17 ± 1	-	35	116	1,085 ± 14	-
3. LF Rotating drum	1.4 ± 0.0	1,016	24	15	22 ± 6	-
4. Polymer solution	- ± -	1,000	1.3	0.82	0.77 ± 0.40	-
5. TF Screw press	23 ± 1	-	24	82	1,502 ± 56	-
6. LF Screw press	8.2 ± 1.7	1,036	16	10	616 ± 83	-
7. VSEP-permeate 1st filtration	- ± -	1,000	1.5	0.95	0.14 ± 0.03	473 ± 67
8. VSEP-concentrate 1st filtration	7.4 ± 0.0	1,045	66	40	56 ± 52	-
9. VSEP-permeate 2nd filtration	- ± -	1,000	0.88	0.56	0.19 ± 0.12	92 ± 42
10. VSEP-concentrate 2nd filtration	0.53 ± 0.00	1,003	14	8.8	5.7 ± 4.0	-
11. Dry end product	76 ± 1	-	26	96	4,498 ± 487	-

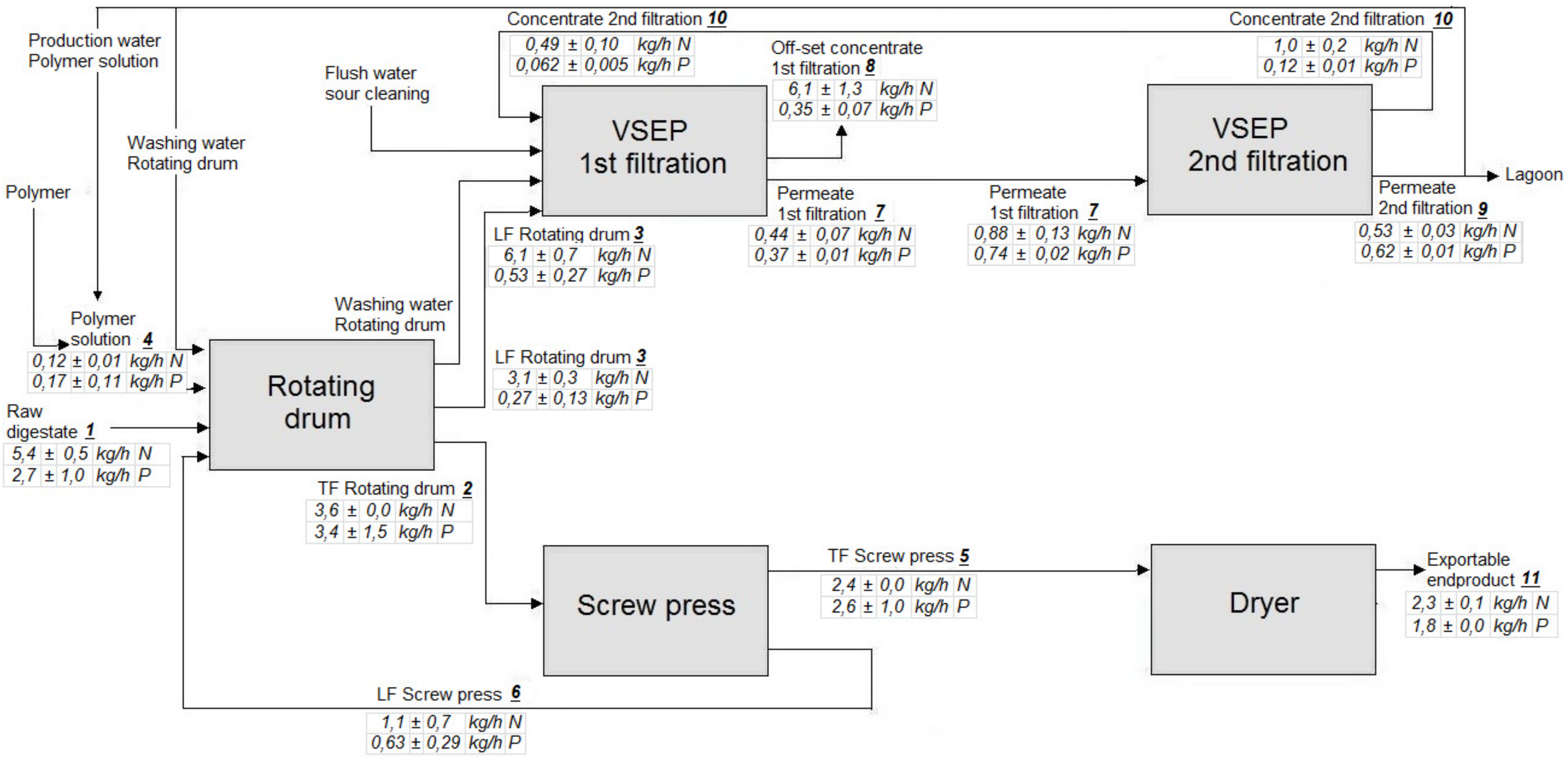

Figure 3.4 Mass balance for nitrogen (N) and phosphorus (P) in kg h^{-1}.
The volumetric flow rates of streams 3, 7, and 10 change during the process.
LF = liquid fraction; TF = thick fraction; VSEP = vibratory shear enhanced processing.

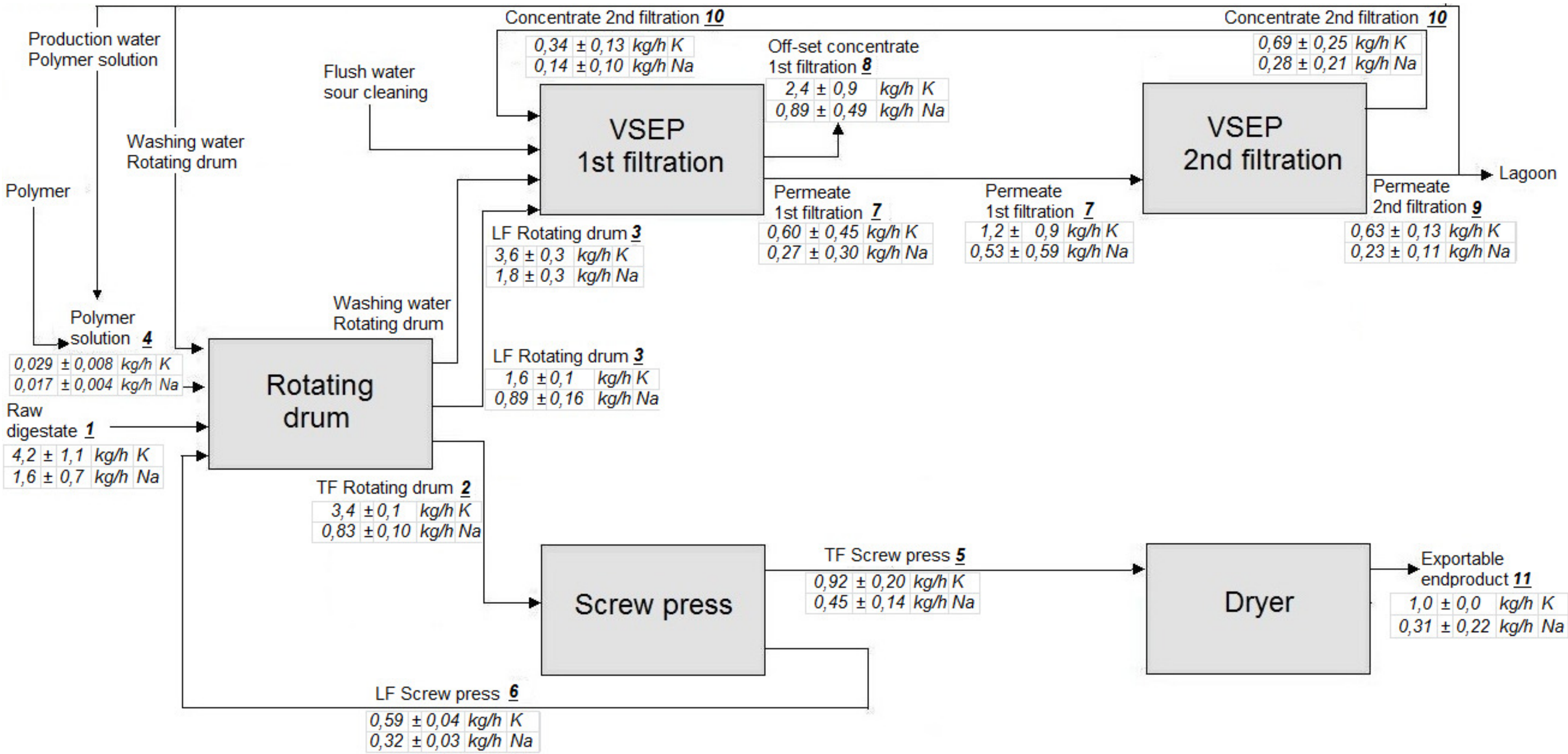

Figure 3.5 Mass balance for K and Na in kg h^{-1}.
The volumetric flow rates of streams 3, 7, and 10 change during the process.
LF = liquid fraction; TF = thick fraction; VSEP = vibratory shear enhanced processing.

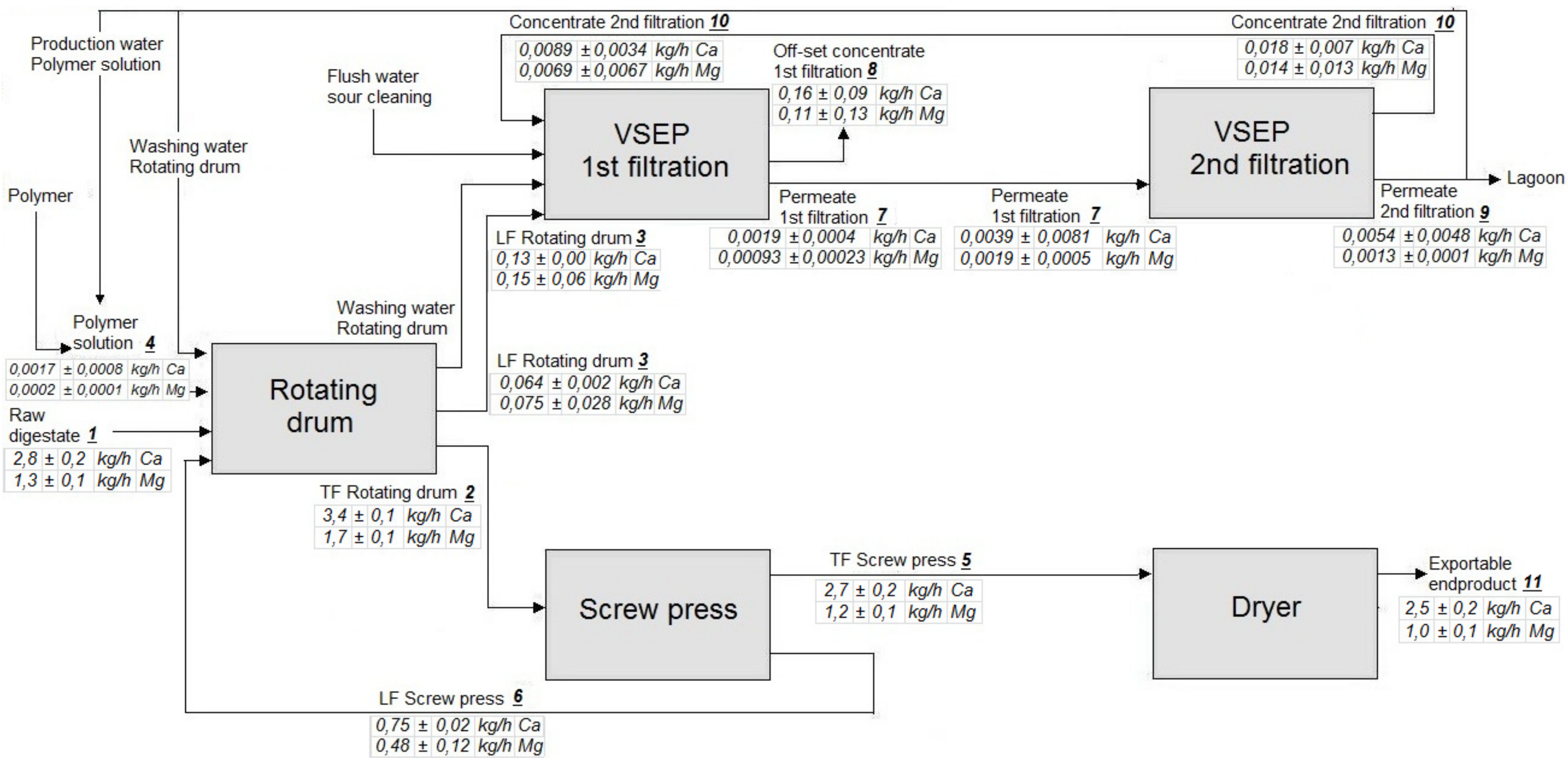

Figure 3.6 Mass balance for Ca and Mg in kg h^{-1}.
The volumetric flow rates of streams 3, 7, and 10 change during the process.
LF = liquid fraction; TF = thick fraction; VSEP = vibratory shear enhanced processing.

3.4. Discussion

3.4.1 Mass balance equilibrium

Total incoming and outgoing mass flows to each particular unit process are approximately equal (Fig. 3.4-3.6), showing that the mass balances are roughly in equilibrium. Small deviations can be caused by the accuracy and precision of the used physicochemical laboratory protocols. Larger deviations can also be caused by biological activity or physicochemical reactions. This can occur, for example, when N escapes from the system as nitrogen gas (N_2) or ammonia (NH_3), or forms ammonium sulfate by reaction with sulfuric acid (H_2SO_4) or hydrogen sulfide (H_2S). Nitrogen losses to air are an important issue in manure and digestate processing. Based on the observed data, it is estimated that the average N losses in the rotating drum, the screw press, and the dryer are 0.85 %, 0.44 %, and 5.0 %, respectively, resulting in a total N loss of 6.3 % over these process steps. The released ammonia is captured in an acidic air scrubber, thereby producing ammonium sulfate as a waste stream. This product could potentially be reused as renewable fertilizer in agriculture in order to close the N cycle (Chapter 2). On the contrary, for the VSEP system, it was observed that total outgoing mass flows can be larger than total incoming flows. This is related to the fact that sludge from previous filtration steps is retained on the membrane surface and can end up in concentrates produced by subsequent filtrations. Finally, the use of washing water can also cause mass balance deviations, for example, when the rotating drum is cleaned with permeate produced by the 1st filtration step.

3.4.2 Digestate pre-treatment

In general, digestate processing tends to be limited to an initial separation and/or dewatering step, producing a liquid and thick fraction with different macronutrient contents (Hjorth *et al.*, 2010). In this particular case, the initial separation occurred using a rotating drum after addition of polymer solution, followed by a screw press for further dewatering of the resulting thick fraction. As expected (Hjorth *et al.*, 2010), most of the P (91 %), Ca (96 %), and Mg (92 %) were recovered in the thick fraction, which can be dried to an exportable (to P-poor regions), organic soil conditioner. In contrast, most of the N (57 %), K (78 %), and Na (72 %) ended up in the liquid fraction. The VSEP system is intended to separate these valuable macronutrients into easily transportable concentrates, producing permeates low in nutrient contents that meet the Flemish legislation criteria for discharge into surface waters.

3.4.3 VSEP performance in water treatment of digestate

Monitoring results for the 1st VSEP filtration step show average removal efficiencies of 93 % for N present in the total incoming feed and 59 % for P, which are insufficient to achieve the Flemish discharge criteria (respectively 15 and 2 mg L^{-1}). Yet, in this study, the N removal was higher than that reported by Johnson *et al.* (2004) for hog manure (79 %), while the P removal was less (86 %). Forwarding the permeate to a 2nd VSEP filtration step resulted in a total N and P removal of 95 % and 69 %, respectively, which is still not sufficient to meet the discharge criteria. Also the COD in the produced permeates was often too high for discharge in surface waters due to intensive cleaning events with citric acid ($C_6H_8O_7$). Further purification in the lagoon through microbiological nitrification-denitrification, nutrient accumulation, plant nutrient uptake (autotrophic photosynthesis), and dilution with rainwater, allowed improving the water quality to the standards for dischargeable water. However, due to technical and mechanical problems, the VSEP performance was instable and legislative levels were also frequently exceeded in the lagoon. Moreover, during the nitrification-denitrification process in the lagoon, N_2 gas is released in the atmosphere and eliminated from the local agricultural cycle. It is therefore advised to further optimize VSEP process parameters, such as vibration frequency and amplitude, filtration time, pH and temperature, as well as conditioning and pre-filtration of the feed (Frappart *et al.*, 2008; Johnson *et al.*, 2004; Petala and Zouboulis, 2006). Johnson *et al.* (2004) and Masse *et al.* (2010) found that pH and temperature have significant effects on the ammonia-ammonium equilibrium and thus on the removal efficiency of N from manure wastewater by VSEP filtration systems. In this context, also the membrane type is of particular importance. During the anaerobic digestion most of the N is transformed into positively charged ammonium, which is better retained using negatively charged membranes.

There exist no discharge criteria for K, Na, Ca, and Mg, though, regarding future water reuse perspectives, these elements are of particular interest. Results show that both the salt content (0.88 mS cm^{-1} or 0.56 g salt kg^{-1} FW) and the total hardness (0.19±0.12 D°H) in the produced permeates were low, making it a valuable source of high-quality water that could potentially be reused, for example, as process water, irrigation water, or drinking water (Vaneeckhaute, 2010). RO-membranes have also been evaluated positively in the past for the elimination of viruses and bacteria from wastewater streams (Gagliardo *et al.*, 1998; Roeper *et al.*, 2007; Tam *et al.*, 2007). The fate of micronutrients and heavy metals in digestate processing was not at the core of the present chapter. However, the concentrations of aluminium (Al), cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), nickel (Ni), and zinc (Zn) in the various process flows were also identified and are given as supplementary information in Appendix 1. The concentrations of these metals in the VSEP-permeates were mostly lower than the respective detection limits of inductively coupled plasma optical emission spectrometry (ICP-OES), again indicating the reuse potential of these water flows for high-quality applications (Vaneeckhaute, 2010). Regarding the worldwide increasing scarcity of water resources and the rising prices of tap water (± € 2 m^{-3}; Flemish Water Supply Company VMW, Leuven, Belgium, personal communication 2011), **it is an important challenge, economically as well as ecologically, to maximally recover this high-quality water source in a sustainable cradle-to-cradle approach**. In addition, water reuse could turn out in economic benefits for anaerobic digestion plants, thereby stimulating the further development of this bio-energy technology in Flanders and abroad.

Compared to other membrane filtration systems, previous studies have shown that the gel layer is much lower in the case of the VSEP, because of the high shear-enhanced forces on the membrane surface during the experiments (Bian *et al.*, 2000; Culkin *et al.*, 1998; Johnson *et al.*, 2004; Wei and Mark, 2008). Though there are currently several VSEPs in operation for agricultural wastewater treatment (New Logic Research Inc., Emeryville, Ontaria, Canada, personal communication 2012), there are little data available on the energy consumption and treatment costs of this technology. Akoum *et al.* (2005) reported on the potential energy saving of the vibratory concept. When 61 cm-diameter membranes are used, a total of 151 m^2 can be installed on a single shaft (VSEP series i-10). The energy consumed per vibration is then 8.83 kW, as it is not much affected by the number of compartments. Energy consumed by the feed pump is also small, as its flow rate does not need to be much larger than the permeate flow rate. They estimated the energy consumed by the recirculation pump at 9.4 kWh per m^3 of permeate in a 154 m^2 membrane area unit. This could be reduced to 6 kWh m^{-3} if plane ceramic membranes were used. Energetic calculations based on these data indicate that large VSEP units will consume significantly less energy per m^3 of permeate than traditional cross-flow filtration. Nevertheless, energy consumption and economic performance remain critical points of attention in evaluating membrane technology.

3.4.4 Agricultural and economic value of concentrates

Membrane technology allows to concentrate nutrients recovered in the liquid fraction of digestate in a small volume that can be transported to agricultural fields. Concentrates produced by the 1st membrane filtration step could potentially be reused as inorganic fertilizers, rich in N and K. The N content was 7.3±1.6 kg ton^{-1} FW, which is comparable to that of conventional pig manure (5-10 kg N ton^{-1} FW; Lemmens *et al.* 2007). The K_2O content was 3.5±0.0 kg ton^{-1} FW, which is lower than predicted literature data (6-12 kg K_2O ton^{-1} FW; Melse and Verdoes, 2002), but slightly higher than that of conventional pig manure (3.3 kg K_2O ton^{-1} FW; Lemmens *et al.*, 2007). As expected, the amount of P in the concentrates was rather low, because most of the P ends up in the separated thick fraction during the pre-treatment. Regarding the P restrictions that become more and more stringent in high-nutrient regions, the use of this P-poor fertilizer could benefit important advantages. Concentrates produced by the 2nd membrane filtration step were poor in macronutrients and have therefore little/no potential for reuse as a fertilizer. This flow is currently recycled within the process.

Although K is an important element for crop production, high ratios of K over N and P are not preferred in every agricultural sector. Especially cattle farmers rather use K-poor fertilizers, because of the potential health risks for cattle (head illness) at high K fertilization (> 50 ton ha^{-1} y^{-1}; Hillel, 2008; Romheld and Kirkby, 2010). Also, high ratios of monovalent cations, such as K and Na, to divalent bases, such as Ca and Mg, may cause degradation of the soil structure, especially when soils are rich in clay (USEPA, 2004). Hence, the soil characteristics, the type of animal production and agricultural crop, as well as the characteristics of the base fertilizer, will all play a role in determining the optimal concentrate dose that ensures sufficient readily available K_2O for plant growth at minimal environmental pollution and health risks (EFMA, 2003; Hillel 2008; Romheld and Kirkby, 2010). Furthermore, concentrates produced by the 1st membrane filtration could have higher salt contents (66 mS cm^{-1}) compared to conventional animal manure (30-50 mS cm^{-1}; Moral *et al.*, 2008). This results in high salt:N ratio's (± 6) for this product. Too high salt contents can cause soil degradation and can dramatically reduce crop production (Verlinden, 2005). Therefore, when using concentrates in agriculture, it will also be important to pay attention to the salt doses per unit N that is applied to the soil. Extensive greenhouse and field-testing will be required to investigate the impact of concentrates on soil and crop production.

Finally, noteworthy is that no products exceeded the legal composition and use requirements in terms of heavy metals (Al, Cd, Cu, Fe, Mn, Pb, Ni, Zn) for reuse as fertilizer and/or soil conditioner in agriculture, as described in Flemish legislation (Vlarea, 1989; Appendix 1). The level of contamination with organic substances and pathogens in these potential fertilizers was out of scope of the present study, but definitely is an important topic for future research.

Next to the potential ecological benefits of recovering nutrients and substituting chemical fertilizers, reuse of concentrates as a renewable fertilizer and/or soil conditioner in agriculture could also result in significant economic benefits. Nowadays, the anaerobic digestion plant has to pay high disposal or treatment costs for the offset of the produced concentrates. In the meantime, prices for chemical mineral fertilizers are increasing and nutrient resources are depleting (Öborn *et al.*, 2005; Ruddock *et al.*, 2003; Smit *et al.*, 2009; Vilalba *et al.*, 2008). Reuse of valuable nutrients coming from digestate processing could therefore also convert the digestate problem into an economic opportunity.

The economic value of concentrates can be calculated based on current cost prices for fossil reserve-based chemical fertilizers/soil conditioners (Table 3.2). The latter were obtained from a price request at Brenntag NV (Deerlijk, Belgium; 2011).

Table 3.2 Economic value (€ ton^{-1} FW; *CAD ton^{-1} FW*) of chemical fertilizers/soil conditioners (Brenntag NV, 2011). FW = fresh weight. € 1 ≈ 1.415 CAD (November 2014).

Chemical fertilizer / Soil conditioner	Economic value (€ ton^{-1} FW; *CAD ton^{-1} FW*)
Ammonium nitrate (27 % N)	165 *(232)*
Tripel superphosphate (46 % P)	268 *(377)*
Potassium chloride (60 % K)	365 *(514)*
Calcium oxide (71.5 % Ca)	165 *(232)*
Kieserite (25 % Mg)	260 *(366)*

The application of concentrates in agriculture could have a value of € 6.3±1.1 *(8.9±1.5 CAD)* ton^{-1} FW, if both N and K are appreciated by the agriculturist. If only N is appreciated, the economic value is € 4.5±1.0 *(6.3±1.4 CAD)* ton^{-1} FW, whereas it amounts to € 1.8±0.1 *(2.5±0.14 CAD)* ton^{-1} FW if only K is of relevance. Unlike traditional mineral fertilizers, these concentrates could also contain significant amounts of organic carbon (24±1 % in this study). Application of concentrates could therefore also have additional values in organic carbon recycling.

3.5 Conclusions and future perspectives

The performance of the VSEP filtration system technically and mechanically proved not yet satisfactory to allow for a reliable, continuous operation. Further technical/mechanical optimization of the process is required in order to implement the VSEP system in full-scale installations.

One VSEP filtration step resulted in an average removal of 93 % N and 59 % P, which was not sufficient to achieve the Flemish legal discharge criteria of 15 mg N L^{-1} and 2 mg P L^{-1}. A second VSEP filtration step allowed to achieve a total average removal efficiency of 95 % N and 69 % P, which was still not sufficient to meet the discharge criteria. A subsequent treatment in an aerated lagoon allowed producing dischargeable water. However, also in the lagoon, the discharge criteria were regularly exceeded due to the instability of the VSEP performance. Optimization of process parameters, such as membrane type, pH, temperature, as well as condition and pre-filtration of the feed, is therefore advised. On the upside, the salt content, the total hardness, and (heavy) metal concentrations in the permeate of the second VSEP filtration step were low, indicating that it could potentially be a water source for reuse in high-quality applications.

Concentrates produced by the first VSEP filtration step were rich in macronutrients and could potentially be reused as a sustainable substitute for fossil reserve-based mineral fertilizers. However, pot and field experiments are required to evaluate its impact on plant growth and soil quality. Reuse of nutrient-rich concentrates produced by VSEP membrane filtration in a sustainable cradle-to-cradle approach might so benefit the economic performance of anaerobic digestion in Flanders (and other high-nutrient regions), thereby stimulating the production of bio-energy in the framework of the 2020 objectives.

The VSEP filtration system has potential for use in the conversion of the liquid fraction of digestates into dischargeable/reusable water and renewable fertilizers, though further optimization and testing in full-scale installations is required.

CHAPTER 4:

ECOLOGICAL AND ECONOMIC BENEFITS OF THE APPLICATION OF BIO-BASED (ORGANO-)MINERAL FERTILIZERS IN MODERN AGRICULTURE

Ammonium sulfate wastewater from acidic air scrubbing (left) and membrane filtration concentrates (right) (Pictures: Vaneeckhaute C.)

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Abstract

During anaerobic digestion and digestate processing, multiple derivatives are produced, some of them possessing potential for reuse as chemical fertilizer substitutes. In-depth research on the composition and properties of these products is scarce, though very relevant, in order to identify bottlenecks for reuse and to evaluate the economic and environmental impact of various bio-based fertilization scenarios. A first aim of this chapter was to characterize in more detail the physicochemical properties of digestates and its derivatives. The fertilizer value and potential bottlenecks for agricultural reuse of these products were identified. Secondly, the economic and ecological (in terms of energy use and associated greenhouse gas emissions) benefits of substituting conventional fertilizers by bio-based alternatives were quantified and evaluated, using the Flanders region (Belgium) as an example. Ammonium sulfate (AmS) wastewater from acidic air scrubbers for ammonia recovery showed potential for application as N/S fertilizer. Analogously, concentrates resulting from membrane filtrated liquid fraction of digestate showed promise as N/K fertilizer. Substituting conventional fertilizers by digestate derivatives in different cultivation scenarios can result in significant economic and ecological benefits for the crop farmer. The most interesting scenario likely exists of an optimal (in terms of effective N over P content) combination of digestate and its liquid fraction as base fertilizer, meanwhile substituting chemical N by recovered AmS or concentrates. Based on the analysis, it was estimated that a marketing value of ± € 0.93 *(1.31 CAD)* kg^{-1} N and ± € 0.60 *(0.85 CAD)* kg^{-1} N could be imposed for the production of acidic air scrubber water and membrane filtration concentrates, respectively, in order to balance with the status quo (= no cost impact for the crop farmer). Starting from theoretical scenarios outlined in the current chapter, field test validation will be required to confirm the potential substitution of fossil reserve-based mineral fertilizers by bio-based alternatives. Moreover, a reconsideration of the legislative categorization of digestate and its derivatives based on their effective fertilizer properties is recommended so as to maximize the beneficial use of these products.

Keywords: *agricultural economics, anaerobic digestion, digestate processing, nutrient recycling, renewable fertilizers, sustainable agriculture.*

Résumé

Pendant la digestion anaérobie et le traitement du digestat, plusieurs dérivés sont produits et certains d'entre eux peuvent servir de substituts aux engrais chimiques. Les recherches approfondies sur la composition et les propriétés de ces produits sont rares, bien que très utiles, afin d'identifier les goulots d'étranglement à la réutilisation et d’évaluer l'impact économique et environnemental de divers scénarios de bio-fertilisation. Un premier objectif de ce chapitre était de caractériser plus en détail les propriétés physicochimiques des digestats et de leurs dérivés. La valeur des engrais et les goulots d'étranglement potentiels pour la réutilisation agricole de ces produits ont été identifiés. Deuxièmement, les avantages économiques et écologiques (en termes de consommation d'énergie et les émissions de gaz à effet de serre associées) de la substitution des engrais conventionnels par des alternatives d'origine biologique sont quantifiés et évalués en utilisant la région des Flandres (Belgique) à titre d’exemple. Les solutions de sulfates d’ammonium (AmS) provenant de récupérateurs d’ammoniac à laveur à air acide ont démontré leur potentiel pour application comme engrais N-S. De manière analogue, les concentrés résultant de la filtration membranaire de la fraction liquide du digestat ont montré promesses à titre d’engrais N-K. La substitution des engrais conventionnels par des dérivés de digestat dans différents scénarios de culture peut entraîner des avantages économiques et écologiques importants pour l'agriculteur. Le scénario probablement le plus intéressant est tiré d’une combinaison optimale (en termes du rapport de N effective sur la teneur en P) du digestat et sa fraction liquide en tant qu’engrais de base, tout en substituant le N chimique par les solutions d’AmS récupérés ou par des concentrés. Basé sur cet analyse, une valeur économique estimée à ± € 0.93 *(1.31 CAD)* kg^{-1} N et ± € 0.60 *(0.85 CAD)* kg^{-1} N pourrait être donnée à la production d’AmS et aux concentrés, respectivement, afin d'équilibrer le statu quo (c’est-à-dire sans impact sur les coûts de l'agriculteur). À partir des scénarios théoriques énoncés dans ce chapitre, la validation sur le terrain sera nécessaire pour confirmer le remplacement potentiel des engrais minéraux non-renouvelables par des alternatives biologiques. En outre, un réexamen de la catégorisation législative du digestat et de ses dérivés en fonction de leurs propriétés réelles d'engrais est recommandé afin de maximiser l'utilisation bénéfique de ces produits.

Mots-clés*: agriculture durable, digestion anaérobie, économie agricole, engrais renouvelables, recyclage des nutriments, traitement du digestat.*

4.1 Introduction

In 2010, chemical fertilizer use in Europe (EU-27) was as high as 10.4 million tons of nitrogen (N), 2.4 million tons of phosphate (P_2O_5), and 2.7 million tons of potash (K_2O) (EFMA, 2010). By 2019/2020, these fertilizer consumption figures are expected to reach 10.8, 2.7, and 3.2 million tons, respectively (EFMA, 2010). Unfortunately, fertilizer production requires significant amounts of fossil energy, prices for mineral fertilizers are increasing, whereas nutrient resources are depleting (Chapter 1; Öborn *et al.*, 2005; Ruddock *et al.*, 2005; Smit *et al.*, 2009; Vilalba *et al.*, 2008). In the transition from a fossil reserve-based to a bio-based economy, it has therefore become an important challenge to maximally recover and recycle valuable nutrients from waste streams in a sustainable and environmentally friendly manner.

In the framework of the 2020 directives, the conversion of biomass, such as energy crops, organic residues, and animal wastes, into biogas through anaerobic (co-)digestion has been evaluated as one of the most energy-efficient and environmentally beneficial technologies for bio-energy production and organic waste valorization (EC, 2011; Fehrenbach *et al.*, 2008; UNEP, 2013). However, in regions facing local manure production excesses, the resulting digestates have to be processed further and cannot or only sparingly be returned to arable land as a fertilizer in its crude, unprocessed form (Chapter 1; Lemmens *et al.*, 2007).

Initial steps of digestate processing generally comprise the use of separation and/or dewatering technologies, using emulsion or powder based polymers for flocculation (Hjorth *et al.*, 2010). The resulting thick fractions (TF) are mostly dried, and as such turned into pasteurized and stabilized exportable organic soil conditioners, high in phosphorus (P) and organic matter (Chapter 3; Umetsu *et al.*, 2002; Vaneeckhaute *et al.*, 2012). The liquid fraction (LF) produced by the separation step contains the majority of the digestate's potassium (K) and inorganic N. This LF can be processed further by ammonia stripping or membrane filtration, for example microfiltration (MF), ultrafiltration (UF), and/or reversed osmosis (RO) (Chapters 2-3; Masse *et al.*, 2007; Vaneeckhaute *et al.*, 2012, 2013a). Each step in a membrane cascade again generates two downstream products, concentrate and permeate, with varying characteristics concerning macro- and micronutrient composition. Alternatively, the LF after separation can be treated biologically, for example by nitrification-denitrification. However, the latter ultimately converts valuable N into nitrogen gas (N_2), which is then eliminated from the local agricultural cycle. In regions where agricultural N emissions to the environment are already excessive and in conflict with the European Nitrate Directive for protection of water bodies, this N elimination may be economically and ecologically sensible for a given portion of the N.

Exhaust gases of the biogas cogeneration engines and driers need to be washed before emission into the atmosphere. This involves the use of acidic, alkaline, and/or oxidative scrubber techniques, again resulting in different types of specific streams, some of which contain large amounts of inorganic nutrients. In acidic air scrubbers, for example, sulfuric acid is dosed to capture ammonia (NH_3) and amines, thereby producing ammonium sulfate (AmS, $(NH_4)_2SO_4$) as a nutrient-rich waste stream (Chapter 2). Alkaline air scrubbers are then used to oxidize organic compounds and to neutralize acidic components that escaped from the system, such as hydrogen sulfide (H_2S) (Bonmati and Flotats, 2003).

Previous chapters have shown that (some of) the above-described derivatives may potentially function as either inorganic or organo-mineral fertilizers and/or soil conditioners, in the meantime providing renewable substitutes for mineral fertilizers, of which the production is based on fossil resources. Such a sustainable development strategy is in line with the cradle-to-cradle approach (Braungart and Mc. Donough, 2003): waste turns into secondary resources (Fig. 4.1).

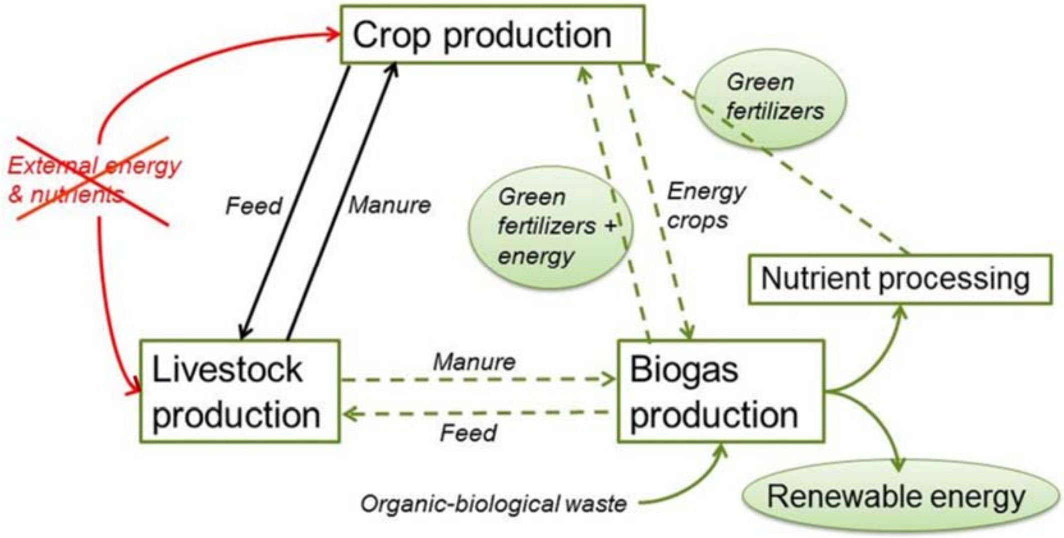

Figure 4.1 Visualization of the cradle-to-cradle concept: biomass waste (manure, organic biological waste, energy crops) is turned into secondary resources (renewable energy and green or renewable fertilizers).

However, in general, the production cost of recovered fertilizers is often still higher than the price of chemical mineral fertilizers (Chapter 2; EC, 2011; Seymour, 2009; USEPA, 2013). Even when producers impose no marketing cost, agricultural acceptance and application is still limited, because there is no common strategy to promote the use of these nutrient sources by farmers (WERF, 2010). To date, only the fertilizer value of digestates in their crude form have been compared with animal manures in comprehensive research (Chapter 2: Section 2.2). Insights in the composition and properties of the more important derivatives are lacking, though very relevant, as the treatment and the transport of these products are expensive and energy consuming, while valuable nutrients are often wasted (Sutton *et al.*, 2013). Due to these flaws, existing economic studies on technology evaluation (Chapter 2) do not take in account the whole-chain benefits of nutrient recovery, although overall costs for the agricultural and waste processing sector may significantly reduce when applying nutrient recovery strategies. Indeed, if a sustainable market for digestate and its derivatives would exist, the digestate problem could be turned into an economic and ecological opportunity (USEPA, 2013; WERF, 2010).

The present chapter first aims to characterize the physicochemical properties of the different derivatives coming from digestate processing, with attention for general conditions such as pH and electrical conductivity (EC), macronutrients and their availability, essential and non-essential trace elements, organic carbon (OC), and nutritive ratios. The fertilizer value and the potential bottlenecks for reuse of these products in comparison with conventional fertilizers are identified. Secondly, based on the characterizations, the economic and ecological (in terms of energy use and the associated carbon foot print) benefits of substituting conventional fertilizers by digestate derivatives are calculated for the most relevant cultivation scenarios in Flanders, a high-nutrient region in the North of Belgium. The knowledge obtained in this research should greatly enhance the understanding and useful application of digestate and its derivatives. Getting a better view on the dilemmas and opportunities posed by these products can in turn help to improve the underlying economics of anaerobic digestion. As such, this study can serve as a catalyst to stimulate this vital, yet fragile, innovative economic activity in the framework of the 2020 objectives.

4.2 Material and methods

4.2.1 Site description and experimental set-up

Samples of the various digestate derivatives were taken in three different full-scale mesophilic (37 °C) anaerobic digestion plants in Belgium: Goemaere Eneco Energy Diksmuide (capacity: 20,000 ton y^{-1}, 378 kW_{el}), Mandel Eneco Energy Roeselare (60,000 ton y^{-1}, 3.033 MW_{el}), and SAP Eneco Energy Houthulst (60,000 ton y^{-1}, 2.83 MW_{el}). The incoming feed to the digesters is composed of animal manure (± 30 %), organic biological waste from the food industry (± 40 %), and energy maize (± 30 %). The following process streams were sampled: digestates, thick fractions (TF) of digestates after separation, TF of digestates after separation and drying, liquid fractions (LF) of digestates after separation, concentrates produced by one vibrating membrane filtration step of the LF using reversed osmosis (RO) membranes, concentrates produced by two subsequent vibrating membrane filtration steps, wastewater from an acidic air scrubber, and wastewater from an alkaline air scrubber. For detailed process description, see Chapter 3.

The samples in the digestion plants were taken on three different points in time over the course of approximately one year (2011-2012). Acidic air scrubber water (AmS) was additionally sampled two times at the pig farm of Ladevo BVBA, Ruiselede, Belgium, and conventional pig slurry was sampled two times at the site of Huisman, Aalter, Belgium. The samples (10 L each) were collected in polyethylene sampling buckets and transported within 1 h from the sampling site to the laboratory, carried in cooler boxes filled with ice. In the laboratory, the replicate samples were stored cool (1-5 °C) and kept separate for replicate analysis.

It should be noted that struvite, although selected as best available technology in Chapter 2, was not sampled for the purpose of this chapter, as at the time of the study (2011) the common practice in Flanders, Belgium (and other high-nutrient regions in Europe) involved the maximum separation of P into the thick fraction for export purposes. Hence, full-scale digestate treatment plants including struvite production were not available. Moreover, the use of struvite for commodity/open-field/broad-acre crops, such as maize, was not attractive due to the strict P fertilization levels. The production of such crops is, however, at the core of the economic and ecological analysis presented below. For struvite characterizations, reference is made to Chapter 6.

4.2.2 Liquid sample analysis

Electrical conductivity (EC) and pH were determined potentiometrically using a WTW F537 conductivity electrode (Wissenschaftlich Technischen Werkstäten, Weilcheim, DE) and an Orion 520A pH meter (Orion Research, Boston, USA), respectively. The salt content was estimated as total dissolved solids (TDS) from the EC using the following approximation: TDS (mg L^{-1}) = EC (µS cm^{-1}) x 0.64 (Ali *et al.*, 2012; Van Ranst *et al.*, 1999). Suspended solids (SS) were determined by vacuum filtration (0.45 µm pores) of 100-300 mL sample and subsequent drying of the filter in a muffle furnace (Memmert, Schwabach, DE) at 105 °C. Total N content was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest, Köningswinter, DE) after digestion of the sample in a sulphuric-salicylic acid mixture. Finally, the captured ammonia in the distillate was titrated with 0.01 mol L^{-1} hydrogen chloride (HCl) in the presence of a methyl red bromocresol green mixed indicator (Van Ranst *et al.*, 1999). The total P content was determined using the colorimetric method of Scheel (1936; Van Ranst *et al.*, 1999) after wet digestion of the liquid samples (2.5 g sample + 2 mL nitric acid, HNO_3, + 1 mL hydrogen peroxide, H_2O_2). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, UK). Calcium (Ca), magnesium (Mg), and (heavy) metals, i.e. aluminium (Al), cadmium (Cd), chrome (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn), were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Vista MPX, Palo Alto, CA, USA) after wet digestion (as described above). Sodium (Na) and potassium (K) in the digested samples (see above) were analyzed using a flame photometer (Eppendorf ELEX6361, Hamburg, DE). Ammonium (NH_4) was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest, Köningswinter, DE) after addition of magnesium oxide (MgO) to the liquid sample (50 mL). Finally, the captured ammonia in the distillate was titrated with 0.01 mol L^{-1} HCl in the presence of a methyl red bromocresol green mixed indicator (Van Ranst *et al.*, 1999). Nitrate (NO_3^-), chloride (Cl^-), and sulfate (SO_4^{-2}) were analyzed using ionic chromatography (Metrohm 761, Herisau, CH) after centrifugation and subsequent vacuum filtration (0.45 µm pores) of the liquid fraction. Total sulfur (S) was analyzed as described by Weaver *et al.* (1994). The procedure involves product ashing, refluxing, and ionic chromatography (Metrohm 761, Herisau, CH). The extractable amount of macronutrients was determined in an NH_4OAc-EDTA pH 4.65 extract of the samples, as recommended by VIAK AS (1993) for determination of plant available nutrients.

4.2.3 Thick sample analysis

Dry weight (DW) content was determined as residual weight after 48 h drying at 100 °C. Ash and organic carbon (OC) were determined by incineration of the dry samples in a furnace

(Nabertherm, Lilientahl, DE) at 550 °C during 4 h. The loss of ignition (= weight loss after incineration) was divided by a conversion factor of 1.8 to calculate OC, which is to date the official factor used for compost products in the Flemish waste and soil remediation decree (CSA, 2012). The EC and pH were measured using a WTW F537 conductivity electrode (Wissenschaftlich Technischen Werkstäten, Weilcheim, DE) and an Orion 520A pH meter (Orion Research, Boston, US), respectively, after equilibration for 1 h in deionized water at a 5:1 liquid to dry sample ratio and subsequent filtering (white ribbon, MN 640 m, Macherey-Nagel, Düren, DE). The salt content was calculated from the EC as described in Section 4.2.2. Total N was determined using the Kjeldahl procedure on fresh weight (FW) content (Section 4.2.2; Van Ranst *et al.*, 1999). For the determination of total P, dry samples were incinerated at 450 °C during 4 h in a muffle furnace (Nabertherm, Lilientahl, DE). The P content was then determined by the colorimetric method of Scheel (1936; Van Ranst *et al.*, 1999) after digestion of the residual ash (1 g ash + 5 mL of 3 mol L^{-1} HNO_3 + 5 ml of 6 mol L^{-1} HNO_3). Ca, Mg, and (heavy) metal (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) contents in the digested samples (see above) were analyzed by means of ICP-OES (Varian Vista MPX, Palo Alto, CA, USA). Na and K in the digested samples (see above) were determined using a flame photometer (Eppendorf ELEX6361, Hamburg, DE). The NH_4 content was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest, Köningswinter, DE) after addition of MgO to the sample (50 mL). Finally, the captured ammonia in the distillate was titrated with 0.01 mol L^{-1} HCl in the presence of a methyl red bromocresol green mixed indicator (Van Ranst *et al.*, 1999). Chloride was determined by means of a potentiometric titration using an automatic titrator (Methrohm, Herisau, CH), provided by a $Hg/(Hg)_2SO_4$ referential electrode (Van Ranst *et al.*, 1999). The extractable amount of macronutrients was again determined in an NH_4OAc-EDTA pH 4.65 extract of the samples (VIAK AS, 1993; Van Ranst *et al.*, 1999).

4.2.4 Economic and ecological analysis

The economic and ecological benefits were calculated for the current most relevant reuse scenarios (Sc) of the renewable fertilizers presented above for the cultivation of maize in Flanders (Table 4.1). Expert advice (Inagro vzw, Beitem, Belgium) was used to draw up the fertilization scenarios.

For each scenario, the total amount of available or effective N applied to the soil was assumed to be 150 kg ha^{-1} y^{-1}, according to the Flemish manure regulation for the cultivation of maize on non-sandy soils (MAP4, 2011). The amount of effective N in both animal manure and organo-mineral digestate derivatives was considered to be 60 % of the total N content, as described by policy (MAP4, 2011). For air scrubber water, an N availability coefficient of 100 % was assumed. Furthermore, the maximum application standard of 250 kg ha^{-1} y^{-1} for total N, 80 kg ha^{-1} y^{-1} for total P_2O_5 (MAP4, 2011), and a total K_2O dose of 220 kg ha^{-1} y^{-1} were respected for each scenario. The different scenarios were compared with the common practice (Sc 0): maximum amount of animal manure (P_2O_5 = limiting factor), chemical mineral starter fertilizer (N, applied to the field at sowing), and additional optimizing fertilization with chemical fertilizers

Table 4.1 Nitrogen (N) and potassium (K_2O) dose (kg ha^{-1} y^{-1}) per product used in the 21 scenarios (Sc) for reuse of digestate derivatives as renewable fertilizers in agriculture. Crop = maize; Soil = non-sandy. Sc 0: common practice; Sc 1-21: reuse of digestate derivatives as renewable fertilizers. Total P_2O_5 dose in all scenarios = 80 kg ha^{-1} y^{-1}. CF = chemical fertilizer; LF = liquid fraction.

(kg ha^{-1} y^{-1})	**Nitrogen (N)**									**Potassium (K_2O)**
	Animal manure	**Digestate**	**LF digestate**	**Mixture**[a]	**Air scrubber**	**Starter CF**[b]	**CF**	**Concentrates**	**Total**[c]	**CF**
Sc 0	117	-	-	-	-	25	55	-	197	156
Sc 1	117	-	-	-	55	25	-	-	197	156
Sc 2	117	-	-	-	80	-	-	-	197	156
Sc 3	-	98	-	-	-	25	66	-	189	154
Sc 4	-	98	-	-	66	25	-	-	189	154
Sc 5	-	98	-	-	91	-	-	-	189	154
Sc 6	-	-	170	-	-	25	23	-	218	55
Sc 7	-	-	170	-	23	25	-	-	218	55
Sc 8	-	-	170	-	48	-	-	-	218	55
Sc 9	-	-	-	170	-	25	23	-	218	126
Sc 10	-	-	-	170	23	25	-	-	218	126
Sc 11	-	-	-	170	48	-	-	-	218	126
Sc 12	-	-	-	187	-	25	-	21	233	102
Sc 13	-	-	-	186	-	-	-	64	250	74
Sc 14	116	-	-	-	-	25	-	93	233	94
Sc 15	115	-	-	-	-	-	-	135	250	66
Sc 16	59	47	-	-	-	25	61	-	192	157
Sc 17	59	47	-	-	-	-	86	-	192	157
Sc 18	87	-	122	-	-	25	-	-	233	55
Sc 19	72	-	178	-	-	-	-	-	250	8
Sc 20	59	-	-	94	-	25	33	-	211	136
Sc 21	59	-	-	94	-	-	58	-	211	136

[a] Mixture of digestate (volume fraction (φ) = 0.5) and liquid fraction of digestate after separation (φ = 0.5).

[b] If starter fertilizer is used (= applied at the moment of sowing), it was supposed to be dosed at 25 kg N ha^{-1} y^{-1}.

[c] In all scenarios the amount of effective N applied to soil was 150 kg ha^{-1} y^{-1}, in compliance with the Flemish manure regulation (MAP4, 2011). The amount of effective N in both animal manure and organo-mineral digestate derivatives was considered to be 60 % of the total N content, as described by policy (MAP4, 2011).

(N, K_2O), in compliance with the maximum allowable levels of N and P_2O_5 application on agricultural land, as limited by the legal fertilization guidelines (MAP4, 2011).

In Sc 1 and 2, chemical N was partially and completely substituted by air scrubber N. In Sc 3-5, animal manure was substituted by digestate (P_2O_5 = limiting factor), with partial, complete, or without the simultaneous substitution of chemical N by air scrubber N. Scenarios 6-8 and 9-11 were similar, but now manure was substituted by (P-poor) LF digestate and an LF digestate/digestate mixture (volume fraction (φ) = 0.5), respectively. Note that for these scenarios the maximum allowable dose of total N from 'animal manure', i.e. 170 kg N ha^{-1} y^{-1}, was also respected. Indeed, currently these products are penalised by the limitations for spreading 'processed manure' in MAP4 (2011). As such, N was the limiting factor for these scenarios. In Sc 12 and 13, the same mixture was used as base fertilizer, but now the product was supposed to be categorized as an 'alternative fertilizer' (= possible at the moment if no addition of animal manure to the digester) and P_2O_5 was assumed to be the limiting factor. Moreover, chemical N was now replaced by membrane filtration concentrates up to the maximum allowable level of 150 kg effective N ha^{-1}, with and without the use of starter fertilizer. Scenarios 14 and 15 are similar as Sc 12-13, but now manure was used as base fertilizer. Finally, in Sc 16-17, 18-19, and 20-21, it was attempted to replace (part of) the chemical N (and animal manure) by digestates, LF digestates, and mixtures (φ = 0.5) of digestate and LF digestate, respectively. In Sc 16-17 and Sc 20-21, 50 % of the P_2O_5 was supposed to come from animal manure and 50 % from raw digestate and the digestate mixture, respectively. In Sc 18, 75 % P_2O_5 was supposed to come from animal manure and 25 % from LF digestate, whereas in Sc 19, 5/8th of the applied P_2O_5 was from manure and 3/8th from LF digestate.

The data used for the economic and ecological analysis of the different cultivation scenarios are presented in Table 4.2. As it concerns a case study for Flanders (Belgium), costs are expressed in euros (€ 1 ≈ 1.415 CAD; November 2014).

The economic and ecological impact of chemical fertilizer production, packing, transport, and application was taken in account. The energy use for transport and application was calculated for a lorry with a capacity of 20 tons and a diesel consumption of 11.6 MJ km^{-1} (Stichting EnergieTransitie Nederland, Boxtel, the Netherlands, personal communication 2011; Wiens *et al.*, 2008). The lorry was supposed to travel from the port of Antwerp, the distribution point in Belgium, to Ypres in the west of Flanders (129 km), the region with the highest nutrient use in Belgium. Next, the impact of transport and application of animal manure and digestate derivatives were incorporated in the calculation (Wiens *et al.*, 2008). It was assumed that the transport distance from the farm/digestion plant to the field is less than 5 km and that a tractor of 88.3 kW is used, with a diesel consumption of 10 L h^{-1}. As such, it is possible to apply 30 tons ha^{-1} h^{-1} of animal manure or digestate derivatives, which is a common figure (Wiens *et al.*, 2008). The transport costs were then calculated based on the current average cost prize for diesel in Europe (€ 1.37 L^{-1}; EU Energy Portal, 2011). Further, it was assumed that an agricultural contractor was paid € 2.5 ton^{-1} FW for fertilizer application (Lemmens *et al.*, 2007).

Table 4.2 Data used for the economic and ecological analysis of the 21 cultivation scenarios. FW = fresh weight; LF = liquid fraction. € 1 ≈ 1.415 CAD (November 2014).

	Item	Value	Reference
COSTS	Cost chemical N production & packaging (€ kg^{-1} N)	1.037	Triferto (2011), pers. communication
	Cost chemical P production & packaging (€ kg^{-1} P_2O_5)	0.956	Triferto (2011), pers. communication
	Cost chemical K production & packaging (€ kg^{-1} K_2O)	0.625	Triferto (2011), pers. communication
	Cost chemical S production & packaging (€ kg^{-1} S)	0.750	Triferto (2011), pers. communication
	Cost chemical fertilizer application (€ ton^{-1} FW)	2.5	Lemmens *et al.* (2007)
	Cost chemical fertilizer transport (€ ton^{-1} FW)	2.85	Calculation, see Section 4.2.4
	Cost animal manure application (€ ton^{-1} FW)	2.5	Lemmens *et al.* (2007)
	Cost animal manure transport (€ ton^{-1} FW)	0.457	Calculation, see Section 4.2.4
	Benefits animal manure (€ ton^{-1} FW)	11.9	Calculation, see Section 4.2.4
	Benefits digestate (€ ton^{-1} FW)	9.99	Calculation, see Section 4.2.4
	Benefits LF digestate (€ ton^{-1} FW)	5.29	Calculation, see Section 4.2.4
	Benefits mixture[a] digestate/LF digestate (€ ton^{-1} FW)	6.91	Calculation, see Section 4.2.4
ENERGY	Production chemical N (GJ ton^{-1} N)	22.6[b]	IFA (2012)
	Packaging chemical N (GJ ton^{-1} N)	2.6	Gellings and Parmenter (2004)
	Production chemical P (GJ ton^{-1} P_2O_5)	7.7	Gellings and Parmenter (2004)
	Packaging chemical P (GJ ton^{-1} P_2O_5)	2.6	Gellings and Parmenter (2004)
	Production chemical K (GJ ton^{-1} K_2O)	6.4	Gellings and Parmenter (2004)
	Packaging chemical K (GJ ton^{-1} K_2O)	1.8	Gellings and Parmenter (2004)
	Transport + application chemical fertilizer (MJ ton^{-1} FW)	74.8	Calculated from data in Section 4.2.4
	Transport + application animal manure (MJ ton^{-1} FW)	12.0	Calculated from data in Section 4.2.4
GENERAL	Energy content diesel (MJ L^{-1})	36.0	Defra (2011a)
	Energy content natural gas (MJ m^{-3})	37.5	Defra (2011a)
	Cost diesel (€ L^{-1})	1.37	EU Energy Portal (2011)
	CO_2 emission diesel (kg L^{-1})	2.668	Defra (2011a)
	CO_2 emission natural gas (kg m^{-3})	2.0196	Defra (2011a)

[a] Mixture of digestate (volume fraction (φ) = 0.5) and liquid fraction of digestate after separation (φ = 0.5).

[b] Note that this number refers to the best available practice anno 2012. The worldwide average anno 2014 is 38 GJ ton^{-1} NH_4 (EFMA, 2014).

Next to these costs, also the economic benefits for the crop farmer (third party) when accepting animal manure or digestate derivatives as base fertilizer were handled. Indeed, due to the overproduction of animal manure in Flanders, to date an income can be received by third parties for spreading excessive animal manure or digestate and LF digestate on agricultural fields. Note that this is the case in most high-nutrient regions. The fee amounts to € 250 ha^{-1} (Lemmens *et al.*, 2007), resulting in € 11.9 ton^{-1} FW or € 1.47 kg^{-1} N for animal manure, based on the maximum allowable dose for total N application from animal manure, i.e. 170 kg N ha^{-1} (MAP4, 2011), and the average N content of this stream (Table 4.3). When animal manure is substituted by digestate, LF digestate, and a mixture of digestate (φ = 0.5) and LF digestate (φ = 0.5), the benefits are € 9.99 ton^{-1} FW, € 5.29 ton^{-1} FW, and € 6.91 ton^{-1} FW, respectively, based on the N content of these streams (Table 4.3). Nevertheless, it is expected that in the future these benefits will have to be calculated using the P content of the product, in line with the legislative standards for soil P application that become the more and more strict (MAP4, 2011).

Based on all these data, the economic impact and energy use for the various cultivation scenarios was calculated using the following functions (Eq. 4.1 and 4.2):

$$\textbf{Net economic cost}\ (€\ \boldsymbol{ha^{-1}y^{-1}}) = CF_{production} + CF_{packing} + CF_{transport} + CF_{application} + DD_{transport} + DD_{application} + AM_{transport} + AM_{application} - AM/DD_{benefits} \qquad \boldsymbol{Eq.(4.1)}$$

$$\textbf{Energy use }(\boldsymbol{GJ\ ha^{-1}y^{-1}}) = CF_{production} + CF_{packing} + CF_{transport} + CF_{application} + DD_{transport} + DD_{application} + AM_{transport} + AM_{application} \qquad \boldsymbol{Eq}.(\mathbf{4.2})$$

where '*CF*' refers to chemical fertilizers*, 'DD'* are digestate derivatives, and '*AM*' is animal manure.

Finally, when fossil reserve-based mineral fertilizers are replaced by digestate derivatives, significant savings in greenhouse gas (GHG) emissions can be expected. The GHG emissions associated to energy use were calculated for the different scenarios in terms of carbon dioxide (CO_2) equivalents (kg ha^{-1} y^{-1}). It was assumed that diesel is used for the transport and application of fertilizers and that natural gas is used for the production of chemical fertilizers.

Note that the scope of this study concerns a cost-benefit calculation for a crop farmer (third party) accepting excessive animal manure or digestate derivatives (for which currently no market exists) in different chemical fertilizer replacement scenarios. It does not take into account the digestate (and its derivatives) production costs, as to date these products are considered as waste streams from bio-energy production through anaerobic digestion, which is an inevitable process for meeting the European 2020 directives. Also, potential GHG emissions, other than those provoked by energy consumption, e.g. nitrous oxide (N_2O) emissions during manure spreading, were not accounted for. For life cycle assessments of anaerobic digestion, digestate processing technologies, and bio-based fertilization strategies, reference is made to Chapter 12. Moreover, it was assumed that there is no difference in crop production between the various scenarios. This should of course be validated at field scale (see Chapter 5).

4.3 Results

4.3.1 Physicochemical analysis

Digestates, thick fractions (TF) and liquid fractions (LF) of digestates after separation, TF of digestates after separation and drying, as well as conventional pig slurry were sampled and physicochemically analyzed (Table 4.3). Also, a mixture of digestate (φ = 0.5) and LF digestate (φ = 0.5) was made and characterized (Table 4.3). The average $N:P_2O_5:K_2O$ *(N:P:K)* ratio (relative by weight) was very variable for the different products: 1.2:1:0.8 *(2.8:1:1.6)* for raw digestates, 0.33:1:0.2 *(0.77:1:0.36)* and 5.8:1:5.6 *(13:1:11)* for TF and LF after separation, respectively, 0.53:1:0.31 *(1.2:1:0.6)* for TF after drying, 2.3:1:1.3 *(5.4:1:2.5)* for the mixtures, and 1.5:1:0.8 *(3.4:1:1.5)* for pig slurry. Hence, most of the P ended up in the thick fraction after solid-liquid separation of digestate, whereas most of the N and K ended up in the liquid fraction. The amount of extractable nutrients and the nitrogen use efficiency (NUE) was always higher in the digestates and its derivatives (up to 100 %) as compared to animal manure, whereas the organic carbon content (on DW %) was lower. Yet, the C:N-ratio was slightly higher for raw digestate and significantly higher for the thick fractions as compared to pig slurry: 5.3 (raw digestate) and 13-17 (TF digestate) vs. 5.0 (pig slurry). Micronutrient contents were in all samples lower than the Flemish legislation criteria for use as fertilizer and/or soil conditioner in

Table 4.3 Physicochemical characterization of pig slurry, digestate, thick (TF) and liquid (LF) fraction of digestate after separation, TF of digestate after separation and drying, and a mixture of digestate (volume fraction, φ = 0.5) and LF digestate (φ = 0.5) (mean ± standard deviation; No of sampling sites = 3 for digestate derivatives, 1 for pig slurry; No. of sampling moments in time = 3 for digestate derivatives, 2 for pig slurry; No of replications per sample = 2). DW = dry weight; EC = electrical conductivity; FW = fresh weight; OC = organic carbon.

Parameter	Pig slurry	Digestate	TF digestate after separation[a]	TF digestate	LF digestate after separation	Mixture[b]
DW (%)	10 ± 1	11 ± 1	23 ± 1	76 ± 1	2.5 ± 0.9	6.2 ± 0.6
Ash (% on DW)	29 ± 1	43 ± 1	42 ± 1	48 ± 13	56 ± 2	35 ± 1
OC (% on DW)	41 ± 1	33 ± 1	33 ± 1	30 ± 8	26 ± 1	37 ± 1
pH (-)	7.4 ± 0.6	7.9 ± 0.6	8.1 ± 0.0	8.2 ± 0.0	7.7 ± 0.5	7.8 ± 0.4
EC (mS cm^{-1})	37 ± 2	43 ± 20	24 ± 1	26 ± 1	30 ± 6	32 ± 6
Salt (g kg^{-1} FW)	24 ± 1	28 ± 10	15 ± 1	17 ± 1	19 ± 4	20 ± 4
Total N (g kg^{-1} FW)	8.1 ± 0.2	6.8 ± 0.8	4.5 ± 0.0	17 ± 1	3.6 ± 0.4	4.7 ± 0.6
NH_4-N (g kg^{-1} FW)	4.9 ± 1.6	5.5 ± 0.8	3.6 ± 0.0	14 ± 1	2.8 ± 0.3	4.0 ± 0.5
Total P (g kg^{-1} FW)	2.4 ± 0.3	2.5 ± 1.1	5.9 ± 2.2	14 ± 0	0.27 ± 0.05	0.87 ± 0.12
Extractable P (%)	97 ± 2	100 ± 0	-	-	90 ± 1	100 ± 0
K (g kg^{-1} FW)	3.6 ± 0.3	3.8 ± 0.8	2.1 ± 0.5	8.4 ± 0.5	2.9 ± 1.1	2.2 ± 0.5
Extractable K (%)	82 ± 2	100 ± 0	-	-	85 ± 2	100 ± 0
Ca (g kg^{-1} FW)	3.0 ± 0.2	2.9 ± 1.8	6.2 ± 0.5	20 ± 2	0.19 ± 0.09	1.5 ± 0.9
Extractable Ca (%)	80 ± 1	100 ± 0	-	-	59 ± 0	100 ± 0
Mg (g kg^{-1} FW)	1.3 ± 0.1	1.2 ± 0.4	2.6 ± 0.5	8.4 ± 0.7	0.058 ± 0.040	0.58 ± 0.14
Extractable Mg (%)	89 ± 0	100 ± 0	-	-	100 ± 0	100 ± 0
S (g kg^{-1} FW)	0.80 ± 0.09	1.2 ± 0.7	-	-	0.19 ± 0.09	0.69 ± 0.42
Na (g kg^{-1} FW)	2.3 ± 0.2	2.8 ± 1.2	1.0 ± 0.3	2.4 ± 1.7	3.1 ± 0.1	2.5 ± 0.5
Extractable Na (%)	44 ± 1	65 ± 0	-	-	50 ± 0	62 ± 1
Cl (g kg^{-1} FW)	3.9 ± -	1.7 ± 0.5	0.68 ± -	3.5 ± -	2.9 ± -	2.7 ± -
Al (g kg^{-1} FW)	0.089 ± 0.025	0.30 ± 0.14	0.70 ± 0.00	2.4 ± 0.3	0.018 ± 0.021	0.088 ± 0.015
Cd (mg kg^{-1} FW)	0.0028 ± 0.0021	0.067 ± 0.090	0.050 ± 0.025	1.3 ± 1.6	< 0.0050 ± 0	0.018 ± 0.006
Cr (mg kg^{-1} FW)	0.57 ± 0.04	-	-	-	0.087 ± 0.001	0.43 ± 0.08
Cu (mg kg^{-1} FW)	35 ± 2	5.7 ± 5.4	22 ± 2	72 ± 9	0.33 ± 0.25	8.5 ± 1.8
Fe (g kg^{-1} FW)	0.15 ± 0.01	1.2 ± 0.1	2.6 ± 1	9.1 ± 2.3	7.3 ± 6.7	4.4 ± 4.0
Mn (mg kg^{-1} FW)	46 ± 1	29 ± 22	96 ± 21	334 ± 22	0.43 ± 0.12	17 ± 4
Ni (mg kg^{-1} FW)	1.0 ± 0.2	1.0 ± 0.5	1.9 ± 0.8	33 ± 8	0.50 ± 0.41	0.56 ± 0.02
Pb (mg kg^{-1} FW)	0.16 ± 0.04	0.48 ± 0.00	1.4 ± 0.0	3.7 ± 0.0	0.028 ± 0.020	0.20 ± 0.06
Zn (mg kg^{-1} FW)	86 ± 4	26 ± 13	45 ± 3	352 ± 126	7.1 ± 6.7	17 ± 6
NUE[c] (%)	60	81	80	78	77	85

[a] Only one installation was sampled in time.

[b] Mixture of digestate (volume fraction (φ) = 0.5) and liquid fraction of digestate after separation (φ = 0.5).

[c] NUE = nitrogen use efficiency: average relative amount of NH_4-N compared to the total amount of N.

agriculture (Vlarea, 1989). Only for one sample of dry thick digestate the amount of Ni slightly exceeded the legal standard: 54 vs. 50 mg kg^{-1} DW. Moreover, for manure, one sample slightly exceeded the legal standard for Zn, 901 vs. 900 mg kg^{-1} DW, while also the Cu concentration was critical, 370 vs. 375 mg kg^{-1} DW. For the sampled digestates, the variation in time and/or between different installations was especially remarkable for the salt content (~ EC and Na), for the macronutrients, P and Ca, and the micronutrients, Cu, Mn, Ni, and Zn. Remarkable for the liquid fraction of digestate after separation was the very high Fe concentration and the high variation in both Fe and Al concentrations. Also the variation in Cu, Ni, Pb, and Zn was very clear. For pig manure, the variation in the NH_4-N concentration in time (note: samples from the same sampling site!) was most expressed.

Furthermore, concentrates produced by one vibrating membrane (RO) filtration step of LF digestate, as well as concentrates following two subsequent vibrating membrane (RO) filtration steps were sampled and physicochemically analyzed (Table 4.4). The $N:P_2O_5:K_2O$ *(N:P:K)* ratio (relative by weight) was 25:1:20 *(58:1:39)* for concentrates following one filtration and 4.3:1:7.7 *(10:1:8.4)* after two filtrations. Results show that concentrates produced by the first filtration not only contained more macronutrients and OC on FW content, but also more salts and trace elements as compared to concentrates produced by the second filtration. Yet, the concentrations of heavy metals were in all concentrate samples below the Flemish legislation criteria for use as fertilizer and/or soil conditioner in agriculture (Vlarea, 1989). Similar as for digestates, especially the salt content (~ EC, Na, and K contents), the P, Mn, and Zn contents were remarkably variable in time and/or between different installations. The NUE was in the range of that for digestates, hence higher than the NUE of pig slurry.

Table 4.4 Physicochemical characterization of concentrates produced by one vibrating membrane (RO) filtration step of the liquid fraction of digestate and concentrates following two subsequent membrane filtration steps (mean ± standard deviation; No. of sampling sites = 3; No. of sampling moments in time = 3; No. of replications per sample = 2). DW = dry weight; EC = electrical conductivity; FW = fresh weight; OC = organic carbon; RO = reversed osmosis.

Parameter	**Concentrate 1st filtration step**	**Concentrate 2nd filtration step**	**Parameter**	**Concentrate 1st filtration step**	**Concentrate 2nd filtration step**
DW (%)	7.0 ± 0.6	0.53 ± 0.02	**SO_4-S (g kg^{-1} FW)**	22 ± 3	0.65 ± 0.10
Density (g L^{-1})	1,041 ± 5	1,004 ± 1	**Na (g kg^{-1} FW)**	3.1 ± 3.0	0.49 ± 0.30
Ash (% on DW)	43 ± 2	66 ± 0	**Cl (g kg^{-1} FW)**	5.1 ± 0.1	2.0 ± 0.0
OC (% on DW)	33 ± 1	20 ± 0	**Al (g kg^{-1} FW)**	0.0035 ± 0.0005	0.00024 ± 0.00018
pH (-)	5.6 ± 0.3	5.8 ± 0.4	**Cd (mg kg^{-1} FW)**	0.011 ± 0.011	<0.0040 ± 0
EC (mS cm^{-1})	60 ± 8	12 ± 3	**Cr (mg kg^{-1} FW)**	0.19 ± 0.00	0.41 ± 0.00
Salt (g kg^{-1} FW)	37 ± 5	7.6 ± 1.7	**Cu (mg kg^{-1} FW)**	0.66 ± 0.20	<0.010 ± 0
Total N (g kg^{-1} FW)	6.4 ± 1.4	0.83 ± 0.20	**Fe (g kg^{-1} FW)**	0.047 ± 0.020	0.0016 ± 0.0007
NH_4-N (g kg^{-1} FW)	5.0 ± 0.3	0.76 ± 0.18	**Mn (mg kg^{-1} FW)**	2.9 ± 1.6	0.061 ± 0.022
Total P (g kg^{-1} FW)	0.11 ± 0.10	0.083 ± 0.050	**Ni (mg kg^{-1} FW)**	0.43 ± 0.03	0.025 ± 0.010
K (g kg^{-1} FW)	4.3 ± 2.7	0.70 ± 0.01	**Pb (mg kg^{-1} FW)**	0.12 ± 0.03	0.025 ± 0.010
Ca (g kg^{-1} FW)	0.20 ± 0.03	0.011 ± 0.010	**Zn (mg kg^{-1} FW)**	6.5 ± 7.1	0.034 ± 0.019
Mg (g kg^{-1} FW)	0.083 ± 0.056	0.014 ± 0.009	**NUE[a] (%)**	79	91

[a] NUE = nitrogen use efficiency: average relative amount of NH_4-N compared to the total amount of N.

Finally, wastewaters produced by both acidic and alkaline air scrubbers (receiving air from digestate driers) were sampled and physicochemically analyzed (Table 4.5). Results show that the pH of the acidic wastewater was continuously in the range of 2 to 3, while the pH of the alkaline water was around 9. The EC and the salt content of the acidic and the alkaline wastewaters were both high. The N content of the acidic wastewater was about three orders of magnitude higher compared to that of the alkaline wastewater, although it was quite low as compared to values provided by technology suppliers anno 2014 (5.3-8.5 % N on FW content; Chapter 2). As expected, the NUE of the acidic air scrubber water was 100 %.

Table 4.5 Physicochemical characterization of acidic and alkaline air scrubber water (mean ± standard deviation; No. of sampling sites = 2; No. of sampling moments in time = 3; No. of replications per sample = 2). EC = electrical conductivity; FW = fresh weight.

Parameter	Acidic air scrubber	Alkaline air scrubber water
Density (g L^{-1})	1,034 ± 3	1,061 ± 4
Suspended solids (g L^{-1})	0.11 ± 0.02	0.057 ± 0.03
pH (-)	2.4 ± 0.3	9.0 ± 0.4
EC (mS cm^{-1})	112 ± 42	68 ± 1
Salt content (g kg^{-1} FW)	72 ± 27	44 ± 1
Total N (g kg^{-1} FW)	23 ± 9	0.071 ± 0.042
NH_4-N (g kg^{-1} FW)	23 ± 9	0.049 ± 0.063
SO_4-S (g kg^{-1} FW)	34 ± 6	0.32 ± 0.16
Cl (g kg^{-1} FW)	2.0 ± 0.2	10 ± 2
NUE[a] (%)	100	69

[a] NUE = nitrogen use efficiency: average relative amount of NH_4-N compared to the total amount of N.

4.3.2 Economic and ecological analysis

Twenty-one different cultivation scenarios were economically (Table 4.6) and ecologically, i.e. in terms of energy use (Table 4.7) and the associated carbon footprint (Fig. 4.2), evaluated. In Sc 3 and Sc 16 to 21, the economic cost was higher than that of the reference scenario. Moreover, in Sc 3, 16, and 17, also the ecological impact was higher as compared to the reference. Interestingly, all the other scenarios under study had a significantly lower ecological and economic impact than the common practice.

Table 4.6 Economic analysis (€ ha^{-1} y^{-1}) of the 21 cultivation scenarios. Sc 0: common practice; Sc 1-21: reuse of digestate derivatives as renewable fertilizers. AM = animal manure; CF = chemical fertilizer; DD = digestate derivatives. € 1 ≈ 1.415 CAD (November 2014).

(€ ha^{-1} y^{-1})	CF production + packaging	CF application	CF transport	DD application	DD transport	AM application	AM transport	AM/DD benefits	Net economic cost[a]
Sc 0	180	2.0	2.3	0	0	36	6.6	172	55
Sc 1	123	1.5	1.7	6.0	1.1	36	6.6	172	4.4
Sc 2	98	1.3	1.5	8.7	1.6	36	6.6	172	-19
Sc 3	191	2.1	2.4	36	6.6	-	-	144	94
Sc 4	122	1.5	1.7	43	7.9	-	-	144	32
Sc 5	96	1.3	1.5	46	8.4	-	-	144	9.1
Sc 6	84	0.67	0.77	118	22	-	-	250	-25
Sc 7	60	0.46	0.52	121	22	-	-	250	-46
Sc 8	34	0.23	0.26	123	23	-	-	250	-70
Sc 9	128	0.97	1.1	90	17	-	-	250	-12
Sc 10	105	0.76	0.86	93	17	-	-	250	-34
Sc 11	79	0.52	0.60	95	18	-	-	250	-57
Sc 12	90	0.66	0.75	108	20	-	-	275	-57
Sc 13	46	0.31	0.35	124	23	-	-	275	-82
Sc 14	85	0.62	0.71	36	6.6	36	6.5	171	0.59
Sc 15	41	0.28	0.31	53	9.6	35	6.5	169	-23
Sc 16	187	2.3	2.6	17	3.2	18	3.3	87	147
Sc 17	187	2.3	2.6	17	3.2	18	3.3	87	147
Sc 18	60	0.46	0.52	85	15	27	4.9	128	65
Sc 19	5.0	0.033	0.038	124	23	22	4.1	106	72
Sc 20	146	1.1	1.3	50	9.1	18	3.3	87	142
Sc 21	146	1.1	1.3	50	9.1	18	3.3	87	142

[a] Net economic cost = $CF_{production} + CF_{packing} + CF_{application} + CF_{transport} + DD_{application} + DD_{transport} + AM_{application} + AM_{transport} - AM/DD_{benefits}$

Table 4.7 Ecological analysis (energy use, GJ ha^{-1} y^{-1}) of the 21 cultivation scenarios. Sc 0: common practice; Sc 1-21: reuse of digestate derivatives as renewable fertilizers. AM = animal manure; CF = chemical fertilizer; DD = digestate derivatives.

(GJ ha^{-1} y^{-1})	**CF production + packaging**	**CF transport + application**	**AM transport + application**	**DD transport + application**	**Total energy use[a]**
Sc 0	3.3	0.061	0.17	0	3.5
Sc 1	1.9	0.046	0.17	0.029	2.2
Sc 2	1.3	0.039	0.17	0.042	1.5
Sc 3	3.6	0.064	-	0.17	3.8
Sc 4	1.9	0.045	-	0.20	2.1
Sc 5	1.3	0.038	-	0.22	1.5
Sc 6	1.7	0.020	-	0.57	2.2
Sc 7	1.1	0.014	-	0.58	1.7
Sc 8	0.45	0.0068	-	0.60	1.0
Sc 9	2.2	0.029	-	0.43	2.7
Sc 10	1.7	0.029	-	0.44	2.1
Sc 11	1.0	0.016	-	0.46	1.5
Sc 12	1.5	0.020	-	0.52	2.0
Sc 13	0.60	0.0090	-	0.60	1.2
Sc 14	1.4	0.019	0.17	0.17	1.8
Sc 15	0.54	0.0082	0.17	0.25	0.97
Sc 16	3.5	0.068	0.087	0.083	3.7
Sc 17	3.5	0.068	0.087	0.083	3.7
Sc 18	1.1	0.014	0.13	0.41	1.6
Sc 19	0.066	0.0010	0.11	0.59	0.77
Sc 20	2.6	0.033	0.087	0.24	2.9
Sc 21	2.6	0.033	0.087	0.24	2.9

[a] Total energy use = $CF_{production} + CF_{packing} + CF_{application} + CF_{transport} + DD_{application} + DD_{transport} + AM_{application} + AM_{transport}$

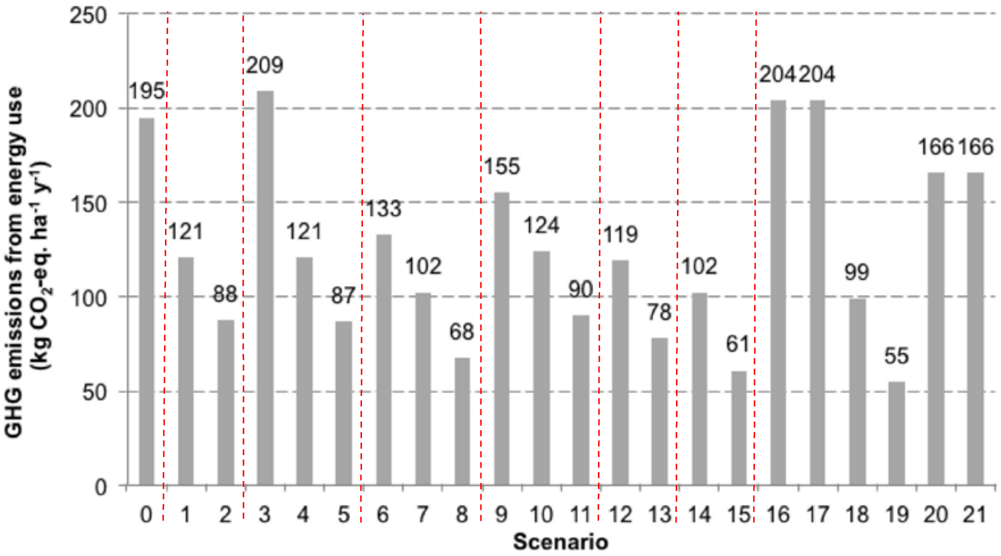

Figure 4.2 Greenhouse gas (GHG) emissions from energy use expressed in terms of CO_2-equivalents (kg ha^{-1} y^{-1}) for the 21 cultivation scenarios. Sc 0: common practice; Sc 1-21: reuse of digestate derivatives as renewable fertilizers. Red dashed lines indicate groups of comparable scenarios (see Table 4.1).

4.4 Discussion

4.4.1 Fertilizer value

In nutrient-rich regions, raw digestates can only for a portion be deposited on available agricultural land. Nevertheless, analytical results show that application of this product can be beneficial. From an agronomic point of view, one of the major advantages when using digestate instead of conventional animal manure is its higher nitrogen use efficiency (NUE) and the higher stability of this property. The NUE represents the relative amount of NH_4-N compared to the total amount of N, i.e. 81 vs. 60 % in average for digestates and pig slurry in this study, respectively (Table 4.3). These findings are completely in line with Calus *et al.* (2007), who reported average values of 82 % for digestate from pig manure and 64 % for pig slurry as such. Indeed, through anaerobic digestion organic N is converted into NH_4, which is directly available for the plant (Calus *et al.*, 2007; Vlaco, 2012). On top of N, the extraction efficiency of other macronutrients (P, K, Na, Ca, Mg), using NH_4OAc-EDTA at pH 4.65 as an extraction agent, was higher (up to 100 %) for digestate derivatives than for conventional pig manure. This measurement can be translated into a higher nutrient availability for plants (VIAK AS, 1993). Moreover, during anaerobic digestion easily biodegradable organic compounds are converted into biogas, while complex molecules such as lignin stay behind (Calus *et al.*, 2007). As such, the relative amount of effective organic carbon (OC) to total carbon (i.e. the OC that contributes to the humus built-up; Chapter 2: Section 2.2) is generally higher for digestate as compared to animal manure: 70-80 % vs. ± 30 % for pig slurry (Vlaco, 2012). Hence, although the C:N-ratio in this study was only slightly higher for raw digestates as compared to pig slurry (5.3 vs. 5.0), the ratio of effective OC to N (and P) can be significantly higher. As such, the digestate exhibits important soil enhancing properties.

Another interesting observation is that the N:P-ratio was about four times higher for liquid fractions (LF) of digestates than for animal manure, i.e. 13 vs. 3.4, and approximately five times higher than for raw digestates, i.e. 13 vs. 2.8. Indeed, most of the P ends up in the thick fraction after solid-liquid separation. In light of P becoming increasingly more restrictive in legislative frameworks for soil nutrient application rates (e.g. MAP4, 2011), this nutrient has become the limiting element in allowed dosage of organic fertilizers, especially in P saturated regions. In this perspective, the use of P-reduced LF digestate is highly interesting because more N can be applied to the soil for the same amount of P. Hence, a reduction in chemical N fertilizer requirements can be expected, which is also the case for K. When mixing digestate ($\varphi = 0.5$) and its LF ($\varphi = 0.5$), the relative amount of N (and K) to P remains high, while also the soil structure enhancing properties (Ca, Mg, OC) are maintained. Note that in this study the ratio of effective N to P was also slightly higher for raw digestates as compared to animal manure, i.e. 2.2 vs. 2.0. **All of these benefits make it an interesting opportunity for livestock farmers to treat their (excess) manure via anaerobic (co-)digestion and reuse the digestate and/or its derivatives on soil**, either as organo-mineral base fertilizer and/or as substitute for fossil reserve-based mineral fertilizers (cfr. Fig. 4.1).

In addition, results indicate that concentrates produced by membrane filtration have potential as N/K fertilizer. The observed N content was 6.4±1.4 kg ton^{-1} FW, which is comparable to the N content in conventional pig manure, i.e. 5-10 kg ton^{-1} FW (Lemmens *et al.*, 2007). The average NUE was 78 %, which is higher than that for conventional pig manure, i.e. 60 % in this study or 64 % in Calus *et al.* (2007). Furthermore, wastewater from acidic air scrubbers shows potential as mineral N/S fertilizer. The N content was 23±9 kg ton^{-1} FW and the S content was 34±6 kg ton^{-1} FW. Both the N and S extraction efficiency were 100 %, which is a prerequisite for recognition as a valuable mineral fertilizer according to the EU requirements for ‘sulfate of ammonia’ (EC 2003/2003; EC, 2003). Note that the same requirement is imposed by the Canadian Fertilizers Regulation (Minister of Justice, 2013). Finally, the wastewater from alkaline air scrubbers was poor in nutrients and therefore exhibits no potential as a fertilizer.

From the above, it can be concluded that **the legislative classification of digestate and its derivatives should be reconsidered on a national, European, and international scale**, with due attention for the qualitative fertilizer properties of these valuable products. The legal categorization of such derivatives as ‘renewable mineral fertilizers’ and/or ‘renewable organo-mineral fertilizers’, next to the existing framework for ‘chemical (= fossil reserve-based) mineral fertilizers’ (EC 2003/2003; EC, 2003), might be indispensable for their success in the European Union. A similar transition will be required in the Canadian Fertilizers Regulation (Minister of Justice, 2013), before effective marketing of bio-based products will be possible. Nevertheless, there are also still some practical bottlenecks for reuse, requiring further research and optimization (Section 4.2.2).

4.4.2 Potential bottlenecks for reuse

When using acidic air scrubber water (AmS-solution) in agriculture, one should be aware of some practical limitations. First of all, the low pH (2 to 3 in this study) of this stream shows that the wastewater not only contains ammonium sulfate, but also significant amounts of sulfuric acid. As a consequence, the product has acidifying and corrosive properties. It is therefore advised to use corrosion-resistant injectors and to avoid direct contact with skin and plants. Another, more practical, solution may be to mix the acidic with the alkaline air scrubber wastewater (pH 9), thereby neutralizing the pH, or at least maintaining a weak acidic pH to avoid unwanted ammonia emissions. Meanwhile, the latter nutrient poor product can also be valorized.

Next, an important note is that during mixing or storing of the acidic waste stream, H_2S can be released which is very toxic even at low concentrations. The production of this toxic gas is related to the presence of sulfate reducing bacteria under low-oxygen conditions, which use sulfates for the oxidation of organic compounds or hydrogen (Kool *et al.*, 2005).

Finally, a critical point when using acidic air scrubber wastewater in agriculture could be the salt content. Results show that the EC of this stream was 112±42 mS cm^{-1}, while that of conventional pig manure amounted to 37±2 mS cm^{-1}, which is in line with literature data, 30-50 mS cm^{-1} (Lemmens *et al.*, 2007; Moral *et al.*, 2008). Nevertheless, when considering the salt doses per kg N applied for air scrubber water and pig manure, i.e. 3.1 vs. 3.0, respectively, only a slight difference can be observed. Moreover, on the basis of the amount of effective N applied, the salt doses for pig manure, i.e. 4.9, was drastically higher than for air scrubber water, i.e. 3.1. Still, when applying AmS as mineral fertilizer (in addition to animal manure or digestate), the salt doses may be significantly higher than when applying traditional concentrated (usually up to 20-30 % N; Triferto, 2015) chemical mineral fertilizers, such as NH_4NO_3. Too high salt doses can cause soil salinization in the long term (depending on soil characteristics and climate) and can dramatically reduce crop production (USEPA, 2004; Verlinden, 2005). Moreover, salts may leach into groundwater, which is undesired from an environmental perspective, nor in view of drinking water extraction. For all the above reasons, **best management practices for implementation and use of wastewater from acidic air scrubbers should be established in order to minimize health risks and to prevent soil and water degradation.**

As for acidic air scrubber water, results show that also membrane filtration concentrates have elevated salt contents, 60±8 mS cm^{-1}, resulting in high salt:N-ratios (up to 6) for this product. Therefore, when using concentrates in agriculture, it may be important to pay attention to the salt doses per unit N applied to the soil. Also high sodium adsorption ratios (SAR), which are ratios of the monovalent cation, Na, to divalent bases, Ca and Mg, can cause degradation of the soil structure, especially when soils are rich in clay (USEPA, 2004). Finally, the K_2O content of the concentrates produced by the first filtration was 5.2±3.2 kg ton^{-1} FW, which is slightly lower than the expected range of Burton (2007), but still higher than that of conventional pig manure, i.e. 4.3±4 kg ton^{-1} FW in this study. Although this element can be important for crop production, high ratios of K to N are not preferred for every agricultural application. Particularly cattle farmers rather use K-poor fertilizers, because of the potential health risks for cattle, such as head illness, at high K fertilization, i.e. > 50 tons ha^{-1} y^{-1} (Hillel, 2008; Romheld and Kirkby, 2010). Hence, when setting up fertilizer recommendations for concentrate dosage, one should take into account the product's K content and that of the base fertilizer, in relation to the type of livestock production, the K demand of the agricultural crop, and the soil characteristics (EFMA, 2003; Hillel 2008; Romheld and Kirkby, 2010).

None of the analyzed products exceeded the legal composition and use requirements in terms of heavy metals (Cd, Cr, Cu, Pb, Ni, Zn) for reuse as fertilizer and/or soil conditioner in agriculture, as described in Flemish legislation (Vlarea, 1989). Only for one sample of dry thick digestate the amount of nickel (Ni) slightly exceeded the legal standard, while for pig manure the zinc (Zn) and copper (Cu) contents were critical. There currently exists no standard for iron (Fe) application, though it should be remarked that some liquid fractions under study contained drastically high Fe concentrations as compared to pig slurry and raw digestate. This is related to the addition of Fe-salts for improved coagulation/flocculation during solid-liquid separation. These high concentrations may cause Fe accumulation in the soil after long-term application, which can impact on the plant availability of important nutrients, mainly P (Hillel, 2008; Sposito, 2008). Field trials are required to evaluate the nutrient availability in soils after long-term bio-based fertilizer application. Moreover, the quality of the resulting fertilizer end products should be (more) considered in the selection of operational strategies, such as the choice of chemical dosing (e.g. Fe/Al-salts).

Furthermore, the larger share of NH_4-N relative to total N in digestates and its derivatives as compared to conventional animal manure (see above) may provoke higher risks for ammonia volatilization. Therefore, emission-poor application techniques, e.g. direct injection, are recommended. Also, fields must be ploughed as soon as possible after application of these fertilizers in order to minimize NH_3 emissions to air.

The microbiological quality of digestate and its derivatives was out of scope of the present dissertation, but definitely is an important topic for future research. An orientating study (Calus *et al.*, 2007) demonstrated that the amount of both aerobic and plant pathogens in digestate is less than in animal manure, while the amount of anaerobic pathogens would be higher. A thorough quantification and comparative study of the microbiological quality and the impact of recovered products on soil organisms is required. Also the degree of contamination with organic substances in the various bio-based products needs to be investigated. All of this may help stimulating the beneficial use of these products in environmental legislations and in the farming community.

4.4.3 Economic and ecological benefits

Reuse of valuable nutrient products from digestate processing as substitutes for chemical fertilizers in agriculture could result in significant fossil energy and CO_2 emission savings, as well as cost savings. Although the present study is based on the Flanders (Belgium) situation, the overall comparative outcomes (not the actual values) are expected to be generalizable for other (high-nutrient) regions.

The energy consumption for chemical fertilizer use (N, P_2O_5, K_2O) in the **reference scenario** was 3.5 GJ ha^{-1}, which resulted in a GHG emission of 195 kg ha^{-1} y^{-1} in terms of CO_2-equivalents, assuming that natural gas is used for the production of chemical fertilizers and that diesel is used for the transport and application of fertilizers. The economic fertilization cost in this scenario amounted to € 55 ha^{-1}.

The **substitution of chemical fertilizers by acidic air scrubber wastewater** resulted in a significantly lower economic and ecological impact (Sc 1-2), especially because of the reduction in chemical fertilizer N production. This was also the case when chemical fertilizers were substituted by membrane filtration concentrates (Sc 14-15). The latter scenarios also resulted in significantly lower chemical K_2O needs as compared to the reference. Based on these scenarios and in order to balance with the status quo (= no cost impact for the crop farmer as compared to the reference scenario), the anaerobic digestion plant may impose a marketing value of € 0.93 *(1.32 CAD)* kg^{-1} N (= € 74 ha^{-1} / 80 kg N ha^{-1} = (cost Sc 0 – cost Sc 2) / N applied as air scrubber water in Sc 2) produced as ammonium sulfate from the digestate or € 0.58 *(0.82 CAD)* kg^{-1} N (= € 78 ha^{-1} / 135 kg N ha^{-1} = (cost Sc 0 – cost Sc 15) / N applied as concentrates in Sc 15) produced as membrane filtration concentrate. Note that this reasoning assumes that there is no impact on crop production when using bio-based alternatives.

Replacing animal manure with digestates as base fertilizer (Sc 3-4-5) resulted in more mineral (chemical) N requirements than the common practice, because the applied effective N:P_2O_5-ratio was lower for the crude digestates than for animal manure. This resulted in a higher economic impact for Sc 3-4-5 as compared to Sc 0-1-2 and a higher ecological impact for Sc 3 (no substitution of chemical N by air scrubber water) compared to the reference. Yet, it should be remarked that in this study the amount of effective N relative to total N in the digestate derivatives was assumed to be 60 %, according to the Flemish manure regulation. Nevertheless, results indicate that the actual amount of effective N in digestate derivatives is significantly higher (± 81 %; Section 4.4.1). Hence, if these products would be used according to their actual fertilizer value, the economic and ecological impact could be seriously lowered. Indeed, it would be possible to apply about 20 % more effective N for the same amount of P, thus the use of chemical N would notably reduce. The implementation of a new legislative categorization for these products (other than ‘animal manure’) is therefore indispensable for their effective and sustainable use in the farming community.

On the other hand, the complete **substitution of animal manure with LF digestate** (Sc 6-7-8) resulted in a significant reduction in chemical K_2O requirements, and hence economic and ecological benefits for the crop farmer. Moreover, due to the very high N:P_2O_5-ratio, the maximum allowable N dose for 'animal manure' can be achieved, without exceeding the maximum P fertilization level. Nevertheless, depending on the soil and crop type, additional mineral (chemical or bio-based) P fertilization may be required (see Chapter 6).

Substituting animal manure by a mixture of digestate ($\varphi = 0.5$) and LF digestate ($\varphi = 0.5$) (Sc 9-10-11) also resulted in lower chemical K_2O requirements than the common practice, while a high N and P_2O_5 dose was maintained. Assuming that no animal manure was added to the digester or that a new categorization for these products (other than 'animal manure') would exist (Sc 12-13), then the highest economic benefits were achieved (Sc 13: € 82 ha^{-1}). In these scenarios also a relative reduction of 60-65 % in the ecological impact was obtained compared to the common practice.

According to the analysis, the **(partial) substitution of chemical fertilizers by digestates** (Sc 16-17) **and mixtures of digestate ($\varphi = 0.5$) and LF digestate ($\varphi = 0.5$)** (Sc 20-21) is not interesting, especially not in terms of economics. This is mainly due to the fact that in this case no revenues were considered for accepting the bio-based products as base fertilizer, next to the higher transportation and application costs for these products as compared to chemical fertilizers. On the other hand, **substituting chemical fertilizers with LF digestate** turned out in significantly lower chemical K_2O requirements, while no chemical N was needed (Sc 19). This resulted in a very low ecological impact, i.e. an energy use of 0.77 GJ ha^{-1} and an associated GHG emission of 55 kg ha^{-1} expressed in terms of CO_2-equivalents. Nevertheless, because the N concentration in the liquid fraction is low, the application and transportation costs in this scenario were again higher than in the common practice (Sc 0).

Overall, based on the analysis, the most beneficial scenario in terms of both economic and environmental impact would exist of an optimal mixture of digestate and its liquid fraction for use as base fertilizer with high effective N content, but low P_2O_5 content (yet high enough to meet crop requirements), combined with a complete substitution of chemical N by air scrubber water or concentrates. A next important task exists in the field-scale evaluation of the impact on crop production and soil quality of such bio-based fertilization scenarios (Chapter 5).

An important remark for the above calculations is that an income was supposed for accepting excessive animal manure, digestate, and LF digestate by third parties, i.e. crop farmers (see Section 4.2.4), as this is currently the situation in Flanders. This may, however, not always be the case, e.g. i) in other regions, ii) in the future, or iii) if the farmer uses its own excessive manure for farm-scale digestion and the resulting digestate for application to his own fields. Note that the latter case also imposes no costs for the farmer for disposal of the excessive manure. When eliminating the benefits from the cost calculations presented in Table 4.6 (so supposing no income for the crop farmer from manure/digestate/LF digestate acceptation and no cost for disposal of these products by the livestock farmer or anaerobic digestion plant), still most scenarios, except for Sc 3, 9, 16-17, and 20-21, pose economic benefits for the crop farmer (Fig. 4.3).

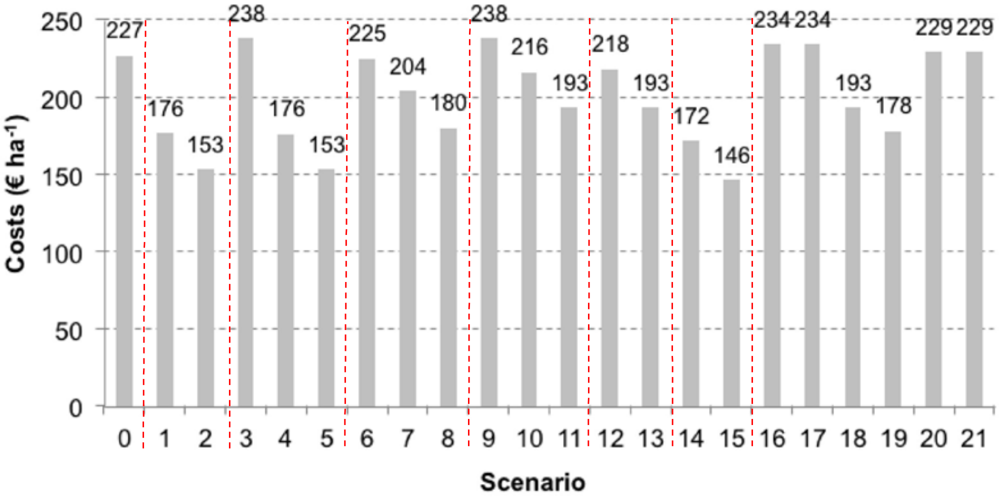

Figure 4.3 Economic analysis (€ ha^{-1}) of the 21 cultivation scenarios supposing no revenues from manure, digestate, and liquid fraction of digestate acceptance. Sc 0: common practice; Sc 1-21: reuse of digestate derivatives as renewable fertilizers. € 1 ≈ 1.415 CAD (November 2014). Red dashed lines indicate groups of comparable scenarios (see Table 4.1).

In this case, the most interesting scenarios involve a complete substitution of chemical N by air scrubber water (Sc 2 and 5) or by membrane filtration concentrates (Sc 15). Based on these results and in order to balance with the status quo (similar as above), the anaerobic digestion plant may now impose a marketing value of € 0.93 *(1.31 CAD)* kg^{-1} N (= € 74 ha^{-1} / 80 kg N ha^{-1} = (cost Sc 0 – cost Sc 2) / N applied as air scrubber water in Sc 2) produced as ammonium sulfate from the digestate or € 0.60 *(0.85 CAD)* kg^{-1} N (= € 81 ha^{-1} / 135 kg N ha^{-1} = (cost Sc 0 – cost Sc 15) / N applied as concentrates in Sc 15) produced as membrane filtration concentrate, which are about the same figures as estimated above.

A final interesting point is that significant amounts of S are applied to the soil when air scrubber water is used (Sc 1, 2, 4, 5, 7, 8, 10, and 11). This could result in an extra economic benefit of € 0.75 kg^{-1} S (Triferto, Ghent, Belgium, personal communication 2011), depending on the S need of the agricultural crops.

4.5 Conclusions and future perspectives

The recovery and cradle-to-cradle reuse of macronutrients from digestate derivatives can be an important aspect in the further development of sustainable agriculture, anaerobic digestion, and green chemistry. Concentrates following membrane filtration through reversed osmosis show potential as renewable N/K fertilizer, whereas wastewater from acidic air scrubbers shows potential as renewable N/S fertilizer. Important bottlenecks for agricultural reuse of concentrates could be the salt content, the sodium adsorption ratio, and the K content, especially for cattle farmers. Bottlenecks for agricultural reuse of acidic air scrubber water could be the pH, the salt content, and its corrosive properties.

Substituting chemical fertilizers by acidic air scrubber water or membrane filtration concentrates theoretically always results in significant economic and ecological benefits for the crop farmer. The highest combined environmental and economic benefits could be obtained by use of an optimal (in terms of effective N over P content) combination of digestate and its liquid fraction as base fertilizer, meanwhile substituting chemical N by air scrubber wastewater or concentrates. Based on the analysis, it is estimated that a marketing value of ± € 0.93 *(1.31 CAD)* kg^{-1} N and ± € 0.60 *(0.85 CAD)* kg^{-1} N could be imposed for the production of acidic air scrubber water and membrane filtration concentrates, respectively, in order to balance with the status quo (= no cost impact for the crop farmer).

Starting from theoretical scenarios outlined in the current study, field test validation will be required in order to evaluate the impact on soil and crop production by application of these new green fertilizers (see Chapter 5). Moreover, a reconsideration of the legislative categorization of digestate and its derivatives based on the effective fertilizer properties is indispensable for the effective use and economic valorization of these products.

CHAPTER 5:

ASSESSING NUTRIENT USE EFFICIENCY AND ENVIRONMENTAL PRESSURE OF MACRONUTRIENTS IN BIO-BASED FERTILIZERS: A REVIEW OF TWO-YEAR FIELD TRIAL RESULTS

Field test site in Wingene, Belgium 2011-2012 (Pictures: Vaneeckhaute C.)

Redrafted from:

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Vaneeckhaute, C., Ghekiere, G., Michels, E., Vanrolleghem, P.A., Tack, F.M.G., Meers, E., 2014. Assessing nutrient use efficiency and environmental pressure of macronutrients in bio-based mineral fertilizers: A review of recent advances and best practices at field scale. Adv. Agron. 128, 137-180.

Abstract

The use of bio-based (organo-)mineral fertilizers in agriculture as sustainable substitute for fossil reserve-based mineral fertilizers can result in serious economic and ecological benefits for the agriculturist. However, the opportunity to close nutrient cycles in this sector has been difficult to realise due to obstacles and inconsistencies in (national) legislative systems, the still limited availability of recovered products to farmers, social perception, and farmers' distrust. As such, to date, the details of their application and potential benefits are not well established in the farming community. Field-scale assessments evaluating the impact on soil and crop production of bio-based fertilization scenarios are lacking, though highly essential. The aim of this study was to evaluate the impact on soil and crop production of using bio-digestion waste derivatives as substitute for chemical fertilizers and/or animal manure. In a two-year field trial, the fertilizer potential of recovered ammonium sulfate from acidic air scrubbers for ammonia removal, digestate, and its liquid fraction produced by mechanical separation was evaluated using high-level performance indicators for measuring farming's pressure on the environment and how that pressure is changing over time. Nutrient balances, nutrient use efficiencies, and apparent nutrient recoveries were assessed. In addition, the biogas yield of the harvested energy crops was determined, and an economic and ecological evaluation was conducted. Fertilizer market trends, and technical and legislative bottlenecks for bio-based fertilizer application were also discussed.

Application of bio-digestion waste derivatives induced small, albeit not always statistically significant, improvement in crop yield compared to current common practices using animal manure and chemical fertilizers. Moreover, the use of these products could stimulate the mobilization of nutrients from the soil, thereby increasing the use efficiency of soil minerals, especially of phosphorus (P) and potassium (K). For all reuse scenarios the calculated economic and ecological benefits were significantly higher than the reference (up to 3.5 and 4.4 times, respectively).

Overall, based on the two-year field trial results, it was concluded that the use of bio-based fertilizers has a positive impact on the economy, agronomy, and ecology of intensive plant production. The proof-of-concept provided in this chapter should help to better classify these bio-based products in environmental and fertilizer legislations, and serve as a support to encourage their use in the farming community. Moreover, this review should stimulate and provide guidance for further field research on bio-based fertilizers, which is highly essential in the development and implementation of more effective and environmentally friendly farming strategies.

Keywords: *agricultural economics, alternative farming strategies, cradle-to-cradle nutrient recycling, energy maize, environmental management, sustainable agriculture.*

Résumé

L'utilisation d'engrais (organo-)minéraux extraits de ressources biologiques en tant que substitut durable aux engrais minéraux à base de ressources fossiles peut engendrer d'énormes avantages économiques et écologiques pour l'agriculteur. Toutefois, la possibilité de fermer les cycles des nutriments dans ce secteur a été difficile à réaliser en raison d'obstacles et d'incohérences présents dans les systèmes législatifs (nationaux), de la disponibilité encore limitée des produits récupérés pour les agriculteurs et de la perception sociale et la méfiance des agriculteurs. En tant que tel, à ce jour, les détails d'une telle utilisation et les avantages potentiels ne sont pas bien établis dans la communauté agricole. Des essais sur le terrain évaluant l'impact sur le sol et sur la production agricole des scénarios de bio-fertilisation font défaut, bien qu'ils soient essentiels. Le but de cette étude était d'évaluer l'impact sur le sol et sur la production agricole de l'utilisation des dérivés de la bio-digestion comme substitut pour des engrais chimiques et/ou des lisiers. Dans un essai sur le terrain de deux ans, le potentiel de fertilisation de sulfate d'ammonium récupéré à l'aide de laveurs à air acide, de digestat et sa fraction liquide produite par séparation mécanique a été évalué en utilisant des indicateurs de performance de haut niveau qui mesurent la pression des pratiques agricoles sur l'environnement et l'évolution de cette pression au fil du temps. Les bilans de nutriments, les efficacités d'utilisation des nutriments, et les récupérations apparentes des nutriments ont été calculés. De plus, le rendement de production de biogaz des cultures énergétiques récoltées a été déterminé, et une évaluation économique et écologique a été menée. Les tendances du marché des engrais, et les goulots d'étranglement techniques et législatifs pour l'application des bio-engrais ont également été évalués.

L'application des dérivés de la bio-digestion induisait une petite, bien que pas toujours statistiquement significative, amélioration du rendement des cultures par rapport aux pratiques courantes utilisant les lisiers et les engrais chimiques. En outre, l'utilisation de ces produits pouvait stimuler la mobilisation des nutriments du sol, augmentant ainsi l'efficacité de l'utilisation des minéraux du sol, surtout du phosphore (P) et potassium (K). Pour tous les scénarios de récupération, les avantages économiques et écologiques calculés étaient significativement plus élevés que le scénario de référence (jusqu'à 3.5 et 4.4 fois, respectivement).

En général, sur la base des résultats de deux ans, il a été conclu que l'utilisation de bio-engrais a un impact positif sur l'économie, l'agronomie et l'écologie de la production végétale intensive. La preuve de concept fourni dans ce chapitre devrait aider à mieux classer ces bio-produits dans les législations environnementales et celles sur les engrais, et servir à encourager leur utilisation dans la communauté agricole. De plus, cette revue devrait stimuler et orienter de futures recherches sur le terrain sur les bio-engrais, ouvrant la porte au développement et à la mise en œuvre de stratégies agricoles plus efficaces et plus respectueuses de l'environnement.

Mots-clés: *agriculture durable, économie agricole, gestion de l'environnement, maïs énergétique, recyclage des nutriments du berceau-au-berceau, stratégies agricoles alternatives.*

5.1 Introduction

Nutrient recovery from digestates and cradle-to-cradle reuse as sustainable fertilizers in agriculture has become an important challenge in the further development of sustainable agriculture, green chemistry, and renewable energy production through anaerobic digestion, both from an economic as well as an ecological point of view (Chapter 4). Previous chapters revealed that ammonium sulfate (AmS, $(NH_4)_2SO_4$) wastewater resulting from NH_3 recovery by an acidic air scrubber could potentially be reused as a formulated N/S fertilizer, whereas concentrates resulting from membrane filtration of liquid digestate could potentially be reused as N/K fertilizer (Vaneeckhaute *et al.*, 2012, 2013b). In this way, sustainable alternatives for fossil reserve-based mineral fertilizers could be provided, while valuable nutrients are being recycled. Furthermore, in light of phosphorus (P) levels for soil application that become more and more strict in (European) fertilizer legislation, reuse of the P-poor liquid fraction (LF) after mechanical separation of raw digestates, or a mixture of raw digestate and its LF might be of important interest in the near future.

Despite the potential economic and ecological benefits (Chapter 4), the opportunity to close nutrient cycles in this sector has been difficult to realise due to obstacles and inconsistencies in (national) legislative systems and lack of insights in the composition and properties of these recovered products, as well as in their impact on crop yield and soil quality. Hence, to date, the details of their application and potential benefits are not well established in the farming community. In 2010-2011, Wageningen UR (the Netherlands) has conducted a field trial aiming to evaluate the fertilizer value of concentrates produced by reversed osmosis membrane filtration of liquid manure and digestate (De Vries *et al.*, 2012). However, field-scale assessments using AmS wastewater from acidic air scrubbers and other digestate derivatives in completely bio-based fertilization scenarios are lacking in literature. Field trials are, however, essential to demonstrate the fertilizer value of (a formulated combination of) these new products in terms of plant nutrient availability and their applicability for several cropping systems. In addition, field trials are crucial to evaluate the effective environmental impact of recovered bio-based products (Johnston, 1997), as well as the economics (crop yield may not be reduced!).

The present chapter aims to demonstrate the fertilizer potential of digestate and its derivatives (in particular recovered AmS) by means of a groundbreaking field trial in which eight different cultivation scenarios are compared. The scenarios were selected based on their beneficial economic and ecological impact as presented in Chapter 4. As such, AmS wastewater from an acidic air scrubber for ammonia removal, liquid fractions (LF) of digestate, and/or optimized mixtures of raw digestate and LF digestate were applied to soil, either as substitute for fossil reserve-based chemical fertilizers and/or as more sustainable and applicable (improved nitrogen to phosphorus, N:P, ratio) organo-mineral equivalent for animal manure. The crop type under study was energy maize. It is hypothesized that the use of these products does not cause significant differences in crop yield and nutrient uptake compared to the common practice using animal manure and chemical fertilizers.

In order to evaluate the potential environmental impact using these bio-based products in agriculture, nutrient use efficiencies, nutrient balances, and apparent nutrient recoveries were assessed. General soil qualitative parameters, such as the salt content, pH, organic carbon (OC) content, sodium adsorption ratio (SAR), as well as P and heavy metal accumulation, were measured in time (two years), while nutrient and OC dynamics were also modelled in the longer term (30 years). In addition, the biogas yield of the harvested energy maize was determined. As such, the nutrients coming from the digestate are cradle-to-cradle recycled to the anaerobic digestion plant and nutrient cycles are maximally closed (cfr. Fig. 4.1). Based on the results, the economic and ecological benefits of the various bio-based fertilization scenarios were recalculated. Due attention was given to the fertilization cost for the various scenarios as well as to the assessment of their carbon footprint (from energy use) and nutrient losses (see Chapter 4). Finally, technical and legislative implications for bio-based fertilizer application, as well as fertilizer market trends and prices, are discussed.

Overall, this chapter may help to better classify these bio-based products in fertilizer and environmental legislations and serve as a support to stimulate their use in the farming community. Moreover, reuse of bio-digestion waste can improve the economic viability of anaerobic digestion plants, especially in high-nutrient regions. In this way, regulatory drivers can be met, while an internal revenue source can be produced, hence the present waste problem could be turned into an economic opportunity. Finally, this chapter aims to stimulate and provide guidance for further field research on bio-based fertilizers. Such studies are highly essential in the development and implementation of more effective and environmentally friendly farming strategies.

5.2 Material and methods: Guidelines for good practice

This section provides guidelines for field experiments aiming to demonstrate the effectiveness of bio-based fertilizers as compared to traditional fertilization using animal manure and chemical fertilizers. The best management practices used in the field tests performed to date using bio-digestion waste are presented based on the two-year field trial under study.

5.2.1 Site description and fertilization strategies

The test site concerns a 0.8 ha large sandy-loam field located in Wingene, Belgium (51° 3′ 0″ N, 3° 16′ 0″ E). The field was divided into four blocks (n = 4), and each block was divided into eight subplots of 9 m by 7.5 m, which were randomly assigned to the eight treatments under study (Figure 5.1). The soil characteristics before the field trial (April 21 2011) can be found in Table 5.1. The methods used for physicochemical analysis are described in Section 5.2.3. Note that the P status of the soil was high, confirming the problem of P accumulation in Flemish soils. The present field was, however, not yet registered as P saturated soil in the Flemish fertilizer legislation at the moment of the field trial.

Figure 5.1 Division of the field into 32 subplots. The first number indicates the repetition (1-4). The last number indicates the fertilization scenario (1-8).

Table 5.1 Soil characteristics before fertilization (April 21 2011): parameter, soil layer, analysis, target zone, limit, and evaluation. Extractable amounts were determined using ammonium lactate/acetic acid (pH 3.75) as an extraction agent. DW = dry weight; OC = organic carbon.

Parameter	Soil layer (cm)	Analysis	Target zone	Limit	Evaluation
Texture	0-23	sandy-loam[a]	-	-	-
Bulk density (kg L^{-1})	0-30	1.45	-	-	-
	30-90	1.5	-	-	-
pH(KCl)	0-23	7.0	5.5-6	5.3	rather high
OC (% on DW)	0-23	1.9	1.3-1.6	0.9	rather high
Extractable Ca (g kg^{-1} DW)	0-23	19	1.0	2.7	high
Extractable K (mg kg^{-1} DW)	0-23	121	140-230	-	rather low
Extractable Mg (mg kg^{-1} DW)	0-23	214	90-160	-	rather high
Extractable Na (mg kg^{-1} DW)	0-23	20	31-67	-	rather low
Extractable P (mg kg^{-1} DW)	0-23	816	120-200	-	high
NO_3-N (kg ha^{-1})	0-30	25	-	-	-
	30-60	10	-	-	-
	60-90	5	-	-	-
NH_4-N (kg ha^{-1})	0-30	4	-	-	-
	30-60	6	-	-	-
	60-90	5	-	-	-

[a] Note: during the experiment in 2011 it was observed that the 0-90 cm soil layer was rather sandy than sandy-loam. Hence, in 2012 the fertilization advice was set for a sandy soil.

Based on the soil characteristics, the fertilization advice was calculated by Inagro vzw, Beitem, Belgium, using the soil balance method. The nutrient inputs considered in this method are the soil nutrient reserves, the release of nutrients from soil organic carbon (SOC), from organic material (crop residues, intercrops, etc.), and organic fertilizers. The nutrient outputs are determined by the crop nutrient uptake and the residual nutrients, such as the NO_3-residue. The difference between the outputs and the inputs determines the fertilization advice. As such, the fertilizer recommendations were formulated at 150 kg effective N ha^{-1} y^{-1} (= maximum allowable dose for the cultivation of maize on non-sandy soils in compliance with MAP4, 2011), 171 kg ha^{-1} y^{-1} potash (K_2O), and 30 kg ha^{-1} y^{-1} magnesium oxide (MgO) in 2011, and 135 (= maximum allowable dose for the cultivation of maize on sandy soils in compliance with MAP4, 2011), 250, and 60 kg ha^{-1} y^{-1}, respectively, in 2012. The fact that the recommended K and Mg dose was higher in 2012 confirms the observed extraction of K and Mg from the soil complex in 2011 (see Section 5.3; Vaneeckhaute *et al.*, 2013c). On the other hand, the recommended N dose was lower in 2012, as high NO_3-N residues were observed at the end of the field experiment in 2011 (see Section 5.3; Vaneeckhaute *et al.*, 2013c). The amount of effective N for the organic and organo-mineral fertilizers was set at 60 % of the total N content, as described in the Flemish manure decree (MAP4, 2011). The nitrogen use efficiency of AmS wastewater from an acidic air scrubber was set at 100 %, similar as for chemical mineral N fertilizers. Furthermore, for phosphate (P_2O_5) the maximum allowable dosage of 80 kg ha^{-1} y^{-1} for the cultivation of maize was respected (MAP4, 2011).

An overview of the eight different fertilization scenarios (Sc 1-8) tested in 2011 and 2012 is provided in Table 5.2. Group 0 (Sc 1) represents the reference scenario in which only animal manure and chemical fertilizers (N, K_2O) were used (cfr. Sc 0 in Chapter 4). In Group I, chemical N was partially (Sc 2) or completely (Sc 3) substituted by AmS wastewater from an acidic air scrubber (cfr. Sc 1-2 in Chapter 4).

In group II (Sc 4-6), animal manure was converted into digestate through anaerobic (co-)digestion and mixtures of digestate and its LF were spread to the field, with partial, complete, or without the simultaneous substitution of chemical N by air scrubber water (cfr. Sc 9-11 in Chapter 4). Based on the product characterizations, an optimal combination was sought between raw digestate and its LF after mechanical separation using the Excel 2010 solver. The aim was to provide a concentrated mixture with high effective N content, but relatively low P_2O_5 content. As such, chemical fertilizer N requirements can be reduced. Hence, while P_2O_5 was the limiting factor for manure application in group 0 and I, N became the limiting factor in group II, as the ratio of P_2O_5 over effective N was lower for the digestate mixtures as compared to animal manure. In 2011, a mixture of 50 volume % ($\varphi = 0.5$) raw digestate and 50 % ($\varphi = 0.5$) LF digestate was used for this purpose. In 2012, the use of a mixture containing 40 volume % ($\varphi = 0.4$) raw digestate and 60 % ($\varphi = 0.6$) LF digestate (Sc 4) could completely fulfill the fertilizer N requirements, without the addition of chemical N and without exceeding the maximum allowable P_2O_5 level. Therefore, in Sc 5-6, the raw digestate was used as such ($\varphi = 1$), with partial or complete substitution of chemical N by air scrubber water.

Table 5.2 Eight different fertilization scenarios (Sc) expressed as effective nitrogen (N; kg ha^{-1} y^{-1}), additional application of chemical potash (K_2O; kg ha^{-1} y^{-1}), and equivalent dosage of phosphate (P_2O_5; kg ha^{-1} y^{-1}). Values represent the intended dosage (based on preliminary product characterizations). Values between brackets represent the actual dosage (based on product characterizations at the moment of fertilizer application).

Group[a]	Sc	Year	Chemical start N	Chemical N[b]	Air scrubber N	Animal manure N	Digestate mixture N	Raw digestate N	LF digestate N	Chemical K_2O[c]	P_2O_5[d]
0	**1**	2011	25	29		96 *(98)*				78	80 *(108)*[g]
0		2012	30	30		75 *(58)*				213	80 *(45)*
I	**2**	2011	25		29	96 *(98)*				78	80 *(108)*[g]
I		2012	30		30	75 *(58)*				213	80 *(45)*
I	**3**	2011			54	96 *(98)*				78	80 *(108)*[g]
I		2012			60	75 *(58)*				213	80 *(45)*
II	**4**	2011	25	18			107[e] *(105)*			29	80 *(74)*
II		2012					134[f] *(139)*[g]			0	80 *(101)*[g]
II	**5**	2011	25		18		107[e] *(105)*			29	80 *(74)*
II		2012	33					102 *(141)*[g]		46	61 *(159)*[g]
II	**6**	2011			43		107[e] *(105)*			29	80 *(74)*
II		2012			33			102 *(141)*[g]		46	61 *(159)*[g]
III	**7**	2011	25			84 *(86)*			35 *(36)*	33	77 *(105)*[g]
III		2012	33			67 *(52)*			35 *(39)*	121	76 *(49)*
III	**8**	2011				78 *(80)*			59 *(60)*	0	76 *(105)*[g]
III		2012			33	67 *(52)*			35 *(39)*	121	76 *(49)*

[a] Group 0 = reference (conventional fertilization): animal manure + chemical fertilizers (N, K_2O); Group I = substitution of chemical fertilizer N by ammonium sulfate (AmS) air scrubber water; Group II = anaerobic (co-)digestion of animal manure and field application of digestate with complete, partial, or without the substitution of chemical fertilizer N by AmS; Group III = use of the liquid fraction (LF) of digestate as P-poor fertilizer in addition to animal manure with or without the substitution of chemical fertilizer N by AmS.

[b] Ammonium nitrate (27 % N).

[c] Patentkali (30 % K_2O, 10 % MgO, 45 % SO_3 by weight).

[d] No chemical P was used.

[e] Mixture (volume percent, φ = 0.5) of raw digestate and LF digestate.

[f] Mixture of LF digestate (φ = 0.6) and raw digestate (φ = 0.4).

[g] Maximum allowable fertilization level was exceeded.

Finally, in group III (Sc 7-8), LF digestate was applied as P-poor fertilizer in combination with animal manure, with or without the substitution of chemical N by air scrubber water (cfr. optimized version of Sc 18-19 in Chapter 4). Although the maximum allowable level for effective N was always respected, it should be noted that for group III it was supposed that i) the LF was derived from a process where no animal manure was added to the digester, or ii) the LF can be classified as 'alternative fertilizer', other than 'animal manure'. As such, its corresponding N dose was not accounted for as 'animal manure N', so the maximum allowable level for total N from animal manure, i.e. 170 kg ha^{-1} (MAP4, 2011), may be exceeded here.

Important to note is that in Sc 3, 6, and 8, as well as in Sc 4 in 2012, no starter fertilizer (= applied to the field at sowing) was used. Furthermore, it should be remarked that the actual rates of application (based on product characterizations at the moment of fertilizer application) were sometimes deviating from the intended doses (based on preliminary product characterizations used for setting up the fertilization scenarios) and at times higher than the maximum allowable level due to differences in organic fertilizer composition over time. Moreover, in 2012 the digestate dosage in Sc 5-6 was higher than intended due to technical issues.

5.2.2 Sampling, fertilizer application, and field follow-up

Product samples were taken for physicochemical characterization before fertilization in order to determine the allowable fertilizer doses in compliance with MAP4 (2011). At the moment of fertilizer application, products were again sampled and analyzed in order to determine the nutrient content of the products that were actually applied to the field (Table 5.3).

Digestate and LF digestate after mechanical separation were sampled at the site of SAP Eneco Energy, Houthulst, Belgium. It concerns a mesophilic (37 °C) anaerobic co-digestion plant (capacity: 60,000 ton y^{-1}, 2.83 MW$_{el}$) with an input feed consisting of 30 % animal manure, 30 % energy maize, and 40 % organic biological waste supplied by the food industry. Pig manure was collected at the pig farm of Huisman, Aalter, Belgium. Acidic air scrubber water was sampled at the piggery of Ladevo BVBA, Ruiselede in 2011 and at Senergho, Hooglede in 2012, both in Belgium.

Two replicate samples of every product were each time collected in polyethylene sampling bottles (10 L), stored cool (± 4 °C), and transported within 1 h to the laboratory for physicochemical analysis. In the laboratory, the replicate samples were kept separated for separate analysis after homogenization of each particular sample. Because the pH of the air scrubber water was very low (2-3), it was neutralized before application to the field. In 2011, the pH-adjustment was conducted by adding sodium hydroxide (1 L NaOH per 200 L acidic wastewater, based on laboratory experiments), whereas in 2012, the pH-adjustment was assessed by mixing the acidic air scrubber water with alkaline air scrubber water from the same site. Hence, the latter provides a more environmentally friendly solution.

Table 5.3 Physicochemical product characterization per year (mean ± standard deviation; n = 2). DW = dry weight; EC = electrical conductivity; FW = fresh weight; N/A = not applicable; OC = organic carbon.

Parameter	Year	Animal manure	Digestate mixture[a]	Raw digestate	Liquid fraction digestate	Air scrubber wastewater (pH-adjusted)
DW (%)	2011	10 ± 0	6.2 ± 0.1	N/A	2.5 ± 0.1	-
	2012	4.3 ± 0.0	7.1 ± 0.0	14 ± 0	2.5 ± 0.0	-
OC (% on DW)	2011	40 ± 0	36 ± 0	N/A	31 ± 0	-
	2012	28 ± 2	34 ± 0	32 ± 0	35 ± 0	-
EC (mS cm^{-1})	2011	35 ± 0	29 ± 0	N/A	34 ± 0	135 ± 0
	2012	31 ± 0	35 ± 0	36 ± 0	34 ± 0	208 ± 0
pH	2011	7.8 ± 0.0	8.2 ± 0.0	N/A	7.4 ± 0	8.5 ± 0.0
	2012	7.7 ± 0.0	8.0 ± 0.0	8.3 ± 0.0	7.8 ± 0.0	6.9 ± 0.0
Total N (g kg^{-1} FW)	2011	8.1 ± 0.0	4.7 ± 0.0	N/A	3.6 ± 0.0	27 ± 0
	2012	5.3 ± 0.0	5.6 ± 0.0	7.4 ± 0.0	4.3 ± 0.0	42 ± 0
NH_4-N (g kg^{-1} FW)	2011	5.6 ± 0.0	3.1 ± 0.1	N/A	2.8 ± 0.0	27 ± 0
	2012	3.2 ± 0.1	3.7 ± 0.1	4.5 ± 0.0	3.2 ± 0.1	41 ± 4
P_2O_5 (g kg^{-1} FW)	2011	5.4 ± 0.2	2.0 ± 0.3	N/A	0.62 ± 0.03	-
	2012	2.4 ± 0.1	2.3 ± 0.2	5.0 ± 0.4	0.57 ± 0.02	-
K_2O (g kg^{-1} FW)	2011	4.7 ± 0.0	3.1 ± 0.5	N/A	3.5 ± -	-
	2012	2.9 ± 1.7	4.0 ± 4.0	5.5 ± 3.0	3.0 ± 1.6	-
Ca (g kg^{-1} FW)	2011	3.0 ± 0.0	1.3 ± 0.3	N/A	0.11 ± 0.00	-
	2012	1.9 ± 0.0	2.1 ± 0.0	6.5 ± 0.0	0.37 ± 0.00	-
Mg (g kg^{-1} FW)	2011	1.3 ± 0.0	0.34 ± 0.04	N/A	0.016 ± 0.000	-
	2012	1.1 ± 0.0	0.86 ± 0.04	2.0 ± 0.1	0.10 ± 0.01	-
Na (g kg^{-1} FW)	2011	2.2 ± 0.0	2.0 ± 0.5	N/A	3.1 ± 0.0	-
	2012	2.2 ± 0.0	3.4 ± 0.1	3.8 ± 0.1	3.1 ± 0.0	-
S (g kg^{-1} FW)	2011	0.80 ± 0.09	0.39 ± 0.01	N/A	0.11 ± 0.01	31 ± 0
	2012	0.42 ± 0.00	0.84 ± 0.30	1.7 ± 0.1	0.27 ± 0.02	48 ± 0

[a] 50 volume % raw digestate and 50 volume % liquid fraction digestate in 2011, 40 volume % raw digestate and 60 volume % liquid fraction digestate in 2012.

It should be remarked that in 2011 the pH after adjustment in practice in the field was slightly higher than predicted under laboratory conditions, i.e. 8.5 instead of 7. However, because of the high solubility of NH_4 and the immediate fertilizer application after sampling, NH_3 losses in the environment were not expected to be significantly influenced by this pH adjustment (Hillel, 2008; Zumdahl, 2005).

Fertilizers were applied to the soil on April 29-30 2011 and May 30 2012 and ploughed one day thereafter. In 2012, the fertilization was conducted late in the season due to the very exceptional wet weather conditions in April of that year (Table 5.4; RMI, 2014).

Table 5.4 Weather conditions in West Flanders (Belgium) in 2011 and 2012, and degree of abnormality by means of the statistical characteristic (SC) based on the reference period 1833-2010 (RMI, 2014).

Month	**Average temperature (°C)**				**Total rainfall (mm)**			
	2011	**SC**[a]	**2012**	**SC**[a]	**2011**	**SC**[a]	**2012**	**SC**[a]
January	4.0	n	5.1	n	90.5	n	86.4	n
February	5.4	n	3.7	va	44.0	n	30.0	n
March	7.7	n	8.9	va	22.4	e	32.9	n
April	14.1	ve	8.4	va	25.8	n	104.1	ve
May	14.8	n	14.3	n	22.5	ve	63.4	n
June	16.8	n	15.4	n	72.3	n	133.1	a
July	16.0	e	17.3	n	55.6	n	115.7	a
August	17.3	n	19.2	n	189.3	ve	22.5	a
September	16.5	a	14.5	n	83.1	n	51.6	n
October	12.1	n	11.1	n	48.8	n	119.4	va
November	8.6	a	7.1	n	8.5	ve	44.7	a
December	6.1	e	5.1	n	152.1	a	172.7	ve

[a] SC = Statistical characteristic: n = normal, a = abnormal (averages one time in 6 y), va = very abnormal (averages one time in 10 y), e = exceptional (averages one time in 30 y), ve = very exceptional (averages one time in 100 y).

Depending on the scenario, starter fertilizers were also applied at the moment of sowing (Table 5.2). On May 5 2011, energy maize of the species *Atletico* (breeder: KWS, Belgium; Food and Agricultural Organisation (FAO) ripeness index: 280) was sown at a seed density of 102,000 ha^{-1}. The crops were harvested on October 7. The preceding crop was fodder maize. On October 22 2011, Italian rye grass was sown as an intercrop, and on June 2 2012 energy maize of the species *Fernandez* (breeder: KWS, Belgium; FAO ripeness index: 260) was sown at a seed density of 100,000 ha^{-1}. Immediately after sampling, pig manure, digestate, and LF digestate were applied to the field by use of pc-controlled injection (Bocotrans, Tielt, Belgium; Fig. 5.2), whereas the pH-adjusted air scrubber water and the chemical fertilizers, ammonium nitrate (27 % N) and patentkali (30 % K_2O, 10 % MgO, 45 % SO_3 by weight), were applied to the plots by hand-application in order to ensure high precision of the applied dosage.

Figure 5.2 Fertilizer application by means of pc-controlled injection (Bocotrans, Tielt, Belgium). Picture: Vaneeckhaute C.

Samples of soils and plants were taken in April, July, September, October (harvest), and November (soil) 2011, as well as in April, August, and November (harvest) 2012. A length measurement was also performed on August 17 2011 (n = 320). At each sampling moment, four homogeneous soil samples were taken per subplot at three depths (0-30 cm, 30-60 cm, 60-90 cm) using a soil core sampler. Six plants were harvested manually by use of trimming scissors in a rectangle (4.5 x 3.5 m) around the boreholes. The samples were collected in polyethylene sampling bags, stored in cooler boxes filled with ice (± 4 °C), and transported within 1 h from the test site to the laboratory. In the laboratory, the replicate samples were again stored cool (1-5 °C) for subsequent separate analysis. The harvest was conducted by use of a maize chopper and the crop fresh weight (FW) yield was determined at the field using a transportable balance (Kubota KA-10-60A, capacity: 0.02-60 kg, Robbe Bascules NV, Torhout, Belgium; Fig. 5.3).

5.2.3 Physicochemical analysis

Note that, unless indicated otherwise, the same analytical devices were used for the soil and plant analyses (Sections 5.2.3.2-5.2.3.3) as described for the products (Section 5.2.3.1).

5.2.3.1 Product analysis

Dry weight (DW) content was determined as residual weight after 72 h drying at 80 °C in an oven (EU 170, Jouan s.a., Saint Herblain, FR). The OC content was determined after incineration of the dry samples during 4 h at 550 °C in a muffle furnace (Nabertherm, Lilientahl, DE). The loss of ignition (= weight loss after incineration) was divided by a conversion factor of

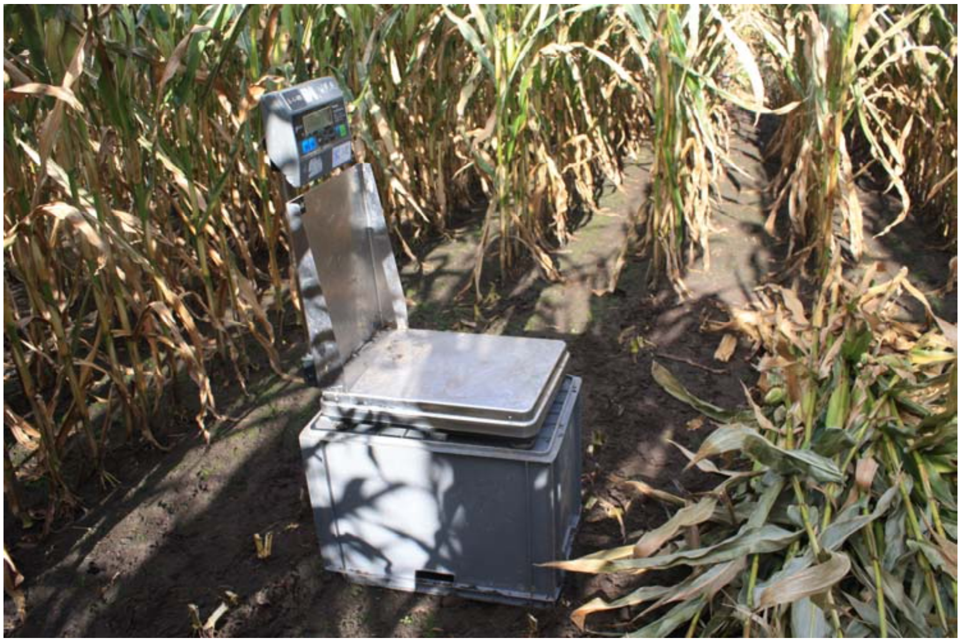

Figure 5.3 Determination of fresh weight biomass yield at the field.
Balance: Kubota KA-10-60A, Robbe Bascules NV, Torhout, Belgium.
Picture: Vaneeckhaute C.

1.8 to calculate OC, which is to date the official factor used for compost products in the Compendium for Sampling and Analysis provided in the Flemish waste and soil remediation decree (CSA, 2012). Note that this factor may be higher for manure and digestate derivatives, though a standard conversion factor for these products is currently not available. Conductivity and pH were determined potentiometrically using a WTW-LF537 (Wissenschaftlich Technischen Werkstäten, Weilcheim, DE) conductivity electrode and an Orion-520A pH-meter (Orion Research, Boston, USA), respectively. The solid samples were first equilibrated for 1 h in deionized water at a 5:1 liquid to dry sample ratio and subsequently filtered (MN 640 m, Macherey-Nagel, DE). Total N content was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest, Köningswinter, DE) after digestion of the sample in a sulphuric-salicylic acid mixture. The captured ammonia in the distillate was then titrated with 0.01 mol L^{-1} hydrogen chloride (HCl) in the presence of a methyl red bromocresol green mixed indicator (Van Ranst *et al.*, 1999). Ammonium (NH_4) was determined using the same Kjeltec-1002 distilling unit after addition of magnesium oxide (MgO) to the sample and subsequent titration (Van Ranst *et al.*, 1999). Total P was determined using the colorimetric method of Scheel (Van Ranst *et al.*, 1999) after wet digestion of the liquid samples using nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, UK). Calcium (Ca), Mg, and (heavy) metals, i.e. aluminium (Al), cadmium (Cd), chrome (Cr), copper (Cu), iron (Fe), lead (Pb), nickel (Ni), and zinc (Zn), were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX, Palo Alto, CA, USA; Van Ranst *et al.*, 1999), whereas sodium (Na) and K were analyzed using a flame photometer (Eppendorf ELEX6361, Hamburg, DE), both after wet digestion of the samples (2.5 g sample + 2 mL HNO_3 + 1 mL H_2O_2; Van Ranst *et al.*, 1999). Nitrate (NO_3^-) and sulfate (SO_4^{2-}) were analyzed using ionic chromatography (Metrohm-761, Herisau, CH) after centrifugation and subsequent vacuum filtration (0.45 µm pores) of the liquid fraction. Total sulfur (S) was analyzed as described by Weaver *et al.* (1994). The procedure involves product ashing, refluxing, and ionic chromatography (Metrohm 761, Herisau, CH).

5.2.3.2 Soil analysis

Soil samples were dried at 50 °C in a soil oven (EU 170, Jouan s.a., Saint Herblain, FR) for minimum 72 h. OC was determined as described for the product analyses (Section 5.2.3.1) using a conversion factor of 1.72 as in CSA (2012). Soil texture was determined manually using the standard method described in CSA (2012). The bulk density of the soil was determined as the mass of dry soil over its total (wet) soil volume (USDA, 2013). Soil conductivity was measured with a WTW-LF537 electrode after equilibration for 30 min in deionized water at a 5:1 liquid to dry sample ratio and subsequent filtration (MN 640 m). To determine the actual soil pH (pH-H_2O), 10 g of air-dried soil was allowed to equilibrate in 50 mL of deionized water for 16 h, while for the potential soil pH (pH-KCl), 50 mL of 1 mol L^{-1} potassium chloride (KCl) was added to 10 g of air-dried soil and allowed to equilibrate for 10 min. The pH of the supernatant was then measured using a pH Orion-520A glass-electrode. Total N in the soil was determined using a Kjeldahl destruction, while total P was determined using the method of Scheel after aqua regia digestion (1 g sample + 7.5 ml HCl, 2.5 ml HNO_3 and 2.5 ml distilled water). NH_4 and NO_3 were determined using an AA3 auto-analyzer (BRAN+LUEBBE, Norderstedt, DE) after extraction with KCl. Na, K, Ca, Mg, and (heavy) metals (Al, arsenic (As), Cd, Cr, Cu, Fe, mercury (Hg), Ni, Pb, Zn) were analyzed using ICP-OES after aqua regia digestion for the determination of total amounts (Van Ranst *et al.*, 1999). Total S was determined using the same ICP-OES after microwave destruction. Therefore, 1 g of dry soil was mixed with 2.5 mL perchloric acid ($HClO_4$) and 3.5 mL HNO_3, allowed to rest for 12 h, and heated in a microwave (CEM MARS 5, Drogenbos, BE) during 40 min at 100 °C and 600 W. Plant available amounts of P, K, S, Ca, and Mg were determined after ammonium lactate/acetic acid (pH 3.75) extraction of the samples (NSI, 2010; VIAK AS, 1993). The SAR, which refers to the ratio of the monovalent cation, Na^+, to the divalent cations, Ca^{2+} and Mg^{2+}, was determined as described by Hillel (2008; Eq. 5.1):

$$SAR = \frac{(Na)}{\sqrt{(Ca) + (Mg)}} \qquad \boldsymbol{Eq. (5.1)}$$

in which (Na), (Ca), and (Mg) represent the ion activities (mmol L^{-1}) of Na, Ca, and Mg, respectively, in the saturation extract of the soil.

5.2.3.3 Plant analysis

Plant samples collected in the field were weighed for determination of the FW biomass yield and oven-dried at 55 °C for determination of the DW content. The dry samples were grinded to pass a 1 mm sieve (Retsch SM-2000, Haan, DE) and incinerated at 550 ℃ during 4 h in order to determine the OC content, similar as described in Section 5.2.3.2. Total N was determined using the Kjeldahl method and total P was determined using the method of Vanadate (Van Ranst *et al.*, 1999) after incineration of the samples during 4 h at 450 ℃ and digestion of the residual ash (1 g ash + 5 mL of 3 mol L^{-1} HNO_3 + 5 mL of 6 mol L^{-1} HNO_3). Total amounts of Na, K, Ca, Mg, and metals (Al, As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, Zn) in the digested samples were determined using ICP-OES. Total S was determined using the same ICP-OES after microwave destruction of 0.2 g dry and grinded plant sample (see Section 5.2.3.2).

5.2.4 Performance indicator calculations

5.2.4.1 Nutrient use efficiency

The nutrient use efficiency (%) was determined using Equation 5.2:

$$\textbf{Nutrient use efficiency}\ (\%) = 100\,.\frac{Crop\ nutrient\ uptake\ (\mathrm{kg\ ha^{-1}})}{Nutrient\ supply\ through\ fertilization\ (\mathrm{kg\ ha^{-1}})} \qquad \boldsymbol{Eq.(5.2)}$$

It gives an indication of the effectiveness of the fertilizers applied (organic + chemical), without taking in account the amount of available nutrients in the soil before fertilization (Parn *et al.*, 2012). Nutrient use efficiencies were evaluated through time for the primary macronutrients, N, P_2O_5, and K_2O, the secondary macronutrients, S, Ca, and Mg, as well as for the micronutrient, Na, in order to evaluate the potential salt accumulation in the soil.

5.2.4.2 Nutrient balances and apparent recovery

Soil nutrient balances provide a method for estimating the annual nutrient loadings to agricultural soils and hence provide an indication of the potential risk associated with losses of nutrients to the environment (leaching, accumulation, volatilization, etc.), which can impact on soil, air, and water quality, and on climate change (Defra, 2011b; Parn *et al.*, 2012). In this study nutrient balances were assessed in two different ways. First, the apparent nutrient surplus was calculated using Equation 5.3:

$$\textbf{Apparent nutrient surplus}\ (\mathrm{kg\ ha^{-1}})$$
$$= nutrient\ inputs\ (\mathrm{kg\ ha^{-1}}) - crop\ nutrient\ uptake\ at\ harvest\ (\mathrm{kg\ ha^{-1}}) \qquad \boldsymbol{Eq.(5.3)}$$

in which the ‘inputs’ refer to the nutrient supply by fertilization and natural deposition, i.e. 30 kg N ha^{-1}, 3 kg P_2O_5 ha^{-1}, and 8 kg K_2O ha^{-1} (van der Burgt *et al.*, 2006). A positive or surplus balance means that less nutrients have been taken out of the field with the harvest than have been put there. In contrast, if the balance is negative or in deficit, more nutrients have been eliminated from the field than have been applied. This balance does not estimate the actual losses of nutrients to the environment, but significant nutrient surpluses are directly linked with these losses.

Secondly, the actual environmental pollution was determined by taking in account the measured changes in soil nutrient reserves over time. It was calculated using Equation 5.4:

$$\textbf{Actual pollution index}\ (\mathrm{kg\ ha^{-1}}) \qquad \boldsymbol{Eq.(5.4)}$$
$$= soil\ nutrient\ reserves\ before\ fertilization\ (\mathrm{kg\ ha^{-1}}) +\ nutrient\ inputs\ (\mathrm{kg\ ha^{-1}}) - soil\ nutrient\ reserves\ at\ harvest\ (\mathrm{kg\ ha^{-1}}) -\ crop\ nutrient\ uptake\ at\ harvest\ (\mathrm{kg\ ha^{-1}}) = soil\ nutrient\ reserves\ before\ fertilization\ (\mathrm{kg\ ha^{-1}}) - soil\ nutrient\ reserves\ at\ harvest\ (\mathrm{kg\ ha^{-1}}) + apparent\ nutrient\ surplus\ (\mathrm{kg\ ha^{-1}})$$

A positive actual pollution index is directly linked to nutrient losses in the environment, e.g. through leaching, whereas a negative pollution index indicates that more nutrients have become available for the plant during the growing season, e.g. via exchange from the clay-humus complex in the soil. These nutrients may, however, be vulnerable for leaching later in the fall and winter, unless they would be captured by an intercrop.

Finally, also the apparent recovery was determined as the percentage of total available nutrients from the soil that are recovered in the crops at the harvest using Equation 5.5:

$$\textbf{Apparent recovery}\ (\%) \qquad \boldsymbol{Eq.(5.5)}$$
$$= 100\ .\frac{crop\ nutrient\ uptake\ at\ harvest\ (\mathrm{kg\ ha^{-1}})}{soil\ nutrient\ reserves\ before\ fertilization\ (\mathrm{kg\ ha^{-1}})\ +\ nutrient\ inputs\ (\mathrm{kg\ ha^{-1}})}$$

in which the ‘inputs‘ refer again to the nutrient supply by fertilization and natural deposition. Hence, it gives an idea of the total amount of nutrients from the soil (not only from the fertilizers applied) that have been taken up by the crops during the growing season. The apparent recovery has become an increasingly important indicator to evaluate the fertilizer performance, next to the nutrient use efficiency, since the awareness of nutrient depletion, especially for P (van Dam and Ehlert, 2008).

5.2.5 Model simulations

Models are useful tools to evaluate environmental impacts associated with nutrient management in cropping systems and to predict them correctly (Cannavo *et al.*, 2008). In this study, simulations of N dynamics were conducted with the computer model NDICEA (Nitrogen Dynamics In Crop rotations in Ecological Agriculture) nitrogen planner 6.0.16 (van der Burgt *et al.*, 2006). It is a process-based simulation model which calculates dynamics of the state variables soil water (m^3 ha^{-1}), soil carbon (kg ha^{-1}), soil organic matter (kg ha^{-1}), apparent initial age of a source of organic matter (year), and soil organic (kg ha^{-1}) and inorganic nitrogen (kg ha^{-1}) for each soil layer over the course of a crop rotation with a time step of one week. The model applies to homogenous layers in well-drained, mineral soils. The purpose of using NDICEA is to reconstruct dynamics of water and nitrogen in cropping system experiments or in farmers' fields. This purpose resulted in a target-oriented approach: the target crop production, expressed in terms of biomass, water use, and nitrogen accumulation is input for the model, and the model ‘reconstructs’ the dynamics of the state variables (van der Burgt *et al.*, 2006).

In this modelling exercise, the physicochemical product analyses, plant yields, crop nutrient uptake data, as well as the soil measurements (e.g. nitrate residue) in time collected during the two-year field trial were used as input to the model. Moreover, the particular weather conditions for the site under study in 2011 and 2012 were automatically selected by NDICEA from online weather station databases. The nutrient balances obtained are thus specific for each scenario. Simulations were conducted over three and thirty years. To this end, crop rotation data from the fertilization year prior to the field experiment (i.e. 2010) were additionally inserted in order to correctly calibrate the model. The set of three-year field-trial data was then calculated after three and thirty years using the 'repeat' function in NDICEA, i.e. a one time and ten times repetition, respectively. The resulting output represents the 2nd (year 4-6) and 11th (year 31-33) cycle, respectively. The first year of the output cycle is not conclusive (only required for model calibration). Hence, only the 2nd and 3rd year of the resulting cycle is presented in the results section below (Section 5.3).

On top of that, carbon dynamics in the long term (30 years) were determined using the 'Koolstofsimulator' software 20110706 (LNE, 2006). To this end, contact was sought with the department of Environment, Nature, and Energy of the Flemish government (LNE, Brussels, Belgium) and the Soil Service Institute of Belgium (Leuven-Heverlee, Belgium) (Tits M., Elsen A., personal communication 2011). Upon request, a modified version of the Koolstofsimulator was prepared in the context of this research and obtained in 2012. It allows the self-insertion and application of new organic/organo-mineral fertilizers. The most important factor in the calculations is the amount of effective organic carbon (EOC), which is the OC that remains in the soil after one year and thus contributes to the humus build-up (Vlaco, 2012). The ratio of EOC over OC in the digestate derivatives can be as high as 0.8 (Vlaco, 2012; Chapter 2, Section 2.2). Nevertheless, in this modelling exercise a conservative standard value of 0.41 was used, as proposed by van der Burgt *et al.* (2011). The standard value for pig manure amounts to 0.31 (LNE, 2006). The initial soil organic carbon (SOC) content was set at 1.9 % (Table 5.1).

5.2.6 Statistical analysis

Statistical analyses were performed using SPSS Statistics 21. A one-way ANOVA model was used to determine the effect of fertilizer type (i.e. the independent variable, between-groups factor) on plant yield and DW content, plant nutrient uptake, nutrient soil contents, and soil quality parameters (i.e. the dependent variable). The condition of normality was checked using the Kolmogorov Smirnov test and QQ-plots, whereas equality of variances was checked with the Levene test. When homoscedascity was found, significance of effects was tested by use of an F-test and post-hoc pair-wise comparisons were conducted using Tukey's honestly significant difference (HSD) test ($\alpha = 0.05$; $n = 4$). When no homoscedascity was found, a Welch F-test combined with a post-hoc Games-Howell test was used ($\alpha = 0.05$; $n = 4$). When the condition of normality was not fulfilled, the non-parametric Kruskal-Wallis test was applied instead of the one-way ANOVA. Significant parameter correlations were determined using the Pearson correlation coefficient (r).

5.2.7 Analysis of biogas potential

In 2011, the biogas potential of the energy maize was determined in the biogas lab of the university college of West Flanders (Innolab, Kortrijk, Belgium) via a mesophillic batch test (Fig. 5.4). Homogenized subsamples of the harvested plant material were taken for the analysis. The four replicate subsamples per treatment were then mixed and again homogenized. A control with inoculum sludge and a flask (5 L) with an equal amount of sludge to which a known amount of dry, grinded biomass was added, were prepared in duplicate (Fig. 5.4A). The organic dry weight load to the reactor was 4 g L^{-1}. The used inoculum was an exhausted digestate, composed of different digestates from stable working biogas reactors. The two controls and the two flasks with inoculum material had the same volume and were incubated at 37 °C. The flasks were connected to gas catch columns, filled with acid water to avoid dissolution of CO_2, and the produced gas was read out on the column (Fig. 5.4B).

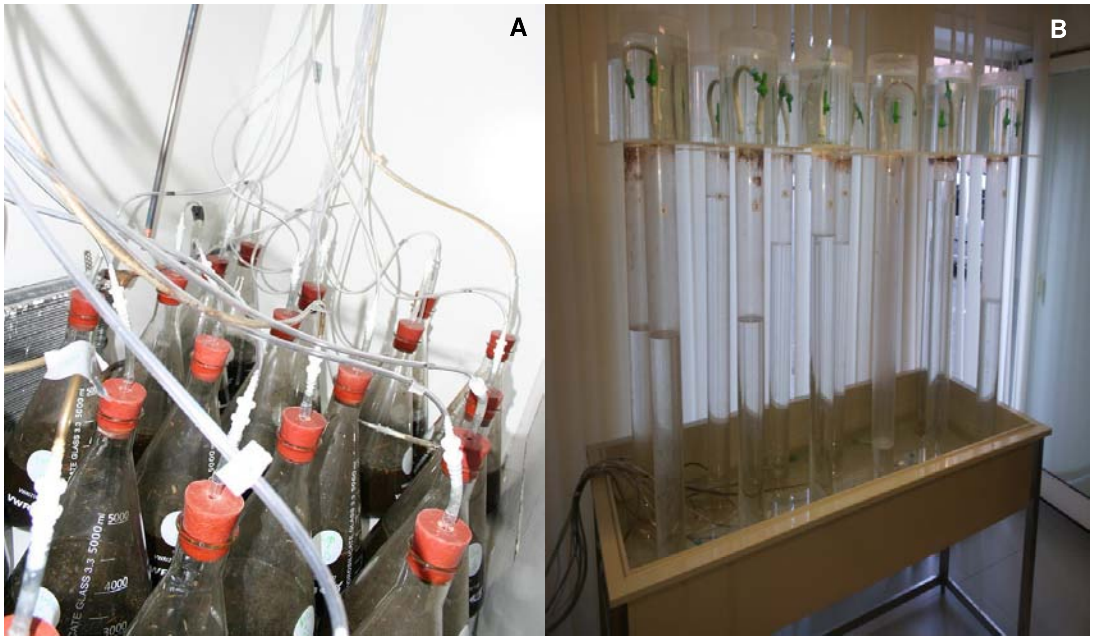

Figure 5.4 Biogas batch test at Innolab, Kortrijk, Belgium.
A: sludge flasks; B: gas catch columns. Pictures: Willems B.

In 2012, the harvested plants were digested in a mesophilic pilot-scale anaerobic digester located at Inagro, Beitem, Belgium.

5.2.8 Economic and ecological benefits

The methodology used for the economic and ecological evaluation of the application of bio-based fertilizers in agriculture can be found in Chapter 4. Attention was given to the fertilization cost and the carbon footprint (energy use and the associated greenhouse gas (GHG) emissions) of the various fertilization scenarios. As the test site is located in Flanders (Belgium), costs are expressed in euros (€ 1 ≈ 1.415 CAD; November 2014).

5.3 Results and discussion

5.3.1 Impact of fertilization strategy on crop production and biogas potential

5.3.1.1 Crop yield

Over the whole experimental period, the mean biomass yields, both on FW and DW content, were the highest when LF digestate was used as P-poor fertilizer in addition to animal manure (Sc 7-8). This effect was significant at the harvest in 2012 (Sc 4 < 1/7/8; Sc 5 < 8) and in 2011 (Sc 2 < 5/7) (Fig. 5.5).

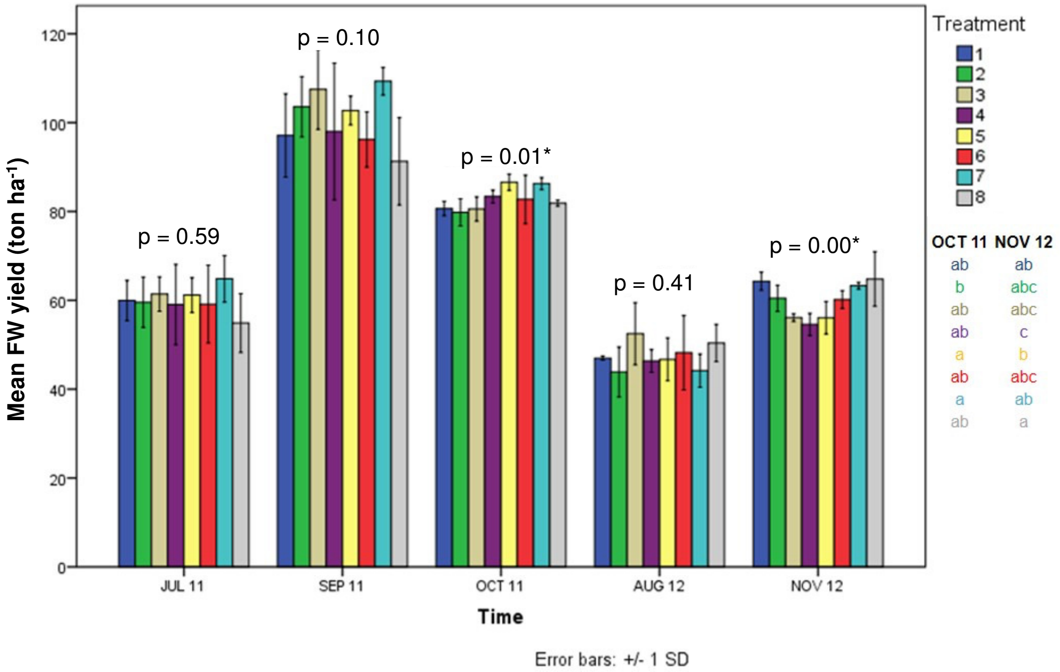

Figure 5.5 Fresh weight (FW) biomass yield (ton ha^{-1}) as a function of time for the eight different fertilization scenarios (mean, error bars: +/- 1 standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

The length measurement in August 2011 showed not much effect of the variable treatment throughout the field (3.61±0.03 m, $p = 0.19$), nor did the cob percentage on DW content (31±3 %). The average DW biomass yield in this study was at the harvest in 2011 approximately 23±1 ton ha^{-1} (*Atletico*), which is regular for the cultivation of this species in Flanders and higher than that of silo maize, i.e. 15 ton ha^{-1} (Ghekiere *et al.*, 2011). However, the DW biomass yield in 2012 was significantly lower for all treatments, i.e. 17±1 ton ha^{-1} in 2012 (*Fernandez*) as compared to the 2011 results. This is most likely related to the exceptional weather conditions occurring in 2012 (Table 5.4). Boerenbond (2012) reported severe damage to maize production all over the West of Flanders in that year. They assigned the cause of the damage to the combination of the cold weather in May, the extremely wet conditions in June and July (leading to nutrient losses and reduced crop nutrient uptake), and the exceptional drought in August (during the most sensitive maize pollination stage).

5.3.1.2 Biogas potential

The DW content of the biomass and DW yield at the harvest are key parameters for determination of the biogas yield (Amon *et al.*, 2007; Calus *et al.*, 2007; Ghekiere *et al.*, 2011; Matjaz *et al.*, 2010). Before energy maize is digested, the maize first has to be ensilaged in order to reach a maximum yield (Amon *et al.*, 2007). Therefore, a minimum DW content in the total plant of 28 % is required in order to prevent sap losses in the silage. The DW content may also not exceed 35 %, because then the fermentation potential diminishes due to the higher lignin content of more ripened maize (Ghekiere *et al.*, 2011). The average DW content in this study at the harvest was 28±1 % in 2011 and 29±0 % in 2012 (Fig. 5.6). Hence, the energy maize was suitable for biogas production (desired: 28-35 %; Matjaz *et al.*, 2010).

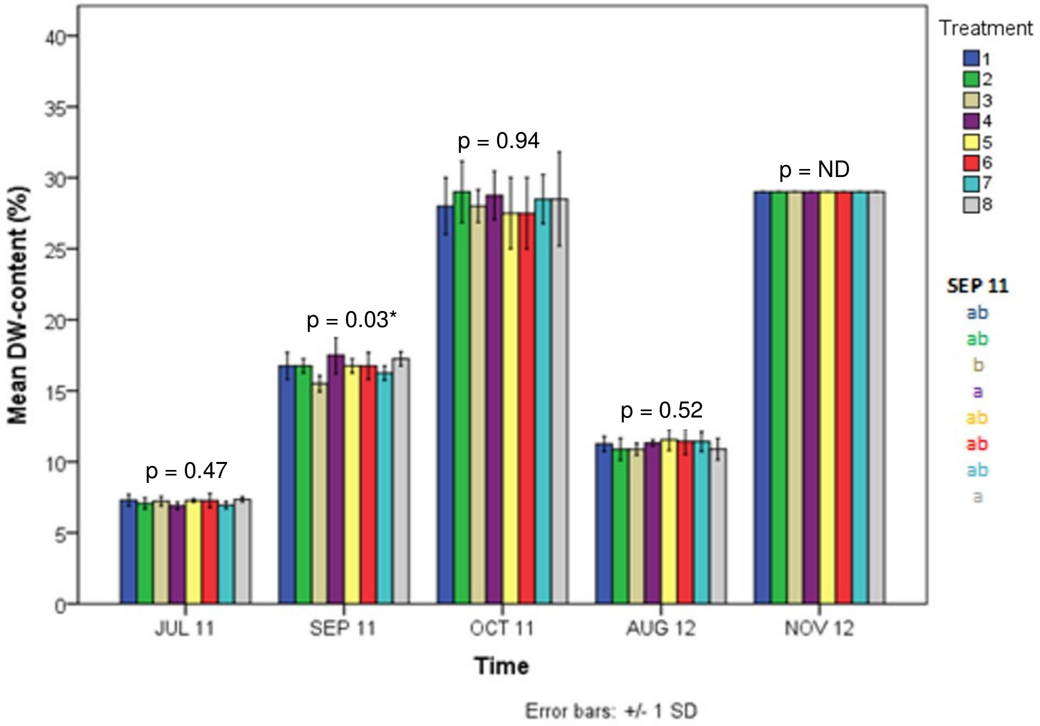

Figure 5.6 Dry weight (DW) content (%) as a function of time for the eight different fertilization scenarios (mean, error bars: +/- 1 standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level. ND = not determined.

Biogas batch tests in 2011 showed little effect ($p = 0.11$) of the fertilizers applied on the biogas potential ($Nm^3\ ha^{-1}$) of the harvested crops (mean ± standard deviation: 349±16 $Nm^3\ CH_4\ ton^{-1}$ DW; Table 5.5). Also, no significant differences were observed in the biomass organic carbon content during the field trial in 2011 ($p > 0.1$). The average plant OC content at the harvest was 95±1 % on DW.

The obtained average methane production potential of the energy maize in this study was in line with the results obtained in Calus *et al.* (2007), who repored an average of 345 $Nm^3\ ton^{-1}$ DW for

Table 5.5 Biogas potential of the harvested energy maize for the eight different fertilization scenarios in 2011 determined by means of a mesophillic anaerobic digestion batch test (mean ± standard deviation; n = 4). DW = dry weight; FW = fresh weight.

Scenario	DW (%)	Residence time (d)	Biogas (Nm^3 ton^{-1} FW)[a]	CH_4[b,c] (Nm^3 ha^{-1})	Energy[d] (GJ ha^{-1})	Electricity[e] (MWh$_{el}$ ha^{-1})	Heat[e] (MWh$_{th}$ ha^{-1})
1	28	42	136	7,765 ± 570	278 ± 20	31 ± 2	34 ± 2
2	29	34	143	7,749 ± 405	277 ± 14	31 ± 2	34 ± 2
3	28	36	135	7,623 ± 126	273 ± 4	30 ± 0	33 ± 0
4	29	39	140	7,879 ± 381	282 ± 14	31 ± 2	34 ± 2
5	27	37	131	8,255 ± 921	296 ± 33	33 ± 4	36 ± 4
6	28	42	135	8,468 ± 443	303 ± 16	34 ± 2	37 ± 2
7	28	41	139	8,403 ± 428	301 ± 15	33 ± 2	37 ± 2
8	29	37	140	8,762 ± 988	314 ± 35	35 ± 4	38 ± 4

[a] Normalized volumetric unit: temperature = 0 ℃ and pressure = 1,013.25 hPa.
[b] Considering a biogas CH_4 content of 65 % (Vaneeckhaute, 2009).
[c] Conversion made using the biomass dry weight content and dry weight biomass yield.
[d] Considering an energetic value of 35.8 MJ Nm^{-3} CH_4 (Vaneeckhaute, 2009).
[e] Conversion of CH_4 into electricity (40 %) and heat (44 %) using a combined heat and power (CHP) engine; 1 kWh = 3.6 MJ (cfr. Eneco Energy biogas installations; Vaneeckhaute, 2009).

seven different energy maize species. However, when taking in account the biomass yield, the methane production potential of the energy maize per hectare was significantly higher for each treatment in this study (8,112±414 m^3 ha^{-1}) compared to the range of 4,856-6,621 m^3 ha^{-1} obtained in Calus *et al.* (2007) and to the average energetic potential of 220 GJ ha^{-1} obtained in Veldeman (2007). Hence, the DW biomass yield obtained in this study for the species *Atletico* was significantly higher than that obtained for the energy maize species in the aforementioned studies. This is in accordance with its higher FAO ripeness index. Indeed, such species bloom later in the season, so that they have a longer vegetative period in which they can grow more biomass (Amon *et al.*, 2007; Matjaz *et al.*, 2010). Interestingly, although there was not much effect of the fertilizers used on the biogas potential per ton fresh weight, the average energetic potential per hectare was higher for Sc 4-8 (= use of digestate) compared to Sc 1-3 (= use of manure) due to the higher mean FW biomass yields obtained in these scenarios (Fig. 5.5). There was also a very strong linear correlation ($Y = 6.1X - 32.8$; $R^2 = 1$) between the biogas potential (Nm^3 ton^{-1} FW; Y) and the DW content of the biomass (%; X), where higher DW contents resulted in a higher biogas potential.

In 2012, the harvested plant material delivered an average methane production of ± 340 Nm^3 CH_4 ton^{-1} DW in a pilot-scale anaerobic digester after ensilaging for about one month. Differences in biogas production between the treatments were not studied here.

5.3.2 Impact of fertilization strategy on nutrient dynamics in the environment

5.3.2.1 Nitrogen dynamics

a) Nitrogen use efficiency, plant N uptake, and soil NO_3-N residue

The NO_3-N residue in the soil profile (0-90 cm) between the 1st of October and the 15th of

November gives an indication of the amount of N that may end up in ground and surface waters. A judicious fertilization is of crucial importance to obtain low NO_3-N residues. During this field trial, no significant differences in NO_3-N residue in the soil were observed between the treatments, except in November 2011 (Fig. 5.7: Sc 5 > 2/4/6/8).

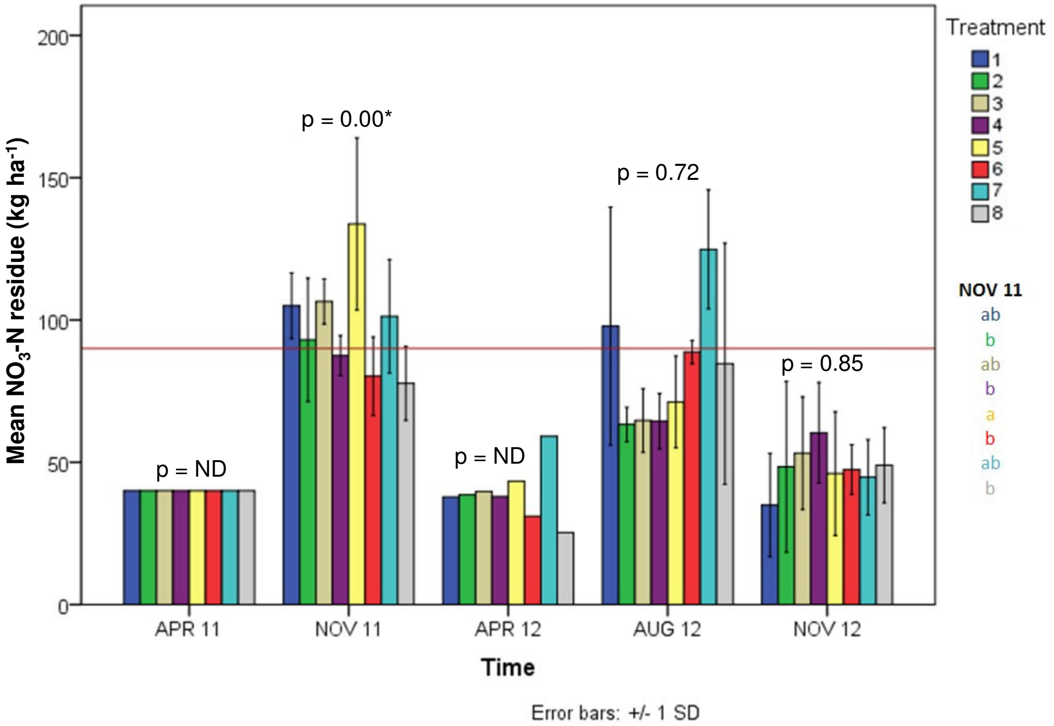

Figure 5.7 Soil NO_3-N residue (kg ha^{-1}) as a function of time for the eight different fertilization scenarios in the 0-90 cm soil layer (mean, error bars: +/- 1 standard deviation; n = 4). Red non-dashed line indicates the Flemish environmental standard of 90 kg NO_3-N ha^{-1} between October 1 and November 15. p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

It should, however, be remarked that at that time all scenarios exceeded the Flemish environmental standard of 90 kg NO_3-N ha^{-1} due to exceptional weather conditions, characterized by an extremely dry spring, wet summer, and hot autumn (Table 5.4; Vaneeckhaute *et al.*, 2013c). The Flemish Land Agency (VLM, 2012) reported that in 2011 approximately 40 % of the NO_3-N residue measurements in West Flanders exceeded the maximum allowable level. Further, it might be possible that the dose of 150 kg ha^{-1} of effective N, which is the maximum allowable dose for the cultivation of maize on non-sandy soils (MAP4, 2011), was too high for the field under study. Indeed, during the experiment in 2011 it was observed that the 0-90 cm soil layer was rather sandy than sandy-loam. In all respects, these high NO_3-N residues may increase the risk for NO_3 leaching to ground and surface waters. Therefore, in 2012, guided measures were implemented at the field (VLM, 2012; Section 5.2.1).

Concerning the intercrop, it is likely that the density of the Italian rye grass was too low and that the grass was sown too late, so that it had not yet taken up its maximum amount of N at the sampling moment (November 25 2011). The N uptake is dependent on the date of sowing and normally ranges for this species between 40 and 60 kg ha^{-1}, and up to 80 kg ha^{-1} under good conditions. In order to reach a maximum N uptake, it is advised to sow the rye grass as soon as possible after the harvest and not later than October 15 (VLM, 2012). Therefore, in 2012, the intercrop was sown immediately after the harvest to optimally enjoy the benefits. In November 2012, all scenarios showed a NO_3-N residue below the limit of 90 kg ha^{-1}.

No significant differences in total soil N content (0-30 cm) were determined during the field trial (Appendix 2: Table A2.1). Nevertheless, there was a strong significant effect of the fertilizers applied on the N use efficiency (NUE; Fig. 5.8) and the plant N uptake (kg ha^{-1}; Table 5.6) in 2012.

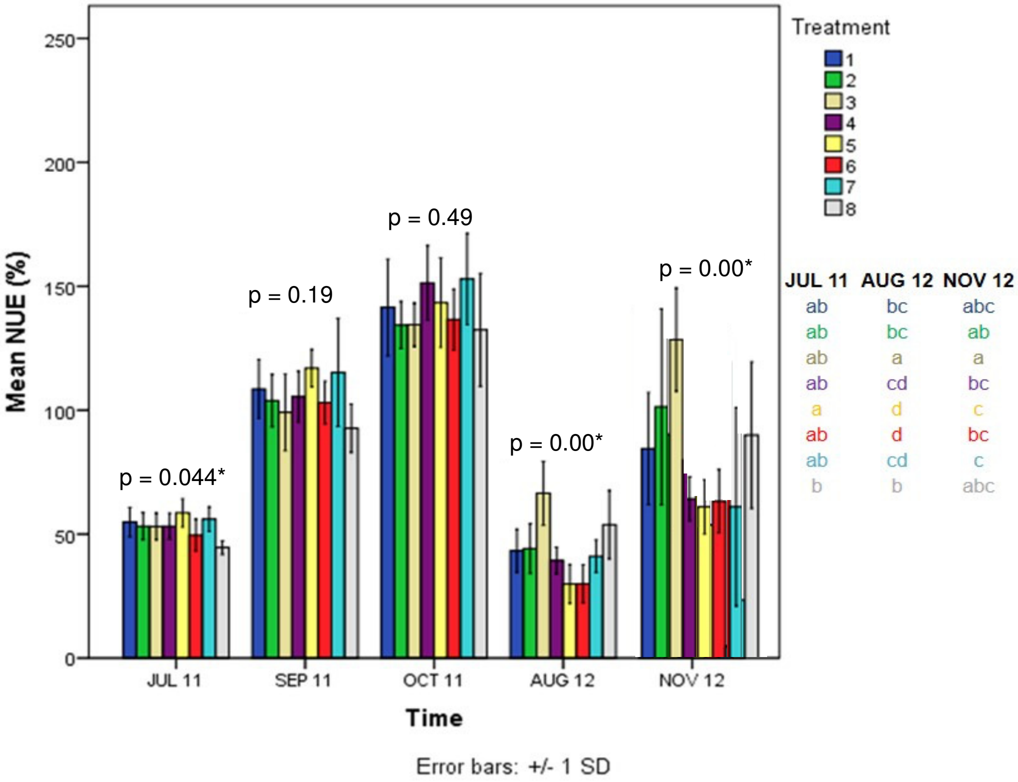

Figure 5.8 Nitrogen use efficiency (NUE, %) as a function of time for the eight different fertilization scenarios (mean, error bars: +/- 1 standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

The scenarios in which chemical fertilizer N was completely replaced by air scrubber water (Sc 3/8) showed the highest NUE and plant N uptake. Furthermore, a strong significant correlation was found between the NUE and the DW biomass yield ($r = 0.80$; $p \approx 0.00$).

Finally, it should be remarked that the plant nitrogen uptake in 2012 was lower for all scenarios as compared to the measurements in 2011, likely due to the unfavorable weather conditions occurring in that growing season (see Section 5.3.1.1). This was also the case for the plant K, S, Ca, Mg, and Na uptake (see Table 5.6). The plant P uptake was less affected, probably due to the large amount of available P in the soil (Table 5.1).

Table 5.6 Plant nutrient uptake (N, P_2O_5, K_2O, S, Ca, Mg, Na; kg ha^{-1}) in time for the eight different fertilization scenarios (mean ± standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

Scenario	Jul/11	Sep/11	Oct/11	Aug/12	Nov/12
N (kg ha^{-1})	**p = 0.11**	**p = 0.33**	**p = 0.68**	**p = 0.00***	**p = 0.032***
1	119 ± 13	235 ± 26	306 ± 42	68 ± 14c	140 ± 23ab
2	119 ± 12	232 ± 24	300 ± 21	69 ± 16c	157 ± 40ab
3	122 ± 13	227 ± 35	308 ± 20	104 ± 20a	195 ± 21a
4	116 ± 11	229 ± 22	329 ± 33	92 ± 13ab	146 ± 9ab
5	130 ± 13	259 ± 17	318 ± 40	81 ± 21b	155 ± 11ab
6	113 ± 15	234 ± 20	310 ± 28	81 ± 21b	165 ± 13ab
7	126 ± 11	260 ± 49	345 ± 42	76 ± 12bc	106 ± 40b
8	103 ± 6	214 ± 22	305 ± 53	100 ± 26a	173 ± 30ab
P_2O_5 (kg ha^{-1})	**p = 0.10**	**p = 0.40**	**p = 0.67**	**p = 0.0010***	**p = 0.010***
1	34 ± 3	101 ± 10	134 ± 18	37 ± 3ab	96 ± 32b
2	32 ± 2	110 ± 16	128 ± 9	37 ± 4b	116 ± 21ab
3	36 ± 2	106 ± 16	135 ± 12	37 ± 4ab	155 ± 23a
4	33 ± 2	94 ± 16	141 ± 12	35 ± 5b	106 ± 16ab
5	35 ± 4	109 ± 9	146 ± 22	34 ± 5ab	124 ± 7ab
6	34 ± 5	105 ± 10	139 ± 4	32 ± 11ab	153 ± 23a
7	38 ± 4	112 ± 4	152 ± 19	33 ± 12ab	118 ± 13ab
8	30 ± 5	97 ± 13	141 ± 30	35 ± 12a	153 ± 13a
K_2O (kg ha^{-1})	**p = 0.18**	**p = 0.94**	**p = 0.0038***	**p = 0.014***	**p = 0.84**
1	164 ± 10	292 ± 29	333 ± 28c	189 ± 28ab	272 ± 92
2	143 ± 9	338 ± 58	346 ± 32b	164 ± 21b	244 ± 52
3	154 ± 9	289 ± 57	352 ± 37abc	204 ± 34ab	199 ± 55
4	161 ± 32	304 ± 92	420 ± 13ab	195 ± 20ab	285 ± 112
5	162 ± 30	321 ± 49	431 ± 39a	196 ± 35ab	224 ± 61
6	176 ± 20	326 ± 44	406 ± 62abc	211 ± 57a	276 ± 38
7	168 ± 7	309 ± 43	366 ± 17abc	182 ± 42ab	254 ± 88
8	153 ± 30	314 ± 85	383 ± 12abc	218 ± 33a	246 ± 37
S (kg ha^{-1})	**p = 0.036***	**p = 0.095**	**p = 0.45**	**p = 0.0080***	**p = 0.035***
1	6.2 ± 0.6ab	18 ± 2	23 ± 3	6.2 ± 0.7ab	14 ± 1ab
2	6.3 ± 0.4ab	17 ± 3	23 ± 1	5.7 ± 1.7b	15 ± 1ab
3	6.4 ± 0.5ab	17 ± 3	24 ± 2	8.2 ± 2.7a	17 ± 2a
4	6.1 ± 0.8ab	16 ± 3	25 ± 3	7.0 ± 1.1ab	13 ± 2ab
5	6.7 ± 0.4ab	13 ± 3	26 ± 3	7.7 ± 1.5ab	14 ± 1ab
6	6.3 ± 0.8ab	14 ± 2	24 ± 1	7.4 ± 3.2ab	16 ± 2ab
7	7.0 ± 0.3a	15 ± 4	26 ± 2	6.1 ± 0.8ab	12 ± 2b
8	5.4 ± 0.4b	13 ± 3	26 ± 4	8.0 ± 2.0ab	15 ± 2ab
Ca (kg ha^{-1})	**p = 0.17**	**p = 0.089**	**p = 0.53**	**p = 0.00***	**p = 0.64**
1	19 ± 2	35 ± 2	48 ± 6	17 ± 2b	21 ± 9
2	16 ± 1	37 ± 5	48 ± 7	14 ± 2b	25 ± 3
3	12 ± 8	34 ± 5	47 ± 7	24 ± 5a	25 ± 10
4	13 ± 4	32 ± 11	48 ± 4	17 ± 5b	31 ± 7
5	13 ± 7	41 ± 4	53 ± 4	16 ± 3b	27 ± 7
6	16 ± 3	31 ± 8	40 ± 8	16 ± 5b	16 ± 5
7	19 ± 3	43 ± 6	47 ± 4	15 ± 8b	23 ± 11
8	12 ± 2	31 ± 4	48 ± 13	18 ± 2ab	23 ± 8
Mg (kg ha^{-1})	**p = 0.16**	**p = 0.13**	**p = 0.56**	**p = 0.18**	**p = 0.22**
1	14 ± 1	29 ± 2	36 ± 4	6.8 ± 0.7	17 ± 3
2	11 ± 1	30 ± 4	36 ± 4	6.1 ± 0.9	14 ± 1
3	9 ± 6	29 ± 4	36 ± 3	7.2 ± 1.6	16 ± 2
4	9 ± 3	26 ± 6	38 ± 3	6.4 ± 1.2	17 ± 1
5	8 ± 4	28 ± 2	37 ± 4	6.3 ± 1.5	15 ± 0
6	12 ± 2	27 ± 4	34 ± 3	7.6 ± 2.6	17 ± 2
7	14 ± 2	34 ± 4	41 ± 4	6.4 ± 1.2	14 ± 2
8	9 ± 2	26 ± 2	38 ± 8	6.5 ± 1.4	15 ± 2
Na (kg ha^{-1})	**p = 0.090**	**p = 0.64**	**p = 0.56**	**p = 0.038***	**p = 0.019***
1	1.2 ± 0.1	3.9 ± 0.8	6.1 ± 1.5	0.40 ± 0.20	1.6 ± 0.4
2	1.7 ± 0.9	4.1 ± 1.0	6.0 ± 1.7	0.43 ± 0.20	1.9 ± 0.3
3	1.1 ± 0.2	4.4 ± 1.6	6.1 ± 1.2	0.41 ± 0.21	1.2 ± 0.3
4	0.95 ± 0.28	3.1 ± 1.6	5.6 ± 0.6	0.44 ± 0.36	1.3 ± 0.2
5	1.1 ± 0.2	4.2 ± 0.7	5.6 ± 1.1	0.42 ± 0.35	1.5 ± 0.2
6	1.2 ± 0.1	3.8 ± 0.6	5.2 ± 1.7	0.34 ± 0.37	2.0 ± 0.4
7	1.4 ± 0.2	4.4 ± 1.5	7.0 ± 0.7	0.33 ± 0.37	1.3 ± 0.4
8	1.0 ± 0.2	3.3 ± 0.7	6.5 ± 0.9	0.22 ± 0.14	1.2 ± 0.1

b) Nitrogen balances and apparent recovery

First, it should be remarked that not all scenarios can be compared with each other as the N delivery was not always equal. This variety was caused by the difference in organic fertilizer composition over time. Especially in 2012, the actual amount of effective N applied to the soil in Sc 5 and 6 was higher than intended, also partly due to technical reasons (Table 5.2). Therefore, for 2012, only Sc 1, 2, and 3 will be compared with each other, and Sc 7 with Sc 8.

A comparison of model simulations over 3 and 30 years (i.e. after one and ten repetitions of the three-year rotation, respectively; see Section 5.2.5) for Sc 1 and 3 using the NDICEA software tool is given in Figure 5.9. The output represents the last two years of the 2nd (year 5-6) and 11th (year 32-33) cycle, respectively (see Section 5.2.5). The mineral balance for Sc 1, 2, and 3 over 3 and 30 years is presented in Table 5.7.

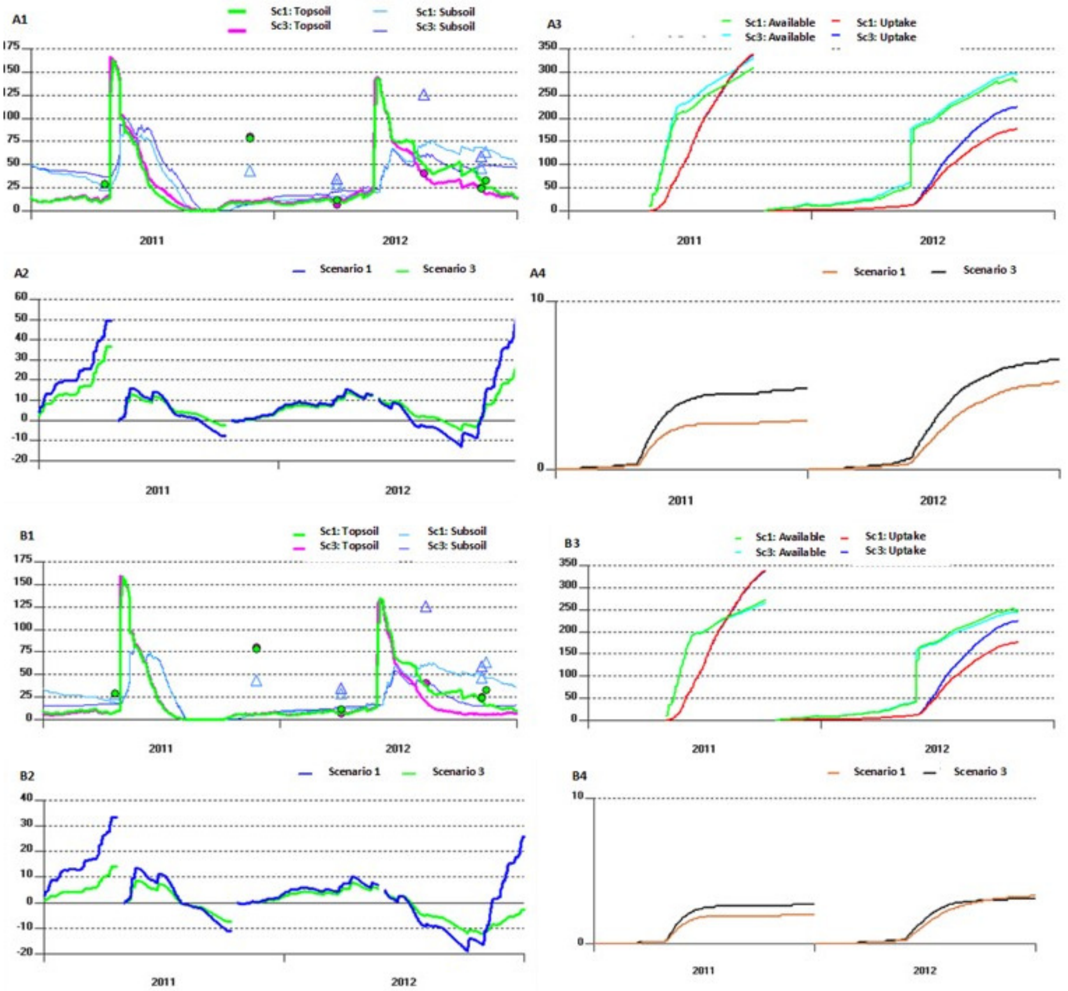

Figure 5.9 Model simulations for Scenario 1 and 3 using the NDICEA software tool over 3 years (A; one repetition of the three-year cycle; see Section 5.2.5) and 30 years (B; ten repetitions of the three-year cycle). 1: evolution of mineral N in topsoil and subsoil (kg ha^{-1}); 2: cumulative leaching and denitrification in subsoil (kg ha^{-1}); 3: cumulative N availability/uptake (kg ha^{-1}); 4: cumulative denitrification in topsoil (kg ha^{-1}).

Table 5.7 Nutrient balances (N, P_2O_5, K_2O; kg ha^{-1} y^{-1}) for Scenarios 1, 2, and 3 simulated with the NDICEA software tool based on the two-year field trial results. Crop type: energy maize. Initial soil characteristics: Table 5.1. N-3: simulation over 3 years (= one repetition of the three-year cycle; see Section 5.2.5); N-30: simulation over 30 years (= ten repetitions of the three-year cycle).

	Scenario 1				**Scenario 2**				**Scenario 3**			
	N-3	**N-30**	**P_2O_5**	**K_2O**	**N-3**	**N-30**	**P_2O_5**	**K_2O**	**N-3**	**N-30**	**P_2O_5**	**K_2O**
Manure application	186	186	76	219	186	186	76	219	186	186	76	219
Nitrogen binding	0	0			0	0			0	0		
Deposition	30	30	3	8	30	30	3	8	30	30	3	8
Total application	216	216	79	227	216	216	79	227	216	216	79	227
Removal with products	228	228	77	301	240	240	76	292	251	251	82	271
Calculated surplus	-12	-12	1	-74	-24	-24	2	-65	-36	-36	-4	-44
Volatilization	15	15			16	16			17	17		
Denitrification	6	3			5	3			6	3		
Leaching	45	24			41	18			31	2		
Organic matter build-up	-50	-20			-66	-21			-82	-20		

The evolution of mineral N in the topsoil and subsoil (Fig. 5.9-1), as well as the cumulative N leaching and denitrification in the subsoil (Fig. 5.9-2 and Fig. 5.9-4), indicate that the amount of N leaching to ground and surface waters decreased significantly as more chemical N was replaced by air scrubber water (Sc 3 < 1). The mineral balance (Table 5.7) shows that the amount of N volatilization simulated over three years was slightly higher for Sc 3 as compared to Sc 1. However, model simulations over 30 years predict that the beneficial effect of reduced N leaching will be more expressed in the long term, while the amount of N volatilization will remain quasi equal. Reasons for these effects are related to the observed differences in plant nutrient uptake, biomass yield, soil nitrate residues, etc. between the different scenarios during the field trial (see above), since these data were used as input to the model. Also, the simulation results of the cumulative N availability/uptake (Fig. 5.9-3) show that in the long term the plant N uptake in Sc 3 will be higher than in Sc 1 (cfr. Fig. 5.8), leading to lower nutrient losses in the environment. Noteworthy, when comparing Sc 7 with Sc 8, these findings could be confirmed (unpublished data).

Furthermore, the two-year field trial results show that for Sc 1-3 and Sc 7-8 the average N uptake by the plant was higher than the available amount through manure application and deposition, resulting in a negative apparent N surplus on the soil balance (Table 5.8). The amount of N extracted from the soil, as well as the apparent N recovery and NUE, increased as more chemical N was substituted by air scrubber water (Sc 3 > 2 > 1; Sc 8 > 7). Consequently, a point of attention when using air scrubber water in agriculture might be the breakdown of soil organic matter (SOM), similar as was found by Minamikawa *et al.* (2005) for the use of chemical ammonium sulfate fertilizer. This can also explain the negative value for SOM build-up obtained with the model simulations (Table 5.7). Indeed, the model results indicated a higher N mineralization from the soil (humus and other intial available SOM) for Sc 3. Nevertheless, when simulating over 30 years, the average SOM breakdown was equal to that of the reference.

Table 5.8 Calculated nitrogen balance (kg ha^{-1}), apparent recovery (%), and nitrogen use efficiency (NUE, %) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Soil layer: 0-30 cm. Average values are marked in bold.

Sc	Year	Available April (kg ha^{-1})	Manure supply (kg ha^{-1})	Deposition (kg ha^{-1})	Total available (kg ha^{-1})	Available November (kg ha^{-1})	Plant uptake (kg ha^{-1})	Apparent surplus (kg ha^{-1})	Actual pollution (kg ha^{-1})	Apparent recovery (%)	NUE (%)
1	2011	29	216	30	275	70	306	-60	-101	111	142
	2012	16	157	30	203	24	140	47	39	69	89
	average	**23**	**186**	**30**	**239**	**47**	**223**	**-6.5**	**-31**	**90**	**116**
2	2011	29	216	30	275	80	300	-54	-105	109	139
	2012	16	157	30	203	27	157	30	-19	77	100
	average	**23**	**186**	**30**	**239**	**53**	**228**	**-12**	**-62**	**93**	**120**
3	2011	29	216	30	275	66	308	-62	-99	112	143
	2012	11	157	30	201	25	195	-8.0	-19	97	124
	average	**20**	**186**	**30**	**238**	**45**	**251**	**-35**	**-59**	**105**	**134**
4	2011	29	217	30	276	100	329	-82	-153	119	152
	2012	11	232[a]	30	273	35	146	116	92	53	63
	average	**20**	**226**	**30**	**275**	**67**	**238**	**17**	**-31**	**86**	**108**
5	2011	29	217	30	276	57	318	-71	-99	115	147
	2012	12	268[a]	30	310	29	155	143	126	50	58
	average	**20**	**243**	**30**	**219**	**43**	**236**	**36**	**14**	**83**	**103**
6	2011	29	217	30	276	71	310	-63	-105	112	143
	2012	11	268[a]	30	309	24	165	103	120	53	62
	average	**20**	**243**	**30**	**222**	**48**	**237**	**20**	**7.5**	**83**	**103**
7	2011	29	225	30	284	71	345	-90	-132	121	153
	2012	12	185	30	227	24	106	79	97	47	57
	average	**21**	**205**	**30**	**208**	**48**	**226**	**-5.5**	**-18**	**84**	**105**
8	2011	29	230	30	289	56	305	-45	-72	106	133
	2012	10	185	30	225	24	173	12	28	77	94
	average	**20**	**210**	**30**	**206**	**40**	**239**	**-17**	**-22**	**92**	**114**

[a] Doses exceeded the maximum allowable fertilization level of 135 kg effective N ha^{-1} in 2012.

As the plant N uptake was higher when more air scrubber water was used, the amount of N provided by the breakdown of harvested crop residues also increased. It is predicted that these residues will deliver a significant amount of direct available N for the plant in the long term. When comparing Sc 7 with Sc 8, these findings could again be confirmed (unpublished data).

5.3.2.2 Phosphorus dynamics

a) Phosphorus use efficiency, plant uptake, and soil availability

The P use efficiency (PUE; Fig. 5.10) was at each sampling moment significantly affected by the treatment.

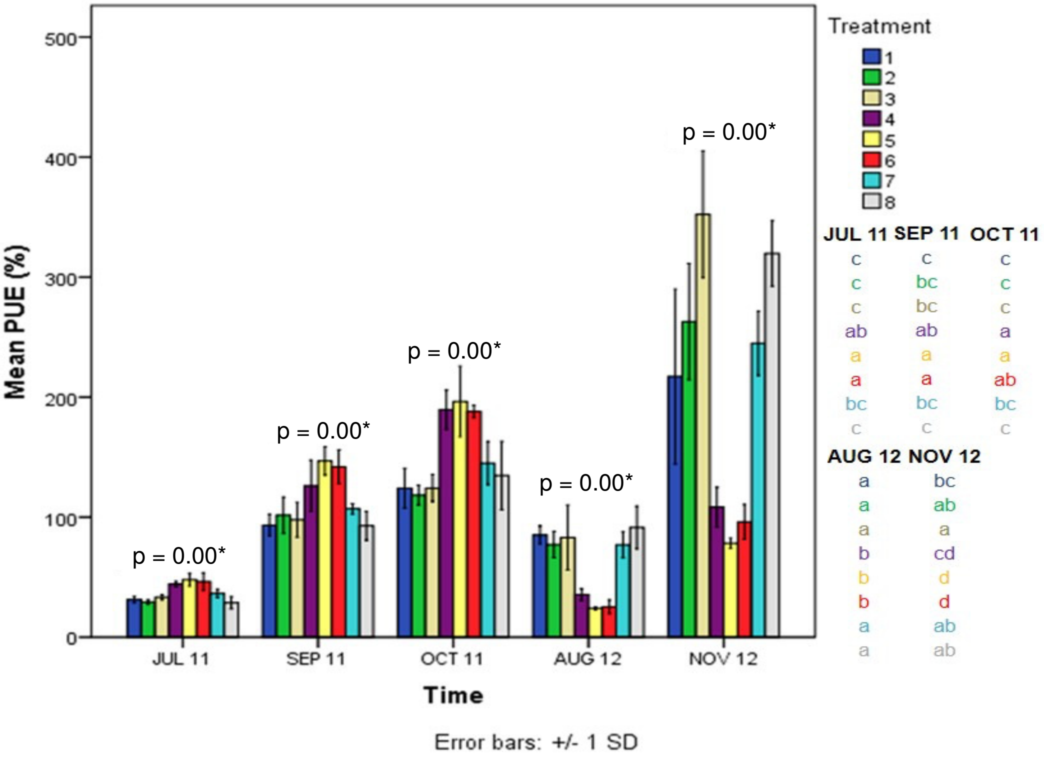

Figure 5.10 Phosphorus use efficiency (PUE, %) as a function of time for the eight different fertilization scenarios (mean, error bars: +/- 1 standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

In 2011, the application of digestate with or without the substitution of chemical fertilizer N by air scrubber water (Group II) resulted in significantly higher PUEs, while the P dosage was the lowest (Table 5.2). However, in 2012, the PUEs were the lowest for this group, while the P dosage was the highest (note: far in excess of the standard due to technical issues). The plant P uptake over time was thus clearly not correlated ($r = 0.091$, $p \approx 0.00$) to the P dosage applied to the field. Therefore, regarding the imminent depletion of P reserves (Neset and Cordell, 2012), the use of products with low (but bio-available) P content seems preferable, at least in P saturated regions. Note that in such regions it is often preferred to apply no P at all, unless for crops with poor, inefficient root systems. Since the ratio of P_2O_5 to effective N is in general lower for digestate derivatives than for animal manure (Table 5.3), as well as the amount of mineralized P over total P, anaerobic (co-)digestion can serve as an interesting step in the treatment of manure. Indeed, sustainable fertilizers could be produced, while renewable energy is provided. Noteworthy in this respect is that both in 2011 and 2012 the PUE was higher for Sc 7-8, in which P-poor LF digestate was applied, as compared to the reference.

In 2012, the plant P uptake was significantly higher when chemical fertilizers were completely substituted by air scrubber wastewater as compared to the reference (Sc 3/6/8 > 1; Table 5.6). The higher P uptake in these scenarios may be attributed to the higher dosage of NH_4-N by the air scrubber water. Indeed, the uptake of NH_4^+ by the roots as well as the nitrification of NH_4^+ into NO_3^- are acidifying processes, which can increase soil P mobilization and uptake in the rhizosphere due to the local pH decrease (Diwani *et al.*, 2007; Timmermans *et al.*, 2012). Hence, the P uptake was also highly correlated to the NUE ($r = 0.93$; $p \approx 0.00$) and the plant N uptake ($r = 0.84$, $p \approx 0.00$). Note that in contrast to the N uptake, the P uptake was less affected by the unfavorable weather conditions in 2012 (see Sections 5.3.1.1 and 5.3.2.1), likely due to the high stocks of available P in the soil. To date, no significant differences were observed in the available (Table 5.9) and total soil P_2O_5 contents between (Appendix 2: Table A2.1) the different treatments. However, these parameters require follow-up in the longer term.

b) Phosphorus balances and apparent recovery

First, it should be remarked that in Sc 5 and Sc 6 the P_2O_5 doses exceeded by far the maximum allowable fertilization level of 80 kg ha^{-1} y^{-1} in 2012 due to technical issues (cfr. N). Therefore, these scenarios are not representative to compare for P_2O_5 balances in 2012. The apparent surplus on the soil balance was for each of the other scenarios negative, indicating that more P_2O was extracted from the soil than was supplied (Table 5.10). With respect to the exhaustive natural P sources and knowing that in many countries some 40 % (15-70 %) of soils test as high and very high in readily available P (EFMA, 2000), this is a very positive and important finding that deserves further study (see Chapter 6).

Moreover, the more chemical N was replaced by air scrubber wastewater (Sc 3 vs. 2 vs. 1, Sc 8 vs. 7), the higher the observed average extraction of P_2O_5 from the soil. This is in line with the higher apparent P recovery and PUE found for these scenarios. Hence, again the synergetic effect between the plant NH_4-N and P uptake is underlined (Diwani *et al.*, 2007; Timmerman *et al.*, 2012). Interestingly, when comparing Sc 1 with Sc 7, it can also be noticed that the use of LF digestate as P-poor fertilizer in addition to animal manure can significantly reduce the amount of P_2O_5 leaching and increase the soil P_2O_5 recovery. Hence, the use of P-poor LF digestate appears again as an interesting alternative.

Table 5.9 Extractable soil nutrient amounts through ammonium lactate/acetic acid (pH 3.75) extraction (P_2O_5, K_2O, Ca, Mg, Na; kg or ton ha^{-1}) in time for the eight different fertilization scenarios (mean ± standard deviation; n = 4). Soil layer: 0-30 cm. p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

Scenario	Apr/11	Jul/11	Oct/11	Apr/12	Aug/12	Nov/12
Extract. P_2O_5 (ton ha^{-1})		**p = 0.78**	**p = 0.71**		**p = 0.84**	**p = 0.31**
1	6.4	5.4 ± 1.3	6.8 ± 0.7	7.5	5.6 ± 1.0	4.1 ± 2.1
2	6.4	5.0 ± 0.4	7.0 ± 0.6	7.5	5.6 ± 0.5	3.9 ± 1.9
3	6.4	5.2 ± 0.2	6.6 ± 0.3	7.5	6.1 ± 0.4	6.0 ± 0.6
4	6.4	5.7 ± 0.8	6.6 ± 1.3	7.5	5.2 ± 0.7	5.5 ± 0.8
5	6.4	5.2 ± 0.4	6.9 ± 1.1	7.5	5.9 ± 0.6	6.4 ± 0.6
6	6.4	5.7 ± 0.2	7.1 ± 0.7	7.5	5.7 ± 0.8	6.1 ± 0.4
7	6.4	5.1 ± 0.2	7.1 ± 0.4	7.5	5.7 ± 0.6	6.1 ± 0.2
8	6.4	5.2 ± 0.5	6.0 ± 0.7	7.5	5.4 ± 0.4	5.6 ± 0.2
Extract. K_2O (kg ha^{-1})		**p = 0.18**	**p = 0.35**		**p = 0.13**	**p = 0.61**
1	496	678 ± 128	332 ± 98	304	451 ± 74	597 ± 76
2	496	756 ± 181	326 ± 201	304	416 ± 44	626 ± 87
3	496	704 ± 18	286 ± 55	304	421 ± 19	690 ± 94
4	496	808 ± 185	354 ± 120	304	464 ± 64	579 ± 162
5	496	854 ± 67	263 ± 67	304	377 ± 56	661 ± 81
6	496	978 ± 226	488 ± 303	304	450 ± 54	706 ± 75
7	496	731 ± 151	469 ± 112	304	407 ± 53	677 ± 9
8	496	821 ± 176	395 ± 65	304	542 ± 80	660 ± 15
Extract. Ca (ton ha^{-1})		**p = 0.22**	**p = 0.40**		**p = 0.76**	**p = 0.74**
1	19[a]	11 ± 2	5.4 ± 0.9	7.3	7.7 ± 1.6	8.1 ± 1.7
2	19[a]	11 ± 2	5.7 ± 0.4	7.3	8.0 ± 1.2	8.4 ± 1.3
3	19[a]	10 ± 3	5.3 ± 0.4	7.3	8.7 ± 0.4	9.2 ± 0.5
4	19[a]	10 ± 2	5.2 ± 0.8	7.3	7.4 ± 2.1	7.8 ± 2.1
5	19[a]	12 ± 1	5.5 ± 1.0	7.3	8.9 ± 1.2	9.4 ± 1.2
6	19[a]	11 ± 1	5.4 ± 0.3	7.3	8.3 ± 0.9	8.9 ± 1.1
7	19[a]	10 ± 1	5.5 ± 0.5	7.3	8.2 ± 0.2	8.7 ± 0.1
8	19[a]	10 ± 1	5.1 ± 0.3	7.3	7.7 ± 0.5	8.2 ± 0.5
Extract. Mg (kg ha^{-1})		**p = 0.45**	**p = 0.67**		**p = 0.15**	**p = 0.45**
1	732	908 ± 234	422 ± 143	541	472 ± 60	393 ± 62
2	732	889 ± 154	410 ± 39	541	493 ± 62	363 ± 29
3	732	859 ± 72	397 ± 45	541	539 ± 66	371 ± 16
4	732	826 ± 173	362 ± 90	541	459 ± 135	404 ± 48
5	732	953 ± 128	373 ± 92	541	522 ± 75	334 ± 50
6	732	994 ± 36	400 ± 41	541	550 ± 49	398 ± 50
7	732	995 ± 137	440 ± 28	541	532 ± 5	357 ± 48
8	732	924 ± 114	376 ± 45	541	520 ± 19	474 ± 65
Extract. Na (kg ha^{-1})		**p = 0.010***	**p = 0.070**		**p = 0.012***	**p = 0.015***
1	68	173 ± 10b	74 ± 16	<68	120 ± 28b	126 ± 29b
2	68	164 ± 66ab	119 ± 53	<68	123 ± 1b	130 ± 5ab
3	68	165 ± 49ab	84 ± 10	<68	141 ± 9ab	149 ± 7ab
4	68	152 ± 4ab	104 ± 19	<68	169 ± 40ab	177 ± 40a
5	68	329 ± 88a	102 ± 22	<68	204 ± 45a	215 ± 51a
6	68	251 ± 49ab	112 ± 29	<68	156 ± 14ab	167 ± 20a
7	68	267 ± 106ab	128 ± 27	<68	147 ± 13ab	155 ± 13a
8	68	242 ± 40ab	122 ± 30	<68	178 ± 13ab	188 ± 15a

[a] Note: extremely high value likely related to a measurement error.

Table 5.10 Phosphorus balance (kg P_2O_5 ha^{-1}), apparent recovery (%), and phosphorus use efficiency (PUE, %) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Soil layer: 0-30 cm. Average values are marked in bold. Available amounts were determined using ammonium lactate/acetic acid (pH 3.75) as an extraction agent.

Sc	**Year**	**Available April** (ton ha^{-1})	**Manure supply** (kg ha^{-1})	**Deposition** (kg ha^{-1})	**Total available** (ton ha^{-1})	**Available November** (ton ha^{-1})	**Plant uptake** (kg ha^{-1})	**Apparent surplus** (kg ha^{-1})	**Actual pollution** (ton ha^{-1})	**Apparent recovery** %	**PUE** %
1	2011	6.4	108[a]	3	6.5	6.8	134	-23	-0.43	2.1	124
	2012	7.5	44	3	7.6	4.1	96	-49	3.3[b]	1.3	218
	average	**6.9**	**76**	**3**	**7.0**	**5.5**	**115**	**-36**	**1.5**	**1.7**	**170**
2	2011	6.4	108[a]	3	6.5	7.3	128	-17	-0.93	2	119
	2012	7.5	44	3	7.6	3.9	116	-69	3.5[b]	1.5	264
	average	**6.9**	**76**	**3**	**7.0**	**5.6**	**122**	**-43**	**1.3**	**1.8**	**192**
3	2011	6.4	108[a]	3	6.5	6.6	135	-24	-0.23	2.1	125
	2012	7.5	44	3	7.6	6.0	155	-108	1.4	2.1	352
	average	**6.9**	**76**	**3**	**7.0**	**6.3**	**145**	**-66**	**0.59**	**2.1**	**239**
4	2011	6.4	74	3	6.5	6.6	141	-64	-0.27	2.2	191
	2012	7.5	98[a]	3	7.6	5.5	106	-5.2	2.0	1.4	108
	average	**6.9**	**86[a]**	**3**	**7.0**	**6.1**	**123**	**-34**	**0.85**	**1.8**	**150**
5	2011	6.4	74	3	6.5	6.9	146	-69	-0.58	2.3	197
	2012	7.5	159[a]	3	7.7	6.4	124	38	1.1	1.6	78
	average	**6.9**	**117[a]**	**3**	**7.1**	**6.7**	**135**	**-15**	**0.27**	**1.9**	**138**
6	2011	6.4	74	3	6.5	7.1	139	-62	-0.77	2.2	188
	2012	7.5	159[a]	3	7.7	6.1	153	9.3	1.4	2	96
	average	**6.9**	**117[a]**	**3**	**7.1**	**6.6**	**146**	**-27**	**0.34**	**2.1**	**142**
7	2011	6.4	105[a]	3	6.5	7.1	152	-44	-0.75	2.3	145
	2012	7.5	48	3	7.6	6.1	118	-67	1.3	1.6	246
	average	**6.9**	**76**	**3**	**7.0**	**6.6**	**135**	**-55**	**0.30**	**2**	**196**
8	2011	6.4	105[a]	3	6.5	6.0	141	-33	0.36	2.2	134
	2012	7.5	48	3	7.6	5.6	153	-102	1.8	2	319
	average	**6.9**	**76**	**3**	**7.0**	**5.8**	**147**	**-68**	**1.1**	**2.1**	**227**

[a] Doses exceeded the maximum allowable fertilization level of 80 kg P_2O_5 ha^{-1}.

[b] Note: very large standard deviation on the result (see Table 5.9).

5.3.2.3 Potassium dynamics

a) Potassium use efficiency, plant uptake, and soil availability

A first interesting observation was that the required amount of chemical K_2O was much lower and sometimes nil in Sc 4 to 8 (Table 5.2), since the ratio of K_2O to effective N was higher for digestate and its LF as compared to animal manure (Table 5.3). Nevertheless, when using digestates or LF digestates (Sc 4-8), the KUE (Fig. 5.11) was significantly higher than in conventional scenarios using animal manure additionally supplied with chemical K_2O (Sc 1-3), both in 2011 and 2012. This indicates that the availability of K_2O in animal manure can be increased by anaerobic (co-)digestion, thereby creating valuable substitutes for chemical K_2O fertilizers. Since K_2O is, similar as P_2O_5, a scarce resource (Born *et al.*, 2005), this may result in significant ecological and economic benefits for the farmer (Chapter 4; Vaneeckhaute *et al.*, 2013b).

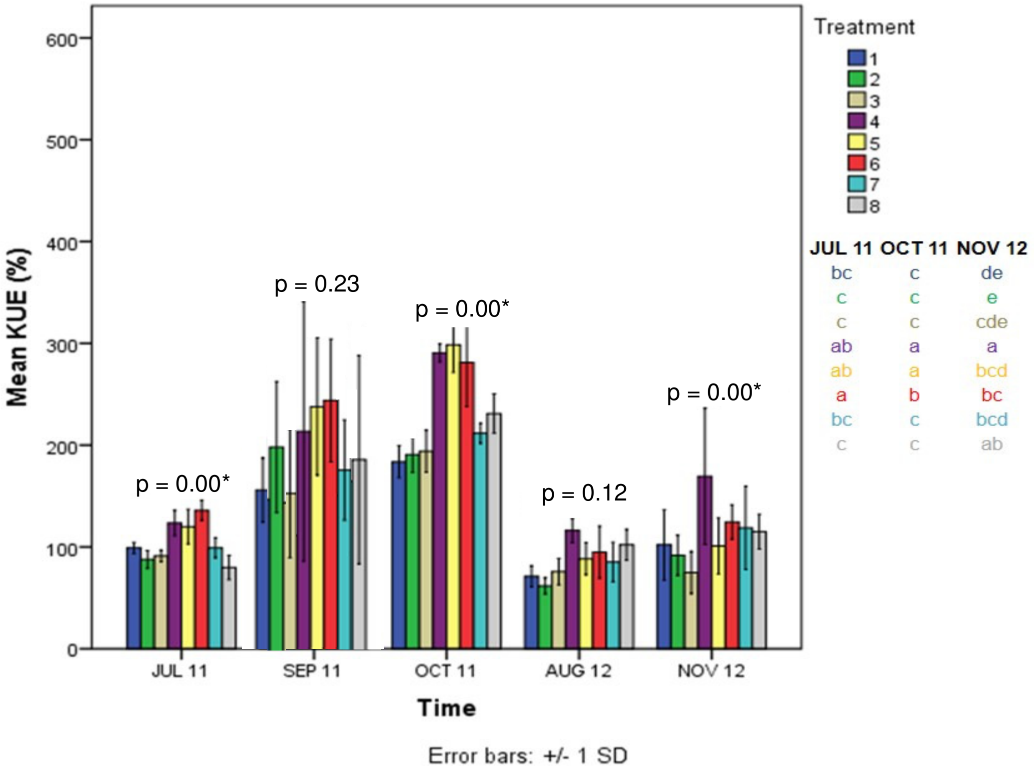

Figure 5.11 Potassium use efficiency (KUE, %) as a function of time for the eight different fertilization scenarios (mean, error bars: +/- 1 standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

Furthermore, the plant K_2O uptake was significantly higher for Sc 5 compared to Sc 3 and for Sc 3 compared to Sc 2 at the harvest in 2011 (Table 5.6). In 2012, a significant effect was found in August, when Sc 6 and Sc 8, in which chemical N was completely replaced by air scrubber water, showed a higher plant K_2O uptake than Sc 2. To date, no significant differences were observed in the available soil K_2O content during the field trial (Table 5.9), nor in the total soil

K_2O content (Appendix 2: Table A2.1), but these are parameters that require long-term follow-up.

b) Potassium balances and apparent recovery

Nutrient balances show that the K_2O uptake by the plant (average over time) was for all scenarios higher than the available amount through manure application and deposition, resulting in a K_2O deficit on the soil balance (Table 5.7) and a negative actual pollution index (Table 5.11). The latter indicates that somehow more K_2O has become available for the plants over time, e.g. via exchange from the clay-humus complex in the soil. The amount of K_2O extracted from the soil and the apparent recovery were much higher when digestate and/or LF digestates (Sc 4-8) were used as compared to animal manure additionally supplied with high amounts of chemical K_2O (Sc 1-3), similar as was observed for the KUE. On the one hand, this natural mining effect of K_2O is interesting regarding its potential depletion (Born *et al.*, 2005). However, if the soil balance is negative for a long period of time, soil fertility will decrease and yields will be reduced. At that time, additional K_2O fertilization will be required. The use of LF digestate, which contains high amounts of soluble K_2O, but low amounts of P_2O_5, seems very useful for this purpose. Furthermore, a valuable and easily transportable N/K fertilizer might exist in concentrates resulting from membrane filtration of LF digestate (Chapters 3-4; Vaneeckhaute *et al.*, 2012, 2013b). Hence, the sustainable production of these products deserves further research, as does the agronomic impact of their use at field-scale.

5.3.2.4 Dynamics of secondary macronutrients

Next to the three principal macronutrients (N, P_2O_5, K_2O), important secondary macronutrients for plants are S, Ca, and Mg. According to United Nation statistics (UN, 2013), deficiency of S became a problem for more than 75 countries, and supply of this nutrient could be efficient by using new (recovered) fertilizers containing available sulfate (Fowler *et al.*, 2007; Till, 2010). In this perspective, an interesting observation was that the average plant S uptake in 2012 significantly increased as more air scrubber water was used (Table 5.6), and that the ratio of mineral S to effective N generally increased through anaerobic (co-)digestion (Table 5.3). Besides, an S deficit may occur when no air scrubber water or no digestates (and no chemical patentkali) is used (Sc 1 and 7; Table 5.12). The latter may cause significant S shortages in the long term, which might result in a yield reduction, depending on the S demand of the agricultural crop.

It should be noted that the common practice of using patentkali as chemical potassium fertilizer in addition to animal manure (Sc 1-3) resulted in significantly higher S surpluses on the soil balance as compared to the use of digestate derivatives (Sc 4-8; Table 5.12). This is due to the higher chemical potassium requirements in these scenarios. Based on the balances, it can be stated that the use of recovered ammonium sulfate fertilizer in addition to digestate derivatives as organo-mineral fertilizer does not have a detiorating impact on the S balance as compared to the common practice using chemical fertilizers (N, K) and animal manure.

Table 5.11 Potassium balance (kg K_2O ha^{-1}), apparent recovery (%), and potassium use efficiency (KUE, %) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Soil layer: 0-30 cm. Average values are marked in bold. Available amounts were determined using ammonium lactate/acetic acid (pH 3.75) as an extraction agent.

Sc	**Year**	**Available April** (kg ha^{-1})	**Manure supply** (kg ha^{-1})	**Deposition** (kg ha^{-1})	**Total available** (kg ha^{-1})	**Available November** (kg ha^{-1})	**Plant uptake** (kg ha^{-1})	**Apparent surplus** (kg ha^{-1})	**Actual pollution** (kg ha^{-1})	**Apparent recovery** (%)	**KUE** (%)
1	2011	496	172	8	676	332	333	-153	11	49	194
	2012	304	266	8	578	597	268	5.7	-288	46	101
	average	**400**	**219**	**8**	**627**	**465**	**301**	**-73**	**-139**	**48**	**148**
2	2011	496	172	8	676	326	346	-166	4.0	51	201
	2012	304	266	8	578	626	243	31	-292	42	91
	average	**400**	**219**	**8**	**627**	**476**	**294**	**-68**	**-144**	**46**	**146**
3	2011	496	172	8	676	286	352	-172	38	52	205
	2012	304	266	8	578	690	198	76	-310	34	74
	average	**400**	**219**	**8**	**627**	**488**	**275**	**-48**	**-136**	**43**	**140**
4	2011	496	145	8	649	354	420	-267	-125	65	290
	2012	304	168	8	480	579	279	-103	-379	58	166
	average	**400**	**156**	**8**	**564**	**467**	**350**	**-186**	**-252**	**62**	**228**
5	2011	496	145	8	649	263	431	-278	-45	66	297
	2012	304	222	8	534	661	222	8.2	-349	42	100
	average	**400**	**183**	**8**	**591**	**462**	**327**	**-135**	**-197**	**54**	**199**
6	2011	496	145	8	649	488	406	-253	-246	63	280
	2012	304	222	8	534	706	277	-47	-450	52	125
	average	**400**	**183**	**8**	**591**	**597**	**342**	**-151**	**-348**	**57**	**203**
7	2011	496	171	8	675	469	366	-187	-160	54	214
	2012	304	214	8	526	677	255	-33	-406	48	119
	average	**400**	**193**	**8**	**601**	**573**	**310**	**-110**	**-283**	**51**	**167**
8	2011	496	171	8	675	395	383	-204	-103	57	224
	2012	304	214	8	526	660	248	-26	-382	47	116
	average	**400**	**190**	**8**	**601**	**527**	**307**	**-115**	**-243**	**51**	**170**

Table 5.12 Sulfur balance (kg S ha^{-1}), apparent recovery (%), and sulfur use efficiency (SUE, %) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Soil layer: 0-30 cm. Average values are marked in bold. N/A = not available. Available amounts were determined using ammonium lactate/acetic acid (pH 3.75) as an extraction agent.

Sc	**Year**	**Available April** (kg ha^{-1})	**Manure supply**[a] (kg ha^{-1})	**Total available**[a] (kg ha^{-1})	**Available November** (kg ha^{-1})	**Plant uptake** (kg ha^{-1})	**Apparent surplus**[a] (kg ha^{-1})	**Actual pollution**[a] (kg ha^{-1})	**Apparent recovery**[a] (%)	**SUE**[a] (%)
1	2011	N/A	16/60	N/A	129	23	-7.2/37	N/A	N/A	145/38
	2012	75	8.0/129	83/204	94	14	-5.8/115	-25/96	17/6.9	173/11
	average	**75**	**12/95**	**83/204**	**111**	**18**	**-6.5/76**	**-25/96**	**17/6.9**	**159/25**
2	2011	N/A	57/101	N/A	128	23	34/78	N/A	N/A	40/23
	2012	75	42/163	117/238	90	15	27/148	12/133	13/6.3	37/9.2
	average	**75**	**50/132**	**117/238**	**109**	**19**	**30/113**	**12/133**	**13/6.3**	**39/16**
3	2011	N/A	93/137	N/A	126	24	69/113	N/A	N/A	26/18
	2012	75	77/198	152/273	123	17	60/181	13/133	11/6.2	22/8.6
	average	**75**	**85/168**	**152/273**	**124**	**20**	**65/147**	**13/133**	**11/6.2**	**24/13**
4	2011	N/A	15/31	N/A	124	25	-11/5.6	N/A	N/A	166/81
	2012	75	35	110	109	13	22	-12	12	37
	average	**75**	**25/33**	**110**	**116**	**19**	**6.0/14**	**-12**	**12**	**101/59**
5	2011	N/A	40/57	N/A	135	26	14/31	N/A	N/A	65/46
	2012	75	54/80	129/155	118	14	40/66	-2.9/23	11/9.0	25/18
	average	**75**	**47/69**	**129/155**	**126**	**20**	**27/49**	**-2.9/23**	**11/9.0**	**45/32**
6	2011	N/A	76/92	N/A	134	24	52/68	N/A	N/A	32/26
	2012	75	92/118	167/193	120	16	76/102	31/57	10/8.3	17/14
	average	**75**	**84/105**	**167/193**	**127**	**20**	**64/85**	**31/57**	**10/8.3**	**25/20**
7	2011	N/A	16/34	N/A	133	26	-10/8.3	N/A	N/A	166/76
	2012	75	11/80	86/155	117	12	-0.77/68	-43/26	14/7.7	107/15
	average	**75**	**13/57**	**86/155**	**125**	**19**	**-5.6/38**	**-43/26**	**14/7.7**	**137/46**
8	2011	N/A	16	N/A	129	26	-10	N/A	N/A	161
	2012	75	49/118	124/193	113	15	34/103	-3.5/65	12/7.8	30/13
	average	**75**	**33/67**	**124/193**	**121**	**20**	**12/57**	**-3.5/65**	**12/7.8**	**95/87**

[a] First number: fertilizer application not taking in account S addition via patentkali (17 % S by weight); second number: application taking in account S addition via patentkali (if applicable).

Furthermore, a remarkable observation was that free Ca and Mg disappeared in the environment in all scenarios (Tables 5.13-5.14: average positive actual pollution index), although Ca and Mg are not considered to be leachable nutrients. Since the CaUE and especially the MgUE were positively correlated with the PUE (2011: $r_{Mg/P} = 0.99$ ($p = 0.00$), $r_{Ca/P} = 0.65$ ($p = 0.079$); 2012: $r_{Mg/P} = 0.89$ ($p = 0.00$), $r_{Ca/P} = 0.61$ ($p = 0.11$)), it is likely that these free cations precipitated with P thereby making this element more slowly available. As digestate generally contains more Ca and Mg than animal manure (Table 5.3), the use of this product seems valuable to reduce P leaching by providing a source of slow-release P, meanwhile maintaining a neutral soil pH and increasing the activity of soil bacteria. Nevertheless, also retrodegradation into immobilized and fixed soil P may occur (Sposito, 2008). Accurate greenhouse experiments are recommended to further study the P release pattern of digestate derivatives in time in comparison with traditional P fertilizers and animal manure (see Chapter 6).

Finally, no effect of the treatment on the total and available soil Ca, Mg, and S contents were observed over time (Table 5.9 and Appendix 2: Table A2.1), but these are again parameters that require long-term follow-up.

5.3.4 Impact of fertilization strategy on general soil quality

Soil organic carbon (SOC) is the most important component in maintaining soil quality because of its role in improving physical, chemical, and biological properties of the soil. Changes in agricultural practices often influence both quantity and quality of SOC and its turnover rates. As such, stagnation or decline in yields has been observed in intensive cropping systems in the last few decades, attributed to the poor quality and quantity of SOC and its impact on nutrient supply (Bhandari *et al.*, 2002). Interestingly, during anaerobic digestion, easily degradable organic matter is converted into CH_4 and CO_2, while complex organic matter such as lignin remains in the digestate, thereby increasing its amount of effective OC (EOC). This is the percentage of OC that remains in the soil after one year and thus contributes to the humus build-up. As such, the digestate contains important soil improving qualities (WPA, 2007).

The level of SOC at a point of time reflects the long-term balance between addition and losses of SOC, particularly C and N, under continuous cultivation (Manna *et al.*, 2005). Overall, significantly more OC was applied to the field in the scenarios in which digestate or its LF was used to (partially) replace animal manure: 217±0 (Sc 1-3) vs. 1,294±240 (Sc 4-6) vs. 329±0 (Sc 7-8) kg OC ha^{-1} in 2012, and 800±0 (Sc 1-3) vs. 835±15 (Sc 4-8) kg OC ha^{-1} in 2011.

As expected, to date, the SOC was not significantly affected by the treatments. Small changes in total SOC between treatments are difficult to detect because of large background levels and natural variability (Carter, 2002). Hence, this parameter requires follow-up in the longer term in order to sustain soil quality and long-term productivity of agricultural systems. Model simulations using the ‘Koolstofsimulator’ (LNE, 2006) over 30 years predict that the SOC content will be reduced from 1.95 to 1.62 % for Sc 1, while it would remain approximately stable when digestate or its LF is used (Sc 4-8).

Table 5.13 Calcium balance (ton ha^{-1}, kg ha^{-1}), apparent recovery (%), and calcium use efficiency (CaUE, %) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Soil layer: 0-30 cm. Average values are marked in bold. Available amounts were determined using ammonium lactate/acetic acid (pH 3.75) as an extraction agent.

Sc	Year	Available April (ton ha^{-1})	Manure supply (kg ha^{-1})	Total available (ton ha^{-1})	Available November (ton ha^{-1})	Plant uptake (kg ha^{-1})	Apparent surplus (kg ha^{-1})	Actual pollution (ton ha^{-1})	Apparent recovery (%)	CaUE (%)
1	2011	19[a]	59	19	5.4	48	11	14	0.25	81
	2012	7.3	35	7.3	8.1	21	14	-0.8	0.29	59
	average	**13**	**47**	**13**	**6.7**	**34**	**13**	**6.6**	**0.27**	**70**
2	2011	19[a]	59	19	5.7	48	11	13	0.25	80
	2012	7.3	35	7.3	8.4	25	10	-1.1	0.34	70
	average	**13**	**47**	**13**	**7.0**	**36**	**11**	**6.0**	**0.30**	**75**
3	2011	19[a]	59	19	5.3	47	12	14	0.25	79
	2012	7.3	35	7.3	9.2	25	10	-1.9	0.34	73
	average	**13**	**47**	**13**	**7.3**	**36**	**11**	**6.1**	**0.30**	**76**
4	2011	19[a]	50	19	5.2	48	1.6	14	0.25	97
	2012	7.3	120	7.4	7.8	31	89	-0.4	0.42	25
	average	**13**	**85**	**13**	**6.5**	**39**	**46**	**6.8**	**0.34**	**61**
5	2011	19[a]	50	19	5.5	53	-2.5	14	0.28	105
	2012	7.3	209	7.5	9.4	27	182	-1.9	0.36	13
	average	**13**	**130**	**13**	**7.4**	**40**	**90**	**6.1**	**0.32**	**59**
6	2011	19[a]	50	19	5.4	40	10	14	0.21	81
	2012	7.3	209	7.5	8.9	16	193	-1.4	0.21	7.8
	average	**13**	**130**	**13**	**7.2**	**28**	**101**	**6.3**	**0.21**	**44**
7	2011	19[a]	54	19	5.5	47	6.9	14	0.25	87
	2012	7.3	36	7.3	8.7	23	13	-1.4	0.32	65
	average	**13**	**45**	**13**	**7.1**	**35**	**10**	**6.3**	**0.29**	**76**
8	2011	19[a]	51	19	5.1	48	3.0	14	0.25	94
	2012	7.3	36	7.3	8.2	23	13	-0.9	0.32	64
	average	**13**	**44**	**13**	**6.6**	**36**	**8**	**6.6**	**0.29**	**79**

[a] Note: extremely high value likely related to a measurement error.

Table 5.14 Magnesium balance (kg ha^{-1}), apparent recovery (%), and magnesium use efficiency (MgUE, %) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Soil layer: 0-30 cm. Average values are marked in bold. Available amounts were determined using ammonium lactate/acetic acid (pH 3.75) as an extraction agent.

Sc	**Year**	**Available April** (kg ha^{-1})	**Manure supply**[a] (kg ha^{-1})	**Total available**[a] (kg ha^{-1})	**Available November** (kg ha^{-1})	**Plant uptake** (kg ha^{-1})	**Apparent surplus**[a] (kg ha^{-1})	**Actual pollution**[a] (kg ha^{-1})	**Apparent recovery**[a] (%)	**MgUE**[a] (%)
1	2011	732	27/43	759/775	422	36	-9.6/6.8	301/317	4.8/4.6	136/84
	2012	541	20/63	561/604	393	17	3.0/46	151/194	3.0/2.8	85/27
	average	**637**	**23/53**	**660/690**	**407**	**27**	**-3.3/26**	**226/256**	**3.9/3.7**	**110/56**
2	2011	732	27/43	759/775	410	36	-9.7/6.8	313/329	4.8/4.6	136/84
	2012	541	20/63	561/604	363	14	6.0/49	184/227	2.5/2.3	70/22
	average	**637**	**23/53**	**660/690**	**386**	**25**	**-1.9/28**	**249/278**	**3.7/3.5**	**103/53**
3	2011	732	27/43	759/775	397	36	-9.5/6.8	325/342	4.8/4.6	135/84
	2012	541	20/63	561/604	371	16	3.7/47	174/217	2.9/2.6	82/25
	average	**637**	**23/53**	**660/690**	**384**	**26**	**-2.9/27**	**250/280**	**3.8/3.6**	**108/55**
4	2011	732	13/19	745/751	362	38	-25/-19	345/350	5.0/5.1	295/200
	2012	541	36	577	404	17	19	156	3.0	48
	average	**637**	**24/28**	**661/664**	**383**	**27**	**-3.0/0.0**	**251/253**	**4.0/4.1**	**172/124**
5	2011	732	13/19	745/751	373	37	-24/-18	335/341	5.0/4.9	291/195
	2012	541	65/74	606/615	334	15	50/59	258/266	2.5/2.4	23/20
	average	**637**	**39/47**	**676/683**	**353**	**26**	**13/21**	**296/304**	**3.7/3.7**	**157/108**
6	2011	732	13/19	745/751	400	34	-21/-15	311/317	4.6/4.5	269/179
	2012	541	65/74	606/615	398	17	48/57	191/200	2.7/2.8	26/23
	average	**637**	**39/47**	**676/683**	**399**	**25**	**13/21**	**251/259**	**3.7/3.7**	**147/101**
7	2011	732	24/31	756/763	440	41	-17/-10	274/281	5.4/5.4	173/132
	2012	541	19/43	560/584	357	14	4.7/29	189/213	2.5/2.4	75/33
	average	**637**	**21/37**	**658/674**	**399**	**28**	**-6.3/10**	**232/247**	**4.0/3.9**	**124/83**
8	2011	732	22	754	376	38	-16	340	5.1	173
	2012	541	19/43	560/584	474	15	3.6/28	71/95	2.7/2.6	81/35
	average	**637**	**21/33**	**657/669**	**425**	**27**	**-6.3/6.0**	**206/218**	**3.9/2.9**	**127/104**

[a] First number: fertilizer application not taking in account Mg addition via patentkali (10 % MgO by weight); second number: application taking in account Mg addition via patentkali (if applicable).

The data obtained from this field trial have also been used by the Swedish University of Agricultural Sciences (Uppsula, Sweden) to study more in depth the effect of using bio-based residues as soil amendments on the SOC content under various cropping scenarios. The results were again most beneficial for Sc 4-6, in which digestate (mixtures) were used instead of animal manure (Appendix 3; Vaneeckhaute *et al.*, in preparation). However, a thorough study comparing and diversifying humification coefficients of various bio-based fertilizers is required for more precise quantification of predicted SOC effects.

Furthermore, in the two years of the field trial, no significant effect of the fertilization strategy on the soil pH(H_2O) (mean ± standard deviation: 6.2±0.3) and pH(KCl) (mean ± standard deviation: 5.2±0.6) was observed (Fig. 5.12). In Aug 2012, a sharp decrease in pH(KCl) values was noticed for all scenarios, while the pH(H_2O) values only slightly decreased. This effect is likely caused by a measurement error, e.g. the use of a slightly more acidic KCl solution at that sampling moment. Still, the results can be used for comparison of soil pH(KCl) values between the different treatments.

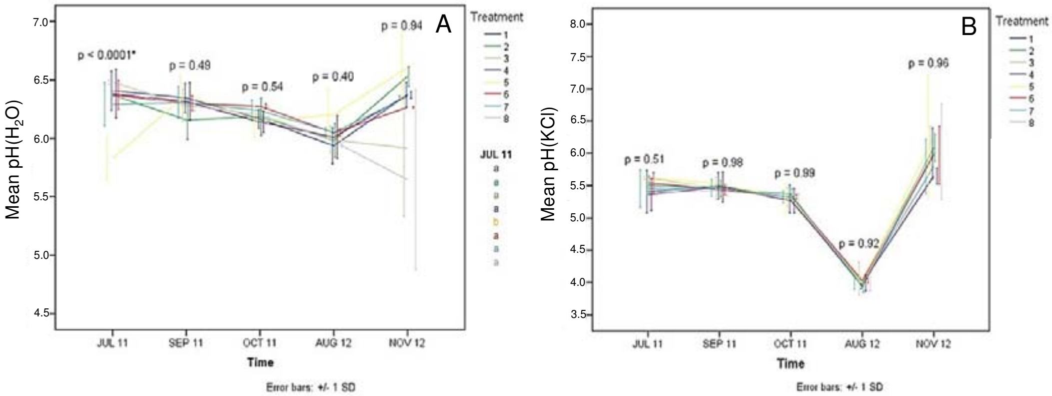

Figure 5.12 pH(H_2O) (A) and pH(KCl) (B) as a function of time for the eight different fertilization scenarios (mean, error bars: +/- 1 standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons.
* = significant difference at the 5 % level.

In Aug 2012, after the second fertilization, the EC was significantly higher as more air scrubber water was used, but this effect disappeared again later in the season (mean ± standard deviation: 107±26 µS cm^{-1}). The total amount of soil Na, which also gives an indication of salt accumulation, was significantly higher for Sc 5 compared to Sc 2 and Sc 3 in July 2011, but thereafter no more significant differences were observed (Appendix 2: Table A2.1). Another issue would be an excess of Na over divalent cations (Ca, Mg), i.e. a high sodium adsorption ratio (SAR), leading to a poor soil structure. A significant effect of the fertilization strategy on the soil SAR was observed in 2012 ($p_{aug} = 0.032$; $p_{nov} = 0.013$), but no statistically significant differences could be detected using post-hoc pair-wise comparison tests. Yet, the SAR was in each case well below SAR 6 (maximum SAR over time: ± 1.75), which is the internationally accepted level, above which soil permeability and structural stability may be affected (Hamaiedeh and Bino, 2010). A soil is referred to as sodic, only when it reaches an SAR of 13 (Hillel, 2008).

Finally, because digestate is the waste product resulting from the co-digestion of animal manure, energy crops, organic biological waste from the food industry, and/or municipal sludge, it could also contain an important amount of micronutrients and heavy metals. Moreover, raw animal manure can contain significant amounts of Cu and Zn (Chapter 4; Dourmad and Jonderville, 2011). On the one hand, Cu, Zn, B, Co, Fe, Mn, Mo, and Ni are all essential trace elements for plants, but on the other hand, there also exist soil environmental quality standards for Cu, Zn, and Ni, as well as for As, Cd, Cr, Hg, and Pb (FSD, 2007). In all scenarios, including the reference, the Flemish soil environmental quality standard for Cu accumulation (17 mg kg^{-1} dry soil; FSD, 2007) was exceeded (mean ± standard deviation: 33±2 mg kg^{-1}; Appendix 2: Table A2.2), but this is likely the legacy of historical manure excesses on the soil balance (Van Meirvenne *et al.*, 2008). No other heavy metal accumulation has been observed thus far. Note that all products applied to soil (Table 5.3) also respected the legal composition and use requirements in terms of heavy metals for reuse as fertilizer and/or soil conditioner in agriculture, as described in Flemish legislation (Vlarea, 1989). Moreover, the harvested plant material met the Vlarea (1989) standards (Appendix 2: Table A2.3). Hence, in terms of heavy metals the energy maize was suitable as input stream for anaerobic (co-)digestion.

5.3.5 Economic and ecological evaluation

The economic benefits for the crop farmer are presented in Figure 5.13A. Figure 5.13B presents the situation when not taking in account potential revenues from (excessive) animal manure, digestate, and LF digestate acceptance (see Chapter 4). The energy use and GHG emissions for the eight different scenarios are presented in Figure 5.14A and 5.14B, respectively.

For all reuse scenarios, the calculated economic benefits were significantly higher compared to the reference (Sc 1), whereas the energy use and the resulting GHG emissions were significantly lower (cfr. Chapter 4). Hence, the application of bio-based fertilizers in agriculture can result in significant economic benefits for the crop farmer, as well as ecological benefits through energy use and associated GHG emission reductions (Chapter 4; Vaneeckhaute *et al.*, 2012). In the present study, the complete substitution of chemical fertilizer N by air scrubber water (Sc 3) almost doubled the economic benefits, while the energy use and GHG emissions were 2.5 times reduced. When meanwhile substituting animal manure by the digestate/LF mixture (Sc 4-6), the observed benefits were even higher, because in these scenarios less chemical N was required due to the higher effective N/P-ratio of the mixture. Also the need for chemical K_2O was less. Both the economic benefits and the reduction in carbon footprint and energy use were the highest for Sc 8, respectively 3.5 and 4.4 times higher than the reference, as both chemical N and K_2O were completely eliminated in this treatment.

When no revenues for the crop farmer were considered for accepting animal manure, digestate, and LF digestate (and hence no cost for disposal of these products by the livestock farmer or anaerobic digestion plant; Chapter 4), the lowest cost scenario was Sc 3, whereas the costs for Sc 4 and 7 were higher than the reference. Also the use of LF digestate (Sc 8) became less

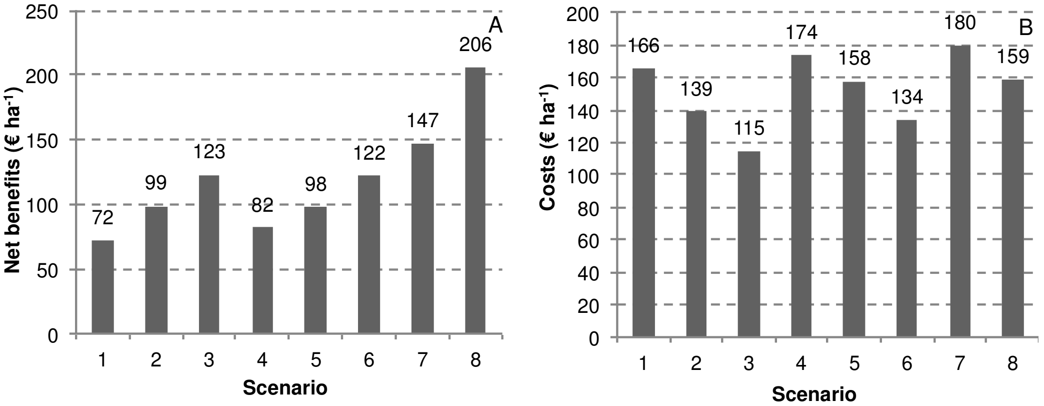

Figure 5.13 Net economic benefits (€ ha^{-1}; A) and costs (€ ha^{-1}; B) for the crop farmer for the eight different fertilization scenarios. Costs: situation where no revenues are obtained for (excessive) animal manure, digestate, and LF digestate acceptance. € 1 ≈ 1.415 CAD (November 2014).

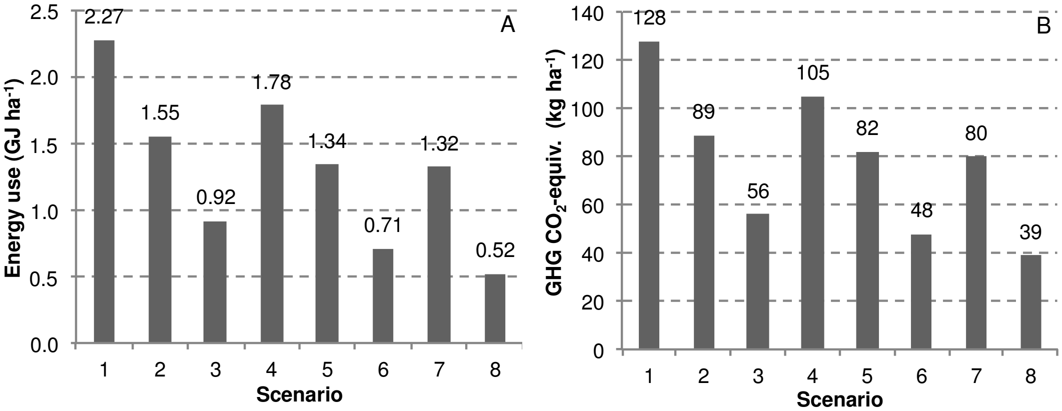

Figure 5.14 Energy use (GJ ha^{-1}; A) and associated greenhouse gas (GHG) emission expressed as CO_2-equivalents (kg ha^{-1}; B) for the eight different fertilization scenarios.

interesting (though still more beneficial than the reference) due to the higher transportation costs related to the lower N concentration of this product. In any case, the beneficial effect of substituting chemical N by air scrubber wastewater is clear from the results. Based on Sc 3 and in order to balance with the status quo (= no economic impact for the crop farmer), the anaerobic digestion plant could impose a price of € 0.94 *(1.33 CAD)* kg^{-1} N (= € 51 ha^{-1} / 54 kg N ha^{-1} = (cost Sc 1 – cost Sc 3) / N applied as air scrubber water in Sc 3), for the production of N fertilizer via acidic air scrubbing.

As such, reuse of bio-digestion waste derivatives can also improve the economic viability of anaerobic digestion plants, especially in high-nutrient regions: no more costs for disposal and/or export, but potential revenues from local fertilizer marketing. This, in turn, can serve as a catalyst to meet renewable energy and waste(water) directives across the world. Note that the above cost calculations do not yet take in account all environmental and health benefits resulting from the improved nutrient use efficiencies when applying bio-based strategies. Holistic life cycle assessments seem relevant and will be aspect of further research (Chapter 12).

5.3.6 Technical implications and recommendations

The reviewed two-year field trial results clearly indicate that ammonium sulfate (AmS) wastewater from an acidic air scrubber for NH_3 recovery can be used as a valuable N/S-rich mineral fertilizer from an agronomic point of view. No (negative) differences in crop yield, soil fertility, and the studied soil quality parameters were observed when using the air scrubber water as compared to the reference, whether it was applied as starter fertilizer at the moment of sowing or right after ploughing (five days prior to sowing). However, there still remain some technical (see below) and legislative (see Section 5.3.7) bottlenecks hindering its use.

First, **the pH** of the acidic air scrubber water in this study amounted to 2, which is practically very low for use as a fertilizer. The low pH could cause corrosion to application instruments, leaf burning, and soil acidification after long-term application. Moreover, it causes a potential hazard for the farmer. It is therefore advised to neutralize the acidic pH. In this study, in 2011, the pH-adjustment was conducted by addition of NaOH. However, environmental-technical solutions are required to neutralize the pH of this waste stream in a practical, economic, and environmentally friendly way. More sustainable options may exist in the addition of wastewater from an alkaline air scrubber (see this study: 2012) or the development of air scrubbers that directly produce air scrubber water at a higher pH. Interesting technology providers in this respect are Anaergia (Ontario, Canada) and RVT Process Equipment (Steinwiesen, Germany), who recently came up with a process that delivers an AmS-solution at pH 5.5 and 6-7, respectively (Chapter 2).

Another technical implication is the way of **spreading the air scrubber water to the field**. As the observed N content of this product was in the range of 20-30 g kg^{-1} FW, approximately 1,000 L ha^{-1} has to be applied for the partial substitution of chemical N in conventional fertilization scenarios. This implies that the farmer must drive much slower than when applying liquid chemical mineral fertilizers, which usually only amounts to 300 L ha^{-1}. Indeed, the product is less concentrated than traditional liquid chemical N fertilizers, such as ammonium nitrate urea solutions, which usually contain about 30 % N (Triferto, Ghent, Belgium, personal communication 2013). One potential way to overcome this problem is to evaporate (part of) the water and crystallize the ammonium sulfate solution, but then significant amounts of energy have to be used. Modified or innovative application techniques should be developed for this new type of fertilizer and/or methods to concentrate the N content in an economic and ecological way should be discovered. Alternatively, the product could be mixed with chemical N fertilizer in order to increase the N content and the pH at the same time. It should, however, be noted that the N content of the air scrubber wastewater in this study was quite low as compared to values currently obtained by technology suppliers (5.3-8.5 % N on FW content; Chapter 2). Nevertheless, application remains a challenge due to the corrosive properties of the product. A corrosion-resistant spoke wheel injector is probably the most feasible application method available today (e.g. *SpikeWheel*, Liquiject, Helix, Oregon, USA). Alternatively, the product can be applied using a peristaltic pump installed on existing machinery, e.g. a sowing machine.

Furthermore, a problem still exists in the variability of manure and digestate composition over time. In order to move towards more sustainable fertilization practices, it is crucial that farmers and operators are able to control and stabilize the nutrient content, mainly N, P, K, but also S, of their end products. **In this respect, the use of mathematical models for nutrient and energy recovery can be very valuable for optimization of both process performance and fertilizer quality.** As to date an adequate integrated biological-physicochemical modelling framework for resource recovery is lacking (Batstone *et al.*, 2012), the development and use of such prototype models will be aspect of further research (Chapters 8-10).

Overall, based on the findings of the two-year field trial, the following **general recommendations** for the use of recovered AmS can be made towards agricultural end-users:

- **Application:**
  - use as starter fertilizer or as chemical fertilizer substitute in spring and summer;
  - avoid contact of fertilizer with plants (risk of leaf burning);
  - verify the S status of the soil and the S demand of the plant. Ideally, the AmS dose should not exceed the plant demand for S. Higher doses may lead to sulfate leaching, which is not desirable from an environmental point of view, nor for drinking water extraction. Simultaneous addition of patentkali or other chemical fertilizers containing sulfate salts is inadvisable;
  - the N working or availability coefficient is 100 %. This value should be accounted for when determining the optimal dose;
  - use corrosion-resistant application techniques. Among the currently available techniques, a corrosion-resistant spoke wheel injector is recommended. Injection is advised so as to minimize ammonia emissions.
- **Transport:** transport in closed truck to avoid environmental pollution and for safety.
- **Safety:**
  - avoid direct contact with the product and wear protective clothing;
  - store in a separate dedicated fluid-tight storage space to avoid soil contamination and for external safety;
  - prevent discharge to a manure cellar in or under a stable (which is in open communication with the animals) in view of the risk for release of the toxic hydrogen sulfide (H_2S) gas.

Finally, upon request of Quebec City, an **official technical fact sheet** with guidelines for application of AmS in Quebec and associated recommendations was developed (Appendix 4). Guidelines for integration of this product in (completely) bio-based fertilization scenarios as function of fertilizer legislations are presented in Chapter 11 (Section 11.2).

5.3.7 Fertilizer market trends and legislations

Besides the technical issues above, AmS wastewater from an acidic air scrubber has not often been applied to date, mainly due to legislative constraints and farmers' distrust in its fertilizer properties. On the other hand, the worldwide supply of AmS has recently increased, in part due to the production of AmS by direct reaction crystallization from (spent) sulfuric acid and NH_3. This additional AmS supply has been absorbed quickly in the marketplace, because of a general increase in fertilizer demand and an increased need for S nutrition in particular (Till, 2010). The current additional production capacity of AmS from waste streams has not even been sufficient to fulfill the market requirements, however, and naturally, this gap in the supply-demand relationship has led to a rise in AmS prices (see Chapter 2: Section 2.4.3). As one might expect, the price of AmS varies with the various types of product quality available. The largest disparity is related to particle size, where up to three times higher prices have been reported for granular (2-3 mm) crystals compared to < 1 mm crystals. This price differential can be a strong incentive to produce large crystals. Hence, the trend of the market is toward the production of the so-called 'granular' AmS quality, with a coarse fraction of 80 % > 1.8 mm, which has a higher sales return compared to standard quality, but requires an improvement of the production process (Gea-Messo, 2013). AmS from acidic air scrubbers can be beneficially used to fill the supply-demand gap, whether or not after crystallization. Therefore, it is highly important that the results obtained in this study are widely spread and that governmental authorities, such as the European Commission (EU) and the Minister of Justice (Canada), stimulate the use of air scrubber water as valuable mineral fertilizer for agricultural purposes, both in fertilizer legislations and in the farming community.

Furthermore, in many regions, an important **legislative bottleneck for the beneficial use of all digestate derivatives** is that, if the biodegradable material fed into an anaerobic digestion plant contains any waste, the digestate produced and its derivatives would normally be classified as waste and be subject to waste regulation controls. Moreover, in the European Union, all derivatives produced from animal manure, including (LF) digestates, are also still categorized as 'animal manure' in environmental legislation and can therefore often not or only sparingly be returned to agricultural land (see Chapter 1: Section 1.1). Yet, the beneficial effects of the substitution of animal manure by recovered organo-mineral fertilizers (digestates and liquid fractions) are clear from the above field-trial results. The nutrient availability of these products is mostly higher than that of animal manure, indicating that they have better mineral fertilizer properties, next to the beneficial organic properties. Therefore, the use of these (organo-mineral) bio-based fertilizers should be stimulated in environmental and fertilizer legislations. The need exists for better classification of these products based on their particular fertilizer characteristics and for greater differentiation between soils, crops, and fertilizer types in the recommendations given on N, P, and K fertilizer requirements. A new legislative framework, in which these products are classified based on their own specific fertilizer properties, instead of straightforwardly obtaining the definition of 'animal manure', may be indispensable for effective fertilizer marketing and application.

5.4 Conclusions and further research

Recent ground-breaking field research shows that the use of wastewater from an acidic air scrubber for NH_3 recovery as sustainable substitute for chemical fertilizer N in agriculture can result in higher N use efficiencies and less N leaching. In addition, the more chemical N was replaced by air scrubber water, the higher the observed P use efficiency and apparent P recovery. Furthermore, the P and K use efficiency could be improved when using digestate and/or its liquid fraction produced by mechanical separation to (partially) replace animal manure. Small, yet not always statistically significant, increases in crop yield were obtained when the liquid fraction of digestate was used as N/K fertilizer in addition to animal manure. In any case, equal to higher yields when using bio-based fertilizers in substitution of their fossil reserve-based counterparts is considered as a positive outcome.

As added benefits to the generation of bio-fertilizers from waste via anaerobic (co-)digestion, renewable energy is produced, negative environmental impacts of untreated animal manure are avoided, while the economics are also improved. Moreover, the use of bio-based fertilizers can result in added supply of (effective) organic carbon, thereby contributing to the struggle against organic carbon depletion in many soils worldwide.

We therefore conclude that the use of bio-based fertilizers has a positive impact on the economy, agronomy, and ecology of intensive plant production. The need exists for better classification of these bio-digestion waste derivatives in fertilizer and environmental legislations based on their particular fertilizer characteristics. Moreover, a greater differentiation between soils, crops, and fertilizer types in the recommendations given on N, P, and K fertilizer requirements is needed. The outcomes obtained in this study should be widely spread as they provide important evidence and guidance for further policy making and bio-based fertilizer scenario implementation. Field-scale experiments using the presented best management practices to evaluate and prove the performance of (different) bio-based fertilizers in the long term are also recommended. As such, the presented field trial was also repeated in 2013-2014 at the same field (Sigurnjak and Vaneeckhaute, in preparation). A parallel field trial was also performed on a different soil type (Bongaman, 2013: MSc Thesis tutored by Vaneeckhaute C.). Moreover, the development and use of physicochemical models to predict, control, and optimize the recovered fertilizer quality seems very valuable (see Chapters 8-10). Finally, a thorough evaluation of the humification coefficients of various bio-based fertilizers is recommended in order to better predict the effect of these products on soil organic carbon. All of this should foster the development and implementation of more sustainable, effective, and environmentally friendly farming practices.

CHAPTER 6:

PHOSPHORUS USE EFFICIENCY IN BIO-BASED FERTILIZERS: A BIO-AVAILABILITY AND FRACTIONATION STUDY

Greenhouse experiment at Ecochem, Ghent University, Belgium
(Picture: Vaneeckhaute C.)

Redrafted from:

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Vaneeckhaute, C., Janda, J., Vanrolleghem, P.A., Meers, E., Tack, F.M.G., 2015b. Phosphorus use efficiency in bio-based fertilizers: A bio-availability and fractionation study. Pedosphere, accepted.

Abstract

Although to date some technologies producing bio-based phosphorus (P) fertilizers have been proposed and implemented, the efficient use of the recovered products is still limited due to legislative constraints, lack of insights in their P release with time, and in the corresponding mechanisms. The aim of this chapter was to evaluate the fertilizer performance in terms of P release and use efficiency of recovered struvite, iron phosphate ($FePO_4$) sludge, digestate, and animal manure as compared to fossil reserve-based mineral triple superphosphate (TSP). First, product physicochemical characteristics and P fractionations in the context of European fertilizer legislation were assessed. Next, a controlled greenhouse experiment was set up to evaluate plant reactions as well as changes in P availability on sandy soils with both high and low P status. P soil fractions were determined in extracts with water (Pw), ammonium lactate (PAl), $CaCl_2$ (P-PAE), and in soil solution sampled with Rhizon soil moisture samplers (Prhizon). Based on all results, long-term field trials evaluating the P release effect of struvite and digestate as compared to animal manure and TSP on different soil types with varying P status appear to be worthwhile. These products show promise as sustainable substitutes for conventional P fertilizers and could contribute to a more efficient use of P in agriculture. A refined classification of P application standards/recommendations in terms of soil P status, texture, and fertilizer characteristics, next to the crop P demand, is recommended. Moreover, the additional use of Rhizon samplers for determination of direct available P, including dissolved organic P, is proposed for better understanding and categorization of different P fertilizers in environmental and fertilizer legislations.

Keywords: *digestate, iron phosphate sludge, nutrient recycling, rhizon soil moisture samplers, struvite, sustainable resource management.*

Résumé

Bien qu'à ce jour certaines technologies produisant des bio-engrais phosphatés aient été proposées et mises en œuvre, la pleine utilisation de ces produits est limitée par des contraintes législatives et une compréhension limitée des mécanismes de libération du phosphore (P) dans le temps. L'objectif de ce chapitre était d'évaluer la performance de libération du P des engrais et de comparer l'efficacité d'utilisation du P provenant de struvite récupérée, de boues de phosphate de fer ($FePO_4$), de digestat et lisiers d'animaux versus les triples superphosphates (TSP) minéraux provenant des réserves fossiles. Tout d'abord, les caractéristiques physicochimiques des produits et le fractionnement du P dans le cadre de la législation européenne d'engrais ont été évalués. Ensuite, une expérience en serre a été mise en place pour évaluer les réactions des plantes, ainsi que les changements dans la disponibilité du P sur les sols sableux avec un état à la fois élevé et bas de P. Les fractions de P dans le sol ont été déterminées dans des extraites avec de l'eau (Pw), du lactate d'ammonium (PAl), du $CaCl_2$ (P-PAE) et dans la solution du sol échantillonnée avec des échantillonneurs d'humidité du sol Rhizon (Prhizon). Sur la base de tous les résultats, les essais sur le terrain à long terme évaluant l'effet de libération de P de struvite et de digestat par rapport aux lisiers et TSP, sur différents types de sols avec un état variable de P, semblent intéressants. Ces produits semblent prometteurs comme substituts durables pour les engrais classiques de P, et pourraient contribuer à une utilisation plus efficace de P dans l'agriculture. Une classification raffinée des normes et recommandations d'application de P en termes de l'état de P du sol, de la texture et des caractéristiques d'engrais, en plus de la demande de P de la culture, est recommandée. De plus, l'utilisation additionnelle des échantillonneurs Rhizon pour la détermination du P directement disponible, y compris le P organique dissous, est proposée pour une meilleure compréhension et catégorisation des différents engrais phosphatés dans les législations environnementales et celles sur les engrais.

***Mots-clés**: boues de phosphates de fer, digestat, gestion durable des ressources, recyclage des nutriments, Rhizon échantillonneurs d'humidité du sol, struvite.*

6.1 Introduction

The rapid and increasing phosphorus (P) consumption in modern agriculture has raised concerns on both its supply security (Elser and Bennett, 2011; Godfray *et al.*, 2010; Neset and Cordell, 2012; Scholz and Wellmer, 2013) and its impact on the environment (soil P accumulation, leaching, and/or eutrophication) (Kang *et al.*, 2011; Ranatunga *et al.*, 2013; Syers *et al.*, 2008). Consequently, the effective use of soil P and P containing mineral and organic fertilizers, as well as the cradle-to-cradle recycling of P from municipal, agricultural, and other biodegradable waste sources as green renewable fertilizers with high P use efficiency (e.g. slow-release granules), has become highly important (Huang *et al.*, 2012; Ma *et al.*, 2011; Schröder *et al.*, 2011; Syers *et al.*, 2008; Zhang *et al.*, 2013a).

Traditional P removal processes from waste(water) streams often involve the addition of iron (Fe) or aluminium (Al) salts, resulting in the production of substantial quantities of Fe/$AlPO_4$-sludge (Sano *et al.*, 2012). Alternatively, in the past decades, the controlled precipitation of struvite ($MgNH_4PO_4{:}6H_2O$) through addition of Mg to the waste flow has gained interest as a route for P recovery (Latifian *et al.*, 2012; Ryu *et al.*, 2012; Shu *et al.*, 2006). Moreover, the anaerobic (co-)digestion of animal manure, sludges, organic biological food waste, and/or energy crops has proven to be an effective technology for bio-energy production and release/mineralization of nutrients, which are concentrated in the remaining digestate (Fehrenbach *et al.*, 2008). During a preceding field-scale assessment (Chapter 5), it has been observed that the use of a formulated mixture of digestate with its liquid fraction (LF) in agriculture as substitute for animal manure may stimulate P mobilization in the soil, thereby increasing the use efficiency of soil minerals (to be confirmed) (Vaneeckhaute *et al.*, 2013c, 2014). Especially in P saturated regions (e.g. Flanders, Quebec, Eastern China, Italy, Northern Spain, etc.; MacDonald *et al.*, 2011), the extraction of P from agricultural fields is relevant, for example, to export the recovered P towards P deficient regions, for local reuse (e.g. in the horticultural sector or for plants with high P demand), and/or for industrial purposes. On the other hand, although the use of LF digestate (with high effective nitrogen (N) over P ratio) is interesting in terms of current legislative fertilization standards, its supply of plant available P may be insufficient, depending on the crop P demand and the soil P status. Hence, additional fertilization with a source of bio-available P may be required.

In this context it must be understood that only a small proportion (15-20 %) of the total amount of P in the plant (uptake: ± 2.5 kg P_2O_5 ha^{-1} d^{-1}; EFMA, 2000) is directly provided by the fertilizer applied to that crop. The remainder comes from soil reserves. Hence, there must be adequate reserves of readily available P in the soil (Syers *et al.* 2008). The P status of European soils has been estimated by EFMA (2000). For many countries, some 25 % (5-55 %) of soils test as very low and low in readily available P. Such soils require significantly more P to be applied than is removed by the crop to increase soil reserves and thus soil fertility. On the other hand, in many countries, some 40 % (15-70 %) of soils test as high and very high in readily available P. On such soils, when crops are grown that have small, inefficient root systems, but a large daily uptake of P at critical growth stages, it may be necessary to apply more starter P fertilizer than required for crop growth to avoid P shortages in the beginning of the growing season. On soils with a medium P analysis value, applications need to sustain the P status. This may require a small extra amount of P on top of that removed with the harvested crop (EFMA, 2000).

All the above clearly indicates the relevance of fundamental comparative research on the P release pattern in time of potential sustainable alternatives for chemical P fertilizers produced from natural and exhaustive phosphate rock and/or for animal manure (products with improved P use efficiency). Such an evaluation is essential to determine the agricultural potential of new fertilizers and their responsible application (Erro *et al.*, 2011). Yet, such studies are currently lacking in literature for the above-mentioned bio-based products (struvite, digestate, Fe/$AlPO_4$-sludge), although their production and availability is on the rise (Chapter 2).

The performance of a fertilizer can be evaluated via i) product fractionation, ii) plant reaction analysis, and/or iii) chemical soil analysis (Dekker and Postma, 2008; Millier and Hooda, 2011; Prummel and Sissingh, 1983; Singh *et al.*, 2005; Sissingh, 1971; van Dam and Ehlert, 2008; Wang *et al.*, 2013). A P fractionation of fertilizers is, in general, based on the P solubility in solvents with different strength and selectivity (e.g. Frossard *et al.*, 2002; He *et al.*, 2004, 2007). With respect to European (EU) legislation, the most important solvents are, ranked from strong to weak: i) mineral acid (MA), ii) neutral ammonium citrate solution (NAC), and iii) water (EC, 2003). Next to the P solubility, the fertilizer performance is usually expressed as bio-availability indices, such as the phosphorus use efficiency (PUE). It can be based on the fresh weight (FW) and dry weight (DW) yield, the growth rate (FW, DW), the P uptake (rate), and the degree and rate in which the P status of the soil changes, as determined by chemical methods (van Dam and Ehlert, 2008). Previous studies have shown that the crop response to P fertilization gives insufficient guidance to determine the fertilizer performance (no correlation), while chemical soil analyses can be conclusive (Árendás and Csathó, 2002; Prummel and Sissingh, 1983; van Dam and Ehlert, 2008). Therefore, most studies evaluating P fertilizers to date are based on soil bioavailability indices. Soil measurements can be divided into P capacity and P intensity of the soil, based on the strength of the extraction method. The P intensity gives an indication of the total amount of P which is directly available for the plant during a short period of time, while the P capacity gives an indication of the amount of P that may be released in the long term, i.e. the backorder capacity (Dekker and Postma, 2008).

In some countries, e.g. the Netherlands, Switzerland, and Norway, fertilizer recommendations are based on the P status of the soil, measured as PAl and Pw number. It corresponds to an extraction with ammonium lactate and water, respectively (Ehlert *et al.*, 2006; Singh *et al.*, 2005; Sissingh, 1971). The PAl number is a measure of the P capacity of the soil, whereas the Pw number reflects a combination of the soil P capacity and intensity. It is not straigthforward to define the boundaries between the different methods, but Figure 6.1 may provide guidance.

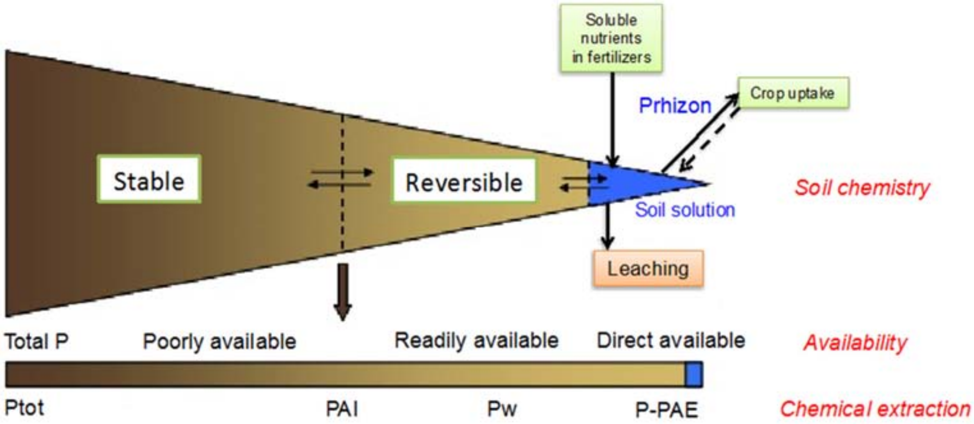


Figure 6.1 P-cycle in the soil-plant system with indication of bio-availability indices. PAl = P extractable with ammonium lactate; Prhizon = P extractable with rhizon soil moisture samplers; P-PAE = plant available elements (= P extractable with $CaCl_2$); Pw = P extractable with water.

In the latest decade, also the PAE method (Plant Available Elements) has received increased attention. It concerns a multi-element extraction with 0.01 M calcium chloride ($CaCl_2$), and hence provides a simple alternative for the many extraction procedures that are currently used for single nutrients (Ehlert *et al.*, 2006; Houba *et al.*, 2000; van Erp *et al.*, 1998). With respect to P (P-PAE), this measurement gives an indication of the P intensity (Houba *et al.*, 2000). An important limitation of all these standard methods is that root formation, soil compaction, and mineralization of organic matter is not or not sufficiently accounted for (Amoakwah *et al.*, 2013; Ehlert *et al.*, 2006; Soine, 2009). Underestimations have been observed in literature, especially for the determination of direct available P (Amoakwah et al., 2013; Sánchez-Alcalá *et al.*, 2014). Alternatively, the use of Rhizon soil moisture samplers (SMS) allows assessing the total amount of P in the actual soil solution (Prhizon), including dissolved organic and inorganic forms (Eijkelkamp, 2003; Fig. 6.1). Besides the ease of sampling, Rhizon SMS for direct extraction of soil moisture also overcomes disadvantages related to traditional sampling using ceramic cups, such as the exchange of (divalent) cations and P (Grossmann and Udluft, 1991). Moreover, in contrast to the above standard methods, the use of Rhizon samplers is not destructive, less laborious and time consuming, and most importantly, it does not change the composition of the soil solution in the process of extracting it (Amoakwah et al., 2013; Sánchez-Alcalá *et al.*, 2014).

The first aim of this study is to evaluate the fertilizer performance of bio-based recovered products (struvite, $FePO_4$-sludge, digestate from co-digestion) and pig manure as compared to fossil reserve-based mineral fertilizer, triple superphosphate (TSP, $Ca(H_2PO_4)_2$:H_2O). After product physicochemical analysis and P fractionation (in the framework of EU legislation), a controlled greenhouse experiment was set up in order to: i) evaluate the PUE based on plant reactions and changes in the chemical soil P bio-availability status during the most critical main growing period, and ii) confirm and further study under precise conditions some nutrient release mechanisms previously observed under practical field conditions (see above; Chapter 5;

Vaneeckhaute *et al.*, 2013c, 2014). A second aim is to overcome the limitations of standard soil extraction methods by using Rhizon SMS to determine the P delivery in the short term. A controlled greenhouse experiment was preferred for this purpose above a field trial so as to minimize potential soil disturbances, e.g. of hydraulic levels, to which the various extraction methods are sensitive (Eikelkamp, 2003). Based on the results, practical implications are discussed and recommendations in terms of legislative revisions and associated further field research are provided. As such, this chapter gives valuable information to guide further efforts to optimize P supply and minimize accumulation and eutrophication risks, aiming at a more responsible and efficient use of P in agriculture.

6.2 Material and methods

6.2.1 Experimental set-up

An overview of the experimental set-up can be found in Figure 6.2. First, a product physicochemical characterization and P fractionation in the framework of EU legislation was conducted (Section 6.2.2). Then, a greenhouse experiment (Section 6.2.3) was set up in order to evaluate the plant reaction and soil P bio-availability status in time (Section 6.2.4). Based on the obtained results, average phosphorus use efficiencies (PUEs) were calculated for the different bio-based fertilizers (including recovered products and pig manure) as compared to a control and a reference TSP (Section 6.2.5).

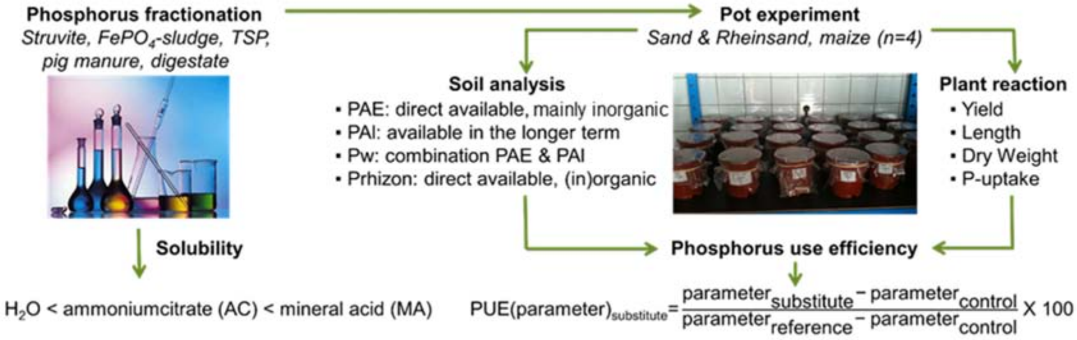


Figure 6.2 Overview of the experimental set-up: phosphorus (P) fractionation and pot (= greenhouse) experiment. PAE = plant available elements (= P extractable with $CaCl_2$); PAl = P extractable with ammonium lactate; Prhizon = P extractable with rhizon soil moisture samplers; PUE = phosphorus use efficiency; Pw = P extractable with water; TSP = triple superphosphate.

6.2.2 Product characterization and phosphorus fractionation

The DW content was determined as residual weight after 72 h drying at 80 °C in an oven (EU 170, Jouan s.a, Saint Herblain, FR). Organic carbon (OC) was determined after incineration of the dry samples during 4 h at 550 °C in a muffle furnace (Nabertherm, Lilientahl, DE). The loss of ignition (= weight loss after incineration) was divided by a conversion factor of 1.8 to calculate OC, hence assuming that organic matter contains 55 % OC (CSA, 2012; Van Ranst *et al.*, 1999). Electrical conductivity (EC) and pH were determined potentiometrically using a WTW-

LF537 (Wissenschaftlich Technischen Werkstäten, Weilcheim, DE) electrode and an Orion-520A (Orion Research, Boston, USA) pH-meter, respectively. The solid samples were first equilibrated for 1 h in deionized water at a 5:1 liquid to dry sample ratio and subsequently filtered (MN 640 m, Macherey-Nagel, DE). Total N content was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest, Koningswinter, DE) after digestion of the sample in a sulphuric-salicylic acid mixture. The captured ammonia (NH_3) in the distillate was then titrated with 0.01 mol L^{-1} hydrogen chloride (HCl) in the presence of a methyl red bromocresol green mixed indicator (Van Ranst *et al.*, 1999). Ammonium (NH_4) was determined using the Kjeltec-1002 distilling unit after addition of magnesium oxide (MgO) to the sample and subsequent titration (Van Ranst *et al.*, 1999). The amount of effective N for organic fertilizers was calculated from the analysis of total N and NH_4-N based on the official formula used by agronomes in Flanders and the Netherlands for determination of fertilizer N recommendations (Inagro, Beitem, BE, personal communication 2012; van Eekeren *et al.*, 2006): Effective N = (N_{tot} – NH_4-N) X 0.475 + (NH_4-N X 0.8). It states that 80 % of the NH_4-N is plant available. On top of that, 47.5 % of the remaining N, i.e. nitrates and organic N, becomes plant available in the short term. Total P was determined using the colorimetric method of Scheel (1936; Van Ranst *et al.*, 1999) after wet digestion of the liquid samples using nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, UK). Calcium (Ca), magnesium (Mg), and potassium (K) were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX, Palo Alto, USA) (Van Ranst *et al.*, 1999) after wet digestion in HNO_3 and H_2O_2. The determination of the fraction of P soluble in water, mineral acid (= mixture of HNO_3 and sulfuric acid, H_2SO_4), and neutral ammonium citrate ($(NH_4)_2C_6H_6O_7$) was determined as described in EC (2003).

6.2.3 Greenhouse experiment

Substrates used in the greenhouse experiment were: i) a nutrient-rich sandy soil with high P status (Pw > 55 mg P_2O_5 L^{-1} soil; Alterra, 2012) from Ranst, Belgium (pH = 5.0; EC = 111 µS cm^{-1}; bulk density = 1.262 kg L^{-1}; oxalate extractable Fe/Al: Fe_{ox} = 34 mmol kg^{-1} soil, Al_{ox} = 66 mmol kg^{-1} soil), and ii) a nutrient-poor, P deficient (Pw < 36 mg P_2O_5 L^{-1} soil; Alterra, 2012) laboratory-grade Rheinsand (pH = 7.9; EC = 67 µS cm^{-1}; bulk density = 1.612 kg L^{-1}). Methods used for soil physicochemical analysis are described in Section 6.2.4. Although Rheinsand is rarely used for agricultural production, tests on this soil may provide additional information on the fertilizer effect itself, i.e. the absolute amount of available P effectively provided by the fertilizers only. Indeed, on P saturated soils (as is often the case in Flanders), differences in the P delivery by the fertilizers themselves may be difficult to detect due to large background concentrations. Moreover, the comparison between the high P and low P soil may provide information on the indirect P liberation from the soil complex as a result of fertilizer application. Hence, comparison with the Rheinsand soil was thought to be useful.

TSP was collected at Triferto, Ghent, struvite at the NuReSys water treatment plant of Clarebout Potatoes, Nieuwkerke-Heuvelland, and $FePO_4$-sludge at the piggery of Innova Manure, Ichtegem, all in Belgium. Animal manure was sampled at the piggery of Ivaco, Gistel, Belgium, and digestate was sampled at the biogas plant SAP Eneco Energy, Houthulst, Belgium. The latter concerns a full-scale mesophilic (37 °C) anaerobic co-digestion plant (capacity: 60,000 ton y^{-1}, 2.83 MW_{el}) with an input feed consisting of animal manure (30 %), energy maize (30 %), and organic biological waste supplied by the food industry (40 %). Two replicate samples of each waste stream were collected in polyethylene sampling bottles (10 L) and transported within 1 h to the laboratory for physicochemical analysis, carried in cooler boxes filled with ice (± 4 °C). In the laboratory, the replicate samples were stored cool (1-5 °C) and kept separated for separate analysis after homogenization of each particular sample. The product characteristics can be found in Table 6.1. The obtained data were used to calculate the maximum allowable product dosage for the different cultivation scenarios in compliance with the Flemish manure decree (MAP4, 2011).

Table 6.1 Product physicochemical characterization (mean ± standard deviation; n = 2). DW = dry weight; EC = electrical conductivity; OC = organic carbon; TSP = triple superphosphate.

Parameter	TSP	Struvite	$FePO_4$-sludge	Pig manure	Digestate
pH	2.6	8.4	4.6	7.7	8.6
EC (mS cm^{-1})	29	547	15	35	37
DW (%)	100	100	2.0 ± 0.0	6.2 ± 0.1	9.8 ± 0.0
OC (% on DW)	1.6 ± 0.0	29 ± 0	25 ± 0	37 ± 1	34 ± 1
Total P_2O_5 (g kg^{-1} DW)	430 ± 5	293 ± 3	26 ± 1	53 ± 0	30 ± 0
Total N (g kg^{-1} DW)	0.49 ± 0.03	52 ± 2	55 ± 0	105 ± 0	67 ± 0
NH_4-N (g kg^{-1} DW)	0.23 ± 0.06	28 ± 1	13 ± 0	74 ± 2	39 ± 0
Effective N (g kg^{-1} DW)	0.31 ± 0.04	34 ± 1	30 ± 1	74 ± 2	45 ± 0
Total K_2O (g kg^{-1} DW)	1.9 ± 0.3	11 ± 0	116 ± 5	74 ± 6	58 ± 0
Ratio effective N:P_2O_5:K_2O	0.00072:1:0.0044	0.12:1:0.038	1.1:1:4.5	1.4:1:1.4	1.5:1:2.0
Total Ca (g kg^{-1} DW)	138 ± 1	0.58 ± 0.00	9.5 ± 0.0	29 ± 0	26 ± 0
Total Mg (g kg^{-1} DW)	2.1 ± 0.0	87 ± 1	5.0 ± 0.0	14 ± 0	6.1 ± 0.0

Plastic containers (height: 14 cm, diameter: 13 cm) were filled with 1 kg of soil and the soil moisture solution was brought to field capacity (23 % for sand and 19 % for Rheinsand by weight; Section 6.2.4). After two days of equilibration (March 16 2012), an equivalent product dose of 80 kg P_2O_5 ha^{-1} was applied to all containers (Table 6.2). This refers to the maximum allowable yearly amount of P application to a sandy soil in Flanders with the purpose of maize cultivation (MAP4, 2011). Simultaneously, a control treatment without P fertilization was set up. Differences in N, K, Ca, and Mg application between the scenarios were corrected by adding the appropriate amount of a 1 M ammonium nitrate (NH_4NO_3), potassium sulfate (K_2SO_4), calcium sulfate ($CaSO_4{:}2H_2O$), and magnesium sulfate ($MgSO_4{:}7H_2O$) solution up to the fertilizer recommendation levels of 135 kg effective N ha^{-1}, 250 kg K_2O ha^{-1}, 100 kg CaO ha^{-1}, and 50 kg MgO ha^{-1}, respectively, and without exceeding the field capacity. Soils were

Table 6.2 Product (ton DW ha^{-1}) and macronutrient (total N, effective N, total P, K_2O, Ca, Mg, and OC; kg ha^{-1}) dosage to soil by bio-based fertilizer application (standardized to 80 kg P_2O_5 ha^{-1}). Differences in N, K, Ca, and Mg application were corrected by adding the appropriate amount of a 1 M NH_4NO_3, K_2SO_4, $CaSO_4{:}2H_2O$, and/or $MgSO_4{:}7H_2O$ solution. DW = dry weight; OC = organic carbon; TSP = triple superphosphate.

Fertilizer type	Product (ton DW ha^{-1})	Total N (kg ha^{-1})	Effective N (kg ha^{-1})	Total P_2O_5 (kg ha^{-1})	Total K_2O (kg ha^{-1})	Total Ca (kg ha^{-1})	Total Mg (kg ha^{-1})	OC (kg ha^{-1})
TSP	0.19	0.093	0.059	80	0.36	26	0.40	3.0
Struvite	0.27	14	9.2	80	3.0	0.16	24	78
$FePO_4$-sludge	3.08	169	92	80	357	29	15	770
Pig manure	1.51	159	112	80	112	44	21	559
Digestate	2.76	185	124	80	160	72	17	938

homogenized and soil moisture content was again brought to field capacity with deionized water. Each treatment was repeated four times, resulting in a total of 48 containers (5 amendments and 1 control, 2 soil types, 4 replications).

After four days of equilibration (March 21 2012), seven energy maize seeds of the species *Atletico* (breeder: KWS, Belgium; Food and Agricultural Organisation (FAO) ripeness index: 280; P demand: high) were sown in each container at a depth of 2 cm. The containers were covered with perforated plastics in order to reduce evapotranspiration. When the plants reached the height of the plastic, the plastics were removed, and the plants were thinned out to five plants per container. In each container a Rhizon SMS (MOM 10 cm male luer, PE/PVC tubing, 9 mL vacuette; Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands) was inserted diagonally from the topsoil through the soil column. A greenhouse bench at ± 20 °C was divided into four blocks representing the four replications, and in each block 12 containers were randomly placed.

The plants were lightened with Brite-Grow bio growing lamps (LUX 1500, 36 W) 50 cm above the plants in a day-night cycle (6 AM till 8 PM). The soils were weighed daily and the soil moisture content was adjusted to field capacity each time. The increasing plant weight was taken into account using the visual estimation method proposed by Datema *et al.* (1986). After one week, leakage of soil solution was visible in two containers: one struvite and one control treatment, both on the sandy soil. These two containers were removed from the experiment.

Homogeneous soil samples (10 g) were taken for analysis of PAl, Pw, and P-PAE by means of a soil auger the first two weeks and the last two weeks of the experiment. Rhizon soil moisture extracts were sampled weekly during the experiment and the P concentration in the soil solution as well as the pH were analyzed each time. Furthermore, the length of the plants was measured weekly. After five weeks of growth, the plants were harvested, their yield was determined, and plant samples were taken for physicochemical analysis. The soils were maintained on the greenhouse bench and were moisturized every week up to field capacity. Finally, PAl, P-PAE, and Pw in the soils were measured again after six months.

6.2.4 Plant and soil analysis

The DW content of the biomass was determined as residual weight after one week drying at 65 °C. Macronutrients (N, P, K, Ca, Mg) in the biomass were determined following the same methodology as described for the product analysis (Section 6.2.2).

Soil pH and EC were determined using the same procedure as described for the products (Section 6.2.2). Field capacities were determined in accordance with the Compendium for Sampling and Analysis provided in the Flemish waste and soil remediation decree (CSA, 2012). Soil bulk densities were determined as the mass of dry soil over its total (wet) soil volume (USDA, 2013).

For the determination of PAl, 2.5 g of soil was mixed with 50 mL of ammonium lactate solution (pH 3.75), shaken for 4 h and filtered until colorless using a white ribbon filter (MN 640 m, Macherey-Nagel, Düren, DE; CSA, 2012). For the determination of Pw, 4 cm^3 of soil and 240 mL of distilled water were mixed in a 250 mL flask, shaken for 1 h and filtered (white ribbon) until colorless (EL&I, 2009; Sissingh, 1971). For P-PAE, 1 g of dry soil was mixed with 25 mL 0.01 M $CaCl_2$ in a 40 mL centrifuge tube, shaken for 1 h, centrifuged during 10 min at 4,000 rpm (Heraeus megafuge 1.0, Kendro Laboratory Products, Hanau, DE), and filtered (white ribbon) (Van Ranst *et al.*, 1999). Note that the P-PAE number is generally expressed as mg P kg^{-1} soil, whereas the Pw and PAl numbers are officially expressed as mg P_2O_5 L^{-1} soil and mg P_2O_5 100 g^{-1} soil, respectively. The total P content in the filtered extraction solutions and Rhizon SMS extracts was then determined using the colorimetric method of Scheel (Section 6.2.2). Finally, in acidic sandy soils, P ions are expected to react with Fe and Al ions to form poorly soluble compounds (Hillel, 2008). Hence, an extraction of the soil with ammonium oxalate ($(NH_4)_2C_2O_4$) and oxalic acid ($H_2C_2O_4$) was also performed in order to determine the active forms of Fe and Al separately. The procedure described in CSA (2012) was used for this purpose.

6.2.5 Phosphorus use efficiency (PUE)

Average PUEs (%) of the bio-based fertilizers were calculated based on the plant reaction and the soil status using the following equation (Eq. 7.1):

$$\mathrm{PUE}(parameter)_{\mathrm{bio-fertilizer}} = \frac{(parameter_{\mathrm{bio-fertilizer}} - parameter_{\mathrm{control}})}{(parameter_{\mathrm{reference}} - parameter_{\mathrm{control}})} . 100 \qquad \textbf{\textit{Eq.}\ (6.1)}$$

where 'bio-fertilizer' refers to the bio-based fertilizers under study, 'control' to the blank treatment, 'reference' to the TSP treatment, and where 'parameter' can refer to:

i. the plant P uptake, the plant FW and DW yield: PUE(uptake), PUE(FWyield), and PUE(DWyield). Here, the PUE refers to the percentage of P in the bio-based fertilizers that has the same effectiveness as the reference fossil reserve-based mineral P fertilizer, TSP;
ii. the PAl, Pw, P-PAE, and the P concentration in the soil solution extracted with Rhizon SMS: PUE(PAl), PUE(Pw), PUE(PAE), and PUE(Prhizon). Here, the PUE

refers to the increment in soil P status by application of the bio-based fertilizers as compared to the increment by application of TSP.

6.2.6 Statistical analysis

Statistical analyses were conducted using SAS 9.3. A one-way ANOVA model was used to determine the effect of the fertilizer type (i.e. the independent variable, between-groups factor) on the different plant and soil parameters (i.e. the dependent variable) per measurement. Furthermore, a two-way mixed ANOVA model was used to determine whether any change in plant and soil parameters (i.e. the dependent variable) was the result of the interaction between the type of treatment (i.e. the between-group factor) and time (in weeks, i.e. the within-group factor). As the interaction term between time and treatment was never significant at the 5 % significance level ($\alpha = 0.05$), it was eliminated from the model. Follow-up tests were performed to determine whether the mean value for each plant and soil parameter was significantly different in time, and whether the average of these parameters over the whole experimental period was significantly different between the treatments. The condition of normality was checked using the Kolmogorov Smirnov test and QQ-plots, whereas equality of variances was checked with the Levene test. When homoscedascity was found, significance of effects was tested by use of an F-test and post-hoc pair-wise comparisons were conducted using Tukey's honestly significant difference (HSD) test ($\alpha = 0.05$). When no homoscedascity was found, a Welch F-test combined with a post-hoc Games-Howell test was used ($\alpha = 0.05$). When the condition of normality was not fulfilled, the non-parametric Kruskal-Wallis test was applied instead of the one-way ANOVA. For convenience of discussion, significant parameter correlations were determined using the Pearson correlation coefficient, r.

6.3 Results

6.3.1 Product characterization and phosphorus fractionation

First, it must be noticed that TSP and struvite were dry, granular products, while the other products were liquids. For recognition of new P fertilizers in the framework of EU fertilizer legislations, the amount of P soluble in water and ammonium citrate, next to the total amount of P must be demonstrated. Moreover, the amount of P soluble in mineral acid must be higher than 2 % (EC, 2003). The extracted P fractions for the different products under study are shown in Table 6.3.

Table 6.3 Phosphorus (P) fractionation: total P, P soluble in water, neutral ammonium citrate (NAC), and mineral acid (MA) (g kg^{-1} DW; mean ± standard deviation; n = 2). DW = dry weight; TSP = triple superphosphate.

Parameter	**TSP**	**Struvite**	**$FePO_4$-sludge**	**Pig manure**	**Digestate**
Total P_2O_5 (g kg^{-1} DW)	430 ± 5	293 ± 3	26 ± 1	53 ± 0	30 ± 0
P_2O_5 extractable in water (g kg^{-1} DW)	413 ± 1	5.0 ± 0.0	1.0 ± 0.0	45 ± 2	23 ± 0
P_2O_5 extractable in NAC (g kg^{-1} DW)	410 ± 1	282 ± 3	25 ± 1	48 ± 0	28 ± 0
P_2O_5 extractable in MA (g kg^{-1} DW)	398 ± 1	288 ± 5	23 ± 0	52 ± 0	30 ± 0

The relative solubility of P in neutral ammonium citrate was high for all fertilizers (91-100 % of total P), similar as the solubility in mineral acid (92-100 %). The amount of P soluble in water was low for struvite (1.7 % of total P) and $FePO_4$-sludge (3.9 %) as compared to TSP (96 %), while their relative amount of P soluble in mineral acid was in the same line as the reference. Digestate had approximately the same P solubility's in the different extraction reagents as animal manure (79-100 % of total P). Compared to TSP, the P solubility of both products in water was lower, while it was higher in mineral acid. Furthermore, the pH of TSP and $FePO_4$-sludge was low (2.6-4.6), while for struvite and digestate it was alkaline (8.4-8.6) (Table 6.1). The pH of pig manure was quasi neutral. Finally, all bio-based fertilizers under study added significantly more organic carbon (OC) to the soil as compared to TSP (Table 6.2).

6.3.2 Plant reaction

6.3.2.1 Biomass yield and phosphorus uptake

On the sandy soil at the harvest all treatments showed a significantly higher FW biomass yield (g FW container^{-1} or kg^{-1} soil; Table 6.4), DW biomass yield (g DW kg^{-1} soil; Table 6.4), and length (cm; Fig. 6.3) as compared to the reference TSP. Conversely, the DW content (%) and P content (mg P kg^{-1} plant DW) of the biomass were significantly higher for the TSP treatment. However, the absolute P uptake per container (mg P container^{-1} or kg^{-1} soil) was only significantly higher for TSP as compared to the control (Table 6.4).

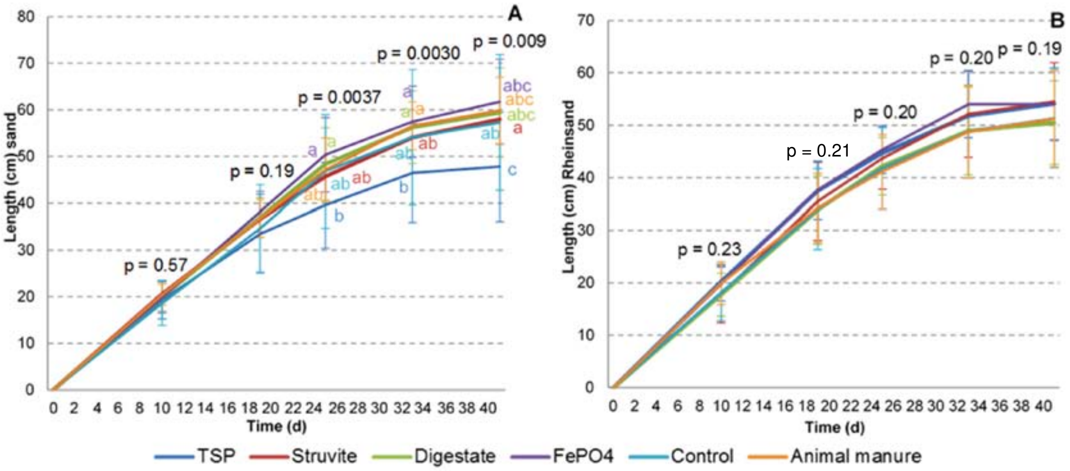


Figure 6.3 Plant length (cm) as a function of time (d) for the different treatments on sand (A) and on Rheinsand (B) (mean, error bars: +/- 1 standard deviation; n = 4). p-values refer to statistical analyses using one-way ANOVA. When a significant difference was observed ($p < 0.05$), post-hoc pair-wise comparisons were added using small letters.

On Rheinsand, no significant differences were observed in the biomass length (Fig. 6.3) and DW yield (Table 6.4). The DW content was significantly lower for TSP and $FePO_4$-sludge as compared to the control and digestate, while $FePO_4$-sludge had a significantly higher FW yield than the control, manure, and digestate. The use of TSP, manure, and digestate resulted in a significantly higher P content (g kg^{-1} plant DW) and absolute P uptake (mg P container^{-1} or kg^{-1}

Table 6.4 Biomass yield (g FW/DW container^{-1} or kg^{-1} soil), dry weight content (%), and phosphorus uptake (mg P kg^{-1} soil) at the harvest (mean ± standard deviation; n = 4), as well as average phosphorus use efficiencies (PUE) based on the plant reaction for the different treatments on P-rich sand and Rheinsand. p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons (α = 0.05). DW = dry weight; FW = fresh weight; TSP = triple superphosphate.

Sand	**Yield** (g FW kg^{-1})	**PUE(FWyield)** (%)	**DW** (%)	**Yield** (g DW kg^{-1})	**PUE(DWyield)** (%)	**P uptake** (mg kg^{-1})	**PUE(uptake)** (%)
	$p < 0.0001$	-	$p < 0.0001$	$p = 0.00021$	-	$p = 0.012$	-
Control	26 ± 2a	0	19 ± 0ab	4.7 ± 0.3a	0	32 ± 2b	0
TSP	20 ± 2b	100	20 ± 2a	4.0 ± 0.2b	100	39 ± 3a	100
Struvite	27 ± 0a	-21[a]	17 ± 0bc	4.7 ± 0.1a	9.6[ab]	34 ± 2ab	22
FePO$_4$-sludge	29 ± 1a	-68[a]	17 ± 0c	4.9 ± 0.1a	-16[a]	33 ± 3ab	16
Pig manure	28 ± 1a	-46[a]	17 ± 0bc	4.8 ± 0.2a	-9.0[a]	35 ± 2ab	37
Digestate	29 ± 1a	-67[a]	17 ± 1c	4.8 ± 0.2a	-15[a]	37 ± 2ab	80
Rheinsand	**Yield** (g FW kg^{-1})	**PUE(FWyield)** (%)	**DW** (%)	**Yield** (g DW kg^{-1})	**PUE(DWyield)** (%)	**P uptake** (mg kg^{-1})	**PUE(uptake)** (%)
	$p = 0.0031$	-	$p < 0.0001$	$p = 0.20$	-	$p < 0.0001$	-
Control	15 ± 1b	0	26 ± 0a	3.9 ± 0.1a	0	5.4 ± 0.7c	0
TSP	16 ± 1ab	100	25 ± 0b	4.0 ± 0.8a	100	9.2 ± 0.6a	100
Struvite	16 ± 2ab	75	25 ± 1ab	3.9 ± 0.3a	67	7.0 ± 1.5bc	42
FePO$_4$-sludge	17 ± 0a	159	24 ± 0b	4.1 ± 0.1a	233	5.6 ± 0.9c	3.3
Pig manure	15 ± 1b	-8.9[b]	26 ± 1ab	3.8 ± 0.1a	-67[b]	8.4 ± 0.8ab	80
Digestate	14 ± 1b	-45[b]	27 ± 1a	3.8 ± 0.1a	-100[b]	7.8 ± 0.5ab	63

[a] PUE shows the opposite sign as results for the reference TSP are lower than the control.

[b] Result for the bio-based fertilizer is lower than the control.

soil) as compared to the control and $FePO_4$-sludge. Moreover, the plant P uptake at the harvest was significantly lower for struvite as compared to TSP on Rheinsand.

6.3.2.2 Phosphorus use efficiency (PUE)

The PUE(FWyield) and PUE(DWyield) on the sandy soil were mostly negative as the yield of the reference TSP was lower than the control (Table 6.4). Among the bio-based products, the best average PUEs based on crop yield were observed for $FePO_4$-sludge and digestate, the latter simultaneously showing the highest PUE(uptake). Also on Rheinsand, the PUE(FWyield) and PUE(DWyield) were the highest for $FePO_4$-sludge, however its PUE(uptake) was the lowest. The PUE(uptake) for manure and digestate were the highest on Rheinsand, yet their PUE(FWyield) and PUE(DWyield) were negative as the yields were slightly lower than the control.

6.3.3 Soil bio-availability indices

6.3.3.1 P-PAE, PAl, and Pw number

Bio-availability curves and corresponding statistics per measurement of P-PAE, PAl, and Pw are presented in Figure 6.4.

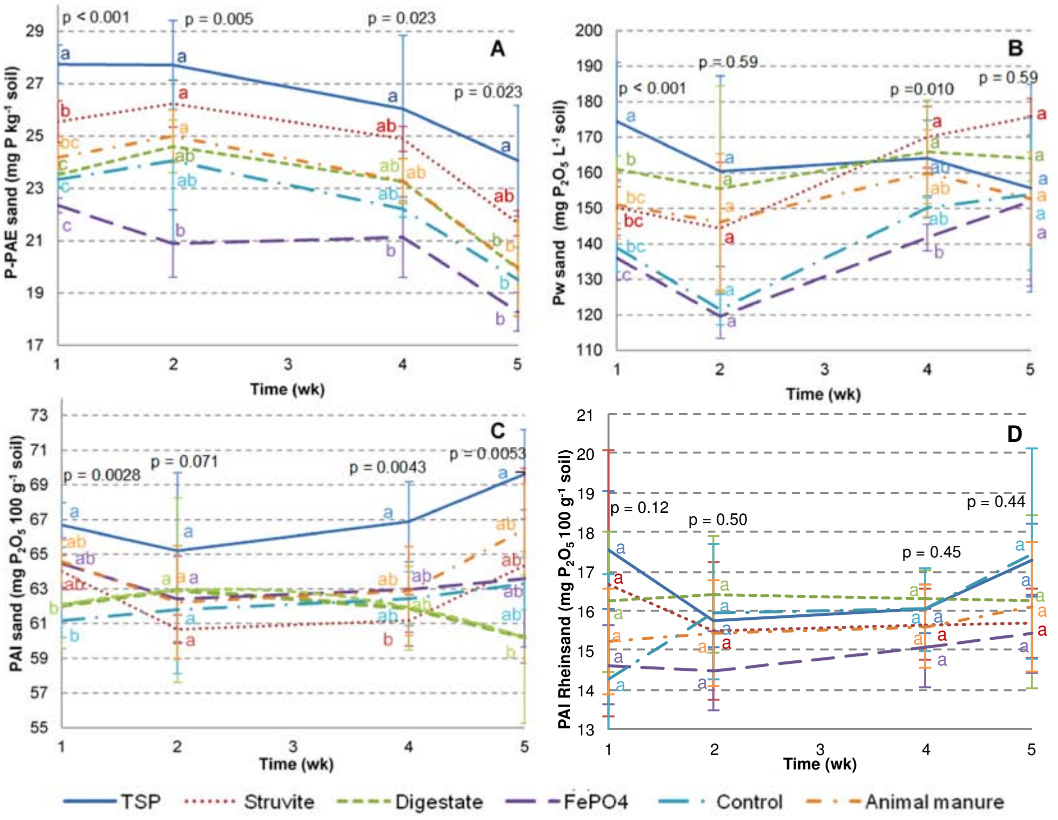


Figure 6.4 P-PAE (A; mg P kg^{-1} soil), Pw (B; mg P_2O_5 L^{-1} soil), PAl on sand (C; mg P_2O_5 100 g^{-1} soil), and PAl on Rheinsand (D; mg P_2O_5 100 g^{-1} soil) as a function of time (wk) after sowing for the different treatments (mean, error bars: +/- 1 standard deviation; n = 4).
p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons (α = 0.05).

First, it must be remarked that P-PAE and Pw could only be detected on the sandy soil as the values on Rheinsand were lower than the detection limit of both the available spectrophotometer (0.66 mg P L^{-1}; Jenway 6400, Barloworld Scientific T/As, Felsted, UK) and the continuous flow analyzer (0.05 mg P L^{-1}; AA3, BRAN+LUEBBE, Norderstedt, DE).

Over the whole experimental period, the mean P-PAE (mg P kg^{-1} soil) was significantly higher ($p < 0.0001$) for TSP as compared to the other treatments and the control, as well as for struvite compared to the control, digestate, and $FePO_4$-sludge (Fig. 6.4A). The effect of $FePO_4$-sludge on the P-PAE number was in average significantly lower ($p < 0.0001$) than that of all other treatments. The two-way ANOVA for P-PAE indicated a significant ($p < 0.0001$) decrease for all treatments from week 2 to 4 and week 4 to 5. The mean Pw over time (mg P_2O_5 L^{-1} soil) for TSP, digestate, and struvite was significantly higher ($p < 0.0001$) than for the control and $FePO_4$-sludge (Fig. 6.4B). A significant decrease ($p = 0.0021$) was observed in week 2 for all treatments. Overall, the mean PAl (mg P_2O_5 100 g^{-1} soil) in time on the sandy soil was significantly higher ($p < 0.0001$) for TSP than for all other treatments (Fig. 6.4C), while on Rheinsand this effect was only significant ($p = 0.030$) compared to $FePO_4$-sludge (Fig. 6.4D). Both on sand and Rheinsand, no significant changes in time were found based on the weekly average PAl ($p > 0.1$). After six months, no more significant effect of the treatment on the P-PAE ($p = 0.15$) and PAl number ($p = 0.10$) was observed, whereas the control showed a significantly higher ($p = 0.0069$) Pw number than struvite, manure, and $FePO_4$-sludge.

6.3.3.2 pH and phosphorus content in the soil solution (Prhizon)

The pH and P content in the soil solution extracted with rhizon SMS are presented in Figure 6.5. On sand, the average pH over time was significantly lower ($p < 0.0001$) for pig manure as compared to all other treatments, as well as for TSP compared to struvite, $FePO_4$-sludge, the control, and digestate (Fig. 6.5A). Conversely, the average Prhizon (mg P_2O_5 L^{-1}) over time was significantly higher ($p < 0.0001$) for manure as compared to struvite, the control, and $FePO_4$-sludge (Fig. 6.5C). The latest showed significantly lower Prhizon values ($p < 0.0001$) than the other treatments and the control, while digestate showed a significantly higher ($p < 0.0001$) average pH than all other treatments, both on sand and Rheinsand (Fig 6.5A,B).

6.3.3.3 Phosphorus use efficiency (PUE)

The average PUE based on the various soil analyses is presented in Figure 6.6 as a function of time. The calculated average values over time are provided in Table 6.5. On the sandy soil, all fertilizers presented a lower PUE(PAE) and PUE(PAl) than the reference TSP during the whole experimental period (Fig. 6.6A,C; Table 6.5). Struvite showed the highest PUE(PAE), while the P-PAE number for $FePO_4$-sludge was even lower than the control. PUE(Pw) increased in time for struvite and digestate relative to TSP (Fig. 6.6B). For $FePO_4$-sludge, it was negative and decreasing. PUE(Prhizon) was very high (up to > 100 %) for pig manure on both sand and Rheinsand (Fig. 6.6E,F). On sand, the curve for struvite showed a similar pattern as for pig manure up to week 3 (Fig. 6.6E). However, on Rheinsand the values for struvite were always lower as compared to the reference and pig manure (Fig. 6.6F).

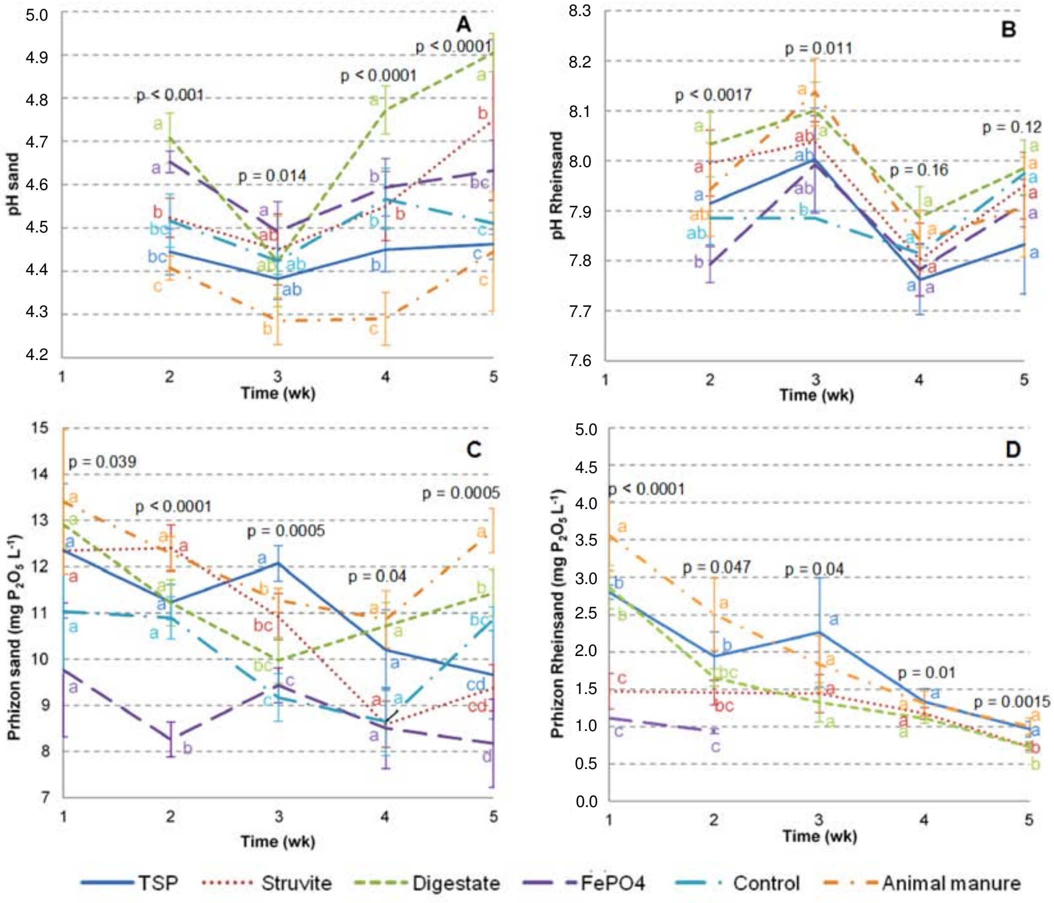


Figure 6.5 pH and P_2O_5 concentration (mg L^{-1}) in the soil solution (Prhizon) as a function of time (wk) after sowing on sand (A, C) and on Rheinsand (B, D) (mean, error bars: +/- 1 standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons (α = 0.05). Detection limit: 0.05 mg L^{-1}.

Table 6.5 Average phosphorus use efficiency (PUE; %) over time based on soil analyses (PAE, Pw, PAl, Prhizon) on sand and on Rheinsand (if detectable) for the different bio-based fertilizers relative to the reference triple superphosphate (TSP; PUE = 100 %). PUE(control) = 0 %.

PUE (%)	PUE(PAE) Sand	PUE(Pw) Sand	PUE(PAl) Sand	PUE(PAl) Rheinsand	PUE(Prhizon) Sand	PUE(Prhizon) Rheinsand
Struvite	57	374	1.6	-94[b]	145	60
$FePO_4$-sludge	-41[a]	-46[a]	23	-606[b]	-131[a]	3.2
Animal manure	21	24	34	-215[b]	130	114
Digestate	14	212	-3.0[a]	453[b]	71	81

[a] Effect of bio-based fertilizer < control.

[b] No significant difference with the control because of high standard error.

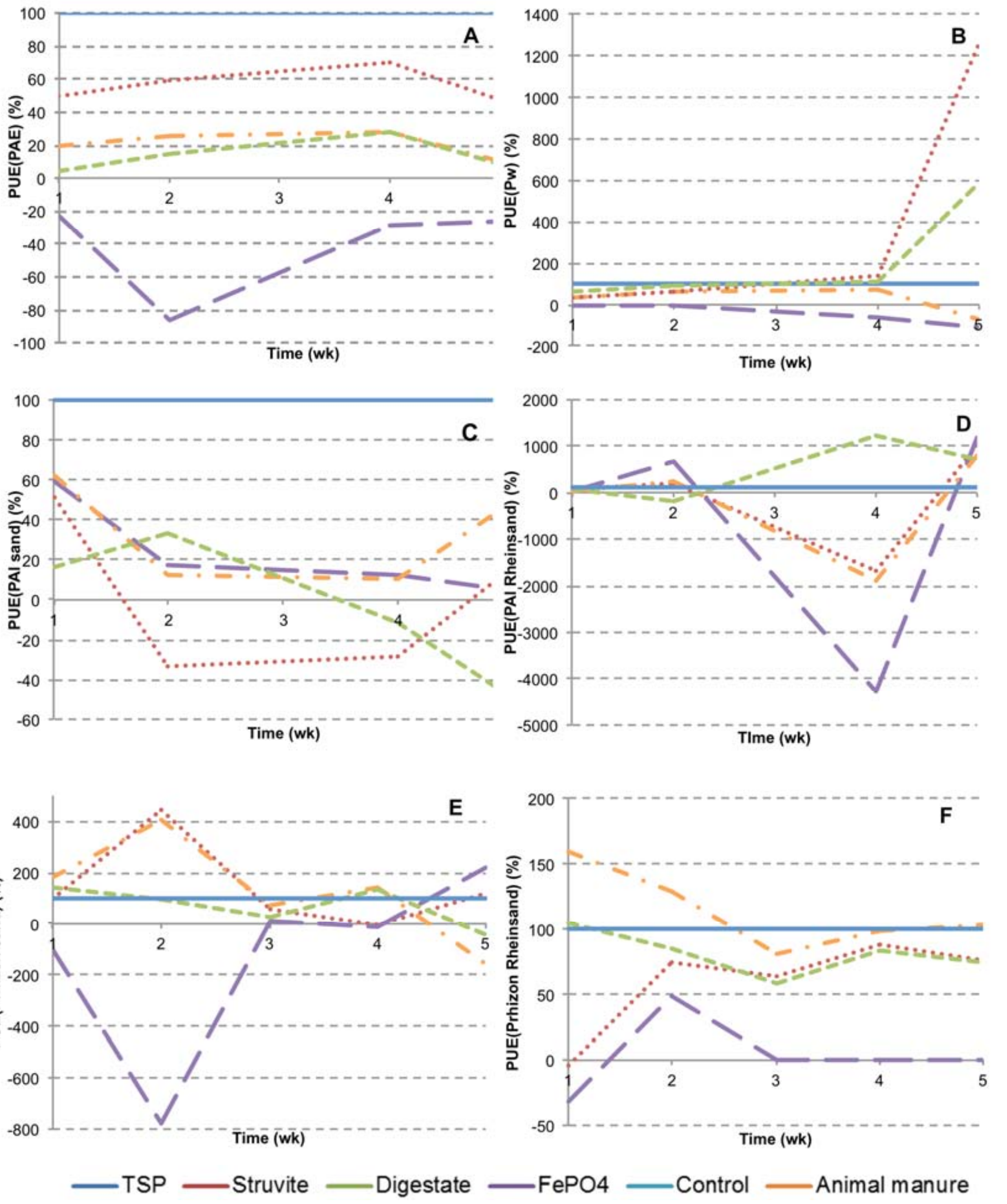


Figure 6.6 Average phosphorus use efficiency (PUE; %) as a function of time (wk) after sowing for the different treatments relative to the reference triple superphosphate (TSP; PUE = 100 %), based on P-PAE (A), Pw (B), PAl sand (C), PAl Rheinsand (D), Prhizon sand (E), and Prhizon Rheinsand (F). PUE(control) = 0 %.

6.4 Discussion

6.4.1 Effect of bio-based fertilizer on the plant reaction

The P use efficiency based on the plant reaction can be expressed in terms of the plant yield and P uptake. However, as the plant yield is mainly influenced by the N effect, as well as multiple other factors, such as micronutrient availability, the effect of P is hard to detect, especially for complex organic P fertilizers. Therefore, in literature the PUE based on the plant reaction is mostly calculated in terms of P uptake, if it is calculated at all (van Dam and Ehlert, 2008; Mohanty *et al.*, 2006). Indeed, some authors showed that there is no correlation between the crop response and the P supply (Árendás and Csathó, 2002; Prummel and Sissingh, 1983; van Dam and Ehlert, 2008).

Also in the present study, **no relevant effect of the fertilizer type on the biomass yield was observed**. For the acidic sandy soil, this is not surprising due to the high P status (Pw control > 55 mg P_2O_5 L^{-1} soil) of Flemish soils, i.e. no response to P in terms of plant growth is expected. Though, an akward observation was that on this high-P sandy soil, the use of the reference TSP resulted in lower yields and lengths as compared to all other treatments under study (Table 6.4; Fig. 6.3). A similar effect was observed in the study of, for example, van Dam and Ehlert (2008), Liu *et al.* (2011), Meena *et al.* (2007), Mohanty *et al.* (2006), and Uddin *et al.* (2012). These authors attributed this phenomenom to the fact that most of the P contained in TSP is water-soluble (96 % in this study) and therefore partly adsorbed and fixed by the substantial amount of Fe and Al oxides in acidic sandy soils (Fe_{ox} = 34 mmol kg^{-1}, Al_{ox} = 66 mmol kg^{-1} in this study). By means of a literature review, van Dam and Ehlert (2008) showed that the relative efficiency in terms of plant yield for animal manure as compared to TSP can vary between 30 and 378 % (140 % in this study). The higher values were, indeed, related to conditions that hinder the operation of the readily soluble P fertilizer reference, such as phosphate fixation by Fe and Al compounds and precipitation with Ca compounds. On Rheinsand, which had a low P level (Pw control < 36 mg P_2O_5 L^{-1} soil), the highest FW biomass yields were obtained for TSP, $FePO_4$-sludge, and struvite (Table 6.4). Hence, the above problem did not (or less) occur in this case.

As mentioned above, a more relevant comparison of the fertilizer effect may be made based on the plant P uptake. The P uptake was the highest for TSP both on sand and Rheinsand. Yet, on the P-rich soil all amendments could cover the crop P demand (no significant difference with TSP), while on the P-poor soil $FePO_4$-sludge and struvite showed a significantly lower P uptake as compared to TSP. This indicates that the initial soil P status plays an important role in determining the plant P availability and uptake. The use of pig manure and digestate resulted in a plant P uptake comparable to TSP on the P deficient soil, indicating that the absolute fertilizer effect in terms of direct available P was similar. The application of $FePO_4$-sludge resulted in the lowest P uptake (Table 6.4), indicating that the P in $FePO_4$-sludge is most fixed. This can be attributed to the lower solubility and stronger P fixation capacity of $FePO_4$ as compared to the Ca/Mg-P precipitates (struvite, TSP) under study (Hillel, 2008; Zumdahl, 2005). In general, it can be stated that **the fertilizers with the highest P solubility in water (i.e. TSP, manure, and digestate) resulted in the highest plant P uptake**.

6.4.2 Effect of bio-based fertilizer on soil phosphorus availability

6.4.2.1 Struvite

The P solubility of struvite in water was much lower as compared to the reference TSP, whereas the solubility in neutral ammonium citrate and mineral acid was relatively high (Table 6.3), in line with literature findings (Barak and Stafford, 2006; Bridger *et al.*, 1962). These measurements indicate that **struvite has slow-release properties**. This was confirmed by the bio-availability curve for Prhizon on P deficient Rheinsand (Fig. 6.6F), which showed an increase in direct available soluble P from ± 0 % to ± 75 % as compared to TSP in approximately two weeks time. Moreover, it is in line with the slow-release properties of this product for NH_4-N found in literature (Latifian *et al.*, 2012; Ryu *et al.*, 2012; Shu *et al.*, 2006; WERF, 2010).

In spite of these findings, struvite demonstrated the highest efficiency (relative to TSP) among the bio-based fertilizers in terms of direct available P on the P-rich sandy soil (Fig. 6.6A,E). This was confirmed by the significant correlation between the P-PAE for struvite and TSP on sand ($r = 0.63$, $p = 0.030$). The high PUE(PAE) and PUE(Prhizon) on sand may be attributed to the higher amount of NH_4-N relative to P_2O_5 in struvite (Table 6.1). In the study of Bridger *et al.* (1962) on struvite and other metal ammonium phosphates, P release appeared to be largely the result of microbial nitrification of the ammonium constituent rather than simple dissolution. The uptake of NH_4^+ by the roots as well as the nitrification of NH_4^+ into nitrate (NO_3^-) are acidifying processes, which can increase soil P mobilization and uptake in the rhizosphere (Bridger *et al.*, 1962; Diwani *et al.*, 2007). Indeed, during the first three weeks of growth on struvite-amended soils, the pH in the soil solution was the lowest (Fig. 6.5A), while the amount of direct available P was the highest (Fig. 6.5C). Note that a similar effect on soil P bio-availability was found when applying bio-based ammonium sulfate (AmS) during the field trials (see e.g. Section 5.3.2.2 in Chapter 5). Other contributing factors to the extra soil P liberation could be the presence of Mg in struvite (~ synergetic effect between Mg and P uptake; Gonzalez-Ponce *et al.*, 2009; Ryu *et al.*, 2012) and/or its high salt content (~ anion exchange with the clay-humus complex of the soil; Hartzell *et al.*, 2010).

At the end of the growing season, PUE(Al) and especially PUE(Pw) increased (Fig. 6.5B,C,D), indicating that struvite addition increased the soil P capacity, mainly the readily available inorganic P pool (Fig. 6.1), for delivery in the longer term. As the plant P uptake was significantly lower for struvite than for TSP on Rheinsand after five weeks of growth (Sections 6.3.2/6.4.1), it is likely that the release and plant uptake of P directly provided by struvite application was not yet completed at the moment of harvest. On the high-P sandy soil, no significant difference in plant P uptake between struvite and TSP was found, indicating that the amount of P liberated from the soil was sufficient to support the crop demand. This difference in soil P uptake on P-rich sand and P-poor Rheinsand confirms again the short-term soil P mobilization provoked by struvite application (see above). Further research on the P delivery and plant P uptake (and the corresponding mechanisms) in the longer term on different soil types with varying P status is advised for this product.

6.4.2.2 Iron phosphate sludge

Iron phosphate ($FePO_4$) sludge showed not useful as starter fertilizer for crop growth, as its P solubility in water was very low (Table 6.3), as were all soil bio-availability indices. In agreement to Hahn *et al.* (2002) and Nieminen *et al.* (2011), the solubility in neutral ammonium citrate was 100 %. Accordingly, the efficiency of this product to supply direct available P was low, and the lowest of all fertilizers under study. Yet, the P capacity over time was slightly increasing, indicating that the addition of $FePO_4$-sludge slowly increased the amount of P that can be released in the longer term. Hence, as expected, the product has slow release properties. This phenomenon was also reflected in the highly significant correlation for PAI on sand between struvite and $FePO_4$-sludge ($r = 0.86$, $p < 0.0001$). Nevertheless, as the P-PAE and Prhizon were even lower than the control, the use of this product for agricultural crop production is discouraged, especially on P-rich soils, so as to avoid further soil P accumulation. On the other hand, the product's ability to fixate P is of increasing interest for forestry on drained peat- and wetlands so as to provide a sustainable alternative for soluble P fertilizers by reducing P leaching and increasing P adsorption (Larsen *et al.*, 1959; Nieminen *et al.*, 2003, 2011; Scheffer and Kuntze, 1999; Silfverberg and Hartman, 1999). P uptake by trees can be supported by tree root/mycorrhiza associations that can release P from highly insoluble forms. Fe-containing fertilizers are not as susceptible to leaching as pure apatites and a higher proportion of added P may thus remain available to the trees. A long study period will, however, be required because of the slow development of active root/mycorrhiza associations that may be necessary for significant P release from Fe-containing P fertilizers (Nieminen *et al.,* 2003, 2011). As such, the duration of the growth response after P fertilization is expected to be over 30 years.

6.4.2.3 Digestate and animal manure

The efficiency of digestate in supplying direct available P was slightly increasing during the greenhouse experiment (Fig. 6.6A), indicating that P from digestate was released slower than from the reference TSP. The product had a relatively high P solubility in water, though lower than TSP, while its solubility in mineral acid was 100 % (Table 6.3). The PUE(Pw) was therefore high (Fig. 6.6B; Table 6.5). Pig manure released direct available P somewhat faster than digestate, as the PUE(PAE) was higher after one week, but equal after four weeks (Fig. 6.6A). In addition, its P solubility in water was slightly higher as compared to digestate, while the solubility in mineral acid was slightly lower (Table 6.3). This is in line with the observed bio-availability indices: P-PAE (Fig. 6.4A) and Prhizon (Fig. 6.5C,D) were higher for pig manure than for digestate, whereas Pw was slightly lower (Fig. 6.4B).

All these results correspond to observations made during a preceding field-scale assessment (Chapter 5, e.g. Section 5.3.2.4; Vaneeckhaute *et al.*, 2013c, 2014) and to literature data (Huang *et al.*, 2012; Möller and Müller, 2012; Güngor *et al.*, 2007; Güngor and Karthikeyan, 2008), indicating that **anaerobic (co-)digestion of animal manure reduces the fraction of direct available inorganic P in the soil solution, whereas it increases the fraction of readily available soil P that can be released in the short term**. This phenomenon would be caused by the enhanced formation and precipitation of calcium phosphate, magnesium phosphate, and/or struvite through mineralization of N, P, and Mg during (co-)digestion in combination with a substantial increase of the manure pH (Hjorth *et al.*, 2010; Le Corre *et al.*, 2009; Möller and Müller, 2012). As a comprehensive example, Güngor *et al.* (2007) showed that 43 % of the mineral P species in dairy manure were struvite and 57 % more weakly bounded dicalcium phosphate ($CaHPO_4$:$2H_2O$), whereas 78 % struvite and 22 % hydroxylapatite ($Ca_5(PO_4)_3(OH)$) were detected in the digested manure sample. Noteworthy in this perspective is that the correlation for both P-PAE and the pH in the soil solution was highly significant between struvite and digestate, with $r = 0.90$ ($p < 0.0001$) and $r = 0.85$ ($p < 0.0001$) for the P-PAE and pH, respectively. Moreover, during the field trial a significant correlation was found between the Ca, Mg, and P use efficiency when applying digestates or its liquid fraction (Chapter 5: Section 5.3.2.4). Consequently, the conversion of animal manure through anaerobic (co-)digestion and the subsequent use of digestate on agricultural fields may offer a solution to control water soluble P in soils, meanwhile supplying sufficient P to support plant growth, similar as was observed during the field trial (Chapter 5).

Another interesting finding is that the P intensity of the soil, measured as P-PAE, was lower for digestate and pig manure than for TSP (Fig. 6.4A), while Prhizon was higher, especially for pig manure (Fig. 6.5C,D). It is likely that this extra amount of soluble P for the organic fertilizers, digestate and pig manure, was attributed to the release of organic P_2O_5 in the soil solution (Huang *et al.*, 2012; Roboredo, 2012), which cannot (or not completely) be measured with the PAE method. Indeed, the P-PAE number was significantly correlated for the mineral fertilizers, struvite and TSP ($r = 0.63$, $p < 0.0001$), but no significant correlation was found between the P-PAE measurements for the other products. On the other hand, on Rheinsand, the correlation of P in the soil solution (Prhizon), which includes dissolved organic forms, between TSP and pig manure ($r = 0.76$, $p < 0.0001$), as well as TSP and digestate ($r = 0.73$, $p < 0.0001$), was significant, although only a relatively weak correlation was found between TSP and struvite ($r = 0.59$; $p = 0.010$). Huang *et al.* (2012) emphasized that this organic dissolved P fraction in soils also plays a role in plant P utilization. Hence, **measurements carried out in the context of fertilizer recommendations and legislative standards should be able to detect both inorganic and organic P fractions**.

As the average PUE(Prhizon) was much higher for pig manure than for TSP, both on sand and Rheinsand (Fig. 6.6E,F), and since pig manure is a liquid fertilizer, application of this product might cause a higher risk of leaching in the field, especially on soils low in Fe and Al (cfr. Kang *et al.*, 2011; Yang *et al.*, 2012). Since also the efficiency in terms of P uptake and yield on sand was slightly higher (Table 6.4) and the soil pH significantly higher for the digestate treatment than for pig manure (Fig. 6.5), treating manure by anaerobic (co-)digestion before field application appears again as an interesting option from an environmental point of view. Meanwhile renewable energy can be produced. Although it is likely that similar results will be obtained for each digestion process fed with animal manure, it should be noted that the present results are based on digestate from co-digestion of pig manure (30 %) with organic biological waste from the food industry (40 %) and energy maize (30 %).

Finally, an interesting point is that all bio-based fertilizers under study, especially digestate, added significantly more organic carbon (OC) to the soil as compared to TSP (Table 6.2). Application of these products could therefore also **contribute to the struggle against OC depletion** in many agricultural soils worldwide.

6.4.3 Practical implications and recommendations

In the wastewater and manure processing industry, Fe- and Al-salts are often used for P removal during solid-liquid separation so as to improve coagulation/flocculation practices and achieve water discharge levels. However, this chapter indicates that the resulting $FePO_4$-sludge is not valuable for reuse as a fertilizer in terms of P release for crop growth. An increased accumulation of P in the soil is expected when using the product for agricultural purposes. Its use may be interesting on drained soils, though this remains to be evidenced. Similar results will likely be obtained for $AlPO_4$-sludge because of the comparable P binding properties of trivalent Fe and Al. However, the fertilizer effect of $AlPO_4$-sludge in terms of P bio-availability remains to be confirmed.

In the transition towards a more efficient use of nutrients in agriculture, alternative P recovery and/or release techniques are recommended instead of the traditional methods for P removal. The present chapter demonstrates that manure treatment via anaerobic (co-)digestion (with other bio-degradable wastes) and/or struvite precipitation may deliver sustainable substitutes (digestate, struvite) for chemical P fertilizers and/or animal manure in agriculture. Moreover, the application of struvite may increase the liberation of P from the soil complex in high-P soils. Field-scale assessments using these bio-based products on soils with different P status are suggested to evaluate the P release and uptake in the long term, and to provide sufficient information for the establishment of responsible fertilizer application recommendations.

Although these new fertilizers are already produced and available today (quantities depend on the region, i.e. legislations, nutrient excesses, etc.; Chapter 2), marketing of these products also depends on the economic viability of the nutrient recovery/release technique in question and the economic competitiveness of the products as compared to commonly used fertilizers (Chapter 2). Herewith another important bottleneck arises: in many regions all derivatives produced from animal manure are currently still categorized as ‘animal manure’ and/or ‘waste’ in environmental and/or fertilizer legislation and can therefore not or only sparingly be returned to agricultural land (see previous chapters). Hence, the need exists for greater differentiation between soils, crops, and fertilizer types in the recommendations given on P fertilizer requirements (EC, 2003), as well as in fertilizer legislations. For example, in the Flemish fertilizer regulation (MAP 4, 2011), currently only one standard for total P application as function of the crop type counts. In contrast to N standards, no distinction is made between P application from animal manure, alternative organic fertilizers, or mineral fertilizers. Moreover, the standard is currently independent of the soil P status and soil texture. Only for P saturated sandy soils one stricter norm exists, but even here no further classification is imposed.

Nevertheless, in the present study, important differences in P solubility and bio-availability for various P fertilizers and different soil P statuses were observed. Hence, a more refined legislative framework in terms of P application is advised. For this purpose, a combination of measurements of the soil chemical P status, texture, and fertilizer properties (mainly P fractionation, NH_4:P-ratio, and P-binding compounds as Fe, Al, Ca, and Mg), in addition to the crop demand for P, is recommended. Regarding the aim to reduce P leaching and run-off, the most important parameter to evaluate is direct available P. As the P-PAE method does not (sufficiently) account for the release of dissolved organic P, measurements with Rhizon SMS are proposed as a valuable complementary method to provide the fundamental information for better categorization of different P fertilizers in environmental and fertilizer legislations. Bio-availability indices based on the crop yield are generally less conclusive, hence their use is less advisable.

Besides pot experiments, the use of Rhizon SMS in field trials is possible, but the samplers have to be inserted in the soil from trenches. Trenches disturb, however, the hydraulic properties of the soil. Less mobile elements may be sampled correctly from trenches, but concentrations of mobile nutrients may differ from those in undisturbed soil due to differing soil water conditions (Eijkelkamp, 2003). An alternative for trenches are manholes, e.g. augered with an Edelman auger. Further research on the soil disturbing impact of the various sampling methods at field-scale compared to results obtained from controlled greenhouse experiments is recommended.

Finally, an important note is that, due to legislative constraints, the current practice of digestate processing in P saturated regions mostly involves a solid-liquid separation step (Chapter 2: Section 2.3.2). The purpose is basically to concentrate the organic matter, P, Ca, and Mg in a thick fraction, which can then be pasteurized and exported (to P-poor regions). As such, the P recovery potential as concentrated and pure struvite from the liquid fraction is limited, although (local) recovery of this mineral fertilizer may be interesting and relevant, e.g. for horticultural purposes or for crops with high (bio-available) P demand. Moreover, through export, the valuable and effective organic carbon (Chapter 2: Section 2.2; Appendix 3) is eliminated from the local agricultural cycle, while organic carbon depletion in many soils worldwide has become an alarming issue. This leads to the suggestion to stimulate the release of P in the liquid fraction for subsequent mineral (and pure) P recovery as struvite. As such, thick fractions with a more interesting (i.e. higher) C:P-ratio for local reuse as soil conditionner can be recovered, and soil organic carbon could be maintained. Pre-treatment methods to improve the release of P in the liquid fraction during solid-liquid separation are therefore gaining importance in P saturated regions. This will be aspect of Chapter 7.

6.5 Conclusions and perspectives

Greenhouse experimental results indicate that some P-containing recovered bio-based products can be used as sustainable substitute for chemical P fertilizers and/or animal manure in agriculture. Struvite provided a high P availability for the plant in the beginning of the growing season, as well as a stock for delayed slow release. The product seems to stimulate the liberation of P from the soil complex, thereby providing sufficient direct plant available P to support plant growth on P-rich sandy soils. The addition of $FePO_4$-sludge proved not useful in terms of short-term P release. Its use as a fertilizer for agricultural crop production should be discouraged. Hence, from an agronomic point of view, the implementation of struvite recovery in waste(water) treatment facilities seems more valuable than traditional practices of P removal using Fe-salts. Moreover, the P use efficiency in animal manure could be improved via anaerobic (co-)digestion and application of the resulting digestate for crop production. As added benefits, negative environmental impacts of untreated animal manure are avoided, renewable energy is produced, important amounts of organic carbon are added to the soil, and the soil pH is maintained.

Furthermore, this study confirmed previous literature findings that chemical soil analyses are more conclusive than the plant reaction in terms of P fertilizer performance. The additional use of Rhizon soil moisture samplers for determination of total direct available P is proposed for better understanding and categorization of different inorganic and organic P fertilizers in environmental and fertilizer legislations. This may contribute to an improved differentiation between soils, crops, and fertilizer types in the recommendations and standards given on P fertilizer requirements. Indeed, a classification of P application standards in terms of the soil P status, texture, and fertilizer properties, next to the crop P demand, is recommended. Based on the results of the presented greenhouse experiment, field-scale validation of recovered struvite and digestates as compared to animal manure and chemical P fertilizers seems worthwhile. Particular attention should be given to the soil bio-availability indices, including Prhizon, on various soil types with different texture and P status. This should further help to refine the P fertilizer legislations and associated recommendations.

CHAPTER 7:

COMPARATIVE EVALUATION OF PRE-TREATMENT METHODS TO ENHANCE PHOSPHORUS RELEASE FROM DIGESTATE

Mechanical solid-liquid separation of digestate (left) and struvite produced from the liquid fraction of digestate (right) (Pictures: Vaneeckhaute C.)

Redrafted from:

Vaneeckhaute, C., Zeleke, A., Tack, F.M.G., Meers, E., in preparation. Comparative evaluation of pre-treatment methods to enhance phosphorus release from digestate.

Abstract

Although struvite may serve as a valuable chemical fertilizer substitute, the potential to recover mineral phosphorus (P) fertilizers from the liquid fraction of digestate is often limited as most of the P ends up in the thick fraction after solid-liquid separation. Moreover, in P saturated regions the thick fraction is usually transformed into an exportable end product, and hence valuable nutrients (P, Ca, Mg) and organic carbon (OC) are eliminated from the local agricultural cycle. The aim of this chapter was to evaluate various pre-treatment methods to improve the amount of P released in the liquid fraction after solid-liquid separation. As such, the P recovery potential from the liquid fraction as concentrated fertilizer product (struvite, Ca/Mg-P precipitates, or P-rich solutions) can be increased, whereas soil OC can be maintained through local recycling of the resulting (P-poor) organic thick fraction. Four different mechanical pre-treatments (microwave heating, conventional heating, ultrasonic treatment, and orbital shaking) were tested in combination with the chemical dosing of three different acids (citric acid, formic acid, and HCl) down to pH 4, 5, and 6. All pre-treatments proved effective in releasing ortho-P into the liquid fraction at all tested pH values, except for orbital shaking, which was of interest only using citric acid at pH 6. The pre-treatments released 13-28 % soluble ortho-P relative to total P. Based on the experimental results, overall the maximum P release efficiency was obtained using microwave heating (1 h at 70 ℃) and citric acid at pH 5. However, when balancing the recovery efficiency with the acid costs, the addition of HCl down to pH 4 under microwave heating was most feasible. Nevertheless, if no pasteurization (defined as 1h heating at 70 ℃) is required for fertilizer marketing, then orbital shaking (i.e. mixing in practice) with HCl addition may be more attractive, considering the ease of implementation and costs of the mechanical treatment. In general, the chemical costs as function of the P release efficiency were high for all pre-treatments: ± € 8-700 *(11-990 CAD)* kg^{-1} P released in addition to the untreated control. Further substantive case studies are required in order to conclude on the economic feasibility of implementing such pre-treatments for P release from digestate at full-scale.

Keywords: *acidification, conventional heating, microwave heating, orbital shaking, pasteurization, ultrasonic treatment.*

Résumé

Bien que la struvite peut servir comme un important substitut aux engrais chimiques, le potentiel de récupération des engrais minéraux de la fraction liquide du digestat est souvent limité car le phosphore (P) se retrouve essentiellement dans la fraction solide après la séparation solide-liquide. De plus, dans les régions saturées en P la fraction solide est généralement transformée en un produit fini exportable, et donc certains nutriments importants (P, Ca, Mg) et le carbone organique (CO) sont éliminés du cycle agricole local. L'objectif de ce chapitre était d'évaluer des diverses méthodes de prétraitement augmentant la quantité de P libéré dans la fraction liquide après séparation solide-liquide. Comme telle, le potentiel de récupération des engrais concentrés (struvite, Ca/Mg-P précipités ou des solutions riche en P) de la fraction liquide peut être augmenté, et le carbone organique du sol peut être maintenu grâce au recyclage local de la fraction solide organique (pauvre en P). Quatre différents prétraitements mécaniques (micro-onde, chauffage conventionnel, traitement par ultrasons et agitation orbitale) ont été testés en combinaison avec le dosage chimique de trois acides différentes (l'acide citrique, l'acide formique et le HCl) à des pH de 4, 5 et 6. Tous les prétraitements se sont avérés efficaces pour la libération de P dans la fraction liquide à toutes les valeurs de pH testées, à l'exception de l'agitation orbitale à pH 6, qui était seulement intéressant en dosant l'acide citrique. Les prétraitements ont libérés 13-28 % d'ortho-P soluble par rapport au P total. D'après les résultats expérimentaux, la meilleure efficacité globale de libération de P a été obtenue en utilisant une combinaison des micro-ondes (1 h à 70 °C) et l'acide citrique jusqu'à un pH de 5. Afin d'équilibrer le rendement de récupération avec les coûts du traitement, l'utilisation de HCl à pH 4 sous micro-ondes était l'option la plus réalisable. Cependant, si aucune pasteurisation (définie comme 1 h de chauffage à 70 °C) n'est nécessaire pour la commercialisation des engrais, alors l'ajout de HCl sous agitation orbitale (c'est à dire mélanger dans la pratique) semble l'option la plus attrayante, compte tenu de la facilité de mise en œuvre et les coûts du traitement mécanique. En général, les coûts des produits chimiques en fonction de l'efficacité de libération de P étaient élevés pour tous les prétraitements: ± € 8-700 *(11-990 CAD)* kg^{-1} P libéré en plus du contrôle non traité. Davantage études de cas approfondies sont nécessaires afin de conclure sur la faisabilité économique de la mise en œuvre de ces prétraitements pour la libération de P à pleine échelle.

Mots-clés: *acidification, agitation orbitale, chauffage conventionnel, traitement micro-ondes, traitement par ultrasons, pasteurisation.*

7.1 Introduction

The recovery and efficient use of phosphorus (P) has become an important challenge in light of natural P resources that are rapidly depleting and the increasingly strict legislative standards for P application to agricultural soils. The latter results from the observed P accumulation in many soils worldwide caused by excessive manure (and sludge) application. Previous chapters (Chapters 5-6) have shown that the P use efficiency (PUE) in animal manure may be increased through anaerobic (co-)digestion. Indeed, during digestion, struvite precipitation may occur, as well as calcium (Ca) and magnesium (Mg) phosphate formation, which both end up in the digestate, thereby improving its slow-release properties (Güngor *et al.*, 2007; Güngor and Karthikeyan, 2008). However, due to legislative constraints, processing of digestate is required (especially in high-nutrient regions) in order to obtain exportable end products, concentrated mineral fertilizers (= chemical fertilizer substitutes), or environmentally neutral compounds. As such, current digestate processing practices mostly involve a solid-liquid separation step. In P saturated regions, the thick fraction is then transformed into an organic end product fit for export, and hence valuable nutrients (P, Ca, Mg) and organic carbon (OC) are eliminated from the local agricultural cycle (Chapters 2-3). As a consequence, also soil organic carbon depletion has become an important issue worldwide (Bhandari *et al.*, 2002; Manna *et al.*, 2005). This leads to the suggestion to enhance the release of soluble orthophosphates (i.e. inorganic soluble PO_4-P) in the liquid fraction during solid-liquid separation (after or prior to digestion) in order to obtain: i) a stabilized carbon-rich soil conditioner with increased local marketing potential, and ii) a P-rich liquid fraction with increased potential for P recovery as high-purity struvite, Ca/Mg-P precipitates, or a concentrated P-solution. A local market for the latter products may exist in the horticultural sector, for crops with high P demand, and/or for industrial purposes.

Methods that have been used to improve the P release from (digested) manure and/or sludge mainly consist of microwave heating, advanced oxidation, and acidification to around pH 4 (Danesh *et al.*, 2006; Harris *et al.*, 2008; Huchzermeier and Tao, 2012; Jin *et al.*, 2009; Qureshi *et al.*, 2008; Zeng and Li, 2006; Zhang *et al.*, 2010). Microwave heating would help in digesting organic P and polyphosphates, i.e. salts or esters of polymeric oxyanions formed from tetrahedral PO_4, that are often available in animal manure (Jin *et al.*, 2009; Qureshi *et al.*, 2008). However, Pan *et al.* (2006) have shown that additional acidification is required in order to effectively improve the P release from dairy manure, which is not the case for sewage sludge (Liao *et al.*, 2005). Acidification followed by solid-liquid separation concerns a potential low-cost option to concentrate P ions in the liquid fraction for direct use in the horticultural sector as concentrated P-solution, or for subsequent precipitation as pure struvite or Ca/Mg-P precipitates. Both organic acids, such as citric acid (Szogi *et al.* 2008) and formic acid (Daumer *et al.*, 2010), and mineral acids, as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) (Müller *et al.*, 2005; Szogi *et al.* 2008), have been used for this purpose.

Although the potential of some of the above techniques to improve the P release in the liquid fraction has already been shown at lab-, pilot-, and even full-scale (e.g. acidification of digested sludge in the Seaborne process; Müller *et al.*, 2005), limited research comparing (combinations of) various pre-treatment methods for P release has been conducted to date, definitely not for the treatment of digestate. As such, the application of efficient and cost-effective pre-treatments is still limited, as there is no common basis comparing the P release efficiency in relation to the costs of the pre-treatment methods involved. Moreover, on top of the above methods, ultrasonic treatment is gaining importance to improve the bio-degradability and/or dewatering of manure or sludge (Ruiz-Hernando *et al.*, 2013; Wu-Haan *et al.*, 2010). Also conventional heating is often applied for product (digestate/manure/sludge) pasteurization (Chapters 2-3; Ruiz-Hernando *et al.*, 2013). Nevertheless, studies on the P release when applying these pre-treatments (whether or not in combination with acidification) are lacking in literature, though relevant because of their increasing use.

This chapter aims to compare (combinations of) promising pre-treatment methods (acidification + mechanical treatment) to improve the P release from digestate. The selected mechanical pre-treatments involve microwave heating, conventional heating, ultrasonic treatment, and orbital shaking (i.e. mixing in practice), whereas the chemical pre-treatments concern the addition of the organic acids, citric acid and formic acid, and the mineral acid, HCl. The heat treatments were applied so as to respect the European standards for product pasteurization, i.e. 1 h heating at 70 °C according to the regulation EG 1069/2009 (formal 1774/2002; EC, 2002, 2009). A comparative economic evaluation of the various treatments based on the chemical cost as function of the P release efficiency is also presented.

Note that these treatments can be applied on liquid waste streams both prior or after anaerobic digestion. In this study, it was aimed to test the treatments on the non-degraded digestate. This is of increasing interest as the thick fraction after pre-treatment and solid-liquid separation can (partially) be fed back into the anaerobic digester for further improved degradation and organic waste stabilization (Lindner *et al.*, 2015). Indeed, during anaerobic digestion only a part of the available organic matter is transformed into biogas. The digestate hence still contains a large fraction of organic matter that potentially can be converted. By application of a disintegration technique (pre-treatments above) on the digestate and subsequent recirculation to the digester, the overall degradation potential could be significantly increased, while reactor dimensions can be reduced and a more stabilized soil conditioner is obtained (Lindner *et al.*, 2015; Müller *et al.*, 2005; Saha *et al.*, 2011). All this may come on top of the potential improved P recovery when applying a pre-treatment. Yet, important is the finding of Jin *et al.* (2006) that H_2SO_4-based pre-treatments result in a low anaerobic digestability due to sulfur (S) inhibition, unlike HCl. Moreover, it leads to high concentrations of hydrogen sulfide (H_2S) in the biogas, which are unwanted in terms of corrosion risks in subsequent piping and equipment. H_2S is also highly toxic to humans, even at low concentrations, and odorous when escaping from the system. Therefore, HCl was selected as mineral acid for the purpose of this study.

7.2 Materials and methods

7.2.1 Experimental set-up

Digestate (20 L) was collected at Wittevrongel Eneco Energy, Aalter, Belgium, and transported to the laboratory within 1 h, carried in cooler boxes filled with ice. It concerns a mesophilic (35 ℃) anaerobic (co-)digestion plant (capacity: 60,000 ton y^{-1}, 3.033 MW_{el}), with an input feed mainly consisting of (dairy) manure, additionally supplied with organic biological by-products provided by the food industry (percentage depends on the availability). The sample was stored at a temperature of 4 ℃ before use. Prior to the pre-treatment, the digestate was homogenized and physicochemically analyzed as described in Section 7.2.2. The product characteristics are given in Table 7.1.

Table 7.1 Physicochemical characteristics of the digestate used for the various pre-treatments (mean ± standard deviation; n = 2). DW = dry weight; EC = electrical conductivity; OC = organic carbon.

Parameter	Value
pH	7.8
EC (mS cm^{-1})	30 ± 0
Density (g L^{-1})	1,047 ± 5
Dry weight (%)	7.4 ± 0.0
OC (% on DW)	31 ± 0
Alkalinity (g HCO_3 L^{-1})	17 ± 0
Total P (mg L^{-1})	422 ± 24
Soluble ortho-P (mg L^{-1})	48 ± 7
Inorganic P (mg L^{-1})	244 ± 12
Organic P (mg L^{-1})	178 ± 31
NH_4-N (g L^{-1})	3.0 ± 0.0
Total Ca (mg L^{-1})	338 ± 80
Total Mg (mg L^{-1})	117 ± 10
Total K (g L^{-1})	4.5 ± 0.0
Total Na (g L^{-1})	2.3 ± 0.1

An overview of the experimental set-up can be found in Figure 7.1.

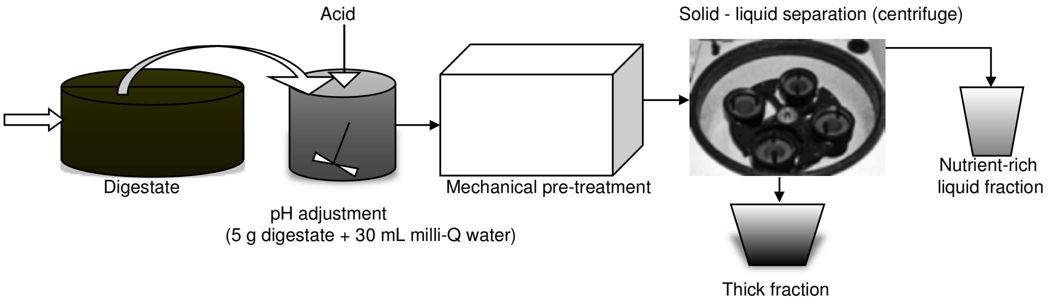


Figure 7.1 Overview of the experimental set-up for pre-treatment (acidification + mechanical treatment) of digestate to improve the P release efficiency in the liquid fraction after solid-liquid separation.

Homogenized subsamples were taken for pre-treatment. Four mechanical pre-treatments were used, each in combination with three different acids and adjusted to three different pH values (4, 5, and 6). For each treatment, 5 g of digestate was weighted on an electronic balance (CP8201, Sartorius, Göttingen, Germany) and 30 mL of milli-Q (i.e. ultrapure) water was added to the sample. The latter was necessary for correct pH-adjustment and to avoid foaming. The samples were adjusted to pH 4, 5, and 6 by addition of the acid (2 M) using a micropipette and a pH-meter, during continuous stirring on a magnetic stirrer (Cenco Instruments b.v., Breda, the Netherlands). The amount of acid required was recorded. In addition, for each treatment, a control (= no acid addition) was prepared, resulting in a total of 48 different pre-treatments (4 mechanical treatments, 3 acids, 3 pH-values, 12 controls). All pre-treatments were prepared in triplicate (= total of 144 treatments).

For the microwave and conventional heating pre-treatments, the samples were weighted before and after the treatments. The water lost through evaporation was added to each sample. All treated samples were transferred to centrifuge tubes (45 mL) and decanted using a laboratory centrifuge (Heraeus megafuge 1.0, Kendro Laboratory Products, Hanau, Germany) at 3,000 rpm for one min. The liquid fractions were separated from the solid fractions, filtered through 0.45 µm pores, diluted with distilled water in 50 mL volumetric flasks, and manually transferred to test tubes for physicochemical analysis of soluble ortho-P (Section 8.2.2).

Organic acids (formic acid, 90 % CH_2O_2 and citric acid, 100 % $C_6H_8O_7$, each 2 M) and mineral acid (hydrochloric acid, 37 % HCl, 2 M) were used. These chemicals were applied to the digestate samples to adjust the pH down to 4, 5, and 6 before using the mechanical pre-treatments. The duration and temperature of the mechanical pre-treatments that involve heat were chosen in line with the European requirements for product pasteurization, i.e. 1 h heating at 70 °C or a proven equivalent (EC, 2002, 2009). As such, the subsequent recovered products (concentrated P-solution, struvite, or Ca/Mg-P precipitates) could be recognized as a valuable chemical fertilizer substitute for horticultural purposes (strict hygienic requirements) and/or for export. Also the remaining organic thick fraction is pasteurized in this way. The following mechanical pre-treatments were applied:

1. A time-controlled orbital shaker (GFL 3015, Gesellshaft für Labortechnik mbH, Burgwedel, Germany): All samples were shaken at 200 rpm during 60 min in 250 mL erlenmeyer flasks;
2. A conventional heating plate (HT22, Harry Gestigkeit GmbH, Düsseldorf, Germany): The temperature was adjusted to 70 °C and the power to 100 watt %. The samples were treated for 60 min in an erlenmeyer flask;
3. A temperature-controlled ultrasonic bath (Bandelin Electronic 12207, Berlin, Germany), with a basket to keep the samples away from the tank base: The basket was filled with distilled water up to the minimum water requirement for use (± 15 cm water height). The temperature was adjusted to 25 °C and the samples were treated for 15 min in 100 mL erlenmeyer flasks;
4. A microwave oven (CEM MARS 5, Drogenbos, Belgium): It concerns an open microwave digester, equipped with a rotating microwave diffuser for homogenous

microwave distribution. The system is capable of accommodating up to 36 volumetric flasks at one run. Centrifuge tubes of 45 mL were used, consisting of a control cap with a vent tube. A temperature sensor was inserted through a hole on top of the microwave oven into the sealed tubes. The temperature was fixed at 70 °C and the power output was fixed at 600 W. The samples were treated for 1h.

7.2.2 Physicochemical analysis

The DW content was determined as residual weight after 72 h drying at 80 °C in an oven (EU 170, Jouan s.a, Saint Herblain, FR). Organic carbon (OC) was determined after incineration of the dry samples during 4 h at 550 °C in a muffle furnace (Nabertherm, Lilientahl, DE). The loss of ignition (= weight loss after incineration) was divided by a conversion factor of 1.72 to calculate OC, hence assuming that organic matter contains 58 % OC (Van Ranst *et al.*, 1999). Electrical conductivity (EC) and pH were determined potentiometrically using a WTW-LF537 (Wissenschaftlich Technischen Werkstäten, Weilcheim, DE) electrode and an Orion-520A (Orion Research, Boston, USA) pH-meter, respectively. Ammonium (NH_4) was determined using the Kjeltec-1002 distilling unit (Gerhardt Vapodest, Köningswinter, DE) after addition of magnesium oxide (MgO) to the sample and subsequent titration (Van Ranst *et al.*, 1999). The initial total P content in the digestate sample was determined using the colorimetric method of Scheel (1936; Van Ranst *et al.*, 1999) after wet digestion using nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). The initial amount of inorganic P was determined by the method of Møberg and Petersen (1982), while organic P was computed by the difference between total P and inorganic P. Soluble ortho-P was analyzed using the method of Scheel (1936) in the liquid fraction after centrifugation and filtration (0.45 µm pores). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, UK). Total calcium (Ca), magnesium (Mg), and potassium (K) were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX, Palo Alto, CA, USA; Van Ranst *et al.*, 1999) after wet digestion in HNO_3 and H_2O_2. Bicarbonate (HCO_3^-) alkalinity was determined by the titration method described by Van Ranst *et al.* (1999).

7.2.3 Statistical analysis

Statistical analyses were conducted using SAS 9.3. A one-way ANOVA model (α = 0.05) was used to compare the effect of the various pre-treatments (i.e. the independent variable, between-groups factor) on the amount of P released (i.e. the dependent variable). For each mechanical treatment, significant differences between the three applied acids were searched per pH value. Moreover, for each acid used, the effect of the mechanical pre-treatment was checked at each pH value under study. The condition of normality was verified using the Kolmogorov Smirnov test and QQ-plots, whereas equality of variances was checked with the Levene Test. When homoscedascity was found, significance of effects was tested by use of an F-test and post-hoc pair-wise comparisons were conducted using Tukey's honestly significant difference (HSD) test (α = 0.05). When no homoscedascity was found, a Welch F-test combined with a post-hoc Games-Howell test was used (α = 0.05). When the condition of normality was not fulfilled, the non-parametric Kruskal-Wallis test was applied instead of the one-way ANOVA.

7.3 Results

7.3.1 Acid requirements

The amount of acid (mol L^{-1} digestate) required to reach pH 4, 5, and 6 is presented in Figure 7.2. The initial pH of the solution (5 g digestate + 30 mL milli-Q water) was about 8.3.

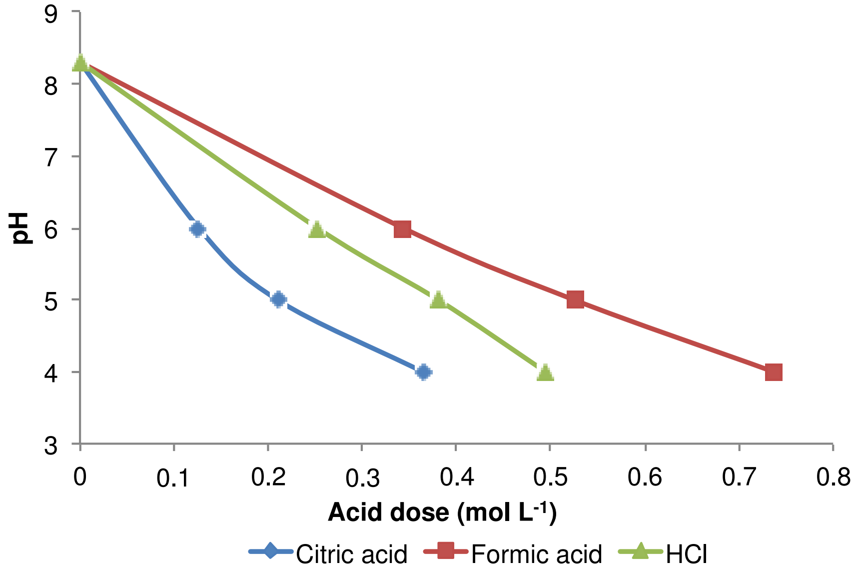


Figure 7.2 Amount of acid (citric acid, formic acid, HCl) used (mol acid L^{-1} digestate) to reach the required pH (4, 5, or 6) for the pre-treatment. Initial pH (5 g digestate + 30 mL milli-Q water) = 8.3.

It can be seen that for the same amount of acid, the obtained pH decreased from formic acid to HCl and citric acid. Hence, the amount of acid needed to obtain a certain pH increased reversely.

7.3.2 Orthophosphate release

The amount of orthophosphate released from digestate (mg P L^{-1}) as function of the pre-treatment is presented in Figure 7.3. The ortho-P release without any pre-treatment (no mechanical treatment and no acidification) was 48±7 mg L^{-1} or about 11 % of the initial total P (Table 7.1). Especially for the microwave and conventional heating pre-treatments, occasionally large standard deviations on the results were obtained. These can be attributed to dilution errors when adding water to replace water lost through evaporation (see Section 7.2.1).

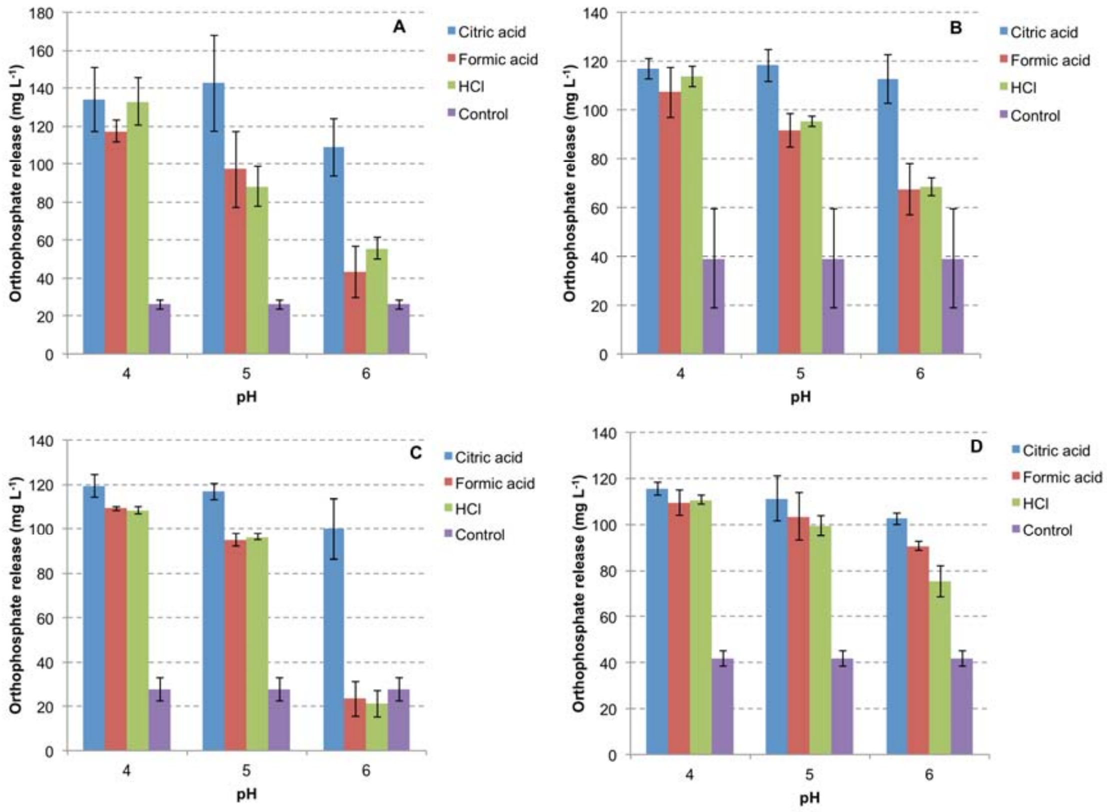


Figure 7.3 Concentration of orthophosphate released from digestate (mg P L^{-1} digestate; mean ± standard deviation; n = 3) after pre-treatment at pH 4, 5, and 6 as function of the chemical (citric acid, formic acid, HCl) and mechanical treatment used: A = microwave heating, B = conventional heating, C = orbital shaking, and D = ultrasonic bath. Control = no acidification. Note: initial ortho-P concentration without pre-treatment = 48±7 mg L^{-1}.

All pre-treatments resulted in a significant effect ($p < 0.05$) on the ortho-P release as compared to the control (no acid addition) and to the untreated digestate, except for orbital shaking in combination with HCl and formic acid at pH 6. Citric acid generally released more soluble ortho-P ions into the liquid fraction as compared to the other acids, which was significant ($p < 0.05$) at pH 6 for all mechanical pre-treatments and at pH 5 for microwave treatment, orbital shaking, and conventional heating. At pH 4, no significant differences ($p > 0.05$) between the different acids per mechanical treatment were found, except for orbital shaking, where the use of citric acid again resulted in the highest ortho-P release. For the ultrasonic treatment, the use of formic acid also resulted in a significantly higher ortho-P release as compared to HCl at pH 6.

Using the same molar concentration of acid (hence the same pH) for all mechanical pre-treatments, no statistically significant difference ($p > 0.05$) between the mechanical pre-treatment methods in releasing soluble ortho-P ions was found with citric acid. For formic acid at pH 6, the ultrasonic treatment showed a significantly higher P release than all other mechanical pre-treatments, while conventional heating also released significantly more P than orbital shaking. These effects disappeared at lower pH values. At pH 4, the microwave treatment showed a significantly higher P release than orbital shaking. No other significant differences between the various mechanical pre-treatments at pH 4 and 5 were observed using formic acid. The P release for HCl at pH 6 was significantly higher for conventional heating and ultrasonic treatment as compared to the microwave treatment, which on its turn showed significantly higher values than orbital shaking. Nevertheless, these effects disappeared at lower pH values, and at pH 4 the microwave treatment showed again a significantly higher effect than all other mechanical pre-treatments under study.

For each mechanical pre-treatment, the maximum obtained ortho-P release (mg L^{-1}) using the different acids is presented in Figure 7.4.

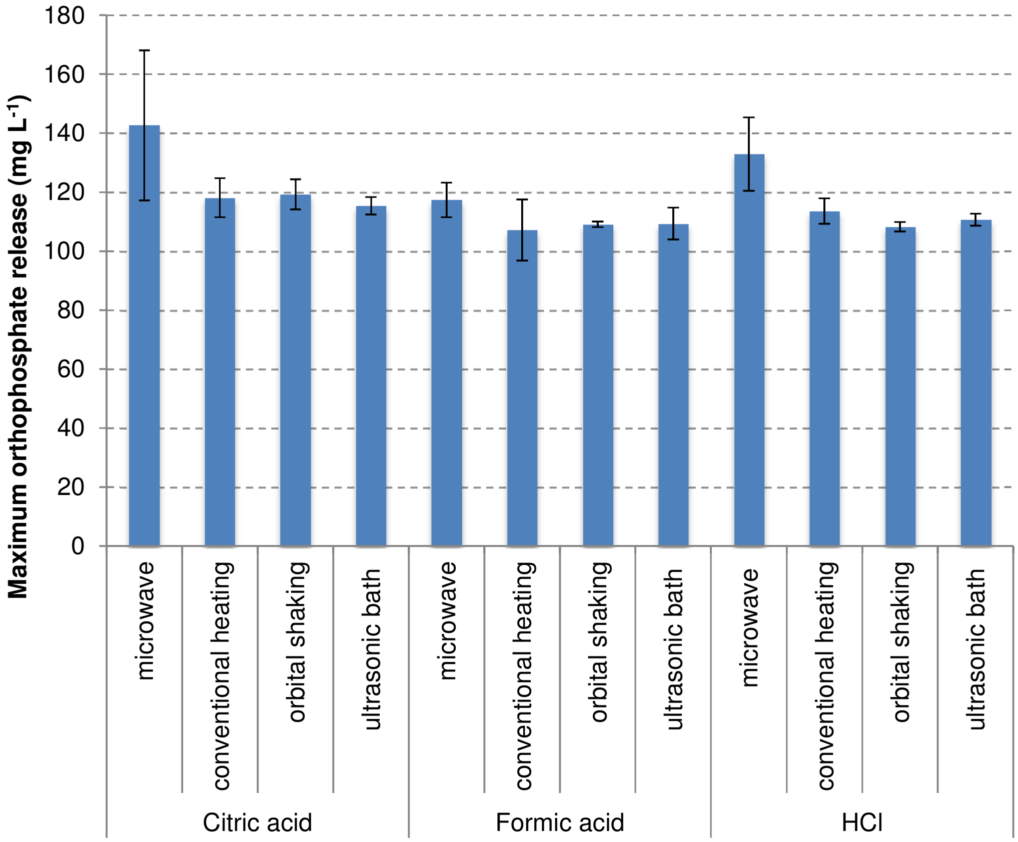


Figure 7.4 Maximum concentration of orthophosphate (mg P L^{-1} digestate; mean ± standard deviation; n = 3) released from digestate as function of the chemical and mechanical pre-treatments used. All results are the maximum concentrations at pH 4, except for citric acid: maximum concentration at pH 5 for microwave and conventional heating.
Note: initial ortho-P concentration without pre-treatment = 48±7 mg L^{-1}.

Interestingly, for citric acid under microwave and conventional heating pre-treatments, the maximum amount of ortho-P released was found at pH 5. For the other acids, the maximum release was found at pH 4, independently of the mechanical treatment. The highest average ortho-P release was found for the combination of citric acid and microwave treatment at pH 5 (143±26 mg L^{-1}), which was comparable to that of HCl and microwave treatment at pH 4 (133±12 mg L^{-1}). The maximum obtained ortho-P release with formic acid was in average slightly lower, i.e. 117±6 mg L^{-1} under microwave heating at pH 4.

7.4 Discussion

All physicochemical pre-treatments used, resulted in higher concentrations of soluble ortho-P ions in the liquid fraction as compared to the control (no acidification) and to the untreated digestate, except for orbital shaking in combination with HCl and formic acid at pH 6. Hence, the combination of the applied mechanical instruments and acids were found to be effective in increasing the release of ortho-P in the liquid fraction of digestate, although orbital shaking at pH 6 was only of interest with addition of citric acid.

It should be remarked that the mechanical treatments alone were not effective in improving the release of ortho-P in the liquid fraction, similar as was previously observed by Pan *et al.* (2006) for microwave digestion of dairy manure. Little to no hydrolysis would occur without acidification. These authors attributed this inconvenience to the inherent characteristics of manure. The phosphorus in manure exists in many forms, such as inorganic residual P, acid-soluble organic P, and lipid P, which are neither very soluble nor easily hydrolised. This was likely also the case for the digestate under study, which was mainly produced from dairy manure. Indeed, in the case of livestock residues, the hydrolysis step in anaerobic digestion is restricted by the presence of fibers, resulting in a low anaerobic degradation, and hence high digestate fiber concentration (Gonzalez-Fernandez *et al.*, 2008; Zwart *et al.*, 2006). In this study the synergetic effect of acidification and mechanical treatment was the most expressed for microwave heating, which at lower pH (4), hence higher acidification, showed a significantly higher P release than the other mechanical treatments when using formic acid or HCl. Looking at all three acids, the ultrasonic treatment seems to be the most capable mechanical pre-treatment for releasing ortho-P from digestate at a higher pH (6). Literature evidence to support this finding is lacking for digestate. However, Saha *et al.* (2011) found that ultrasonic treatment was more effective than microwave heating (without acidification) for COD (chemical oxygen demand) solubilization of various sewage sludges. This may support the improved P release found in this study at relatively high pH (6) for HCl and formic acid under the ultrasonic treatment. Interestingly, when using citric acid, all mechanical pre-treatments were very effective at pH 6 (see below).

The maximum P release efficiency (%) provoked by the various pre-treatment methods is presented in Figure 7.5. It was calculated as the difference between the maximum amount of ortho-P release achieved with the pre-treatment at the respective pH (Fig. 7.4) and the ortho-P release without pre-treatment (48±7 mg L^{-1}), relative to the total initial amount of P in the digestate (Table 7.1). **The pre-treatments released 12-28 % soluble ortho P.** Alternatively, the absolute (maximum) P release compared to total P (hence not correcting for the untreated control) ranged from 25 to 40 %, which is about 2.3 to 3.6 times higher as compared to not applying a pre-treatment at all (± 11 %). Note that the latter value corresponds well to the value obtained at full-scale during solid-liquid separation in Chapter 3, i.e. ± 9 % of the total P ended up in the liquid fraction (Vaneeckhaute *et al.*, 2012).

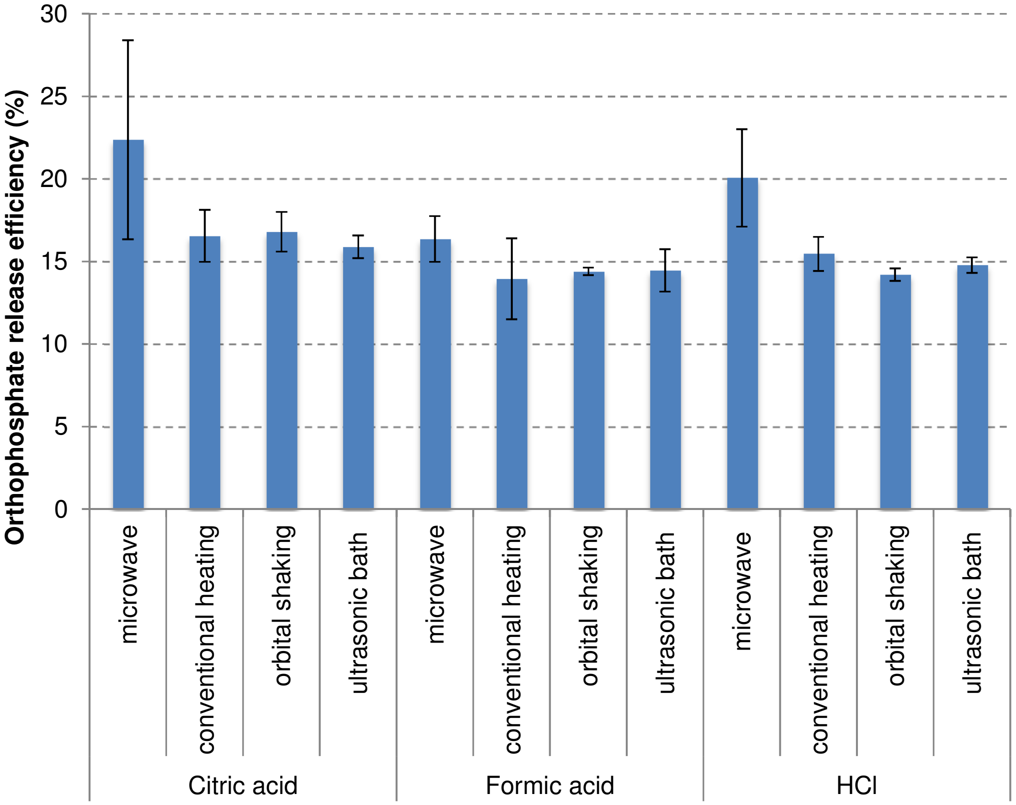


Figure 7.5 Maximum orthophosphate release efficiency (%) from digestate by the pre-treatments at the respective pH (mean ± standard deviation; n = 3). All results are calculated based on the maximum P release at pH 4, except for citric acid: maximum P release at pH 5 for microwave and conventional heating. Efficiency = ((maximum ortho-P release with pre-treatment) – (ortho-P release without pre-treatment, i.e. 48±7 mg L^{-1})) / (total initial P).

Looking at the maximum obtained P release efficiencies, **among the mechanical pre-treatments, the microwave treatment was generally most effective in releasing ortho-P**. The obtained ortho-P release efficiencies are in line with Jin *et al.* (2009), who reported values in the range of 13 to 30 % using microwave digestion and various chemicals (NaOH, CaO, H_2SO_4, HCl) for the treatment of dairy manure. Moreover, the P release obtained in this study was similar to that in Pan *et al.* (2006) using a closed vessel microwave with addition of H_2SO_4 (1:50-ratio) at 60 °C for dairy manure treatment (115±3 mg P L^{-1} or 40 % of total P). Differences can be attributed to the different chemicals used, the heating temperature, the pH, the microwave system used (open system for this study), and differences in initial P content and animal diet (He *et al.*, 2004; Szogi *et al.*, 2008), next to the fact that in this study the manure was subjected to anaerobic (co-)digestion prior to the microwave treatment.

The improved P release may be attributed to the ability of microwave digestion to convert other forms of P, such as polyphosphates and organic phosphates, into orthophosphates via hydrolysis at 70 °C as compared to mesophilic anaerobic digestion at 35 °C (Jin *et al.*, 2009; Qureshi *et al.*, 2008). The fact that microwave digestion was able to release more ortho-P than conventional heating is likely due to an increased solubilization of lignocelluloses under microwave heating at low pH. Also Jin *et al.* (2009) previously observed this effect. Orbital shaking and ultrasonic treatment, both without imposed heat supply, showed similar maximum release efficiencies as conventional heating at low pH. Hence, from a technical point of view, if pasteurization is targeted, microwave heating may be preferred above conventional heating in order to simultaneously maximize the P release efficiency, at least when working at low pH.

The differences between the three acids can be attributed to the strength and individual properties of the acids. Citric acid generally released more soluble ortho-P ions into the liquid fraction under all pre-treatments (Fig. 7.3). Even at high pH (6), high ortho-P release efficiencies were obtained under all mechanical treatments. Moreover, less acid was required to reach a certain P release and pH as compared to the other chemicals under study (Fig. 7.2, 7.3). The improved P release is probably caused by complex formation of citrate with cations in the solution (Ca^{2+} and Mg^{2+}), which reduced the availability of Ca^{2+} and Mg^{2+} as free cations to precipitate with P (FAO, 2004b; Zumdahl, 2005). Formic acid showed a lower P release, likely because formic acid is a monodentate (only one atom in the ligand can bind to the metal), whereas citric acid is a multidentate (FAO, 2004b). Citric acid also generally released more P than HCl from digestate, which is in line with the findings of Szogi *et al.* (2008) for poultry litter. Overall, in this study, HCl and formic acid showed similar release efficiencies at the same pH. However, less acid was required when using HCl to obtain a particular pH. HCl also seems to be more effective when heat (microwave or conventional heating) is involved, though this could statistically not be evidenced.

Although citric acid seems the most interesting chemical to use, the choice of the acid also depends on its price. The estimated acid cost for each pre-treatment is presented in Table 7.2. It was calculated from the cost price of the used acids, as offered by the chemical provider (Brenntag NV, 2012). Also the average amount of additional ortho-P release above that obtained without pre-treatment (48±7 mg L^{-1}) is presented.

Table 7.2 Acid dose (mol L^{-1} digestate), estimated acid cost (€ m^{-3} digestate), and additional ortho-P released from digestate under the various pre-treatments (g m^{-3} digestate) relative to the P released without pre-treatment (48±7 g m^{-3}). Acid prices: HCl: € 0.0014 mol^{-1}, citric acid: € 0.13 mol^{-1}, formic acid: € 0.02 mol^{-1} (Brenntag NV, 2012). € 1 ≈ 1.415 CAD (November 2014).

Acid	**pH**	**Acid dose (mol L^{-1})**	**Acid cost (€ m^{-3})**	**Average additional P release (g m^{-3}) compared to no pre-treatment**			
				Microwave Heating	Conventional Heating	Orbital shaking	Ultrasonic bath
HCl	6	0.25	0.35	8.0	21	0	27
	5	0.38	0.53	40	47	48	51
	4	0.49	0.69	85	66	60	63
Citric acid	6	0.13	16.39	61	64	52	54
	5	0.21	27.31	95	70	69	63
	4	0.36	47.34	86	69	71	67
Formic acid	6	0.34	6.86	0	19	0	43
	5	0.53	10.50	49	44	47	55
	4	0.74	14.73	69	59	61	61

Although the combination of microwave treatment and citric acid at pH 5 resulted in the highest average ortho-P release, the cost of this treatment (only for the acids) was about 50 times higher as compared to the use of HCl. In this respect, it seems more interesting to use HCl down to pH 4 (hence more acid required), which still resulted in high P release efficiencies under the various mechanical pre-treatments, though significantly reduced the acid costs. Moreover, if no pasteurization is required for effective fertilizer marketing, then orbital shaking may be considered as mechanical treatment (in combination with HCl addition down to pH 4), due to its generally lower operational cost and energy use, but still relatively high P release efficiency. In practice, this pre-treatment can easily be realized by addition of the acid into a continuously stirred tank reactor, for example, a digestate storage tank. The choice and cost of the mechanical treatment will also depend on the local availability of (recovered) heat. This will not be further discussed here.

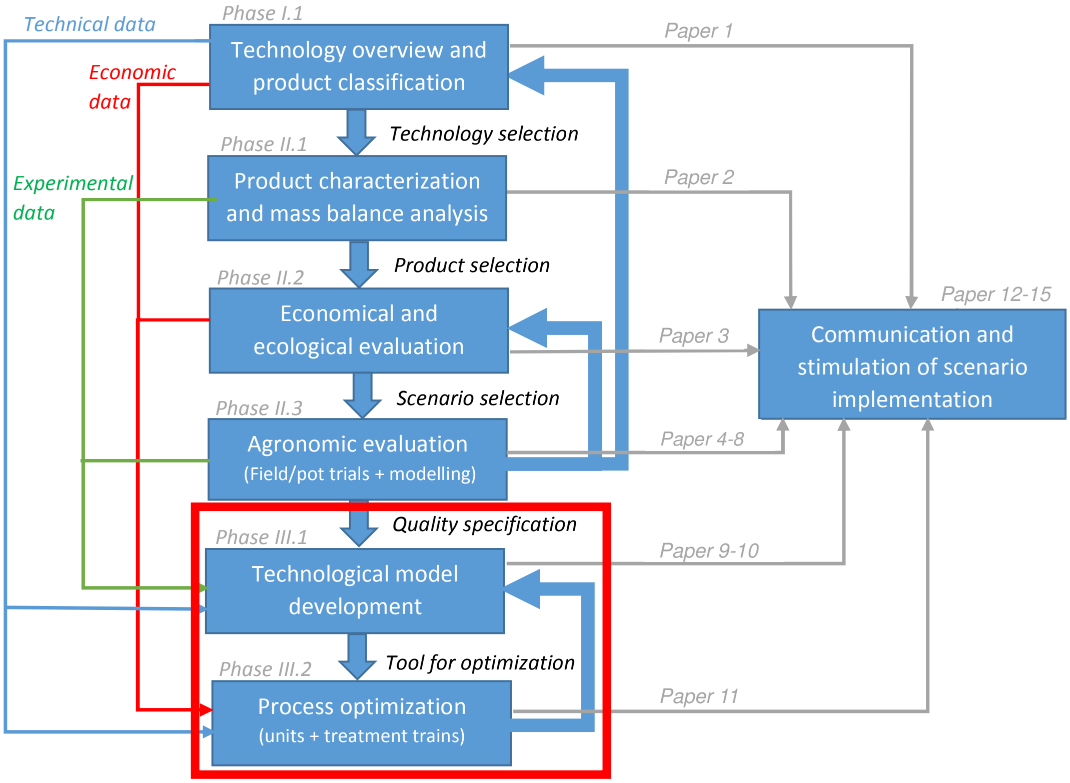
Although the above estimated costs seem fairly high, the results are comparable to the findings of Daumer *et al.* (2010) for the treatment of raw pig slurry using formic acid down to pH 5, i.e. € 8 *(11 CAD)* m^{-3}, only taking in account the acid costs. Hence, the findings were believed to be realistic. Looking on a phosphorus base, the costs are even more discouraging, ranging from € 8 *(11 CAD)* (microwave heating, HCl, pH 4) to ± € 700 *(990 CAD)* (ultrasonic bath, citric acid, pH 4) per extra kg of P released as compared to not applying a pre-treatment at all. To this, the costs for a Mg-source will have to be added if struvite is to be produced, next to the costs for the mechanical treatment. On the other hand, a reduction in transport costs (estimated at € 1.2 *(1.7 CAD)* ton^{-1} km^{-1}; Daumer et al., 2010) can be obtained as the resulting organic thick fraction should have increased local valorization potential (higher C:P-ratio). Moreover, the thick fraction may (partially) be recycled to the anaerobic digester prior to marketing in order to enhance biogas production and further stabilize the organic amendment. It should, however, be remarked that the fertilizer value and characteristics of such organic thick fractions remain to be explored. The carbonate content, for example, may be reduced during acidification.

Revenues can also be obtained from (local) struvite fertilizer marketing, ranging from ± € 45 to 1,400 ton^{-1} anno 2014 *(± 64-2000 CAD* ton^{-1}; Chapter 2: Table 2.4). On top of that, the production and transport costs for chemical P fertilizers may be reduced or even eliminated. Hence, **the economic feasibility of implementing a pre-treatment will have to be evaluated for each specific case**.

Next to the costs and technical performance, another important factor influencing the chemical choice is related to the acid composition. Mineral acids supply anions (chloride in this case) at high concentrations. These soluble anions increase the salinity of the final effluent. On the other hand, organic acids increase the easily degradable carbon content of the effluent (Daumer *et al.*, 2010). Hence, the acid to be preferred will also depend on the required effluent quality. Note that when simultaneously applying a mechanical treatment, further COD degradation is expected to occur. Also pathogens can be further killed off during the pre-treatment. Moreover, next to P, (heavy) metals can be released, which could be recovered prior to struvite precipitation, meanwhile improving the struvite purity and effluent quality (Müller *et al.*, 2005). The Ca/Mg-dose needed for P precipitation may also be reduced, due to the potential improved Mg release. Yet, the pH will have to be increased after the pre-treatment to allow for precipitation to occur. Finally, acids of reduced quality could be used, which may significantly reduce the acid costs, but again impact on the fertilizer and effluent quality. These aspects were out of scope of the present study, but should be taken in account when selecting the technically and economically most feasible pre-treatment for each particular case.

7.5 Conclusions and perspectives

The P release potential of various combinations of mechanical (microwave heating, conventional heating, orbital shaking, ultrasonic bath) and chemical (acidification using HCl, citric acid, and formic acid down to pH 4, 5, and 6) pre-treatments was studied. All pre-treatments were effective in increasing the release of P from digestate, although orbital shaking at pH 6 was only of interest with addition of citric acid. Based on the experimental results, overall the maximum P release efficiency was obtained using citric acid under microwave heating at pH 5. However, when comparing the P release efficiency and the chemical costs for the various pre-treatments, acidification with HCl down to pH 4 under microwave heating was the most feasible option. Nevertheless, if no pasteurization is required for fertilizer marketing, then orbital shaking (i.e. mixing in practice) in combination with HCl may be more attractive, considering the ease of implementation and costs for the mechanical treatment. In general, the chemical costs as function of the P release efficiency were high for all pre-treatments. Further substantive case studies are required so as to conclude on the economic feasibility of implementing such treatments for P release from digestate at full-scale. Aspects as improved COD degradation and biogas production, chemical fertilizer replacement, local fertilizer markets, the fertilizer value of the remaining organic thick fraction, transport costs, and pasteurization will have to be considered in the evaluation.

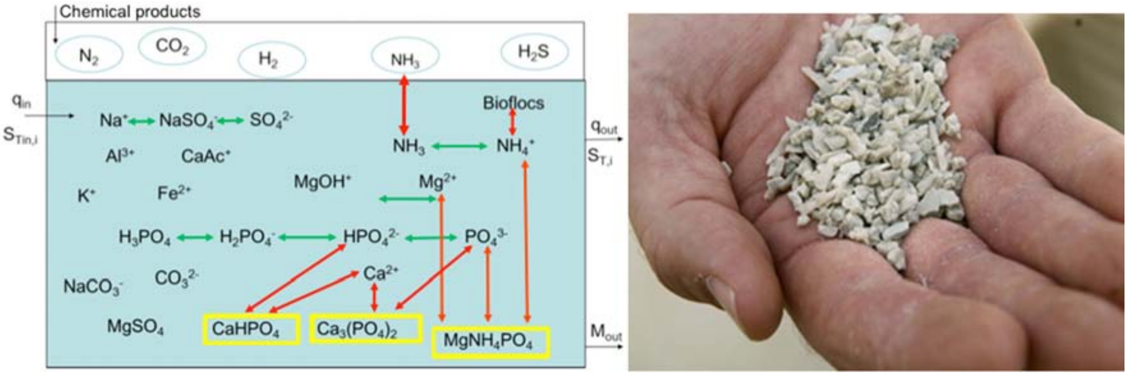


PHASE III

PROCESS MODELLING AND OPTIMIZATION

CHAPTER 8

MODELLING AND OPTIMIZATION OF NUTRIENT RECOVERY SYSTEMS: ADVANCES AND LIMITATIONS



From complex waste matrix (left) to recovered high-quality fertilizer (right): challenge?!
(Pictures: Lebuf V., Vaneeckhaute C.)

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Abstract

Mathematical models have become very important tools for technology design, optimizing performance, and process troubleshooting as they are both time and cost efficient. Although a number of models of waste(water) treatment facilities have been developed and applied extensively, these state-of-the-art models lack the inclusion of key fundamental physicochemical processes that play a major role for nutrient recovery. Critical elements to be dealt with include accurate descriptions of acid-base reactions, slow precipitation kinetics, liquid-gas exchange, and ion pairing in the complex mixture of chemical entities that the recovery systems in place deal with. Moreover, nutrient recovery models should provide information on the physicochemical characteristics (e.g. purity, particle diameter, density, etc.) of the recovered products under varying conditions (input composition, pH, temperature, reagents, etc.) in order to determine and control their fertilizer properties. Hence, considerable research is required before integrated models will be available that allow designing and optimizing recovery facilities at the same level as is now possible for traditional biological nutrient removal systems. This chapter first gives a brief overview of important fertilizer quality specifications for effective product marketing. Secondly, this chapter elaborates on the modelling advances and limitations involved in the transition from nutrient removal to nutrient recovery models. Finally, the chapter provides recommendations for the development of a generic physicochemical modelling framework in view of nutrient recovery. It is expected that the establishment of a generic nutrient recovery model library can greatly facilitate the implementation and optimization of full-scale treatment trains for nutrient recovery. A compromise should be found between model accuracy and simulation times.

Keywords: *anaerobic digestion, fertilizer quality, mathematical modelling, nutrient recovery model library, physicochemical framework, treatment train.*

Résumé

Les modèles mathématiques sont devenus des outils très importants pour la conception de la technologie, l'optimisation de la performance et le dépannage des processus car ils sont à la fois efficaces et économiques. Bien qu'un certain nombre de modèles pour des installations de traitement des déchets et eaux usées aient été mis au point et largement appliqués, ces modèles ne tiennent pas compte de processus physicochimiques fondamentaux jouant un rôle majeur dans la récupération des nutriments. Les éléments clés à traiter incluent une description précise des réactions acido-basiques, la cinétique lente de la précipitation, l'échange gaz-liquide et la sorption/désorption dans le mélange complexe d'espèces chimiques qui se produisent dans les systèmes de récupération. En outre, les modèles de récupération des nutriments devraient fournir des informations sur les caractéristiques physicochimiques (par exemple la pureté, le diamètre des particules, la densité, etc.) des produits récupérés dans des conditions variables (composition de l'affluent, le pH, la température, les réactifs, etc.) afin de déterminer et de contrôler leurs propriétés fertilisantes. Ainsi, une recherche considérable est nécessaire avant que des modèles intégrés seront disponibles, qui permettent la conception et l'optimisation des installations de récupération à un niveau similaire à ce qui se fait dans le domaine de l'épuration biologique. Ce chapitre examine d'abord en bref les spécifications qualitatives requises pour la commercialisation de bio-engrais. Deuxièmement, ce chapitre explore les défis de modélisation impliqués dans la transition des modèles d'élimination des nutriments à des modèles de récupération. Enfin, le chapitre fournit des recommandations pour le développement d'un cadre générique de modélisation physicochimique pour la récupération des nutriments. Il est prévu que la mise en place d'une librairie générique de modèles pour la récupération des nutriments peut grandement faciliter la mise en œuvre et l'optimisation des chaînes de traitement pour la récupération des nutriments à pleine échelle. Un compromis devra être trouvé entre la précision des modèles et le temps de simulation.

Mots-clés: *cadre physicochimique, chaîne de traitement, digestion anaérobie, librairie de modèles de récupération des nutriments, modélisation mathématique, qualité des engrais.*

8.1 Introduction

Driven by economic, ecological, and community considerations, waste(water) treatment plants (WWTPs) are increasingly transformed into waste(water) resource recovery facilities (WRRFs). Next to the long recognized and successfully recovered resources, water itself and energy, attention is growing to extract other valuable products from waste(waters), in particular nutrients. Although to date many processes for the recovery of nutrients from waste(water) have been proposed and applied to varying degrees (Chapter 2; Vaneeckhaute *et al.*, 2013a), challenges remain in improving their operational performance, decreasing the economic costs, and recovering the nutrients as pure marketable products with added value for the agricultural sector.

Previous chapters provide evidence of the agronomic value of recovered products. However, a prerequisite for marketing and recognition in environmental legislations is that these bio-based fertilizers can compete with conventional fertilizer quality specifications, as summarized in Chapter 2 (Section 2.4). The fact that the WRRFs aim at delivering high-value products that can partially replace those produced by other means (e.g. chemical mineral nitrogen (N) production through the Haber-Bosch process) leads to a paradigm shift in specifications of the outputs of the facility: no longer treated wastewater and biosolids (i.e. organic thick fractions), but products that have to compete with what is already on the market. Previous chapters demonstrated that there are still some qualitative bottlenecks for product reuse requiring further optimization. Moreover, a problem still exists in the variability of digestate (and manure) composition over time. Hence, in order to move towards more sustainable fertilization practices, it is crucial that farmers and operators are able to predict the macronutrient content, mainly N, phosphorus (P), potassium (K), and sulfur (S), of their end products.

From the literature (Chapter 2; Vaneeckhaute *et al.*, 2013a), the techniques for nutrient recovery from digestate available or under development today and the recovered fertilizer products (between brackets) are: 1) chemical precipitation/crystallization (struvite, calciumphosphates), 2) gas stripping (ammonia, NH_3) and absorption (ammoniumsulfate (AmS) solution), 3) acidic air scrubbing (AmS-solution), 4) membrane separation (N/K-concentrates), 5) ammonia sorption (N-zeolites), and 6) biomass production and harvest (biomass). Hence, in contrast to the traditional biological nutrient removal technologies used in WWTPs, e.g. the activitated sludge (AS) system for N removal, the main unit processes considered in WRRFs rely on (changes in) the physicochemical properties of the solution. Important properties are, for example, ion activities, the chemical redox state, and the degree of solution supersaturation, to effectively perform precipitation, extraction, stripping, phase separation, crystallization, sorption, and filtration processes for recovery. On their turn, these fundamental properties are determined by the underlying chemical solution speciation, which is the detailed distribution of total component amounts between the ionic species physically present in the system. Consequently, the production of a pure and marketable fertilizer product from a complex waste matrix is challenging.

Resource recovery treatment trains are being conceived to maximize the recovery of interesting products from waste streams (WWTP sludge, manure, etc.) at minimal cost and environmental impact. A state-of-the-art example is given in Figure 8.1 and further examples can be found in Verstraete and Vlaeminck (2011). However, finding the appropriate combination of technologie(s) for a particular waste flow and the optimal operational conditions for the unit processes in the overall treatment train is a key concern.

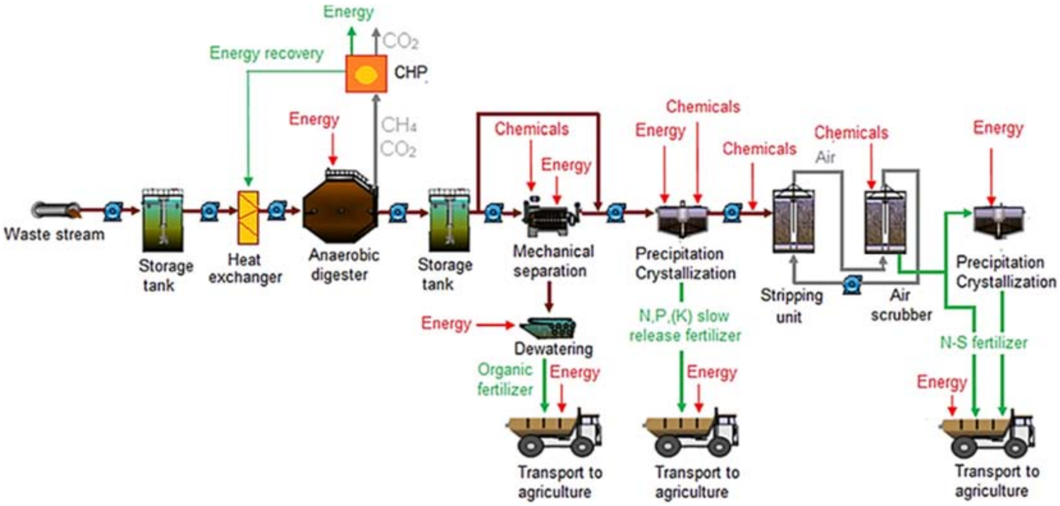


Figure 8.1 Treatment train for recovery of energy, organic fertilizer, ammonium sulfate fertilizer, and N/P/K slow-release fertilizer from a waste stream.
CHP = combined heat and power generation.

Mathematical models have become very important tools for technology design, optimizing performance, and process troubleshooting of treatment systems as they are both time and cost efficient (Rieger *et al.*, 2012). Moreover, models can fill the gap between lab/pilot-scale experiments and commercial scale operation (Yu *et al.*, 2011). Although a number of models of treatment facilities have been developed and applied extensively (Henze *et al.*, 2000; Rieger *et al.*, 2012), these state-of-the-art models focus on biological processes for the removal of nutrients (N, P) and chemical oxygen demand (COD). Fundamental physicochemical properties of the solution (see above) are not (or not sufficiently) accounted for, although they clearly play a major role in resource recovery.

In order to integrate nutrient and energy recovery processes in the existing model libraries and/or to predict the physicochemical waste input properties (sludge, manure, etc.) for a nutrient recovery treatment train (Fig. 8.1), existing models will have to be extended so that they allow for physicochemical transformations to occur. Critical elements to be dealt with include accurate descriptions of acid-base reactions, slow precipitation kinetics, liquid-gas exchange, and sorption/desorption in the complex mixture of chemicals that the systems in place deal with (Batstone *et al.*, 2012). Moreover, WRRF models should provide information on the physicochemical characteristics (e.g. macronutrient content, particle diameter, density, etc.) of the recovered products in order to determine and control their fertilizer properties (Vanrolleghem and Vaneeckhaute, 2014). Hence, considerable research is required before integrated models will be available that will allow designing and optimizing WRRFs in the same way as is now possible for traditional biological WWTPs.

First important steps were made towards a physicochemical modelling framework compatible with the current more biological process-oriented modelling frameworks (Batstone *et al.*, 2012; Fernández *et al.*, 2014; Grau *et al.*, 2007b; Hauduc *et al.*, 2014; Lizarralde *et al.*, 2014; Takacs *et al.*, 2006). However, these modelling studies focus on the integration of simplified physicochemical models in the existing (biological) nutrient removal models, e.g. the P precipitation model in the Activated Sludge Model 2d (ASM2d; Hauduc *et al.*, 2014). Moreover, the scope of the existing studies stops at the anaerobic digestion of mainly WWTP sludge, where it mostly aims at the prediction of uncontrolled struvite precipitation during digestion. **No work has been done on the development of generic models for the controlled nutrient recovery treatment train following the digester (Fig. 8.1).** Consequently, models to adequately put together a nutrient recovery treatment train of unit processes and their operating conditions to maximize resource recovery and fertilizer quality in a sustainable and cost-effective way are missing, although the need clearly exists.

This chapter first gives a brief overview of the most important fertilizer quality specifications (Section 8.2) based on the findings of the previous chapters, in order to compile essential model outputs with focus on fertilizer commercialization. Next, the chapter elaborates on the limitations and advances in nutrient recovery process modelling and optimization (Section 8.3). The focus is on anaerobic digestion and the best nutrient recovery systems available, as selected in Chapter 2. Finally, based on the findings of the review, objectives and recommendations for future work (Section 8.4) in terms of nutrient recovery model development and implementation are provided. As such, this chapter aims to build up the fundamental basis for the modelling work that is subsequently presented in Chapters 9 and 10.

8.2 Fertilizer quality specifications

For generic fertilizer quality specifications, reference is made to Chapter 2 (Section 2.4).

From the agronomic results presented in Phase II (Chapters 3-7) of this dissertation, the most important physicochemical qualitative fertilizer properties that deserve attention when using bio-based products in agriculture can be derived. It concerns: i) the pH, ii) the salt content, iii) the sodium adsorption ratio (SAR), iv) the macronutrient (N, P, K, S, calcium (Ca), magnesium (Mg)) and (organic) carbon content, v) the macronutrient use efficiency, and vi) impurities, e.g. iron (Fe) and aluminium (Al) compounds. Important factors determining the product's economic value, next to the nutrient content, are the density for liquid fertilizers and the particle size for granular fertilizer products. Hence, WRRF models should allow to accurately predict these product characteristics under variable operating conditions and variable input compositions.

8.3 Modelling and optimization: Advances and limitations

The present section describes in more detail the advances and limitations in modelling and optimization of anaerobic digestion (Section 8.3.1) and of the best available nutrient recovery technologies selected in Chapter 2 (Vaneeckhaute *et al.*, 2013a): P precipitation/crystallization (Section 8.3.2), NH_3 stripping and absorption (Section 8.3.3), and acidic air scrubbing (Section 8.3.4).

8.3.1 Anaerobic digestion

The reaction system in anaerobic digestion is complex with a number of sequential and parallel steps. These reactions can be divided into biochemical reactions, which act on the pool of biologically available organic components, and physicochemical reactions, which are not biologically mediated and encompass liquid-liquid reactions (i.e. ion association/dissociation), gas-liquid exchange (i.e. gas transfer), and liquid-solid transformation (i.e. precipitation and dissolution of ions). Anaerobic digestion is affected by several operating conditions, such as the specific characteristics of the waste stream, temperature, pH, macro- and micronutrients, inhibition (NH_3, volatile fatty acids (VFA), shock loading), toxicity, retention time, mixing conditions, and feeding strategy (Astals *et al.*, 2013; Bhuiyan *et al.*, 2009; Hafner and Bisogni, 2009; Zhang and Jahng, 2010). Monitoring VFAs and alkalinity during digestion is particularly essential for efficient digester process control because the acid/alkalinity ratio will change before the pH begins to drop (which is fatal for methanogenic bacteria) (Vanrolleghem and Lee, 2003). In recent years, several authors underlined the importance of modelling the physicochemical system in anaerobic processes. The following arguments were used:

i. A number of biological inhibition factors can be expressed physicochemically, such as pH, free acids and bases, and dissolved gas concentrations (Batstone *et al.*, 2002);
ii. Major performance variables such as gas flow and carbonate alkalinity are dependent on correct estimation of physicochemical transformations (Batstone *et al.*, 2002);
iii. Often, pH control with a strong acid or base is the major operating cost. In this case, the control setpoint (pH) must be calculated from the physicochemical state (Batstone *et al.*, 2002; Lauwers *et al.*, 2013);
iv. The acid-base subsystem is vitally important to calculate gas transfer (lots of gases are also acids or bases), while gas transfer has a significant impact on the acid-base subsystem through its effect on pH (Batstone *et al.*, 2012);
v. Chemical speciation of major solutes in digestion is required, e.g. to understand the toxicity of NH_3 and VFAs and to mitigate uncontrolled struvite precipitation in the reactor, piping, and equipment (Bhuiyan *et al.*, 2009; Hafner and Bisogni, 2009);
vi. Precipitation processes are critical in modern waste(water) treatment, as they describe the behavior of P in all stages, e.g. struvite formation, especially during digestion of sludge from enhanced biological P removal (EBPR) (Ikumi, 2011), precipitation of Fe and Al with P after addition of Fe/Al-salts (Hauduc *et al.*, 2013), as well as Ca and Mg scaling (Batstone *et al.*, 2012; Brouckaert *et al.*, 2010; Harding, 2009; van Rensburg *et*

al., 2003);

vii. The presence of precipitates provides a slow buffer to changes in pH, and emerging processes such as P recovery are highly dependent on metal ion precipitation (Brouckaert *et al.*, 2010; Kim *et al.*, 2004).

The lack of ion activity correction (at low conductivity), ion pairing (at high conductivity), precipitation, and P modelling are assumed the main limitations of the Anaerobic Digestion Model No. 1 (ADM1), which is the generic anaerobic digestion model currently provided by the International Water Association (Batstone *et al.*, 2012; Lauwers *et al.*, 2013). Due to lack of activity corrections, ADM1 also fails to predict pH correctly. pH is vital for proper precipitation prediction (Ganigue *et al.*, 2010). In recent years, some attempts have been made to improve the predictability of anaerobic digestion by integrating physicochemistry, mainly in order to overcome the nuisance problem of struvite precipitation. Research groups that have been working on this issue are the University of Cape Town (South Africa; Musvoto *et al.*, 2000b; Sotemann *et al.*, 2005; van Rensburg *et al.*, 2003) and KwaZulu-Natal (South Africa; Brouckaert *et al.*, 2010), the Center of Studies and Technical Research (CEIT, San Sebastian, Spain; Lizarralde *et al.*, 2013, 2014), Cornell University (New York, USA; Hafner and Bisogni, 2009), and EnviroSim (Ontario, Canada; Takacs *et al.*, 2006). However, **to date, no generic approach has been agreed upon to incorporate solution speciation based on ion activity, and the kinetics of precipitation of multiple minerals that share common ions, as well as competing reactions, such as ion pairing, in an anaerobic digester for organic waste treatment.**

Furthermore, the ADM1 application has practical problems related to the characterization of the digester feedstock and the associated model definition of the enzymatic disintegration and hydrolysis steps. As biological wastes are heterogeneous and dynamically changing in composition, it is difficult to find unique parameter values that are applicable to all possible combinations and ratios of wastes together with decaying anaerobic biomass. Since ADM1 has been published, several methods have been developed to overcome such parameter estimation and substrate fractionation problems. These approaches are based on elemental analysis (Grau *et al.*, 2007a; Kleerebezem and van Loosdrecht, 2006; Zaher *et al.*, 2009a), physicochemical analysis (Batstone *et al.*, 2009), the conversion of other model outputs, e.g. activated sludge models (ASM), to ADM1 state variables (Copp *et al.*, 2004; Vanrolleghem *et al.*, 2005; Zaher *et al.*, 2007), or anaerobic respirometry (Girault *et al.*, 2012; Zaher *et al.*, 2009b). A powerful dynamic interface to ADM1 to simulate the digestion of any combination of waste streams by evaluating their independent hydrolysis rates and operational settings (optimal feed ratio, hydraulic retention time, etc.) is the general integrated solid waste co-digestion (GISCOD) modelling tool, developed by Zaher *et al.* (2009a).

8.3.2 Phosphorus precipitation/crystallization

The ability to predict the P precipitation potential from a waste(water) flow is an important consideration for designers and operators to determine the feasibility and economics of nutrient recovery, e.g. as struvite ($MgNH_4PO_4{:}6H_2O$), and for the subsequent design and operation of reactors for P crystallization. For good product quality control, it is essential to know the best conditions under which the target precipitation reaction is likely to occur. Based on experimental studies conducted thus far, P recovery through crystallization was found to be mainly affected by the following operating factors: supersaturation (Bouropoulos and Koutsoukos, 2000; Ohlinger *et al.*, 1998), pH (Doyle *et al.*, 2002; Münch and Barr, 2001; Nelson *et al.*, 2003), Mg to P molar ratio in case of struvite (Adnan *et al.*, 2003; Jeong and Hwang, 2005; Le Corre *et al.*, 2007b; Münch and Barr, 2001; Nelson *et al.*, 2003), crystal retention time (Adnan *et al.*, 2003), recycle ratio, i.e. the ratio between the feed flow and the recycle flow (Adnan *et al.*, 2003), reactor seeding (Ohlinger *et al.*, 1998; Wu and Bishop, 2004), temperature (Bhuiyan *et al.*, 2009; Doyle *et al.*, 2000), turbulence and mixing (Ohlinger *et al.*, 1998; Regy *et al.*, 2002). The crucial value to control is the supersaturation value, next to the total crystal surface, retention time, and flow pattern. To optimize the size of recovered crystals, researchers have often tested crystallization onto seed materials such as sand (Battistoni *et al.*, 2002) or preformed crystals (Shimamura *et al.*, 2003). Seeding clearly impacts the final particle size distribution (PSD).

Especially struvite solubility is widely studied. However, the conditions reported to be optimal for struvite crystallization vary from publication to publication (Andrade and Schuling, 2001; Huang *et al.*, 2011; Le Corre *et al.*, 2009), and to date the purity of the product precipitated cannot be guaranteed due to the availability of foreign ions and co-precipitation. Recently, Schneider *et al.* (2013) underlined the importance of modelling solution thermodynamics and the presence of foreign ions in nutrient recovery systems, as the constituent species concentrations, the solution pH, and ionic strength directly determine the generation of supersaturation.

Although a substantial number of models have been developed for P precipitation and/or crystallization, these models mostly focus on the precipitation of one target compound, e.g. struvite (Bhuiyan *et al.*, 2007; Celen *et al.*, 2007; Miles and Ellis, 1998; Mohan *et al.*, 2011; Wu and Zhou, 2012; to mention a few), $Ca_5(PO_4)_3OH$ (Maurer *et al.*, 1999), or $FePO_4$ (Hauduc *et al.*, 2013, 2014), accounting only for the solubility product and supersaturation ratio of the target species, e.g. for struvite based on the three main constituents, Mg^{2+}, PO_4^{3-}, and NH_4^+. Besides the equilibrium model developed by Lee *et al.* (2013) for struvite formation with simultaneous Ca precipitation, no other models have been described in the literature for simulation of P recovery as a pure target product (e.g. struvite) under the competitive inhibition of other ions, e.g. Ca and Fe ions. Moreover, no models applied for nutrient recovery from waste(water) by means of precipitation/crystallization account for supersaturation ratios and solubility products of multiple competing precipitation reactions based on a detailed solution speciation, including e.g. PO_4^{3-}, HPO_4^{2-}, Ca^{2+}, Fe^{3+}, and Al^{3+} ionic species, and the time-dependent behaviour of supersaturation. As a result, given the complex nature of (digested) waste and the multiple competing processes (complex formation, ion exchange, co-precipitation, etc.), the current models often overestimate removal efficiencies (Rahaman *et al.*, 2008, 2014) or underpredict the precipitate formation potential (Doyle and Parsons, 2002; Parsons *et al.*, 2001). Hence, pilot testing is still indispensable for proper design and process performance evaluation. Besides, the product's fertilizer potential is affected by concurrent precipitation. For example, in Chapter 6 it was observed that $FePO_4$-sludge is not an interesting product in terms of P release for agricultural crop growth because of its high P-binding capacity, in contrast to the valuable slow-release struvite fertilizer (Vaneeckhaute *et al.*, 2015a, 2015b).

Next to the simplified thermodynamic approach of the current models for P precipitation/ crystallization, another limitation is that most of the present studies focus on the development of a thermodynamic chemical equilibrium model. Much less work has been carried out to couple solution thermodynamics to the fundamental kinetics of P crystallization, which involves the relatively slow processes of nucleation, crystal growth, agglomeration, and breakage, and hence should be modelled dynamically**.** The main research groups that have been working on modelling these phenomena are the Australian universities, James Cook and Queenland (Ali and Schneider, 2008; Galbraith *et al.*, 2014; Harrison *et al.*, 2011), Cranfield University (Bedford, UK; Le Corre *et al.*, 2007a,b), and the University of British Columbia (Vancouver, Canada; Bhuiyan *et al.*, 2008; Rahaman *et al.*, 2008). These studies focus on the production of N-struvite only, and are limited to crystal growth and occasionally nucleation, described by empirical power laws. Only Le Corre *et al.* (2007a,b) studied aggregation and suggested that aggregation without the addition of coagulants is not significant in the case of struvite. However, recently, Galbraith *et al.* (2014) proposed a generalized model for P crystallization driven by the three key mechanisms of nucleation, growth, and aggregation. Nevertheless, this model is likely too complex for direct application to real-world, large-scale nutrient recovery systems, since it employs complex crystal population dynamics. To date, it has only been tested on synthetic solutions containing principal reactants, while it is expected that the presence of competing ions and suspended particles in the complex matrix of (digested) waste flows will significantly influence the rate of crystal formation and its purity (Quintana *et al.*, 2005). Hence, as in all other kinetic modelling efforts described above, a significant problem of this model is the fact that the underlying kinetic equations are all driven by solution supersaturation, which is not adequately accounted for due to the simplified thermodynamic approach (even though the kinetics are described in a very complex way).

Ideally, a more easily-applicable generic modelling approach for real waste flows would build up a detailed chemical speciation model to correctly predict supersaturation of multiple precipitates, coupled to a simplified classical kinetic model (e.g. Perez *et al.*, 2008) to describe the main slow mechanisms involved in crystal formation. As such, the model can provide accurate information on product quantity and quality, such as purity and particle size, which is essential to obtain marketable end products acceptable for agricultural use.

8.3.3 Ammonia stripping and absorption

The operational pH and temperature are the most important factors in the NH_3-NH_4^+ equilibrium. Above pH 10, NH_3 predominates in the solution and an increased temperature enhances NH_3 stripping (Saracco and Genon, 1994). However, as for P precipitation, optimal conditions for

NH_3 removal reported in literature are very variable. Lemmens *et al.* (2007) state that for optimal NH_3 removal, the pH of the liquid fraction should be around 10 and the temperature around 70 °C. However, Liao *et al.* (1995) and Gustin and Marinsek-Logar (2011) found no appreciable improvement in NH_3 removal by changing the temperature at high pH (10.5-11.5), while other studies showed that 'complete' removal without chemical addition is possible at a temperature of 80 °C (Bonmati and Flotats, 2003) and 60 °C (Campos *et al.*, 2013). The latter would be caused by the transformation of bicarbonate (HCO_3^-) to carbonate (CO_3^{2-}) at higher temperature, resulting in a pH increase through carbon dioxide (CO_2) stripping. Hence, the alkalinity of the feed flow is also very important in determining optimal process conditions and costs. **This underlines the essence of modelling treatment trains for resource recovery, as alkalinity is also a key operational factor for anaerobic digestion. Hence, process optimization of these systems is interconnected.**

The rate of mass transfer of a compound is proportional to the contact area, which is determined by the specific surface area ($m^2\ m^{-3}$) and the degree of wetness of the packing material (if there is any), which, in turn, is affected by the means of wetting, such as trickling, spraying, and submerging, and the liquid flow rate (Collivignarelli *et al.*, 1998; Melse and Ogink, 2005). In practice, air stripping in packed towers typically leads to scaling and fouling of the packing material due to reactions between CO_2 in the air and some metal ions in the waste(water). Slaked lime is therefore often added to adjust the pH of the waste flow and reduce the carbonate content before entering the stripping tower (Alitalo *et al.*, 2012; USEPA, 2000). Alternatively, calcium carbonate ($CaCO_3$) could simultaneously be recovered in the stripping column (GNS, 2014). In case of high buffering capacity, an additional CO_2 stripper before the NH_3 stripping process might be economical (RVT Process Equipment, Steinwiesen, Germany, personal communication 2014).

With the purpose of improving the mass transfer and eliminating scaling problems, in recent years some new gas-liquid contactors without packing have been used for the gas-liquid operation, such as the water-sparged aerocyclone (Bokotko *et al.*, 2005; Quan *et al.*, 2009, 2010) and bubble column reactor (BCR) (Collivigneralli *et al.*, 1998; Powers *et al.*, 1987). In these systems the gas film resistance is decreased and the gas-liquid contact area increased. This accelerates the mass transfer of NH_3 (which has a low Henry coefficient or very high solubility) from the liquid to the gas phase (Mattermuller *et al.*, 1981; Powers *et al.*, 1987).

Mathematical models are particularly important for process optimization and scale-up of stripping systems in order to fill the information gap between lab/pilot- and full-scale (Collivignarelli *et al.*, 1998; Yu *et al.*, 2011). For example, most laboratory stripping experiments use blowers instead of fans, because there are no appropriate fans available for lab-scale NH_3 stripping experiments. At a commercial scale, though, it is possible to achieve a large volume of airflow with small air pressure by fans, which require minimal electrical consumption.

Previously reported theoretical modelling studies are mostly based on empirical methods, such as mass transfer correlation of the volatile compound under study, and assume that the flow in stripping towers is homogenous, i.e. spatially independent (Arogo *et al.*, 1999, Katechis *et al.*, 1998). Collivigneralli *et al.* (1998) and Powers *et al.* (1987) developed steady state models for BCRs and accounted for the entrainment of NH_3 in bubbles, as well as for the temperature and pH dependency of the Henry coefficient. Recently, Yu *et al.* (2011) showed that the distribution of temperature and liquid volume fraction in a packed tower is not homogenous. The authors underlined the importance of considering liquid residence time in the design. Little efforts have been made to connect mass and heat transfer with chemical reactions, other than the NH_3-NH_4^+ equilibrium, occurring in stripping towers for N recovery. For instance, $CaCO_3$ precipitation, which mainly causes the above-mentioned blocking and scaling problems, may occur and should be quantified. Also the simultaneous removal of other volatile compounds, such as amines, from the waste flow may not be underestimated in view of odor emission control. Moreover, a series of strippers could be implemented for combined N and S recovery (Lee *et al.*, 2002). Yet, again, because of the complex nature of (digested) waste material, **modelling the chemical speciation and solution thermodynamics, next to an appropriate rate-based mass transfer model, is essential to improve process design, operational performance, and recovered product quality.**

8.3.4 Acidic air scrubbing

The equipment most often used for acidic air scrubbing to capture NH_3 are packed towers and venturi scrubbers. The pH is controlled, usually at a value below 4, by addition of acid (typically sulfuric acid, H_2SO_4; Chapter 2) to the recirculation water in order to enhance the mass transfer and absorption process. A minimum water discharge rate is required to prevent precipitation of ammonium sulfate ($(NH_4)_2SO_4$, AmS) on the packing column, which causes blocking and clogging of the system. At an NH_3 removal efficiency of 95 %, the discharge water production is about 0.2 m^3 kg^{-1} NH_3 (Melse and Ogink, 2005). Melse and Ogink (2005) reported that the AmS concentration of acidic air scrubbers is usually controlled at a level of ± 150 g AmS L^{-1}, which is roughly 40 % of the maximum solubility at pH 4. However, commercial processes combining stripping and NH_3 absorption seem to achieve more concentrated solutions, i.e. 25 % AmS (*ANAStrip*, GNS, Halle, Germany, personal communication 2014) to 38 % AmS (RVT Process Equipment, Steinwiesen, Germany, personal communication 2014) and 40 % AmS (*Amfer*, Colsen, Hulst, the Netherlands, personal communication 2014). From literature and contact with technology providers, process control with pH measurement and automatic water discharge appears to be sufficient to guarantee adequate NH_3 recovery. In order to simultaneously capture sour reacting components, e.g. hydrogen sulfide (H_2S) and CO_2, often a two-stage scrubber is used in the field of gas purification, capturing these compounds in an alkaline aqueous solution, such as sodium hydroxide (NaOH) (Brettschneider *et al.*, 2004; See Chapter 4: alkaline air scrubber water). Using a subsequent bioreactor, elemental S could simultaneously be recovered after biological oxidation (Lens *et al.*, 2006). Furthermore, a recent study (Jiang *et al.*, 2014) demonstrated the economic viability of integrating NH_3 stripping, absorption, and biogas purification (H_2S and CO_2 absorption) for both N and S recovery.

The rate of mass transfer of a compound to the liquid phase is proportional to the concentration gradient between the gas and liquid phase. The concentration in the liquid phase is determined by the component solubility, the rate of water discharge and fresh water supply, the pH, and if applicable, the transformation of NH_3 (or H_2S, etc.) into other compounds (Manuzon *et al.*, 2007). Furthermore, the empty bed air residence time, which can be calculated by dividing the reactor volume by the air flow rate, determines the total mass transfer and depends on solubility. Simplified models have been developed in literature to predict the performance of a counter-current gas absorption tower based on the above mass transfer principles (Calvert and Englund, 1984, Fair *et al.*, 1997, Manuzon *et al.*, 2007). Manuzon *et al.* (2007) designed and optimized a prototype acid spray wet scrubber for single-stage and multi-stage NH_3 absorption, while commercial scale H_2S stripping columns have also been modelled (Taylor *et al.*, 2010). Nevertheless, **no generic absorber model with the purpose of nutrient recovery, taking in account ion activity and other physicochemical reactions than the targeted gas-liquid equilibrium (e.g. NH_3-NH_4^+), such as precipitation (e.g. AmS) and simultaneous absorption/volatilization of multiple compounds, has been proposed.**

Finally, several technologies are commercially available for the crystallization of AmS. It involves both evaporative crystallizers for undersaturated solutions (external heat is required to obtain supersaturation) and reaction crystallizers for concentrated reactants (use of dissolution and reaction heat only). Examples are the Oslo type and Draft Tube Baffled (DTB) type crystallizers (Hofmann *et al.*, 2009). Currently 80-90 % of the AmS crystallizers operate in evaporative mode and DTB is recommended (Gea-Messo, 2013), resulting in crystal sizes of 2-2.4 mm. Mathematical models of FBR crystallizers for AmS production from NH_3 and H_2SO_4 have been reported on in literature (Belcu and Turtoi, 1996; Daudey, 1987; Kubota and Onosawa, 2009) because of their long-time record for industrial application. Usually the process is described in terms of dynamic heat and mass balances, combined with a dynamic population balance, which describes the crystal size distribution (CSD). The nucleation rate is traditionally described using an empirical power law based on supersaturation, which is the main driving force (Daudey, 1987). However, as supersaturation is difficult to measure, it is often replaced by the growth rate, which is also a function of supersaturation, but which can be estimated experimentally. **Because such experiments are expensive and time-consuming, models that are able to adequately predict solution supersaturation or sensors that allow online monitoring of this control parameter would be valuable tools for crystallization process and product quality optimization** (cfr. Section 8.3.2)**.**

8.4 Recommendations for research

8.4.1 Definition of modelling objectives

From the literature review above, it is clear that a first important research objective should involve the development of generic integrated biological-physicochemical three-phase process models for anaerobic digestion and for the best nutrient recovery systems available to date. The models should include an accurate chemical solution speciation as well as reaction dynamics, though a balance must be found between model accuracy, complexity, and simulation times (Section 8.4.3).

Secondly, the generic model library should be applicable as a tool for process optimization of single nutrient recovery systems, as well as for determination of optimal unit process combinations, in order to maximize resource recovery (nutrients, energy) from a particular waste stream and minimize energy and chemical requirements. Modelling of treatment trains is important as a combination of suboptimal unit processes may lead to an overall optimal output. Moreover, modelling of treatment trains can help identifying bottlenecks in operational strategies and treatment processes upstream. For example, the use of Fe and/or Al salts to improve separation/dewatering has a huge impact on the P bio-availability (Chapter 6; Vaneeckhaute *et al.*, 2015a) and limits the potential for P recovery as valuable fertilizer product downstream.

In summary, a common base for modelling is required, which should not only facilitate process and treatment train implementation, but also serve as a generic framework allowing to make outcomes more comparable and compatible.

8.4.2 Recommended model properties

The generic models should be based on mass balances to describe physicochemical and biochemical transformation and transport processes, as well as on accurate calculation of water chemistry in order to correctly define solution speciation and driving forces for component transformation (e.g. supersaturation). A dynamic modelling approach, i.e. one that accounts for time-dependent changes in the state of the system, is recommended, because the models should be applicable to real-time situations and (variable) operating conditions, such as i) periodical load variations, e.g. absence of operators in weekends/evenings, seasonal variations, etc., ii) individual disturbances, e.g. rain events and incorrect control manipulations, and iii) systems that are operated intermittently or cyclically as is the case for multiple nutrient recovery processes, e.g. intermittent aeration in stripping systems and (semi-)batch processes to obtain target fertilizer specifications, e.g. a target AmS concentration via acidic air scrubbing.

The system to be described consists of interactions between three phases: liquid, solid, and gas. Both heterogeneous transfer reactions that occur between phases (gas transfer, liquid-solid transfer) and homogenous transformation reactions that occur within a single phase (bio-degradation, acid-base chemistry, ion pairing) must be taken in account. Model outputs should involve fertilizer quality and quantity measurements. Based on the literature review above, desired outputs for each discussed resource recovery process are compiled in Table 8.1.

Via the interrelated chemical and biological processes, the mass balance and continuity based process models fix quantitatively the relationship between all components considered in the system so that the system's output is governed completely by the input waste stream characteristics and the applied process conditions. Factors that are expected to influence the process outputs and hence must be included as model inputs are presented in Table 8.2.

Table 8.1 Recommended model outputs for each unit process. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripping; Scrub = scrubbing.

Model outputs	AD	Prec	Strip	Scrub
Biogas volume and composition	X	-	-	-
Consumables (air, chemicals, heat, etc.)	X	X	X	X
Fertilizer quantity	X	X	X	X
Fertilizer (and/or effluent) quality				
Dry weight content / density	X	X	(X)[a]	X
Macronutrient content (N, P, K, S, Ca, Mg)	X	X	X	X
Macronutrient use efficiency (N, P, K, S)	X	X	(X)[a]	X
Micronutrient content	X	X	(X)[a]	(X)[b]
Organic carbon content	X	X	(X)[a]	-
Particle size	-	X	-	-
pH	X	X	(X)[a]	X
Purity	-	X	X	X
Salt content	X	X	(X)[a]	X
Scaling potential	X	X	X	X

[a] Values between brackets refer only to the effluent quality from the stripping unit, not to the stripped gas.

[b] Depending on the origin of the acid used in the air scrubber, micronutrients can be taken in account or ignored.

Table 8.2 Factors that potentially influence the model outputs per unit process and reference for corresponding equations. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripping; Scrub = scrubbing.

Influencing factors	AD	Prec	Strip	Scrub	Reference
Aeration (air flow rate)	-	(X)[a]	X	X	Tchobanoglous *et al.* (2003)
Alkalinity (addition/removal)	X	-	X	-	Crittenden *et al.* (2012)
Bubble size	-	-	X	X	Gujer (2008)
Chemical pH-adjustment (acid/base dose)	X	X	X	X	Crittenden *et al.* (2012)
Feed composition	X	X	X	X	-
Feed flow rate	X	X	X	X	-
Heating (temperature)	X	X	X	X	Tchobanoglous *et al.* (2003)
Mixing ($\bar{G}$ value)[b]	X	X	-	-	Crittenden *et al.* (2012)
Reactor seeding	-	X	-	-	Schneider *et al.* (2013)
Reactor height	-	-	X	X	Gujer (2008)
Residence time (liquid, air, crystals)	X	X	X	X	Tchobanoglous *et al.* (2003)

[a] Value between brackets represents the use of air instead of chemicals for pH increase.

[b] $\bar{G}$ is the root mean square velocity gradient $[\mathrm{Time}^{-1}]$, which depends on the power input (Camp and Stein, 1943).

Evidently, the mathematical models should allow evaluating how a change in these model inputs will impact on the value of the process outputs. As such, the models could be used as a valuable tool for process optimization.

8.4.3 Numerical solution

When combining biological and chemical reactions, the numerical solution is a critical step because of the stiffness that arises when considering reactions with very different conversion rates, i.e. the range of the time constants is large (Lizarralde *et al.*, 2014). Because they are much more rapid, the homogenous physicochemical reactions can be assumed at equilibrium compared to the time scale of heterogeneous physicochemical reactions and biological reactions (Batstone *et al.*, 2012). Therefore, for the fast reactions the steady state solutions can be perfectly adequate and a thermodynamic equilibrium approach may be applied. However, for slower reactions, a kinetic approach must be applied because one is interested in the time-variable or dynamic variation of the constituents. This makes the simulation of such a system challenging, and in order to avoid excessively long simulation times, one needs to be somewhat creative when implementing the model.

In the case of dynamic models, two possible solution procedures have been applied to date for stiff systems:

1. ODE (ordinary differential equation) approach: All reactions are calculated simultaneously using ODEs as in Musvoto *et al.* (2000a, b) and Sotemann *et al.* (2005);
2. DAE (differential algebraic equation) approach: The slower reactions are represented by differential equations (ODE) and the fast reactions are calculated by use of algebraic equations (AE) at each iteration step as in Batstone *et al.* (2012), Brouckaert *et al.* (2010), Volcke *et al.* (2005), or Rosen *et al.* (2006). The modeller can choose between having a tailored code to solve water chemistry or using an external software tool such as PHREEQC (Parkhurst and Appelo, 2013) or Visual MINTEQ (Allison *et al*., 1991) at each iteration step.

The use of an external geochemical software tool with designated thermodynamic databases is interesting so as to accurately calculate chemical speciation and pH. Software tools as PHREEQC and MINTEQ are generally accepted tools for equilibrium water quality modelling and have a dedicated and proven solver for chemical speciation calculations. However, simulation times using the full PHREEQC/MINTEQ thermodynamic databases for chemical speciation may be longer than when an integrated code is used (Lizarralde *et al*., 2014). On the other hand, the latter may be less flexible and complete. Hence, **an important challenge exists in the development of an efficient methodology for solving the (stiff) equations in nutrient recovery models. A compromise should be found between model accuracy and simulation times.**

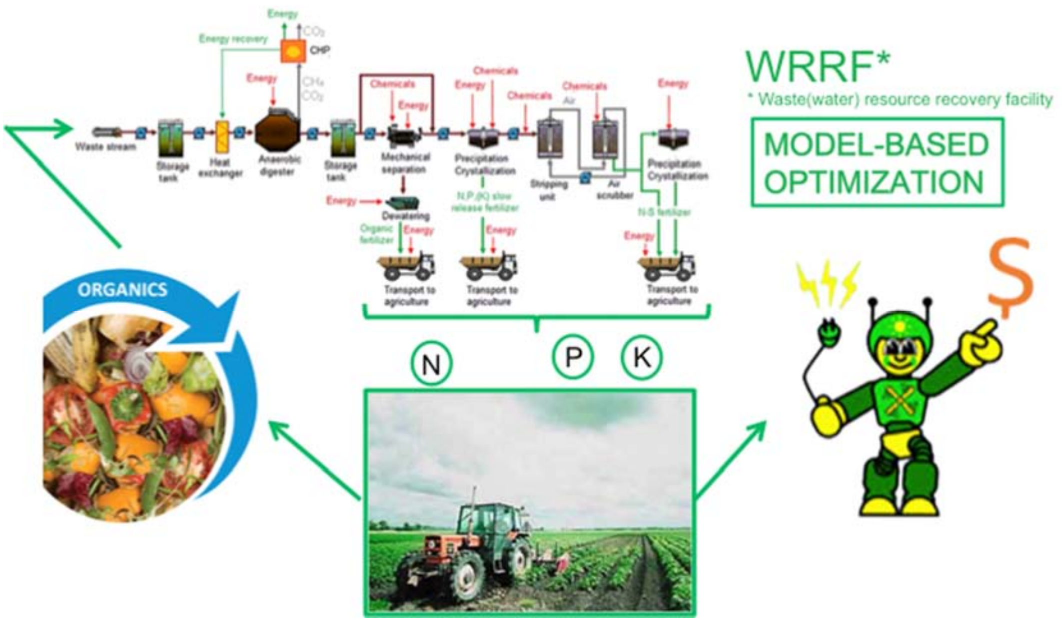
8.5 Conclusions and perspectives

The advances and limitations in modelling and optimization of nutrient recovery systems were reviewed. In order to select important model outputs, a brief overview of relevant fertilizer quality specifications was also provided. Based on the findings, recommendations for model development in view of nutrient recovery were specified.

Further research should involve the construction of a generic nutrient recovery model library based on detailed solution speciation and reaction dynamics aiming at fertilizer quantity and quality as model outputs. The library should be applicable as a generic tool for process optimization of single nutrient recovery systems, as well as for determination of optimal unit process combinations, in order to maximize resource recovery (nutrients, energy) from a particular waste stream and minimize energy and chemical requirements. Finally, numerical solution should be regarded as a critical step in resource recovery modelling, requiring further research and optimization. Starting from the modelling objectives and recommended model properties outlined in the present chapter, the development and implementation of a generic nutrient recovery model library will be aspect of Chapter 9.

CHAPTER 9:

DEVELOPMENT, IMPLEMENTATION, AND VALIDATION OF A GENERIC NUTRIENT RECOVERY MODEL (NRM) LIBRARY



Towards a generic modelling framework for nutrient recovery processes

Redrafted from:

Vaneeckhaute, C., Claeys, F.H.A., Tack, F.M.G., Meers, E., Belia, E., Vanrolleghem, P.A., submitted. Development, implementation, and validation of a generic nutrient recovery model (NRM) library.

Abstract

In the transition from waste(water) treatment plants (WWTPs) to waste(water) resource recovery facilities (WRRFs), the construction of accurate mathematical models at minimal computational effort is becoming an important challenge to hasten process and treatment train implementation and optimization. The present chapter aimed at the development of a generic nutrient recovery model (NRM) library based on detailed solution speciation and reaction kinetics, with focus on fertilizer quality and quantity as model outputs. The purpose was to provide a common base that compiles the large body of knowledge on nutrient recovery processes currently available from research studies and operational experience. To this end, dynamic physicochemical three-phase process models for precipitation/crystallization, stripping, and acidic air scrubbing as key units were developed, as well as four ancillary units. In addition, a compatible combined biological-physicochemical anaerobic digester model was constructed. The latter includes sulfurgenesis, biological N/P/K/S release/uptake, interactions with organics, among all other relevant processes, such as precipitation, ion pairing, and liquid-gas transfer.

In order to facilitate numerical solution, an efficient procedure for calling PHREEQC selected chemical speciation outputs from the Modelica coded kinetic transformation models using the Tornado(/WEST) software kernel was developed. A reduction of execution time was established at two critical points during model simulations: i) the uploading and reading of the database and input files (through PHREEQC model reduction), and ii) the transfer of data between PHREEQC and Tornado (through tight model coupling). An average improvement of model simulation speeds of 64±10 % an 79±7 % was obtained using the developed reduced models as compared to full PHREEQC and MINTEQ databases, respectively. An important discovery concerns the omission of essential physicochemical components/species/reactions in view of nutrient recovery, e.g. aluminum phosphate, potassium struvite, and ammonium sulfate precipitation, in the existing standard geochemical databases. Because of these flaws, a generic database with the purpose of nutrient recovery was created for future applications.

The models were successfully validated against experimental results at steady state. Their functionality in terms of increased process understanding and optimization was also demonstrated. All model results were found very sensitive to the input waste flow composition through its direct effect on pH. For optimization of process performance and sustainability, a more detailed input characterization than is common for WRRFs today is advised. Based on the results, recommendations for further experimental research in order to fully calibrate the NRMs were provided.

Keywords: *combined chemical equilibrium-kinetic modelling approach, chemical speciation, generic physicochemical framework, numerical solution, process optimization, reduced PHREEQC.*

Résumé

Dans la transition des stations d'épuration d'eaux usées (STEP) vers des stations de récupération des ressources de l'eau et des déchets (StaRRED), la construction des modèles mathématiques précis à l'effort de calcul minimal devient un défi important pour accélérer la mise en œuvre et l'optimisation des processus et des chaînes de traitement. Le présent chapitre vise le développement d'une librairie générique de modèles pour la récupération des nutriments (MRN) basée sur la spéciation chimique de la solution et sur la cinétique détaillée des réactions, tout en mettant l'accent sur la qualité et la quantité des produits fertilisants en sortie de modèle. L'objectif était de fournir une base commune qui compile le grand corpus de connaissances sur les processus de récupération des nutriments actuellement disponibles à partir des études de recherche et d'expérience opérationnelle. À cette fin, des modèles dynamiques et physico-chimiques de processus en trois phases pour la précipitation/cristallisation, le stripage et le lavage à air acide comme unités clés ont été développés, ainsi que quatre unités auxiliaires. En outre, un modèle combinant la biologie et la physicochimie de la digestion anaérobie a été construit. Ce dernier inclut la genèse de soufre, la libération/absorption biologique de N/P/K/S, les interactions avec les matières organiques ainsi que tous les autres processus pertinents, comme les précipitations, les couplages des ions et les transferts gaz-liquide.

Afin de simplifier la solution numérique du modèle, une procédure efficace capable d'extraire les sorties d'intérêt du modèle de spéciation chimique PHREEQC et de les transmettre au modèle développé en Modelica, utilisant le logiciel Tornado/WEST, a été développée. Une réduction du temps d'exécution a été établi à deux points critiques pendant les simulations de modèle: i) l'ajout et la lecture des bases de données et des fichiers d'entrée (par la réduction du modèle PHREEQC), et ii) le transfert de données entre PHREEQC et Tornado (par le fort couplage des modèles). Une réduction moyenne des temps de simulation de modèle de 64±10 % et 79±7 % a été obtenue en utilisant les modèles réduits développés versus un modèle utilisant les bases de données complètes de PHREEQC et MINTEQ, respectivement. Une découverte importante concerne l'omission des composants/espèces/réactions physico-chimiques essentielles en vue de la récupération des nutriments, par exemple la précipitation de phosphate d'aluminium, de struvite de potassium et de sulfate d'ammonium, dans les bases de données géochimiques existantes. En raison de ces défauts, une base de données générique visant la récupération des nutriments a été créé pour les applications futures.

Les modèles ont été validés avec succès par comparaison avec les résultats expérimentaux à l'état d'équilibre. Leur fonctionnalité accrue en termes de compréhension et optimisation des processus a également été démontrée. Tous les résultats des modèles ont été trouvés très sensibles à la composition des flux de déchets d'entrée par leur effet direct sur le pH. Pour l'optimisation de la performance et de la durabilité des processus, une caractérisation des flux d'entrée plus détaillée que la caractérisation réalisée dans les StaRRED actuellement est recommandée. Basé sur ces résultats, des recommandations pour la poursuite des recherches expérimentales afin de calibrer entièrement les MRN ont été fournies.

Mots-clés: *approche de modélisation d'équilibre chimique–cinétique combinée, cadre physicochimique générique, optimisation des processus, PHREEQC réduite, solution numérique, spéciation chimique.*

9.1 Introduction

In the transition from waste(water) treatment plants (WWTPs) to waste(water) resource recovery facilities (WRRFs), mathematical models are becoming important tools to hasten nutrient recovery process implementation and optimization (Chapter 8). Indeed, models may aid in technology development, process operation, optimization, and scale-up in a cost-effective way (Rieger *et al.*, 2012; Yu *et al.*, 2011). Although to date many processes for the recovery of nutrients from waste(water) have been proposed and applied to varying degrees, no generic models for nutrient recovery aiming at the construction and optimization of treatment trains for resource recovery are currently available. Moreover, existing model libraries for WWTPs, e.g. activated sludge models (ASMs), do not allow the integration of nutrient recovery unit processes and/or the coupling of a nutrient recovery treatment train. This is due to the omission of key fundamental physicochemical components and transformations that are essential to describe nutrient recovery (Chapter 8). Consequently, the potential to adequately put together an optimal treatment train of unit processes and their operating conditions that maximize nutrient recovery and fertilizer quality is missing.

This research aimed at developing generic integrated biological-physicochemical three-phase mathematical process models for the best nutrient recovery systems currently available (as selected in Chapter 2). The models are based on detailed solution speciation and reaction kinetics. This **nutrient recovery model (NRM) library is a compilation of the large body of knowledge** on nutrient recovery processes that is currently available from research studies and operational experience. In contrast to existing model libraries for waste(water) treatment (Chapter 8), e.g. the ASM library, the scope of the NRM library starts at the anaerobic digester and focusses on the nutrient recovery treatment train following the digester (Fig. 9.1). In addition to the development of a generic physicochemical modelling framework, a critical and challenging step when combining (stiff) biological and physicochemical differential equations is the numerical solution (Chapter 8). Hence, a generic methodology to allow for accurate chemical speciation at minimal computational effort is also proposed.

The development of such a common basis for modelling of nutrient recovery systems requires considerable testing and validation, and comes along with the discovery of new data gaps and needs for experimentation. In fact, there is a long development path before new models may actually be used by the different stakeholders in the field. To speed up this process, three different nutrient recovery model user objectives (NRM-UOs) were aimed from short to longer term:

1. NRM-UO I: Use of models for increased process understanding and optimization;
2. NRM-UO II: Use of models for process design and control (e.g. fertilizer quality) operations;
3. NRM-UO III: Use of models to assess environmental nutrient pollution (greenhouse gases (GHGs), nutrient leaching, etc.) over the whole waste-nutrient-soil-plant system.

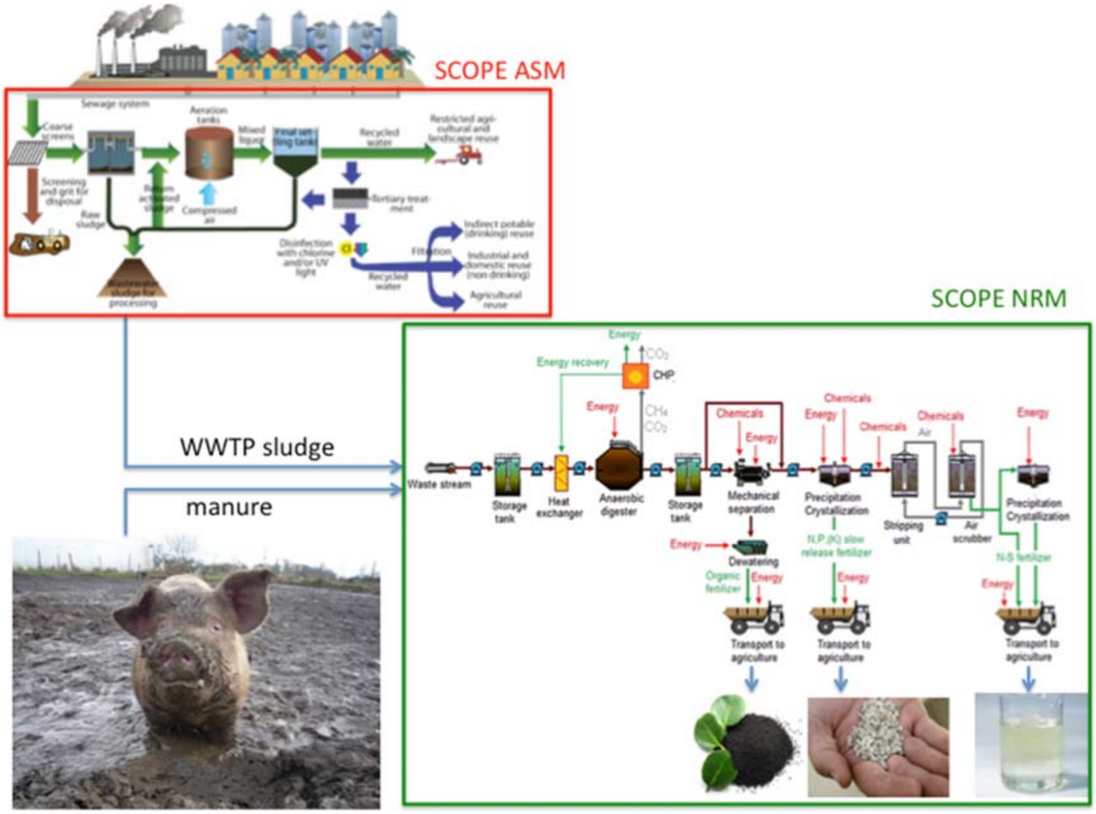


Figure 9.1 Scope of the nutrient recovery model (NRM) library as compared to the activated sludge model (ASM) library.

The present chapter describes the specifications, the development methodology, and implementation of the generic refined NRM framework. Aiming at the first stage of use (NRM-UO I), the **functionality of the models in terms of increased process understanding and optimization is demonstrated through testing and validation**. Recommendations for further experimental research required to fully calibrate the models, as well as case-specific potential extensions, are provided. As such, in a second phase (NRM-UO II; beyond this PhD), the fine-tuned models may allow for technology design and process control. In a third phase (NRM-UO III; beyond this PhD), the models may be coupled to soil nutrient balance models (e.g. the NDICEA software tool used in Chapter 5) to allow for environmental pollution assessments, which may aid in governmental decision-making (e.g. setting nutrient pollution levels, subsidies, etc.), as well as agricultural decision-making (e.g. timing of fertilizer application, fertilizer mixing, etc.). The expected benefits from this first phase of development for the different stakeholders are:

i. Increased process understanding (consultants, operators, researchers, technology developers);
ii. Increased use of models to specify operational conditions (consultants, operators);

iii. Increased use of models to select important factors for monitoring (consultants, operators);
iv. Increased use of models to set up an optimal treatment train for nutrient recovery (consultants, researchers);
v. Optimization of process performance (consultants, operators, researchers, technology developers);
vi. Optimization of fertilizer quality (consultants, operators, researchers, technology developers);
vii. Increased thinking prior to decision-making, e.g. through study of 'what if' scenarios (consultants, operators, researchers, technology developers);
viii. Increased technology transfer from research to industry (researchers, operators, technology developers);
ix. Common basis for further model development and validation studies to make outcomes comparable and compatible (consultants, operators, researchers, technology developers).

All these benefits should hasten and facilitate the implementation of cost-effective full-scale treatment trains for anaerobic digestion and nutrient recovery from biodegradable waste(water) flows.

9.2 Nutrient recovery model (NRM) methodology

The methodology used for NRM development can be represented by six steps, shown in Figure 9.2 and described in detail in the sections below.

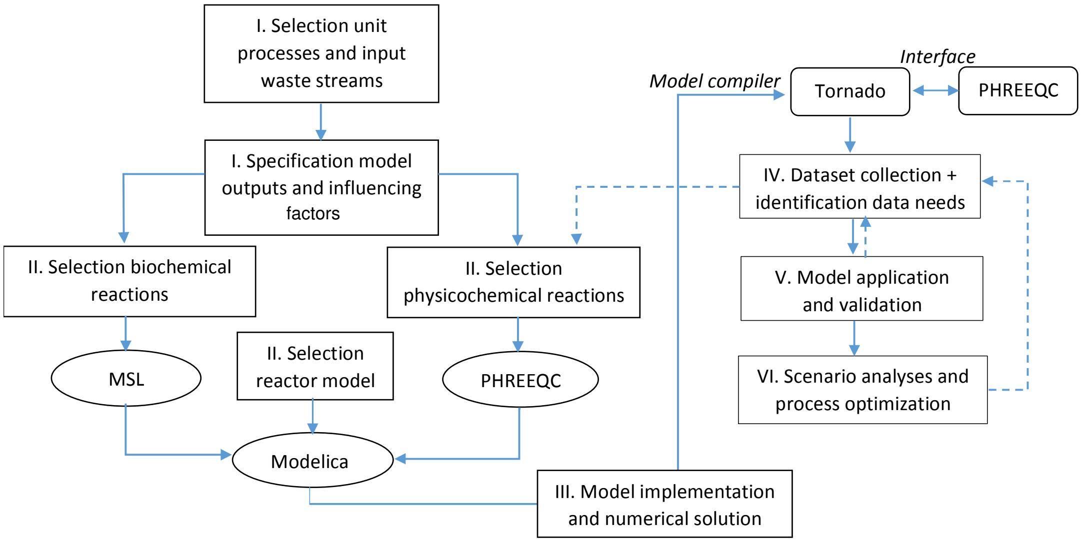


Figure 9.2 Six-step model development scheme. Step I: definition of modelling objectives; Step II: theoretical model development. MSL = model specification language.

The generic models are based on mass balances to describe physicochemical and biochemical transformation and transport processes, as well as an accurate calculation of water chemistry in order to correctly define solution speciation and driving forces for component transformation. Two key features of the models should be clear. First, a dynamic modelling approach, i.e. one that accounts for time-dependent changes in the state of the system, was applied, because the models should be applicable to real-time situations and (variable) operating conditions, such as i) periodical load variations, e.g. absence of operators in weekends/evenings, seasonal variations, etc., ii) individual disturbances, e.g. rain events and incorrect control manipulations, and iii) systems that are operated intermittently or cyclically as is the case for multiple nutrient recovery processes, e.g. intermittent aeration in stripping systems and (semi-)batch processes to obtain target fertilizer specifications, e.g. a predefined ammonium sulfate (AmS) concentration in the acidic air scrubber (Chapter 8).

Secondly, the geochemical modelling software tool PHREEQC, i.e. PH REdox EQuilibrium in C language (Parkhurst and Appelo, 2013), was used for two purposes in the development of the NRM library:

1. **PHREEQC for NRM building** (Section 9.2.2.1), which involves the selection of species and reactions to be included in the models, the preparation of a reduced PHREEQC model database, and the definition of PHREEQC selected outputs;
2. **PHREEQC for NRM simulation** (Section 9.2.3), which involves the tight coupling of the reduced PHREEQC model to a kinetic and mass balance model in order to accurately calculate speciation and driving forces for component transformations at each time step during the model simulations.

As such, a methodology to allow for accurate chemical speciation at minimal computational effort was developed (see below).

Note that in the following sections, variables will be defined with their dimension given in straight brackets: $[M]$ for mass, $[L]$ for length, and $[T]$ for time.

9.2.1 Step I: Definition of modelling objectives

9.2.1.1 Selection of unit processes and input waste streams

A literature review on nutrient recovery technologies (Chapter 2; Vaneeckhaute *et al.*, 2013a) was conducted in order to select the best available technologies as key unit processes for modelling (Table 9.1: four key units). The selection was made based on the economic feasibility, full-scale application at this stage, and the potential to produce marketable end products for agricultural applications (see Chapters 2-8; Vaneeckhaute *et al.* 2013a,b,c; 2014, 2015a,b,c). With the purpose of modelling treatment trains, four ancillary units were additionally selected (Table 9.1).

Table 9.1 Key units and ancillary units included in the nutrient recovery model (NRM) library.

Type	Unit	Model name
Key unit	Anaerobic digester	NRM-AD
Key unit	Precipitation/crystallization unit	NRM-Prec
Key unit	Stripping unit	NRM-Strip
Key unit	Air scrubber	NRM-Scrub
Ancillary unit	Settling tank	NRM-Settle
Ancillary unit	Storage tank	NRM-Store
Ancillary unit	Chemical dosing unit	NRM-Chem
Ancillary unit	Heat exchanger	NRM-Heat

As mentioned above, in contrast to existing studies, the scope of the present research starts at the anaerobic digestion unit and focusses on the nutrient recovery treatment train following the digester (Fig. 9.1). No recycle flows to upstream facilities in the WRRF, e.g. to an activated sludge (AS) system, were currently considered. In later stages, the proposed NRM models could be coupled to activated sludge models (ASMs), if a compatible generic physicochemical framework is also integrated in the ASMs.

As input waste stream to the digester, manure and sludge (primary and secondary sludge, and mixtures of these) from WWTPs removing nitrogen (N) and chemical oxygen demand (COD) were considered for NRM-UO I (Fig. 9.1). Digestate (the remaining product after digestion) was considered as input stream to the key units for controlled nutrient recovery following the digester. WWTP sludge was selected, next to manure, as the current most advanced models for anaerobic digestion originate from the municipal wastewater and sludge treatment sector (Chapter 8). Nevertheless, for future applications, the generic NRM-AD implementation allows easy extension to co-digestion of other organic-biological wastes, e.g. using the general integrated solid waste co-digestion (GISCOD) modelling tool proposed by Zaher *et al.* (2009b) (Chapter 8: Section 8.3.1). The NRM-AD model can also be extended to allow for specific reactions occurring during the treatment of sludge from enhanced biological phosphorus (P) removal (EBPR) as e.g. in Ikumi (2011), but this was considered to be outside the scope of NRM-UO I.

9.2.1.2 Specification of model outputs and influencing factors

In order to develop valuable tools for process optimization, the desired model outputs and factors that may affect these outputs were defined for each NRM key unit (see Chapter 8: Tables 8.1-8.2).

Obviously, the total content of **principal macronutrients**, N, P, and potassium (K), in the fertilizer product and the amount of **biogas production** are important model outputs, so as to quantitatively and qualitatively determine the overall resource recovery. Next to the three principal macronutrients, N, P, and K, previous chapters have shown the relevance of the **secondary macronutrient**, sulfur (S), in the context of nutrient recovery. Some motivations for inclusion of S in the models were: i) the demand for S fertilization in agriculture is increasing, hence its recovery deserves attention (Till, 2010), ii) S may precipitate with iron (Fe), making Fe less available for P precipitation, iii) sulfate reducing bacteria (SRBs) compete with methane (CH_4) producing bacteria for the same substrate, hence at high sulfate concentrations CH_4 production may be reduced (UCT, 2007), iv) hydrogen sulfide (H_2S) is an important inhibitor of CH_4 producing bacteria (UCT, 2007), and v) high biogas H_2S values cause important concerns (toxicity, corrosion, biogas pollution, etc.), e.g. in the paper industry (Reiter and Piccot, 2004). Calcium (Ca) and magnesium (Mg) are also of importance, mainly for their soil improving properties and their interaction with P (Chapters 5-6).

For all nutrient recovery systems, the **percentage recovery of the target nutrient** is a key performance measure. It was calculated using Equation 9.1:

$$\% \, Recovery = \frac{S_i^{i} . Q_{in} - S_i^{out} . Q_{out}}{S_i^{in} . Q_{in}} . 100 \qquad \boldsymbol{Eq. (9.1)}$$

in which S_i^{in} and S_i^{out} are the in- and outgoing liquid flow activities for component i $[\mathrm{M\ L^{-3}}]$, and Q_{in} and Q_{out} are the in- and outgoing flow rates $[\mathrm{L^3\ T^{-1}}]$.

Furthermore, the **macronutrient use efficiency** (N, P, K, S) in the fertilizer end products is an important factor in determining the agronomic potential and sustainability of the produced fertilizers (Chapters 5-6). It was evaluated as the percentage available or mineralized nutrient content over the total nutrient content, e.g. NH_4-N/total N, ortho-P/total P, etc. This is possible by means of a solution speciation calculation (Section 9.2.2.1).

Next, the fertilizer **pH and salt content** are of important concern as they may impact on soil quality (Chapters 5-6). The pH was directly calculated from solution speciation. Salts were characterized using the sodium adsorption ratio (SAR), i.e. the relative amount of available sodium (Na) over divalent cations, Ca and Mg (Hillel, 2008; Chapter 5: Eq. 5.1).

Factors that may additionally determine the value of the recovered product are the **particle size** (for solid fertilizers), the **density** (for liquid fertilizers), and the **product purity** (Chapters 2, 4-5). To date (with the purpose of NRM-UO I), the particle size was evaluated as mean particle diameter (Section 9.2.2.2), but in future research one may be interested in particle size distributions (PSDs) (Nopens *et al.*, 2014; Perez *et al.*, 2008). Hence, PSDs may be included for future applications, e.g. using the generic approach presented by Perez *et al.* (2008).

For the NRM-Prec unit, product purity was evaluated by calculating the fraction of precipitated target mineral(s) over the total product collected, taking in account the presence of multiple competing and concurrent precipitation reactions. To this end, also the precipitation of principal **micronutrients** occurring in waste(water) treatment, such as Fe and aluminium (Al), were evaluated, as these precipitates may negatively impact on the fertilizer P release in the soil (Chapter 6). Moreover, pollution with **organics** was accounted for. For the NRM-Strip/NRM-Scrub units, purity was evaluated by calculating the amount of volatile target component(s) captured over the total amount of gas/liquid captured.

Finally, the **formation of scale** within the treatment module is an important operational bottleneck for multiple nutrient recovery technologies. Especially calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) formation in the stripping and scrubbing units are of concern (Chapters 2, 8). To determine scale formation, the amount of $CaCO_3$ and $MgCO_3$ precipitates formed were evaluated in time, next to other relevant precipitation reactions. The scaling potential was then examined by using the scaling criteria of the Ryzner Index (Tchobanoglous *et al.*, 2003).

9.2.2 Step II: Theoretical model development

The dynamic mathematical model of each unit process was built using (Fig. 9.3): i) the definition of a chemical speciation model by means of geochemical modelling software (PHREEQC for model building, Section 9.2.2.1), ii) the description of a kinetic physicochemical and biochemical transformation model tailored to the models developed in the first step (Section 9.2.2.2), and iii) the selection of a reactor mass balance model to describe the (time-dependent) process conditions (Section 9.2.2.3).

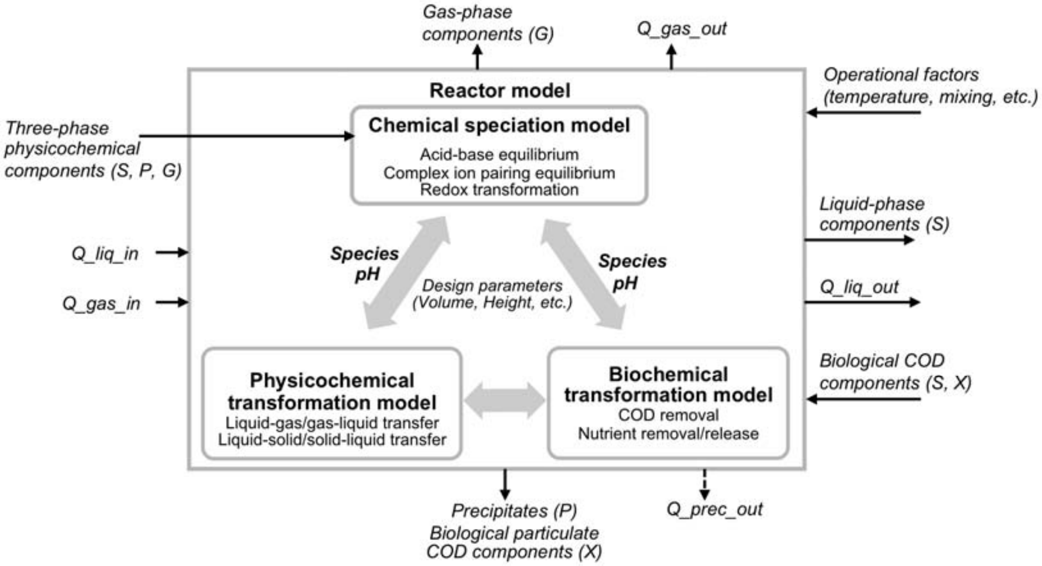


Figure 9.3 Development of combined physicochemical-biological three-phase (liquid-solid-gas) process models. COD = chemical oxygen demand; G = gas; P = precipitate; Q_gas = gas flow rate; Q_liq = liquid flow rate; Q_prec = precipitate extraction rate (for NRM-Prec); S = soluble; X = biological particulate COD.

9.2.2.1 Chemical speciation model: PHREEQC for NRM building

In order to describe the water chemistry in each system, first the potentially present chemical components and species were defined, and the possible heterogeneous physicochemical transformation reactions (gas transfer, precipitation) were selected using generally accepted geochemical software for equilibrium water quality modelling, PHREEQC 3.0.6 (Parkhurst and Appelo, 2013). Visual MINTEQ 3.1 was used as a control (Allison *et al.*, 1991). As the involved homogeneous reactions (acid-base, ion pairing) in a speciation calculation are very rapid compared to heterogeneous physicochemical reactions and biological reactions (Batstone *et al.*, 2012), instantaneous equilibrium was assumed to be adequate for solving water chemistry in NRMs. A reduced PHREEQC database and input script with definition of selected model outputs were developed for each key unit, so as to compromise between model accuracy and simulation times when coupling the speciation model to the kinetic mass balance model (Section 9.2.3.1). The proposed four-step procedure used for NRM building, involving the selection of the relevant species/reactions and the preparation of the reduced PHREEQC chemical speciation model, is presented in Figure 9.4 and further described below.

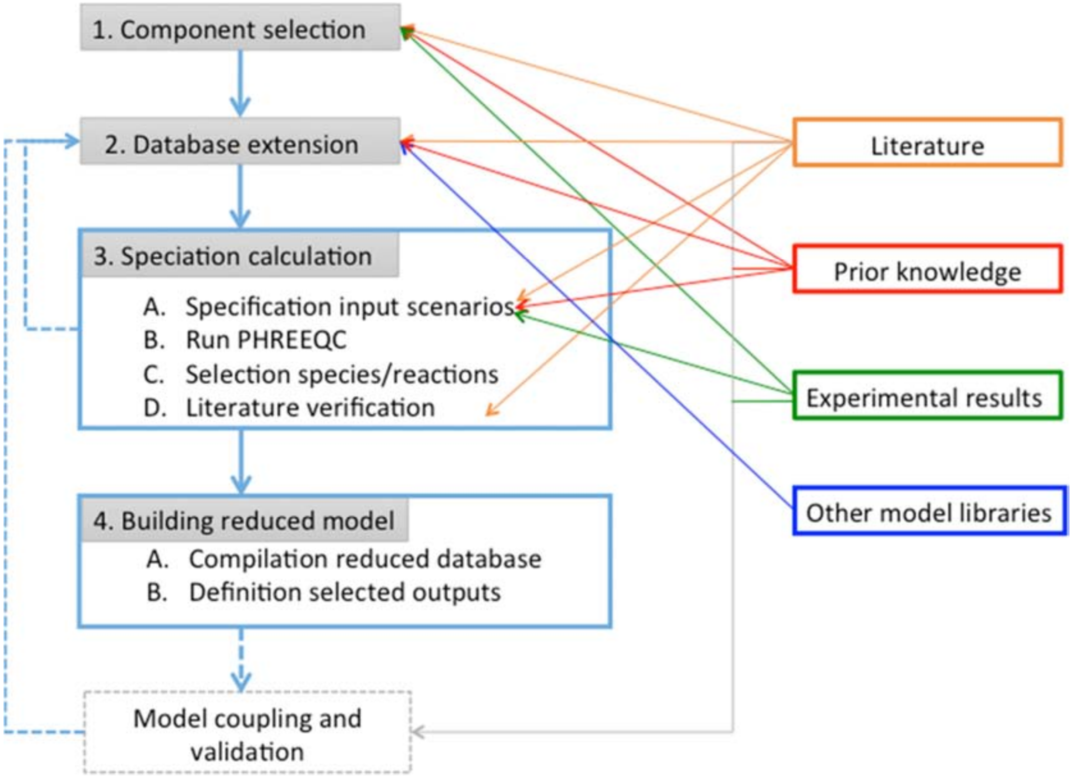


Figure 9.4 Use of PHREEQC for nutrient recovery model (NRM) building: methodology for selection of relevant species and reactions per key unit and development of a reduced PHREEQC chemical speciation model.

Step 1: Selection of relevant components for each unit process

Based on literature, collected experimental data, and prior knowledge (Section 9.2.4 + Chapters 2-8; Vaneeckhaute *et al.* 2012, 2013a,b,c, 2014, 2015b,c), the most important physicochemical dissolved components to include in models for nutrient recovery from both (digested) manure and sludge were selected for each key unit process (Table 9.2). In line with the selected model outputs (Section 9.2.1.2), it was aimed to represent **five important component classes**:

1. All important macronutrients for recovery in line with the findings of the previous chapters (~ determine recovery efficiency and fertilizer value);
2. Gaseous compounds (~ determine biogas production, volatilization, odors, greenhouse gas emissions, etc.);
3. Salts (~ impact on ionic strength and soil quality);

4. Inorganic and organic carbon compounds (~ impact on biogas production, product purity, and scaling);
5. Micronutrients that may occur in large quantities in waste(water) treatment, e.g. Fe and Al as a result of coagulation/flocculation practices (~ impact on product purity and recovery potential).

Table 9.2 Dissolved physicochemical components selected for each key unit in the nutrient recovery model (NRM) library. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripping; Scrub = scrubbing. Component names are given by their valence state.

Symbol	Component	AD	Prec	Strip	Scrub	Symbol	Component	AD	Prec	Strip	Scrub
S_Acetate	Acetate	X	X	X	-	S_K	Potassium	X	X	X	-
S_Al	Aluminium	X	X	X	-	S_Mg	Magnesium	X	X	X	-
S_Butyrate	Butyrate	X	X	X	-	S_Na	Sodium	X	X	X	-
S_Ca	Calcium	X	X	X	-	S_N_min3_	Nitrogen (-III)[f]	X	X	X	X
S_C_4_	Carbon (+IV)[a]	X	X	X	X	S_N_0_	Nitrogen (0)[g]	X	(X)[l]	X	X
S_Cl	Chloride	X	X	X	-	S_N_5_	Nitrogen (+V)[h]	X	X	X	X
S_C_min4_	Carbon (-IV)[b]	X	-	X	X	S_O_0_	Oxygen (0)[i]	-	(X)[l]	X	X
S_DOM	Dissolved OM[c]	X	X	X	-	S_P	Phosphorus	X	X	X	-
S_Fe	Iron	X	X	X	-	S_Propionate	Propionate	X	X	X	-
S_H_0_	Hydrogen (0)[d]	X	-	X	X	S_S_min2_	Sulfide (-II)[j]	X	X	X	X
S_H_I_	Hydrogen (+I)[e]	X	X	X	X	S_S_6_	Sulfate (+VI)[k]	X	X	X	X
S_H2O	Water	X	X	X	X	S_Valerate	Valerate	X	X	X	-

[a] carbonate species; [b] CH_4(aq); [c] OM = organic matter; [d] H_2(aq); [e] refers to pH; [f] ammonia species; [g] N_2(aq); [h] nitrate species; [i] O_2(aq); [j] sulfide species; [k] sulfate species; [l] values between brackets represent the use of air instead of chemicals for pH-adjustment.

Since redox reactions too were considered, components that exist in more than one valence state in solution were identified by their component name followed by their valence. For instance, i) the component S_C_4_ constitutes CO_3^{2-} plus HCO_3^- plus H_2CO_3 (or $CO_{2,aq}$) plus various other carbonate complexes present in the solution, such as $MgCO_3$ and $CaHCO_3^+$, and ii) S_N_min3_ constitutes both NH_4^+ and dissolved NH_3, as well as its various complexes. Only for Fe, the two valence states, Fe (+II) and Fe (+III), were lumped together into one component for total Fe, as the measurement of its valency is complicated and generally not provided in practice in WRRFs, nor in literature. Yet, in the speciation calculation, the Fe (+II) / Fe (+III) redox equilibrium was considered, as calculated from the occurring redox potential. The input Fe redox states can optionally be specified, if such data are available.

As it is well-known that the presence of organic compounds may influence the purity of the recovered products (Kozic *et al.*, 2011), relevant interactions between inorganic and organic components were also accounted for. Among the organic biological components considered (see Section 9.2.2.3), volatile fatty acids (VFAs) up to valerate were included as individual components in the physicochemical models. Oh and Martin (2010) indeed emphasized the particular importance of their physicochemical behaviour in WRRFs. The remaining soluble organic chemical oxygen demand (COD) fractions (see Section 9.2.2.3) were lumped into one component, i.e. dissolved organic carbon (DOC; 1 g DOC ≈ 0.33 x g COD). For DOC, the complexation with metals (Ca, Mg) was computed using a competitive Gaussian model for dissolved organic matter (DOM; 1 mol DOC ≈ 8.6×10^{-2} mol DOM; USEPA, 1999). This simplified approach may be further refined for future applications, if more insights in the physicochemical behaviour of each particular COD fraction become available.

Finally, it should be remarked that heavy metals, such as cadmium (Cd), copper (Cu), and zinc (Zn), were not yet included in the speciation models. Nevertheless, heavy metals and the corresponding reactions are available in PHREEQC. Hence, the generic approach used for chemical speciation allows easy extension of the models to incorporate heavy metals for future applications.

Step 2: Addition relevant components/species/reactions to generic geochemical databases

To verify completeness, the generic PHREEQC (Phreeqc.dat) and Visual MINTEQ (minteq.v4.dat) databases were compared with each other, as well as with prior knowledge and with literature. Two observations were made: 1) the generic MINTEQ database is more complete than the PHREEQC one in view of WRRFs, 2) some important components, species, and reactions that can be expected in WRRFs are not included in either database. Hence, the generic database files were extended prior to use for speciation calculation (Table 9.3). The corresponding acid-base constants, ion pairing constants, solubility products, and other thermodynamics were taken from literature or other model libraries, as indicated in Table 9.3.

Table 9.3 Extensions made to the generic PHREEQC (P; Phreeqc.dat) and/or MINTEQ (M; minteq.v4.dat) database files, and the reference for thermodynamic data. DOM = dissolved organic matter.

Extension	**Name**	**Database**	**Reference**
Components	acetate, butyrate, propionate, valerate, DOM	P	M, USEPA (1999)
Species	Ca(acetate)$^+$, Ca(butyrate)$^+$, CaCl$^+$, Ca-DOM, $CaNH_3^{2+}$, $Ca(NH_3)_2^{2+}$, Ca(propionate)$^+$, Ca(valerate)$^+$, $FeH_2PO_4^+$, $FeNH_3^{2+}$, $Fe(NH_3)_2^{2+}$, H(acetate), H(butyrate), H-DOM, H(propionate), H(valerate), K(acetate), KCl(aq), KOH, KPO_4^{2-} Mg(acetate)$^+$, Mg(butyrate)$^+$, MgCl$^+$, Mg-DOM, $Mg(NH_3)_2^{2+}$, Mg(propionate)$^+$, Na(acetate), NaCl(aq), NaH_2PO_4(aq)	P	M, USEPA (1999)
	NH_2COO^-	P + M	Hafner and Bisogni (2009)
Precipitates	FeS(ppt), Mackinawite (FeS)	P	M
	$AlPO_4$, $K_2NH_4PO_4{:}6H_2O$, $(NH_4)_2SO_4$	P + M	NIST (2001)
	K-struvite ($MgKPO_4{:}6H_2O$)	P + M	Chauhan *et al.* (2011)

It should be noted that in the context of nutrient recovery from waste(water) flows as fertilizer products, the database extensions provided concern a fundamental contribution to the field. For example, K-struvite is (next to N-struvite) an interesting fertilizer (Chapter 2), though its precipitation reaction is not included in the standard databases. Also precipitation of aluminium phosphate ($AlPO_4$) is highly important in waste(water) treatment as often Al-salts are dosed for sludge conditioning, whereas the precipitation reaction of ammonium sulfate ($(NH_4)_2SO_4$) is essential for description of the scrubbing process. Noteworthy is also the clear impact of the omission of the species monosodium phosphate, i.e. NaH_2PO_4(aq), on the simulation results, that was found during model validation of the NRM-Prec (see Section 9.3.3.1). The generic extended database in view of nutrient recovery was named *'Nutricover.dat'* and will be made available for inclusion in future PHREEQC and Visual MINTEQ software packages.

Step 3: Speciation calculation - Selection relevant species and reactions

As mentioned above, the speciation calculation was conducted using PHREEQC 3.0.6, and Visual MINTEQ 3.1 was used as a control. An advantage of PHREEQC compared to most chemical software for water treatment is that saturation indices (SI's) are calculated by PHREEQC with the free ions only, for instance Ca^{2+} instead of total Ca, which increases the accuracy of precipitation reaction calculations (Parkhurst and Appelo, 2013).

The following methodology was used for selection of the relevant species and reactions:

A. *Specification of input scenarios (components + operational conditions);*
B. *Run PHREEQC under the various conditions defined in A;*
C. *Select relevant species and reactions based on the PHREEQC outputs;*
D. *Verify the selection of species and reactions with literature.*

A: Specification of input scenarios

Realistic ranges for the input component concentrations and operational conditions (pH, temperature, etc.) for the speciation calculations were adopted from literature and experimental data as described in Section 9.2.4, as well as through contact with technology providers (Chapter 2). The operational conditions and input streams tested for each key unit process are the following:

- Anaerobic digestion: no oxygen, pH: 5-8.5, temperature: 20-55 °C, input: sludge and manure;
- Precipitation unit: pH: 7-11, temperature: 20-50 °C, with and without $Ca(OH)_2$, CaO, $MgCl_2$, $Mg(OH)_2$, or MgO dosing (0-500 mol m^{-3}), input: digestate;
- Stripping unit: pH: 7-11, temperature: 20-70 °C, with and without NaOH, $Ca(OH)_2$, CaO, $Mg(OH)_2$, or MgO dosing for pH-increase (0-500 mol m^{-3}), input: digestate;
- Air scrubber: H_2SO_4-solution at pH: 1-4 and temperature: 15-25 °C, input: stripped air.

PHREEQC makes calculations using an input script in which the problem is specified via 'KEYWORDS' and associated datablocks. First, all possible realistic scenarios were introduced using the maximum/minimum values of all operational factors and input variables for each unit separately. Next, for each unit the composition of 20 different possible input flows (from literature: Astals *et al.*, 2013; Bhuiyan *et al.*, 2007; Cesur and Albertson, 2005; Martin, 2003; Mattocks *et al.*, 2002; Tchobanoglous *et al.*, 2003; Vaneeckhaute *et al.*, 2012, 2013b,c, 2014; Vlaco, 2012; Zaher *et al.*, 2009) was used for simulation under variable operating conditions. To this end, a PHREEQC input script was developed for each unit, involving the identification of the input waste flows (PHREEQC data blocks: 'SOLUTION' and/or 'GAS'). A batch reaction calculation was also coded if there is both a gas and liquid input, which is the case for the stripper and scrubbing unit (PHREEQC data block: 'REACTION'). Then, one factor at a time was allowed to increase within its range (e.g. PHREEQC code: REACTION_TEMPERATURE 20.0 – 70.0 in 51 steps), while the other factors were kept fixed. As such, a broad range of input scenarios was screened.

Note that contact was sought with the PHREEQC development center (Parkhurst D., personal communication 2014) to obtain feedback on the selection procedure presented above. However, currently in PHREEQC, no more feasible strategy is available for selection of the various simulation scenarios. Yet, the development of an adequate, but more time-efficient, procedure to go through a multidimensional set of factors will be aspect of further research. It is likely more practical to use PHREEQC coupled to another programming language, e.g. Tornado (Modelica) (Section 9.2.3), to go through a set of many combinations.

***B*: Run PHREEQC**

Speciation calculations in PHREEQC/MINTEQ are made using designated thermodynamic databases which include a wide range of data for mineral phases and compounds. The calculations are based on three types of equations: 1) equilibrium relationships, 2) concentration conditions or mass balances (one per component), and 3) electro-neutrality conditions or charge balances (Chapra, 2008; Stumm and Morgan, 1996). By inclusion of oxidation/reduction reactions in the database, also the components' redox states were defined in the speciation calculations. The pH may be defined or adjusted to achieve the charge balance. The Davies equation was selected for ion activity correction in the NRMs, similar to Ali and Schneider (2008), Galbraith *et al.* (2014), Lizarralde *et al.* (2013), and Ohlinger *et al.* (1998). The Davies ion activity correction was also recommended by Hafner and Bisogni (2009) above other relevant approaches, such as the Pitzer ion interaction approach. Moreover, the Peng-Robinson equation of state, which corrects for the nonideal behavior of gases, was used for calculating partial pressures (p) and solubilities (Parkhurst and Appelo, 2013). Furthermore, the temperature dependency of the thermodynamic equilibrium coefficients was expressed by means of the Van't Hoff relationship (Zumdahl, 2005), while the value of the water dissociation constant (K_w) at different temperatures (other than 25 ºC) was computed using the equation of Harned and Hamer (1933).

***C/D*: Selection criteria + verification**

From the speciation calculations the distribution of aqueous species (= ion activities) and saturation indices (SI) for phases (= driving forces for precipitation and gas transfer) were obtained. Soluble species with an insignificantly low activity, i.e. less than 0.01 % of the total component activity, were excluded from the NRMs. Solids that may potentially precipitate ($SI \geq |0|$) as well as gases that may volatilize (partial pressure (p) > 0) in the different units were selected. Conditions (pH, temperature) and rates for precipitation of the various forms of the selected minerals were also researched in the literature. The aim was to confirm the exclusion of the selected insignificant species and precipitates, while further identifying potential species and reactions that should be included in the database for each unit.

The number of species and reactions that were found to be relevant according the speciation calculations and that were included in each NRM are presented in Table 9.4. The list of species involved and the transformation reactions included in each model are presented in

Table 9.4 Number of selected species and reactions for each key unit in the nutrient recovery model (NRM) library resulting from speciation calculations using PHREEQC (and Visual MINTEQ as control) modelling software. AD = anaerobic digestion; Prec = precipitation/ crystallization; Strip = stripping; Scrub = scrubbing.

	NRM-AD	NRM-Prec	NRM-Strip	NRM-Scrub
No. of dissolved ionic species	**80**	**86(87)[a]**	**80**	**18**
No. of reactions				
Acid-base reactions	12	11	10	6
Ion pairing	48	55	47	2
Redox reactions	6	4/(5)[a]	7	6
Precipitation/Dissolution	27	28	30	1
Liquid-gas/Gas-liquid exchange	7	0/(5)[a]	7	7

[a] Values between brackets represent the use of air instead of chemicals for pH-adjustment.

Appendix 5 (Table A5.1 and Tables A5.2-5.6, respectively).

Step 4: Building of a reduced model

Knowing that the generic geochemical model databases contain more than 3,000 species (Allison *et al.*, 1991), it was expected that the elimination of irrelevant species and reactions can have a significant impact on the simulation speed. As such, with the purpose of reducing model complexity and simulation times when coupling PHREEQC for NRM simulation (Section 9.2.3), a new PHREEQC database file including only the selected reactions and species was set up for each unit process. Moreover, a ‘SELECTED_OUTPUT’ data block was coded in the input script for each unit in order to transcribe only the appointed species and driving forces to the resulting outputfile. The latter is required for efficient coupling of the selected outputs to the kinetic and mass balance model (Section 9.2.3).

The chemical speciation scripts developed above were run in PHREEQC using the full Phreeqc.dat (P) and minteq.v4.dat (M) databases, both available in the PHREEQC 3.0.6 release. A comparison of simulation times using the full databases and the corresponding reduced database is presented in Table 9.5.

Table 9.5 Simulation times (s) and improvement (%) using the reduced PHREEQC database as compared to the full Phreeqc.dat (P) / minteq.v4.dat (M) databases for simulation of the chemical speciation scripts developed for each key unit in the nutrient recovery model (NRM) library. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripping; Scrub = scrubbing.

Key unit	**Simulation time (s) Reduced PHREEQC**	**Simulation time (s) Full PHREEQC (P) / MINTEQ (M)**	**Improvement (%)**
NRM-AD	0.031	0.094 (P) / 0.185 (M)	67 (P) / 83 (M)
NRM-Prec	0.047	0.094 (P) / 0.172 (M)	50 (P) / 73 (M)
NRM-Strip	0.047	0.156 (P) / 0.172 (M)	70 (P) / 73 (M)
NRM-Scrub	0.020	0.066 (P) / 0.157 (M)	70 (P) / 87 (M)

An average improvement of model simulation speeds of 64±10 % and 79±7 % was obtained using the reduced database as compared to full Phreeqc.dat and minteq.v4.dat, respectively. The observed deviation between PHREEQC and MINTEQ shows again the higher completeness of the MINTEQ database. Note that the presented simulation times in Table 9.5 concern the chemical speciation model only, so without the coupling to the kinetic and mass balance model. Yet, this model reduction is clearly relevant in terms of WRRFs, since the speciation model is run at every time step during NRM model simulations (Section 9.2.3.3). Evidently, it is important for model validation to keep in mind that a model reduction was performed. As such, for example, it was discovered during initial validation of the NRM-Prec model that the species NaH_2PO_4(aq) was lacking in the reduced database, though essential for correct prediction of P recovery (Section 9.3.3.1).

9.2.2.2 Physicochemical transformation model

Heterogeneous physicochemical reactions, such as liquid-gas transfer and precipitation, occur much slower than the homogeneous reactions involved in the speciation calculations presented above. Hence, a kinetic approach was applied in order to allow for the dynamic variation of the constituents.

a) Liquid-gas / gas-liquid transfer

Gas exchange processes in resource recovery systems can occur passively, i.e. without intensive gas bubbling (NRM-AD), or actively, i.e. with gas bubbling driven by an external air flow (NRM-Strip, NRM-Scrub). For both cases similar kinetic gas exchange formulations, based on the concentration driving force between the liquid and gas phases, apply (Eq. 9.2):

$$\rho_{T,i}\ [\mathrm{M\ L^{-3}\ T^{-1}}] = K_{L/G,i}.\,a\,.\,(S_{liq,i} - H_{T,i}.\,p_{gas,i}) \qquad \boldsymbol{Eq.(9.2)}$$

where $S_{liq,i}$ is the liquid phase activity of component i $[\mathrm{M\ L^{-3}}]$, $p_{gas,i}$ is the partial pressure in the gas phase of component i (atm), $H_{T,i}$ is the temperature-dependent Henry coefficient $[\mathrm{M\ L^{-3}\ atm^{-1}}]$, $H_{T,i}.\,p_{gas,i}$ represents the saturation concentration of gas component i in the liquid, $K_{L/G,i}$ is the overall liquid-gas mass transfer coefficient $[\mathrm{L\ T^{-1}}]$, and a is the specific surface of the gas bubbles per reactor volume $[\mathrm{L^{-1}}]$. Temperature dependency of H was described by a Van't Hoff relationship (Powers *et al.*, 1987), while temperature dependency of $K_{L/G,i}a$ was described using the Arrhenius equation (Chapra, 2008). Through the coupling with PHREEQC (Section 9.2.3.1), both $S_{liq,i}$ and $p_{gas,i}$ can be calculated at every time step during the simulations. The total gas phase pressure was computed using Dalton's law of partial pressures (Stumm and Morgan, 1996).

Furthermore, for calculation of $K_{L/G,i}a$, a distinction was made between active and passive systems, as the values may differ significantly in practice (Chapra, 2008; Sotemann *et al.*, 2006; Tchobanoglous *et al.*, 2003). Moreover, a second distinction was made depending on the solubility of the gas considered, which determines whether mass transfer is liquid film controlled (for low to moderate soluble gases: H > 0.55, i.e. CH_4, CO_2, H_2, H_2S, N_2, O_2 = all gases considered in the NRMs, except for NH_3) or gas film controlled (for very soluble gases: H < 0.55, e.g. NH_3). If the resistance to mass transfer is on the liquid side, the overall liquid mass transfer coefficient, $K_{L,i}$, can be perfectly adequate, while the overall gaseous mass transfer coefficient, $K_{G,i}$, provides a good estimation if the resistance is on the gas side. The relationship between the two coefficients can be represented by Equation 9.3:

$$\frac{1}{K_{L,i}} = \frac{H_{T,i}\,.R.T}{K_{G,i}} \qquad \boldsymbol{Eq.(9.3)}$$

in which R is the universal gas law constant (0.082 L atm mol^{-1} K^{-1}) and T the temperature (K). It should be noted that the above-mentionned overall mass transfer coefficients are actually derived from the individual mass transfer coefficients by Equation 9.4 (combined with Eq. 9.3 for $K_{G,i}$):

$$\frac{1}{K_{Li}} = \frac{1}{k_{L,i}} + \frac{H_{T,i}\,.R.T}{k_{G,i}} \qquad \boldsymbol{Eq.(9.4)}$$

in which $k_{L,i}$ and $k_{G,i}$ are the individual mass transfer coefficients that depend on the conditions at the interface and the bulk of the liquid and gas phase, respectively (Chapra, 2008; Tchobanoglous *et al.*, 2003). Nevertheless, since the concentrations at the interface are difficult to measure, the overall mass transfer coefficient is generally used for practical purposes.

As such, **four potential mass transfer scenarios** were considered:

1) Active liquid-gas/gas-liquid transfer (NRM-Strip, NRM-Scrub) of low to moderately soluble gases.

In this case, the penetration theory of Higbie (1935) was used to calculate the liquid mass transfer coefficient, $K_L a$ $[\mathrm{T}^{-1}]$. It states that diffusion is a non-steady state process and that the molecules of the solute are in constant random motion. Clusters of these molecules arrive at the interface, remain there for a fixed period of time, and some of them penetrate while the rest mixes back into the bulk of the phase. The transfer velocity was then formulated in terms of the average contact time of a gas bubble at the interface (Eq. 9.5; Chapra, 2008; Gujer, 2008):

$$K_{L/G}a = K_L a\,[\mathrm{T}^{-1}] = \sqrt{\frac{4.D_l.u}{\pi.d}}.\frac{\theta_{gas}.6.Q_{gas_{in}}}{d.V_{liq}} \qquad \boldsymbol{Eq.(9.5)}$$

in which d is the average gas bubble diameter (default = 3 mm; Gujer, 2008), u is the rise velocity of the gas bubbles (default = 0.3 m s^{-1}; Gujer, 2008), $\theta_{gas} = \frac{V_{gas}}{Q_{gas}}$ is the mean residence time of a gas bubble in the reactor $[\mathrm{T}]$, V_{gas} is the volume of all bubbles in the reactor or the total gas volume $[\mathrm{L}^3]$, and D_l is the liquid phase diffusion coefficient $[\mathrm{L}^2\,\mathrm{T}^{-1}]$. The latter was calculated at 298 K using the equation proposed by Schwarzenbach *et al.* (1993) (Eq. 9.6) based on the component's molecular weight (MW, $[\mathrm{M}\,\mathrm{M}^{-1}]$):

$$D_l\,[\mathrm{L}^2\,\mathrm{T}^{-1}] = \frac{2.7.10^{-4}}{MW^{0.71}} \qquad \boldsymbol{Eq.(9.6)}$$

The obtained D_l values using Equation 9.6 showed good equivalence with D_l values found in literature for wastewater systems (Chapra, 2008; Gujer, 2008; Tchobanoglous *et al.*, 2003).

2) Active liquid-gas/gas-liquid transfer (NRM-Strip, NRM-Scrub) of very soluble gases. In this case, Equation 10.5 was again applied, but now the gaseous phase diffusion coefficient (D_g) was used (Arogo *et al.*, 1999).

3) Passive liquid-gas/gas-liquid transfer (NRM-AD) of low to moderately soluble gases. In this case, the mass transfer rate needs to be calibrated based on experimental results, e.g. as in Tourlousse and Ahmad (2007), because the rise velocity of gas bubbles is usually not measurable or very difficult to measure. For convenience, the $K_L a$ is usually calculated from the $K_L a$ of oxygen gas (O_2) as a reference compound, as rate constants for volatile solutes can be assumed proportional to each other (Chapra, 2008; Ikumi, 2011; Mackay and Yeun, 1983; Munz and Roberts, 1989; Musvoto *et al.*, 1997). However, the use of O_2 as a reference compound, as selected by Musvoto *et al.* (1997), is quite odd for anaerobic digestion, because normally no O_2 is present in such reactors. Therefore, in the NRM-AD model, H_2 was used as volatile reference compound occurring in digesters, similar as in Pauss *et al.* (1990; Eq. 9.7):

$$K_{L/G}a = K_L a\ [\mathrm{T^{-1}}] = K_{L,H_2}\, a \,.\left(\frac{D_l}{D_{l,H_2}}\right)^{0.5} \qquad \boldsymbol{Eq.(9.7)}$$

4) Passive liquid-gas/gas-liquid transfer (NRM-AD) of very soluble gases.

In this case, the mass transfer rate should be determined independently of the low to moderately soluble gases above (Sotemann *et al.*, 2005). If no experimental data are available, the $K_G a$ value for NH_3 in anaerobic digestion is usually set to a very low value ranging from 1.92 to 3.2 (default in NRM-AD = 3.2; Ikumi, 2011; Musvoto *et al.*, 2000a; Sotemann *et al.*, 2005). This is to ensure an extremely low loss from the liquid phase through stripping. However, as the transfer rate depends much on design, operating conditions, and characteristics of the waste flow to be treated, it is advised to determine the $K_{G,NH_3}a$ under actual environmental conditions, as e.g. in Arogo *et al.* (1999) and Vaddella *et al.* (2013).

b) Liquid-solid / solid-liquid transfer

The kinetic liquid-solid/solid-liquid transfer mechanisms described in all NRMs are nucleation (= birth of crystals), crystal growth, and redissolution. For the NRM-Prec, a generic approach for floc agglomeration and break-up as function of mixing energy was also included. All reactions were represented by an empirical power law (Eq. 9.8) using **relative supersaturation ($\boldsymbol{S-1}$)** as driving force (Ali and Schneider, 2008; Galbraith *et al.*, 2014; Harrison *et al.*, 2011; Nielsen, 1984):

$$\rho_{T,i}\ [\mathrm{M\ L^{-3}\ T^{-1}}] = k_T.(S-1)^n \qquad \boldsymbol{Eq.(9.8)}$$

in which S is the saturation ratio ($=\left(\frac{IAP}{K_S}\right)^{1/v}$), v refers to the stoichiometric precipitation coefficient which represents the total number of species involved in the precipitation reaction, IAP is the ion activity product $[\mathrm{M\ L^{-3}}]$, K_s is the solubility product $[\mathrm{M\ L^{-3}}]$, k_T is the temperature dependent transfer coefficient $[\mathrm{M\ L^{-3}\ T^{-1}}]$, and n is the reaction order. The value of S was directly derived from the saturation index, SI ($= \log\left(\frac{IAP}{K_s}\right)$), which is calculated by PHREEQC at every time step during model simulations. The temperature dependency of the reaction rate was modelled by means of the Arrhenius equation (Greenberg and Tomson, 1992; Nielsen, 1984).

Using literature values for the molecular weight (MW) and density of the different precipitates, the total volume ($V_{fertilizer}$), total mass/moles ($M_{fertilizer}$), and MW ($MW_{fertilizer}$) of the recovered fertilizer product (composed of the various precipitates) was calculated at every time step. The time-dependent number of particles (N_{part}) was then determined using the Avogadro constant (N_A = 6.022 x 10^{23} mol^{-1}). The mean particle diameter (d_p) of the precipitates was calculated assuming spherical particles using Equation 9.9:

$$d_p\ [\mathrm{L}] = \sqrt[3]{\frac{V_{fertilizer}}{N_{part} \cdot \frac{\pi}{6}}} \qquad \boldsymbol{Eq.(9.9)}$$

The kinetic precipitation/dissolution coefficient k_T and the reaction order n in Equation 9.8 were adjusted according to the liquid-solid/solid-liquid transfer mechanism occuring: $k_{G,T}$ and n_G for growth, $k_{B,T}$ and n_B for nucleation, $k_{D,T}$ and n_D for dissolution. The prevalent mechanism depends on the value of S and the amount of seed material in the reactor. Hence, these values were checked at every time step. As such, four possible scenarios were considered:

1) Supersaturation occurs ($S > 1$; $SI > 0$) and seed material is available.

In this case, the crystallization of sparingly soluble salts in WRRFs is mainly controlled by surface spiral growth. This means that the integration of the cations into crystal lattice positions at kinks in the surface is the rate-determining molecular mechanism (Galbraith *et al.*, 2014; Koutsoukos *et al.*, 1980; Musvoto *et al.*, 2000b; Nielsen, 1984). The kinetic precipitation coefficient (Eq. 9.10) was then assumed to be proportional to the available seed material (cfr. Koutsoukos *et al.*, 1980; Parkhurst and Appelo, 2013):

$$k_T\ [\mathrm{M\ L^{-3}\ T^{-1}}] = k_{G,T}\ .\ a_{seed} \cdot \frac{M_{seed}}{V_{liq}} \qquad \boldsymbol{Eq.(9.10)}$$

in which $k_{G,T}$ is the temperature dependent growth rate coefficient $[\mathrm{M\ L^{-2}\ T^{-1}}]$, a_{seed} is the specific area of surface per gram of seed material before the seed crystals start to grow in the crystallizing solution $[\mathrm{L^2\ M^{-1}}]$ (default = 600 m^2 g^{-1}; Parkhurst and Appelo, 2013), and M_{seed} is the time-dependent mass of seed material in the reactor $[\mathrm{M}]$ (default initial mass = 0.0005 kg; Parkhurst and Appelo, 2013). The latter is calculated at every time step by means of mass balances on the seed material for each precipitate (Section 9.2.2.4), taking in account the mass of newly formed precipitates and redissolution. The default reaction order for surface controlled growth (n_G) was set at 2, which generally provides a good approximation to represent precipitation in WRRFs (Bouropoulos and Koutsoukos, 2000; Mehta and Batstone, 2013; Musvoto *et al.*, 2000b; Nielsen, 1984).

2) Supersaturation occurs ($S > 1$; $SI > 0$), but no seed material is available and/or the crystal size is not large enough to have any influence on the process, i.e. the induction time is

not exceeded.

In this case, primary nucleation occurs, which was often not accounted for in previous studies (Harrison *et al.*, 2011; Nielsen, 1984; Schneider *et al.*, 2013), though very relevant (Bhuiyan *et al.*, 2008). The value of k_T and n in Equation 9.8 are then switched to the nucleation rate, $k_{B,T}$ (default = 10^6 nuclei L^{-1} s^{-1}; Mehta and Batstone, 2013), and the nucleation reaction order, n_B. The latter is usually higher for nucleation than for growth (3-4; default = 3; Tavare, 1995). The induction time is inversely proportional to the logarithm of S, and should be estimated experimentally for each precipitate (Bhuiyan *et al.*, 2008; Mehta and Batstone, 2013).

3) The solution is undersaturated (S < 1; SI < 0) and precipitate is present in the system. In this case, the NRMs allow for precipitate redissolution until equilibrium is reached using the reverse reaction of Equation 9.8 (Morse and Arvidson, 2002). However, the kinetic dissolution rate ($k_{D,T}$) and the reaction order for dissolution (n_D) may be different than those for precipitation. Significantly more work is needed to better understand the dissolution behaviour of the various precipitates in complex waste(water) matrices (Greenberg and Tomson, 1992; Morse and Arvidson, 2002).

4) Equilibrium occurs (S = 1; SI = 0).

In this case, the liquid-solid / solid-liquid transfer rate was set at 0.

Finally, for the NRM-Prec, a generic mechanism for **agglomeration and floc break-up** through the effect of mixing was included using the spherical particle model for macroscale flocculation (Crittenden *et al.*, 2012). The net rate of floc appearance (Eq. 9.11) was written as:

$$\rho_{aggl}\,[\mathrm{L}^{-3}\,\mathrm{T}^{-1}] = K_a.\bar{G}.\frac{N_{part}}{V_{liq}}.\frac{V_{fertilizer}}{V_{liq}} - K_b.\bar{G}^{\delta} \qquad \boldsymbol{Eq.(9.11)}$$

in which K_a $[-]$ is the aggregation constant (= $4\alpha/\pi$ for laminar flow where α is the collision efficiency factor; default for turbulent flow = 5 x 10^{-4}), K_b $[\mathrm{T}^{\delta-1}.\mathrm{L}^{-3}]$ is the floc break-up constant (= 0 for laminar flow; default for turbulent flow = 10^{-7}; Crittenden *et al.*, 2012), $\bar{G}$ is the root mean square velocity gradient $[\mathrm{T}^{-1}]$ which depends on the power input (Camp and Stein, 1943), and δ is the turbulence constant. Under turbulent conditions, the values of K_a and K_b should be determined empirically in laboratory or pilot-scale tests (Argaman, 1971; Parker *et al.*, 1972). Note that when the $\bar{G}$ value is set to 0, it is assumed that no agglomeration occurs.

A time-dependent agglomerate number balance was also provided (Section 9.2.2.4). By division of the total fertilizer volume by the number of agglomerates, the agglomerate volume was obtained. The mean agglomerate diameter can then be computed in the same way as the particle diameter (Eq. 9.9).

It should be remarked that mixing energy may also have to be included in Equation 10.8. Growth can be assumed surface integrated controlled when the system is well mixed, so the mixing effect can be neglected for the growth equations in units with proper mixing (Galbraith *et al.*, 2014; Rahaman *et al.*, 2014). However, mixing may affect the nucleation mechanism and induction time through microscale flocculation (Ohlinger *et al.*, 1998). This mechanism is very site and species specific, hence it was not included in the generic approach for NRM-UO I. However, by selecting a generic empirical equation based on S (Eq. 9.8), the models could easily be extended to include mixing effects (Galbraith *et al.*, 2014; Perez *et al.*, 2008; Vicum and Mazzotti, 2007), if appropriate parameter correlations are available. As mentioned above, future extensions may also involve particle size distributions (PSDs) (Nopens *et al.*, 2014; Perez *et al.*, 2008).

9.2.2.3 Biochemical transformation model

a) Anaerobic digestion

Biochemical processes and state variables are clearly important for the NRM-AD model. The description, stoichiometry, and kinetics of biochemical transformations that may be expected in the NRM-AD were based on the Anaerobic Digestion Model No. 1 (ADM1; Batstone *et al.*, 2002). The biochemical processes involved are: 1) disintegration from homogeneous particulates to carbohydrates, proteins, and lipids, 2) extracellular hydrolysis of these particulate substrates to sugars, amino acids, and long chain fatty acids (LCFAs), 3) acidogenesis from sugars and amino acids to VFAs and hydrogen, 4) acetogenesis of LCFAs and VFAs to acetate, and 5) methanogenesis from acetate and H_2/CO_2 to CH_4, resulting in a total of 19 processes (Appendix 6: Table A6.1). pH, H_2, and NH_3 inhibition expressions were also taken from Batstone *et al.* (2002).

In view of nutrient recovery, three important extensions were included in the NRM-AD as compared to the ADM1 model (see below). The detailed stoichiometric matrix and kinetic transformation equations can be found in Appendix 6 (Table A6.2-A6.4).

Extension 1:* *Inclusion of physicochemical-biological interactions

At present, the only physicochemical processes included in the ADM1 are the acid-base systems NH_4^+/NH_3, CO_2/HCO_3^-, VFA/VFA$^-$, and H_2O/OH^-/H^+, and the three main gas-liquid exchange processes for CO_2, CH_4, and H_2, as well as for water vapour. Hence, the model was extended with the physicochemical components and processes (acid-base reactions, ion pairing, liquid-solid transfer, liquid-gas transfer, redox transformations) selected in Section 9.2.2.1 (Appendix 6: Table A6.1, Extension 1). Note that ion pairing of cations with VFAs was also accounted for.

When including these physicochemical state variables and reactions in the biological model, additional relevant biochemical transformation processes had to be included as well (Vanrolleghem *et al.*, 2014) (see below).

Extension 2:* *Sulfurgenesis

To describe the sulfur system, a set of transformations describing biological sulfate reduction (= sulfurgenesis) was considered based on the model proposed by Knobel and Lewis (2002) and thereafter used by Lizarralde *et al.* (2010) (Appendix 6: Table A6.1, Extension 2). Motivations for inclusion of biological sulfur degradation were given above (Section 9.2.1.2). It mainly concerns the competition of sulfate reducing bacteria (SRBs) with CH_4 producing bacteria for the same substrate, the toxic effect of H_2S, and biogas pollution with H_2S (UCT, 2007; Reiter and Piccot, 2004). The decay of SRBs was included in the same way as the decay of other organisms described in the ADM1 model (Batstone *et al.*, 2002). An inhibition term for H_2S was incorporated in the appropriate bio-kinetics (I_{H2S}), similar as in Lizarralde *et al.* (2010). Moreover, its transfer to the gas phase was included as described in Section 9.2.2.2.

Extension 3:* *Biochemical P, K, and S release/uptake

A third extension (Appendix 6: Table A6.1, Extension 3) of the ADM1 model concerns nutrient release from biological cells and disintegration of other biochemical components, as well as nutrient uptake by growing biomass.

First, the inclusion of nutrient release from the biological cells, other than N (average 12 % on dry weight (DW); Tchobanoglous *et al.*, 2003) was considered. Based on the theoretical composition of bacterial cells (primary and activated sludge) compared to the magnitude of the components in the liquid phase, it was estimated that this process may be relevant for P (average 2 % on DW; Tchobanoglous *et al.*, 2003), K and S (average 1 % on DW; Tchobanoglous *et al.*, 2003). Hence, the release of these components was additionally included in the ADM1 stoichiometric matrix, in the same way as for N. The remaining physicochemical state variables were supposed not to be significantly influenced by biological transformations, because they usually comprise less than 0.5 % of the bacterial cell (Tchobanoglous *et al.*, 2003). This was found to be insignificant as compared to the average composition of the mixed liquor. An exception is EBPR sludge for which the release of Ca and Mg, next to P and K, from polyphosphates should be accounted for according to Ikumi (2011). Modelling of EBPR sludge was considered beyond the scope of NRM-UO I (Section 9.2.1.1), but for future applications the NRM-AD could further be extended using equations from Ikumi (2011) (Appendix 6: Table A6.1, Potential extension 4).

Secondly, N, P, K, and S uptake for biomass growth were included in line with the corresponding removal of organic substrates (aminoacids, acetate, butyrate, LCFAs, H_2, propionate, monosaccharides, valerate). Finally, N and P release through disintegration of complex particulates, P release from lipid hydrolysis, N release from protein degradation and aminoacid uptake, as well as the N and P content of soluble and particulate inerts were also accounted for.

b) Nutrient recovery key unit processes following the digester

The biological (dead) solids leaving the digester were supposed to end up mainly in the solid fraction after solid-liquid separation of the digestate. Hence, in the succeeding key units for nutrient recovery (Fig. 9.1), it was assumed within the scope of NRM-UO I that biochemical particulate transformations do not play a significant role. Nevertheless, in order to allow coupling of NRMs to activated sludge models (ASMs) in a later stage (through return liquors, for instance), the biological state variables were integrated in all NRMs. Note that the physicochemical interactions with the remaining soluble COD components were included in all models (Section 9.2.2.1).

9.2.2.4 Reactor model

For each unit process, a mass balance was written, not only for all components in the liquid phase (S), e.g. Equation 9.12, but also for all components in the gas phase (G), all precipitated components (P), and all particulate biological solids (X), including both a transport term (based on in- and outgoing flow rates) and a transformation term (involving liquid-gas/gas-liquid transfer, liquid-solid/solid-liquid transfer, and biochemical transformations):

$$\frac{d\left(S_{liq,i}.V_{liq}\right)}{dt}\,[\mathrm{M\ T^{-1}}] = S_{liq_{in},i}.Q_{liq_{in}} - S_{liq,i}.Q_{liq_{out}} + V_{liq}.\sum_{j=1:n}\rho_j.v_{i,j} \qquad \boldsymbol{Eq.(9.12)}$$

where $\sum_{j=1:n}\rho_j.v_{i,j}$ is the summation of the specific kinetic process rates for process j (ρ_j, $[\mathrm{M\ L^{-3}\ T^{-1}}]$) multiplied by the stoichiometric coefficient for component i on process j ($v_{i,j,}$ $[\mathrm{M\ M^{-1}}]$), $Q_{liq_{in}}$and $Q_{liq_{out}}$ are the in- and outgoing liquid flow rates $[\mathrm{L^3\ T^{-1}}]$, V_{liq} is the bulk reactor volume $[\mathrm{L^3}]$, and $S_{liq_{in},i}$ and $S_{liq,i}$ refer to the activities of the in- and outgoing liquid components $[\mathrm{M\ L^{-3}}]$.

In addition, a mass balance for the seed material in the reactor was included, similar as Equation 9.12. The mass of seed material was adjusted in time according to the mass of precipitates present in the reactor and the liquid volume. Hence, it was assumed that newly formed crystals act as seed material for precipitation, similar as was experimentally discovered by Le Corre *et al.* (2007a,b) and Shimamura *et al.* (2003). External seed material can also be added.

For the precipitation unit (NRM-Prec), also particle and agglomerate number balances were implemented. The number of free precipitated particles was assumed to reduce according to the agglomerates formed, as in Crittenden *et al.* (2012). Note that agglomeration was only accounted for when mixing is present in the reactor (Section 9.2.2.2).

The used reactor design and the default specifications and features for each unit process are compiled in Table 9.6.

9.2.3 Step III: Model implementation and numerical solution

9.2.3.1 Model coding and state vector definition

The main coding language used in this study was Modelica, which is a high-level, declarative, and object-oriented modelling language (Claeys *et al.*, 2006; Elmqvist *et al.*, 1999). It is similar to the model specification language (MSL), which is currently used in Tornado/WEST (mikebydhi.com; Vanhooren *et al.*, 2003), one of the most common softwares used in waste(water) quality modelling. However, Modelica has a better readability and expressiveness, and because of the more important industrial use (Audi, Ford, Siemens, etc.) of Modelica compared to MSL, the wastewater modelling community using WEST recently decided to convert all conventional models for waste(water) treatment from MSL to the more powerful and more widely supported Modelica coding language.

Table 9.6 Reactor design, default specifications and features for each unit in the nutrient recovery model (NRM) library. AD = anaerobic digestion; AmS = ammonium sulfate; Chem = chemical dosing; CSTR = continuously stirred tank reactor; Heat = heater; TSS = total suspended solids; P = precipitates; Prec = precipitation/crystallization; Scrub = scrubber; Settle = settler; Store = storage tank; Strip = stripper; WRRF = water resource recovery facility; X = biological particulate solids.

Unit	Reactor design	Default specifications and features
NRM-AD	CSTR (based on Gujer, 2008)	- Constant liquid volume; - Sealed gas phase at atmospheric pressure; - Gas removed to downstream treatment/process.
NRM-Prec	CSTR (as generally used for coagulation / flocculation units; Crittenden *et al.*, 2012)	- Variable volume as function of retained precipitant volume; - Precipitate flow rate (Q_prec) extracts fraction of the precipitates continuously or at specific times when selected specifications are reached, e.g. target particle diameter, purity, etc.; - Allows to study the effect of mixing power and reactor seeding on, e.g., the mean particle/aggregate diameter; - Optional: use of gas flow instead of chemicals for pH-increase in the reactor; - Potential extension: inclusion of particle (differential) settling velocity (Crittenden *et al.*, 2012).
NRM-Strip	Stirred tank for active liquid-gas exchange (based on Gujer, 2008)	- Continuous in- and outgoing liquid and gas flows; - Newly formed gas bubble enters the reactor at an initial gas phase concentration; - Model parameters averaged over all bubbles; - Heterogenous gas transfer throughout the reactor height; - User-selectable number of liquid layers to represent spatially dependent liquid transfer.[a]
NRM-Scrub	Stirred tank for active gas-liquid exchange (Gujer, 2008)	- Similar specifications as NRM-Strip, but: i) Default use of sulfuric acid solution at pH 1.3 for NH_3 absorption; ii) AmS recycle flow (Q_rec) with extraction as fertilizer flow when user-selected AmS specifications (usually 25-40 % AmS concentration) are reached (cfr. semi-batch process).
NRM-Store	Tank with gas recovery for digestate storing	- Continued (non-controlled) anaerobic digestion and biogas recovery; - Continuously emptied to a user-specified minimum level, default = 15 % (*AgriDigestore*, Ludlow, UK) → Complete digestion, energy recovery ↑, digestate nutrient availability ↑.
NRM-Settle	Point settler	- Simplified design based on TSS removal efficiency and TSS settleability (Hendricks, 2010), default = 0.5 % non-settleable *X* and 10 % non-settleable *P*; - Potential extension: inclusion of particle (differential) settling velocity (Crittenden *et al.*, 2012) → No longer simplified design.
NRM-Chem	Point mixer	- Closed tank to avoid NH_3 emissions through pH-increase; - Allows addition of the most important amendments in WRRFs: i) $MgCl_2$, $Mg(OH)_2$, and $Ca(OH)_2$ prior to P precipitation, ii) NaOH and $Ca(OH)_2$ prior to stripping (goal = pH ↑, $CaCO_3$ scaling ↓); - Usually followed by NRM-Prec to allow for species precipitation and flocculation.
NRM-Heat	Point heater	- Colder fluid gaining heat from a hot gas/steam flow or a hot liquid flow; - Generic equation based on the specific heat of the fluid, the surface area of the heat exchanger, and the overall heat transfer coefficient (AIC, 2014); - Application prior to NRM-AD and NRM-Strip.

[a] Some literature studies show that hydraulic levels and reactor design have no effect on the NH_3 recovery efficiency as equilibrium conditions are reached in a very small time interval (Chapter 8; Arogo *et al.*, 1999; Collivignarelli *et al.*, 1998; Gujer, 2008; Powers *et al.*, 1987). However, other studies believe that liquid transfer should be modelled heterogeneously, i.e. spatially dependent (Yu *et al.*, 2011). Because of this discussion, an option was included in the NRM-Strip and NRM-Scrub to calculate NH_3 removal and absorption for a user-selectable number of liquid layers. The Gujer (2008) model is based on homogeneous liquid transfer.

As mentioned above (Section 9.2.2.1), a PHREEQC script was written for each unit process separately in order to include water chemistry. A 'SELECTED_OUTPUT' statement involving the selected species activities, saturation indices (SI's), partial pressures (p's), as well as the pH, temperature, alkalinity, and ionic strength was defined. The obtained SI's and p's are then used as driving forces for precipitation and gas transfer in the Modelica code describing the slow transformation processes (Eq. 9.2 and 9.8).

As only small differences exist between the selected components for the different NRMs (Table 9.2), it was decided to define one generic component state vector for each different phase. As such, five different NRM component state vectors were enumerated (Appendix 7: Table A7.1):

1. *Components_S1*: the components in the liquid phase, i.e. the main waste flow:
    a. *Components_S1_PC:* soluble components involved in physicochemical transformations (mol-base);
    b. *Components_S1_Bio:* soluble components involved in biological COD transformations (COD-base);

2. *Components_S2:* the components in the H_2SO_4-solution used in NRM-Scrub (mol-base);
3. *Components_G:* the components in the gas phase (mol-base);
4. *Components_P*: the components in the precipitated phase (mol-base);
5. *Components_X*: the particulate biological solids (COD-base).

The *Components_S1* state vector was further split into a *Components_S1_PC* and *Components_S1_Bio* state vector in order to describe physicochemical transformation and biological COD transformations separately. All state variable quantities involved in the physicochemical calculations (*Components_Gas*, *Components_P*, *Components_S1_PC*) were expressed on a molar base, whereas the state variables only involved in biological transformations (*Components_X*, *Components_S1_Bio*) were expressed on a COD-base. Moreover, for each model separately, a species state vector was enumerated referring to the PHREEQC selected output (which is different for each unit process).

Parameters and equations for the (slow) physicochemical and biochemical transformations, and mass balances for all total components were implemented in Modelica using a multi-matrix structure. The Tableau method matrix implementation of Morel and Herring (1993) was used as generic method for linking total soluble component activities to species activities and total precipitated component concentrations to precipitate concentrations in the NRMs, whereas the Gujer (2008) matrix implementation was used to describe the biochemical reactions involved.

9.2.3.2 Numerical solution and model execution procedure

When combining biological and chemical reactions, numerical solution becomes a critical issue, because of the stiffness of the set of differential equations that arises when considering reactions with very different conversion rates, i.e. the range of system time constants is large (Chapter 8: Section 8.4.3; Batstone *et al*., 2012; Brouckaert *et al*., 2010; Garneau *et al*., 2009; Lizarralde *et al*., 2014; Musvoto *et al*., 2000a,b; Rosen and Jeppson, 2006; Sotemann *et al*., 2005). To overcome this problem, the slower reactions (Sections 9.2.2.2-9.2.2.4) and mass balances (Section 9.2.2.5) were represented by ordinary differential equations (ODE) coded in Modelica, while the fast reactions (Section 9.2.2.1) were calculated algebraically by use of algebraic equations (AE) at each iteration step using the software tool PHREEQC (Parkhurst and Appelo, 2013). The models coded in the Modelica language (with invocations of the PHREEQC engine for speciation calculation) were then executed through the Tornado(/WEST) framework (mikebydhi.com; Vanhooren *et al*., 2003) for modelling and virtual experimentation on the basis of sets of complex ODEs and AEs.

The use of a geochemical software tool to solve water chemistry was brought forward, as PHREEQC has a dedicated and proven solver (Newton Raphson) for the set of implicit non-linear equilibrium equations involved. Moreover, it has a high flexibility for model extension to include other (case-specific) components, e.g heavy metals, and the associated species and equilibrium reactions. PHREEQC was preferred over other geochemical models (e.g. Visual

MINTEQ, WHAM, and WATEQ4F), because of its ease of integration with diverse scripting languages and other model libraries, next to its apparent more suitable methodology in terms of precipitation calculations (Charlton and Parkhurst, 2011). Recently, a C-callable API (Application Programming Interface) for the PHREEQC engine has become available under the name IPhreeqc. It allows for easily coupling the PHREEQC engine to software developed in other programming languages. The API provides direct access to the geochemical processes in the PHREEQC library, as well as support for new PHREEQC specification keywords that allow for easier manipulation of PHREEQC input and output data (Charlton and Parkhurst, 2011).

In this PhD, a generic mechanism for calling IPhreeqc (hereafter referred to as PHREEQC) from Modelica-specified models using Tornado has been developed (Fig. 9.5).

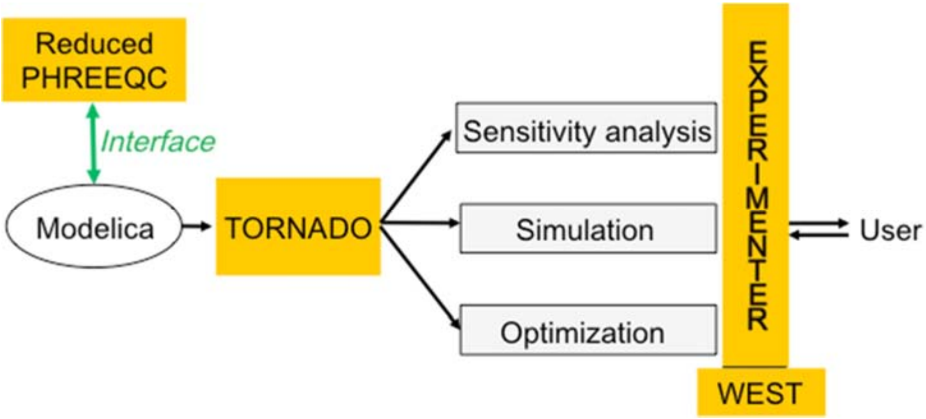


Figure 9.5 Tight coupling of reduced PHREEQC to Modelica code and model execution in Tornado.

It consists of a Tornado-specific PHREEQC wrapper library containing only a predefined set of methods to be used in Tornado, as well as a reduced PHREEQC database and a PHREEQC script with selected outputs (Section 9.2.2.1). Any PHREEQC code can now be run, using input data supplied by Tornado and providing output data to be used by Tornado, in a flexible manner without the need for any case-specific C/C++ code modifications by the user. The underlying PHREEQC-Tornado interface is further described in Section 9.2.3.3. As a result, the combined kinetic-equilibrium models can now be used in Tornado for simulation and other tasks such as parameter estimation, optimization, scenario analysis, Monte Carlo simulation, sensitivity analysis, and steady-state analysis (i.e. so-called virtual experiments), through the Tornado CUI (Command-line User Interface) tool and the user-friendly Tornado Experimenter GUI (Graphical User Interface) (Fig. 9.5).

Finally, for numerical solution in Tornado, two different solvers, RK4ASC (Runge Kutta 4 Adaptive Step size Control integration algorithm; Press *et al.*, 1992) and VODE (Variable-coefficient Ordinary Differential Equation solver; Brown *et al.*, 1989), were compared. The RK4ASC algorithm was retained, as simulation times were much faster and results more stable. This is likely related to its higher ability to solve models with certain discontinuities and dynamic inputs/disturbances.

9.2.3.3 PHREEQC-Tornado interface

In order to connect state vectors used by PHREEQC (C code) and Tornado (Modelica code), a PHREEQC-Tornado interface was developed (Fig. 9.6). The interface makes special use of the data defined by the ‘SELECTED_OUTPUT’ data blocks (Section 9.2.3.1), and allows this array of data to be returned to Tornado without the necessity to read or write files. Hence, the data can be transferred between PHREEQC and Tornado through internal computer memory. This method of tigth model coupling has significant merits with respect to calculation time and programming: a PHREEQC instance is only created once and is subsequently reused, preserving its internal state. In general, an order of magnitude decrease in run times is obtained compared to a loosely-coupled model, which requires starting PHREEQC as an external process for each time step (Müller *et al.*, 2011). On top of that comes the gain in simulation time by using the developed reduced PHREEQC databases and scripts (with selected outputs) instead of full PHREEQC (Section 9.2.2.1). Hence, a reduction of execution time is obtained at two critical points during model simulations: i) the uploading and reading of database and input files, and ii) the transfer of data between PHREEQC and Tornado. As such, running a complete digestate treatment train (e.g. Fig. 8.1) under dynamic conditions for one year would take approximately 15 min (depending on the operating conditions and input characterization) using the reduced PHREEQC model, whereas it would take 45 min using the full PHREEQC model, both with tight model coupling to the kinetic model developed in Tornado.

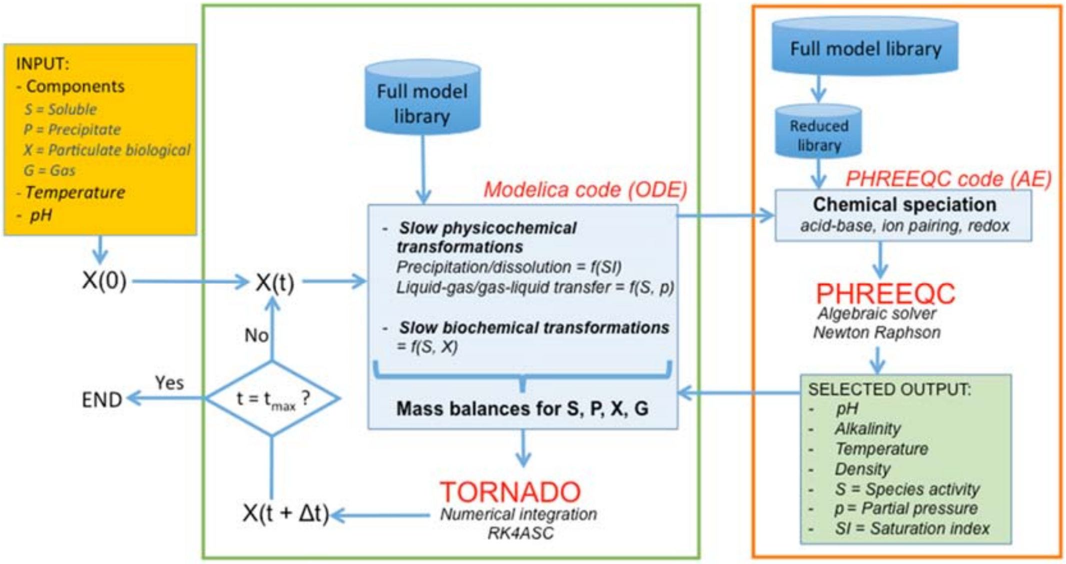


Figure 9.6 Overview of the PHREEQC-Tornado interface coupling chemical speciation calculations at every time step to slow physicochemical and biochemical dynamic transformations. AE = algebraic equations; ODE = ordinary differential equations; X(0) = initial state of the system; X(t) = state of the system at time t.

9.2.3.4 Model verification and debugging

After implementation, the models were subjected to a battery of tests to ensure implementation correctness, also referred to as model verification (Dochain and Vanrolleghem, 2001). A generic

six-step procedure for model verification of NRMs was developed and applied to each unit process separately:

1. Verification PHREEQC-Tornado interface: Comparison of speciation calculations in Tornado (with tight coupling to reduced PHREEQC) with simulation results from the independent full PHREEQC engine;
2. Verification physicochemical transformation model: Implementation of slow physicochemical transformations in Modelica code, execution in Tornado, and mass balance check;
3. Verification biochemical transformation model: Implementation of slow biochemical reactions in Modelica code, execution in Tornado, and i) mass balance check, ii) check against independent implementations, e.g. ADM1 (Batstone *et al.*, 2002) and model for anaerobic S degradation (Lizarralde *et al.*, 2010);
4. Verification(/validation) at steady state: Performance of steady state simulations using different initial values from literature and comparison with experimental literature results;
5. Verification(/validation) of dynamics: Performance of dynamic simulations using realistic databases and check effect of disturbances (e.g. different loading scenarios) on model outputs (comparison with prior knowledge and literature);
6. Verification of generic NRM implementation: Comparison of simulation results obtained with individual equation implementation and with generic compact matrix-based implementation. Hence, two different implementations are available of each unit process model: one based on all separate individual equations and one based on vectors and matrices.

As such, typing errors, inconsistencies, gaps, and conceptual errors were eliminated, while software bugs were discovered and dealt with.

9.2.4 Step IV: Dataset collection and identification of data needs

One of the issues in the development of new models is the necessity to provide data for the estimation of model parameters and as input variables. The different types of data required for each key NRM and the datasets that were used are provided in Appendix 8 (Table A8.1).

A thorough review of literature and existing models was conducted to provide default values for the different parameters involved. Physicochemical stoichiometry and thermodynamic parameters are incorporated in the PHREEQC and Visual MINTEQ modelling softwares, where they are mainly taken from the National Institute of Standards and Technology (NIST, 2001) database. Default values for the kinetic precipitation coefficients were taken from literature, while default values for biomass kinetic coefficients were taken from the ADM1 model (Batstone *et al.*, 2002), except for the SRB kinetics for which the parameters were taken from Knobel and Lewis (2002) and Lizarralde *et al.* (2010).

Next to literature studies, also new experimental data aiming at NRM validation were collected through lab/pilot-scale testing and contact with industry. For NRM-AD, full-scale data at steady state from an anaerobic reactor treating S-rich paper mill sludge located at the WRRF Holmen Paper, Madrid, Spain has been obtained from the Center of Studies and Technical Research (CEIT, San Sebastian, Spain; Appendix 8: Table A8.2). An input fractionation was conducted following the procedure proposed by Grau *et al.* (2007a).

For validation of the NRM-Prec, lab tests were conducted for P recovery from digestate under different operating conditions, i.e. different Mg:P-ratios, contact time, etc. For this purpose, two different digestates were sampled at the full-scale biogas installations of SAP Eneco Energy, Houthulst, Belgium and Wittevrongel Eneco Energy, Aalter, Belgium, which both treat agricultural wastes, mainly manure. The experimental set-up is shown in Figure 9.7.

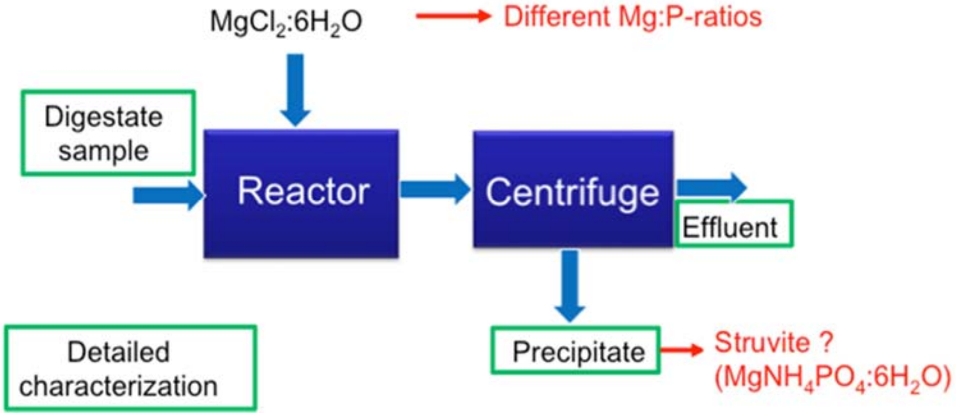


Figure 9.7 Experimental set-up: lab-scale experiment for P recovery from digestate.

A detailed input characterization was performed prior to the experiment (Appendix 8: Table A8.3). The precipitate was separated from the effluent by means of a centrifuge (5 min at 2,000 rpm; Heraeus megafuge 1.0, Kendro Laboratory Products, Hanau, Germany), after which both fractions were also physicochemically analyzed. The P recovery efficiency (%) was then calculated using the P recovery of a control (no Mg addition) as a reference. For detailed methodology and experimental results, reference is made to the MSc Thesis of De Corte (2012), tutored by Vaneeckhaute C.

To obtain data for the NRM-Strip/NRM-Scrub, a technical and financial survey for a case treating 2,000 m^3 d^{-1} of digestate at 200 mol NH_4-N m^{-3} (more details: Appendix 8: Table A8.4) was carried out at various key suppliers in the field. As such, insights in the variability of the processes available today were obtained, e.g. different target ammonium sulfate concentration, operational pH and temperature, consumables, etc. (see also Chapter 2). These detailed data provided by the suppliers were used for further model refining and validation.

Finally, it should be stated that during model development new data needs appeared for which to date literature references are lacking. Such data gaps were identified and recommendations for future experiments and data collection are provided further in this chapter (Section 9.3.5).

9.2.5 Step V: Model validation

Model validation was performed in four different ways: i) validation against prior knowledge, ii) validation against existing models, iii) validation against literature or technical inquiries, and iv) validation against collected experimental results. In all cases, the default stoichiometric and kinetic parameter values were used as determined in Section 9.2.4. Input stream compositions, design data, and operational conditions were taken from the dataset involved. During the validation procedure, attention was given to the reduced PHREEQC database used. If required, an extra evaluation was conducted using the full PHREEQC and/or Visual MINTEQ database and missing species/reactions were additionally added to the reduced database.

9.2.6 Step VI: Scenario analyses and process optimization

To obtain more insights in the results and to further explore the model outcomes, scenario analyses were performed in Tornado(/WEST) (Claeys, 2008). Moreover, the applicability of the models for process optimization was demonstrated by running optimization experiments in Tornado(/WEST) (Claeys, 2008).

9.3 Results and discussion

The implementation of the models developed in Section 9.2 was verified and validated. General verification results and a verification example showing the correctness of the PHREEQC-Tornado interface are given in Section 9.3.1. An example of model validation against experimental results, including scenario analyses and/or process optimization, is given for each NRM in Sections 9.3.2-9.3.4. Finally, recommendations for further research are provided in Section 9.3.5.

9.3.1 Model verification

9.3.1.1 General results and issues

During model verification, various software bugs were discovered and communicated to DHI, Merelbeke, Belgium, who successfully resolved the issues. As such, this PhD also contributed to the development of the Tornado/WEST software kernel.

Each step in the verification procedure was completed successfully. First, the PHREEQC-Tornado interface was found to be effective (see Section 9.3.1.2). Next, the mass balance check provided good results for each NRM. The step-by-step comparison of the Gujer matrix with other digester implementations showed that the biochemical reactions were correctly implemented. Tests performed to check the ability of the models to realistically respond to model inputs, both under steady state and dynamic conditions, eliminated small implementation errors. Some examples of tests and effects performed for model verification/validation can be found in Appendix 9. Finally, simulation results obtained from the two different implementations of each unit process, i.e. using individual equations and using a multi-matrix structure, were identical.

Three important general issues were observed during model verification, to which future model developers must pay attention. First, it was found that some components, species, and precipitates that are highly important for modelling of WRRFs are not yet included in the generic PHREEQC and/or MINTEQ databases (Section 9.2.2.1: Table 9.3). Hence, for each new nutrient recovery model, the chemical speciation calculation should be verified with multiple softwares, with literature, and with prior knowledge in order to comprehensively select which components, species, and precipitates to be included in the model and which ones to be excluded.

Secondly, if an input to PHREEQC is set to 0 or if a species is not defined or not present in the calculation, then a value of -999.999 is printed as output for this component's species distribution and the corresponding saturation indices and partial pressures. In the Modelica code, these outputs are then used as driving forces for slow transformations, which makes that the calculations are incorrect. This issue was solved by introduction of an if-then-else statement in the PHREEQC-Tornado interface.

Finally, attention should be paid to the use of units for input and output variables. Input concentrations in PHREEQC are expressed by default as mol m^{-3}, whereas the outputs are given by default as kmol m^{-3}. Deviations from these standard units should be declared in the PHREEQC script.

9.3.1.2 Verification PHREEQC-Tornado interface

When comparing simulation results using the stand-alone full PHREEQC engine and Tornado (with tight coupling to reduced PHREEQC), identical model outputs were obtained for all NRMs. As an example, the results for the NRM-Scrub are given in Table 9.7.

Table 9.7 Verification PHREEQC-Tornado interface: example NRM-Scrub. Left: gas phase speciation (atm). Right: ammonium sulfate fertilizer speciation (mol m^{-3}) after gas-liquid exchange. log(p) = logarithm of the partial pressure (p) in the gas phase.

Gas	**Input p** (atm)	**Output full PHREEQC log(p)** (atm)	**Output Tornado**[a] **log(p)** (atm)
CH_4	0.001	-6.12	-6.12
CO_2	0.006	-7.55	-7.55
H_2	0.001	-6.13	-6.13
H_2S	0.001	-1.43	-1.43
H_2O	0.0001	-1.50	-1.50
N_2	0.1	-0.03	-0.03
NH_3	0.8	-6.23	-6.23
O_2	0.09	-71.0	-71.0

[a] With tight coupling to the developed reduced PHREEQC model.

Soluble species	**Output full PHREEQC** (mol m^{-3})	**Output Tornado**[a] (mol m^{-3})
NH_3	0.0361	0.0361
$NH_4SO_4^-$	0.00179	0.00179
NH_2COO^-	1.96	1.96
NH_4^+	6.46	6.46

An initial gas phase flow with high NH_3 load (coming from the NRM-Strip) was given as input to the NRM-Scrub and brought into contact with a sulfuric acid solution for NH_3 absorption. The outputs, i.e. the logarithm of the partial pressures ($\log(p)$, atm) in the purified gas phase and the acitivities (mol m^{-3}) of some species in the ammonium sulfate solution after gas-liquid exchange, obtained with both the stand-alone PHREEQC engine and Tornado-PHREEQC are presented. It can be concluded that the implementation of the PHREEQC-Tornado interface and the PHREEQC invocation in Modelica are correct.

9.3.2 NRM-AD validation

9.3.2.1 Case study anaerobic tank at Holmen Paper Madrid (Spain)

The NRM-AD model was validated using experimental results collected under steady state conditions from an anaerobic digester for the treatment of S-rich paper mill sludge from a full-scale WRRF located at Holmen Paper, Madrid, Spain. The same case was previously used for validation of the Lizarralde *et al.* (2010) model for anaerobic S reduction. The input sludge characteristics, design parameters, initial reactor state variables, and operating conditions are given in Appendix 8 (Table A8.2). Kinetic and stoichiometric parameters were set at default (Section 9.2.4). A comparison of experimental and simulation results using the NRM-AD and the model proposed by Lizarralde *et al.* (2010) is given in Table 9.8.

Table 9.8 NRM-AD validation based on experimental results from Holmen Paper, Madrid, Spain at steady state and comparison with the Lizarralde *et al.* (2010) model for anaerobic S removal. ND = not determined.

Output	**Variable**	**Unit**	**Experiment**	**Simulation NRM-AD**	**Simulation Lizarralde *et al.* (2010)**
Biogas	CH_4	%	80	81	70
	CO_2	%	13	15	8
	H_2S	%	6	2	22
Digestate	pH	-	7.21	7.21	7.6
	NH_4-N	mol m^{-3}	123	130.04	ND
	PO_4-P	mol m^{-3}	12.63	12.48	ND
Removal efficiency	ηCOD	%	61	63	62
	ηSO_4	%	78	63	81

Simulation results using the NRM-AD show a good agreement with the experimental results for COD removal and biogas CH_4 and CO_2 composition at a particular pH. The model also seems to give a very good prediction of the digestate pH and P content, and a relatively good prediction for NH_4-N in the digestate. The slightly higher digestate nutrient value for NH_4-N obtained with the NRM-AD may be attributed to losses of NH_3 during digestate sampling and analysis, although potential model deficiencies may not be excluded.

The NRM-AD seems to underpredict the biological SO_4 removal and corresponding H_2S production by SRBs, as will be explored below. However, from a pure validation perspective, when comparing with the Lizarralde *et al.* (2010) model, overall the performance of the NRM-AD is significantly better, very probably due to the underlying detailed chemical speciation and the inclusion of multiple competing physicochemical transformation reactions.

9.3.2.2 Exploration of hypothesis regarding S cycle measurements

Through model scenario analyses, four potential explorations were brought forward for the underestimation of biological SO_4 removal in the above case study. First, it was observed that the biogas H_2S concentration was very sensitivite to variations in pH (cfr. Al-Zuhair *et al.*, 2008). Model simulations were carried out at the digestate pH (7.21). However, the input pH was significantly lower (6.66) and the digestate pH may be influenced through contact with air. Hence, there exists some uncertainty about the actual reactor pH.

To further explore this hypothesis, a scenario analysis was conducted in order to evaluate the effect of pH (variable) on the % CH_4, CO_2, and H_2S in the biogas at fixed waste input COD:SO_4-ratio. Assuming that the pH in the reactor ranged from 6.66 (waste input pH) to 7.21 (digestate pH), the biogas composition varied from 61 % CH_4, 34 % CO_2, 2.94 % H_2S to 80 % CH_4, 16 % CO_2, 1.90 % H_2S. Hence, under the present implementation, it was not possible to obtain 6 % H_2S in the biogas at a pH in that range.

It should be remarked that the biogas H_2S content of 6 % experimentally obtained is extremely high compared to literature values. Typical biogas H_2S values for similar concentrated sulfurous streams from the paper industry range between 1-2 % H_2S (Reiter and Piccot, 2004). Hence, a second reason for the uncertainty may be related to the analysis itself conducted by the operators.

A third explanation may be the exclusion of lactate in the present NRM-AD implementation. Lactate is a preferred substrate for sulfate reducing bacteria and would thus aid in increasing SO_4 removal and H_2S production (UCT, 2007). This may explain the slight overestimation of biogas CO_2 production and underestimation of H_2S production. In the present case, no lactate measurements were available, but future research should consider this component.

Furthermore, the non-consideration of reactions (precipitation/ion pairing) with Al and Fe, due to lack of input Al/Fe measurements at the WRRF, may explain the lower SO_4 removal found through simulation (cfr. Zhang *et al.*, 2013b). This can also declare why model predictions for COD removal and CH_4 production were good, while additional COD would be required for SO_4 removal by SRBs. Based on a similar reasoning, Lizarralde *et al.* (2010) assigned potential sulfate precipitation to the highly overestimated H_2S production found with their model.

An attempt to calibrate Al in the present case study showed that a reactor concentration of 276 mol Al m^{-3} resulted in a SO_4 removal of 78 % (= experimental value) and a biogas H_2S concentration of 3 %. However, in this scenario the pH lowered to a value of 6.26. The higher SO_4 removal found through addition of Al was likely the result of a combination of multiple effects. It was, for example, observed that the addition of Al impacted on the amount of Ca/Mg sulfates and Ca/Mg precipitates formed. The addition of Fe resulted in a lower H_2S production because of FeS precipitation, but it did not aid in SO_4 removal.

Finally, other model gaps can of course not be ruled out and it should be beared in mind that the above validation is based on a one-time test.

It can be concluded that more detailed waste(water) input characterizations, including all selected components for the NRM-AD unit process (Section 9.2.2.1: Table 9.2), as well as instantaneous pH measurements in the reactor, are required in order to correctly calibrate the model for biological S removal. Nevertheless, clearly, exploration using the NRM-AD leads to increased insights and better understanding of the various interacting processes occurring in digesters. Hence, the model can meet the objectives set for NRM-UO I.

9.3.3 NRM-Prec validation

9.3.3.1 Phosphorus precipitation at different Mg:P-ratios

For validation of the NRM-Prec model, batch experiments were carried out in the lab for P recovery from two different crude digestates (Section 9.2.4; Appendix 8: Table A8.3). Different Mg:P-ratios, obtained through addition of $MgCl_2$:6H_2O, were applied aiming at the production of N-struvite ($MgNH_4PO_4$:6H_2O or MAP) or K-struvite ($MgKPO_4$:6H_2O or MKP) fertilizer. Initial simulation results showed a large deviation from the experimental results (Table 9.9). After evaluation using the full PHREEQC and MINTEQ databases, this deviation could be attributed to ion pair formation of NaH_2PO_4, a species that was initially not included in the reduced PHREEQC database, nor in the generic PHREEQC database (Table 9.3). Indeed, due to the high Na concentration of both digestates, Na coupled with P, making it less available for precipitation. When NaH_2PO_4 was added as species to the reduced database, a very good agreement between the simulation and the experimental results was obtained for P recovery at steady state (after 12h; Table 9.9).

Table 9.9 NRM-Prec validation based on experimental batch tests at lab-scale at steady state (after 12h).

Mg:P	% P recovery digestate 1			% P recovery digestate 2	
	Experiment	NRM-Prec without NaH_2PO_4	NRM-Prec with NaH_2PO_4	Experiment	NRM-Prec with NaH_2PO_4
1:1	41	95.60	41.32	28	27.76
2:1	44	97.91	43.62	29	29.29

This finding is in line with the results obtained by Li *et al.* (2012), who found a ± five times higher residual effluent P concentration when NaH_2PO_4 + $MgCl_2$:6H_2O were dosed for struvite precipitation, compared to the dosing of H_3PO_4 + $MgCl_2$:6H_2O. Moreover, recently Chauhan and Joshi (2014) found that at high Na:NH_4-ratios, NaH_2PO_4 is formed instead of or next to $NH_4H_2PO_4$, the precursor for MAP precipitation. In turn, this compound may be transformed into Na-struvite through the following reaction:

$$NaH_2PO_4{:}2H_2O + Mg(CH_3COO)_2{:}4H_2O + H_2O \rightarrow NaMgPO_4{:}7H_2O + 2CH_3COOH$$

The formation of Na-struvite was not yet included in the NRM-Prec model due to lack of knowledge on the existence, the stoichiometry, and the kinetics of this precipitation reaction. However, knowing that current practice often involves the addition of NaOH for pH-increase prior to struvite crystallization, the case study above clearly shows the relevance of further research on Na-P ion pair formation and Na-struvite precipitation kinetics in waste(waters). The phenomenon may not only impact on the effluent quality, but also on the quality of the resulting recovered fertilizer product, i.e. a potential mixture of N/K- and Na-struvite may appear.

9.3.3.2 Exploration for process understanding and optimization

Two questions arise from the experimental (and simulation) results presented above (Table 9.8):

1. Why is the P recovery efficiency rather low for both digestates?
2. Why does increasing the Mg dose not improve the P recovery efficiency?

The ability of the models to find an answer to such questions is presented below.

First, it was observed experimentally and through simulations that the main precipitated components, next to P, were Al, Ca, Fe, K, Mg, and N(-III). Hence, the product recovered was definitely not pure MAP or MKP. A scenario analysis including these components was conducted for both digestates in order to obtain more insights in the results (Fig. 9.8). The digestate compositions under study are marked as stars in Figure 9.8.

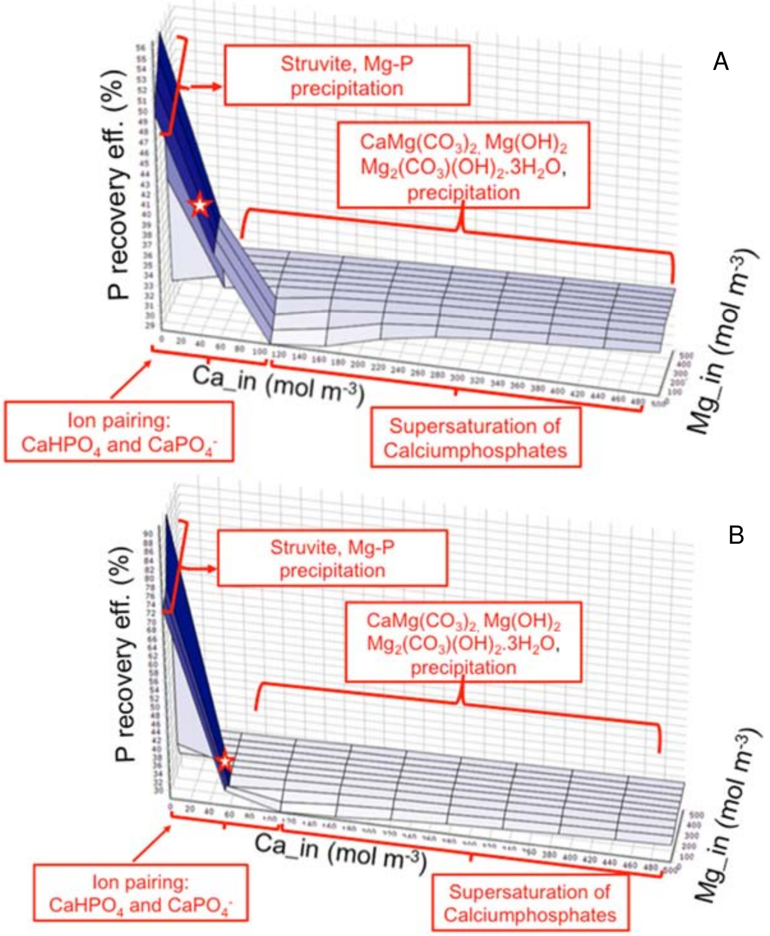


Figure 9.8 P recovery efficiency (%) as function of input Mg and Ca concentration (mol m^{-3}) for streams with high (A: digestate 1) and low (B: digestate 2) Fe and Al input concentrations. Red stars indicate the digestate compositions of the case studies.

The maximum achievable P recovery as function of the input Mg and Ca content was 56.2 % for digestate 1 (Fig. 9.8A), whereas it amounted to 90.7 % for digestate 2 (Fig. 9.8B). This discrepancy can be attributed to the higher concentration of Fe and Al in digestate 1 compared to digestate 2 (Appendix 8: Table A8.3). Indeed, at high concentrations of both Fe and Al mainly Hercynite ($FeAl_2O_4$) precipitation occurs, whereas at low concentrations P recovery increases through precipitation of $AlPO_4$ and Vivianite ($Fe_3(PO_4)_2{:}8H_2O$). Furthermore, the inhibition of P precipitation due to the presence of soluble Ca is very clear for both cases (see details Fig. 9.8). Up to ± 110 mol m^{-3} of input Ca (the margin in which the digestates under study are situated), mainly ion pairing of $CaHPO_4(aq)$ and $CaPO_4^-$ was observed, which decreased the amount of P available for precipitation (cfr. Lin, 2012). Above a value of ± 110 mol m^{-3}, calcium phosphates became oversaturated, precipitation occurred, and P recovery increased. This effect of Ca inhibition observed through model simulations is in agreement with the experimental findings of Huchzermeier and Wengdong (2012). The latter concluded that struvite purity decreased because of the formation of calcium phosphates when the Ca:P activity ratio was greater than 0.5 to 1.

Secondly, the fact that the P recovery in the present experiment was not much influenced by increasing Mg:P-ratios, can, according to the model, be attributed to the formation of dolomite ($CaMg(CO_3)_2$), as well as $Mg(OH)_2$ and $Mg_2(CO_3)(OH)_2{:}3H_2O$ at higher Ca and Mg concentrations. Indeed, higher Ca and Mg doses are associated with a pH-increase, which favours carbonate and hydroxide precipitation (Zumdahl, 2005). When the input Ca concentration would be 0, one can see an increase in P recovery with increasing Mg dose due to the formation of MKP (lots of K in the input) and Mg-phosphates. This competitive effect between Mg, Ca, and P found through NRM-Prec simulations is in agreement with the findings of Lin (2012), who obtained a precipitate mixture of struvite, dolomite, $Mg(OH)_2$, calcium phosphates, and $CaCO_3$ in experiments on P recovery from digested swine manure.

Based on the above-mentionned findings, **two optimizations of the process can be proposed** if the aim would be to produce high purity struvite:

1. Removal of $CaCO_3$ through precipitation prior to the experiment, e.g. using a filtration system as in Huchzermeier and Wengdong (2012);
2. Elimination or reduction of the use of Fe and Al in the WRRF processes upstream of the precipitation unit, e.g. for improved sludge dewatering. This measure could also be assessed by locating the struvite precipitation unit (with optional pre-treatment; Chapter 7) upstream in the WRRF, e.g. immediately after the activated sludge (AS) system (cfr. combined use of the *WASSTRIP* and *Pearl* process for improved P release and struvite recovery; Ostara, Vancouver, British Colombia, Canada; Ostara, 2014). In fact, the AS system itself could also (partially) be replaced by a strip/scrub system.

When applying these proposed measures in a treatment train for digestate 1, the maximum achievable P recovery through simulation became 91 %, consisting of MKP, $Mg(OH)_2$, and $Mg_3(PO_4)_2$. Hence, a pure Mg/P/K fertilizer would be obtained (Fig. 9.9). Remark that the main precipitate found, MKP, is not included in the generic PHREEQC/MINTEQ databases. Hence, **the extensions provided to the database are clearly relevant** (Section 9.2.2.1).

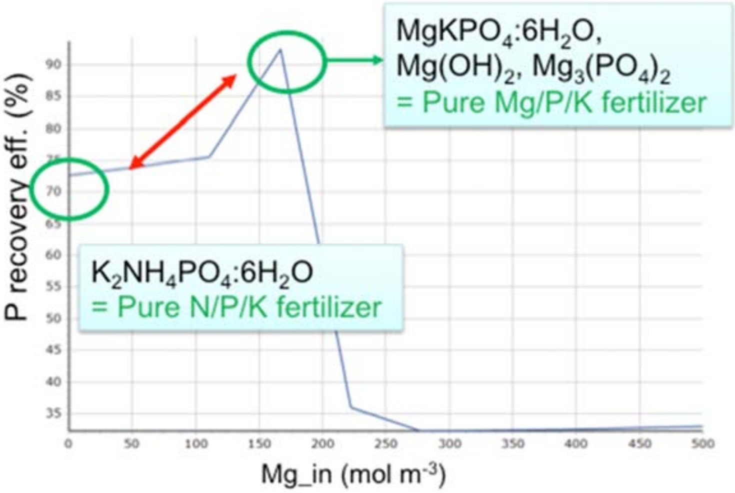


Figure 9.9 P recovery efficiency (%) as function of input Mg (range: 0-500 mol m^{-3}) for digestate 1 after $CaCO_3$ removal (= optimization 1) and exclusion of Fe/Al addition in processes upstream (= optimization 2).

Also note that in Figure 9.9, the Mg dose was allowed to change within the range of 0 to 500 mol m^{-3} (so no point measurements). Hence, the abrupt changes in slope are related to changes in precipitation mechanisms.

Moreover, an interesting observation made through model simulations was that a high P recovery efficiency of 72 % could be obtained without any addition of Mg. This could be appointed to the precipitation of $K_2NH_4PO_4$:$6H_2O$ (= pure N/P/K fertilizer) due to the high amounts of available K in the digestate (Appendix 8: Table A8.3). In this case, an economic analysis is recommended to select a target fertilizer, thereby taking into account local fertilizer market demands, and environmental and fertilizer regulations. On the one hand, the use of chemical Mg may increase the operational costs of P recovery, but, on the other hand, a higher recovery efficiency can be obtained, while also the mean particle diameter of the recovered precipitates (mainly MKP) predicted with the NRM-Prec was larger. The latter generally increases the revenues from fertilizer sales (see Chapter 2).

9.3.4 NRM-Strip/NRM-Scrub validation

9.3.4.1 NH_3 recovery at different operating conditions

During validation of the NRM-Strip and NRM-Scrub models, NH_3 stripping was found to be very sensitive to the total and relative input concentration of carbonates, Ca, and Na, as they determine the input alkalinity and pH. Since operators usually focus on the measurement of NH_3 and pH (+ sometimes total alkalinity) only, an identifiability problem arises. For example, when using the design parameters and input flow characterizations (S_N_min3_, pH) of Collivignarelli *et al.* (1998), a good agreement was obtained between experimental and simulation results for NH_3 recovery (Table 9.10).

Table 9.10 NRM-Strip/NRM-Scrub validation based on experimental literature results (Collivignarelli *et al.*, 1998) at different operating conditions at steady state (after 6h).

Test	Operational factor	Input		Recovery efficiency	Output	
		Experiment	Model		Experiment (6h)	Model
1	V_liq (m^3)	0.84	0.84	NH_3 recovery (%)	32	34.26
	Height (m)	2	2			
	S_N_min3_in (mol m^{-3})	147	147			
	Q_air (NL L^{-1} h^{-1})[a]	120	120			
	pH	8.5	8.52[b]			
	Temperature (ºC)	293.15	293.15			
2[c]	Q_air (NL L^{-1} h^{-1})[a]	200	200	NH_3 recovery (%)	50	50.12
	pH	12	12.03[b]			
3[c]	Q_air (NL L^{-1} h^{-1})[a]	70	70	NH_3 recovery (%)	59	58.44
	pH	10	9.97[b]			
	Temperature (ºC)	323.15	323.15			

[a] NL = normalized liter: temperature = 273.15 K, pressure = 1 atm.
[b] Calculated by PHREEQC based on the (calibrated) input composition.
[c] Other factors are similar as for Test 1.

However, due to lack of some fundamental input flow characteristics for pH calculation using the NRM-Strip model, the input composition had to be chosen (i.e. calibrated) in order to approximate the operational pH. Evidently, there are multiple ion combinations possible to obtain the specified pH, but the choice of the combination may influence the model outputs. Hence, in order to effectively use the NRM-Strip/NRM-Scrub models for process optimization, the initial waste flow composition should be characterized in more detail than is usually done at WRRFs today. Irrespective thereof, it can be seen in Table 9.10 that the model responded correctly to disturbances / operational decisions, such as an increase in pH, temperature, and air flow rate (cfr. Collivignarelli *et al.*, 1998).

9.3.4.2 Treatment train for NH_3 recovery

In order to overcome the above-mentioned identifiability issue, a technical survey was sent out to key suppliers of strip/scrub units for the treatment of a particular digestate flow (Section 9.2.4). Using the predefined input characteristics (Appendix 8: Table A8.4), as well as the dimensions, operating conditions, the effluent quality, and stripping performance offered by the different suppliers, the models were again validated for the different set-ups received. To this end, first a treatment train consisting of NRM-Chem, NRM-Strip, and NRM-Scrub was built to reflect a full-scale installation. Then, model simulations using the design data were conducted and scenario analyses were performed to check the performance guaranteed by the suppliers.

The most detailed reply was received by company X and is presented below as an example. The company guaranteed an NH_3 recovery efficiency of ± 90 % at 55 ºC, when increasing the pH to a value of 10.3 by addition of 102.5 mol m^{-3} NaOH d^{-1} under the design conditions provided in Appendix 8 (Table A8.4). The same results were obtained through treatment train simulation (Table 9.11).

Table 9.11 Validation treatment train (NRM-Chem, NRM-Strip, NRM-Scrub) based on technical inquiry provided by company X.

Variable	Output Company X	Output Model
S_NH_3_out (mol m^{-3})[a]	20	19.87
NH_3 recovery (%)	± 90	90.02
Operational pH[b]	10.3	10.30
Fertilizer pH[a]	6.3-6.8	6.33

[a] Ammonium sulfate (AmS) solution = output NRM-Scrub.
[b] NRM-Strip.

Finally, company X also advised to remove excess input carbonate buffer capacity prior to the treatment, e.g. through CO_2 stripping, in order to minimize NaOH consumption for pH-increase as well as $CaCO_3$ precipitation in the reactor (Pérez, 2002; Technology provider X, 2014). This recommendation could be confirmed using the NRM-Strip model: Figure 9.10 shows the decreasing NH_3 recovery efficiency as function of carbonate buffer capacity, if the NaOH consumption and other operating conditions would not be adjusted. Hence, the more carbonate is stripped off, the higher the reactor pH and the higher the NH_3 recovery efficiency. Note that, based on this principle, some technology suppliers provide an integrated CO_2 and NH_3 stripping process without using NaOH for pH-increase (e.g. Anaergia, Ontario, Canada and Colsen, Hulst, the Netherlands; Chapter 2: Section 2.3.4).

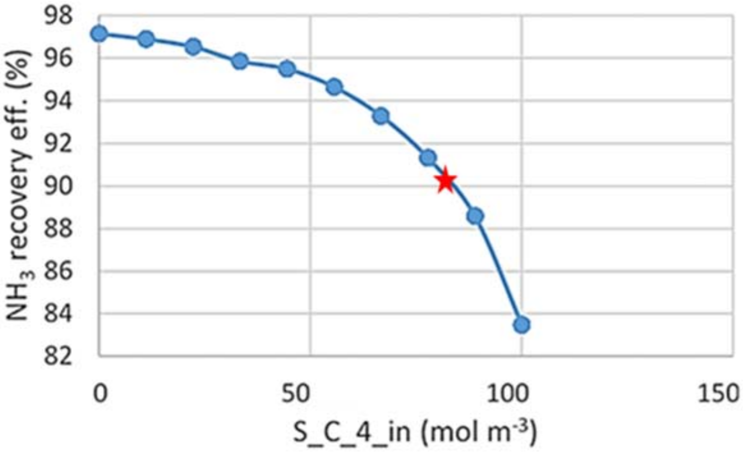


Figure 9.10 Simulated NH_3 recovery efficiency (%) as function of carbonate alkalinity (S_C_4_in, mol m^{-3}) using the NRM-Strip model. The red star indicates the digestate composition under study.

9.3.5 Recommendations for further experimental research

The results show that the performance of all resource recovery systems under study is very sensitive to the input waste stream composition, e.g. through its direct effect on the pH. In order to obtain good model predictions for a particular waste flow, the input flow should therefore be characterized in more detail than is usually done at WRRFs today. This observation is similar to activated sludge modelling in which influent characterization is considered as the most important step (Rieger *et al.*, 2012).

It is clear that a better characterization of the input composition may help to adjust the use of consumables (e.g. chemical dose, air requirements, etc.) to a minimum, thereby reducing the operational costs. As such, the models can be used as an invaluable tool for process optimization (= NRM-UO I). New experimental results, including detailed input characterizations, are currently being collected at pilot/full-scale under dynamic conditions in order to further calibrate and validate the proposed NRMs. To this end, collaboration was sought with various companies active in the field of anaerobic digestion and nutrient recovery, including, for example, Ekobalans (Lund, Sweden), Greenwatt (Heverlee, Belgium), Waterleau (Leuven, Belgium), and NuReSys (Waregem, Belgium).

A second issue observed is that values for the kinetic precipitation (k_T) and gas transfer coefficients ($K_{L/G}a$) used from literature are commonly determined under ideal conditions, i.e. gas transfer in clean water and precipitation in a synthetic solution containing only the target species involved in the reaction, e.g. Mg, NH_4, and P for MAP precipitation. However, the estimation of these parameters may be highly influenced by the complex matrix of the waste streams involved, e.g. through ion pairing (Section 9.3.3.1), concurrent and competing precipitation reactions (Section 9.3.3.2), and the presence of seed material. Studies evaluating kinetic rates under actual process conditions are lacking in literature, but should be the focus of further research in order to correctly calibrate these parameters in the NRMs. Moreover, rates and mechanisms for nucleation, agglomeration, and dissolution of various precipitates are still unknown and should be further studied. In this sense, the use of the simple empirical equation (Eq. 9.8) for liquid-solid/solid-liquid transfer in the NRMs is interesting compared to previously used approaches in wastewater treatment (e.g. Hauduc *et al.*, 2014; Lizarralde *et al.*, 2014; Mousvoto *et al.*, 2000a,b). Indeed, in a plot of $\log(\rho_{T,i})$ vs. $\log(S-1)$ the intercept will be k_T and the slope n. Hence, parameter estimation can be relatively easy.

Another important complication is related to the characterization of the precipitates formed. X-ray diffraction is the commonly used technique to characterize precipitates in pure solutions. However, it generally requires pure crystals of high regularity to solve the structure of a complicated arrangement of atoms. Also, the results usually represent a very local microstructure, and it requires a lot of work to obtain a certain statistical reliability on the results (Tanigawa *et al.*, 2003). More research is required on the development of a generic and cost-effective experimental method to accurately characterize the different precipitated species from a complex waste matrix. Such a procedure may not only be used to determine the precipitated species in precipitation units, but also, for example, the precipitates in the digestate leaving the digester. The latter is relevant as these precipitates may act as seed material for precipitation downstream.

Finally, interesting model extensions have been identified. They lead to the inclusion of:

i. Lactate as specific substrate for biological sulfate removal in the NRM-AD, e.g. as in UCT (2007);

ii. A transformer tool in the NRM-AD to allow for co-digestion of multiple input streams, e.g. the GISCOD tool (Zaher *et al.*, 2009b);
iii. Biochemical transformations of EBPR sludge in the NRM-AD, e.g. as in Ikumi (2011);
iv. Sludge retention in the NRM-AD, e.g. as in Cesur and Albertson (2005);
v. Microscale flocculation in the NRM-Prec, e.g. as in Crittenden *et al.* (2012);
vi. Particle size distributions in the NRM-Prec, e.g. as in Perez *et al.* (2008);
vii. Differential settling in the NRM-Settle and (if relevant) in the NRM-Prec, e.g. using the Stokes equation (Crittenden *et al.*, 2012);
viii. Heavy metals (and other contaminants) in all NRM models.

These extensions will of course lead to further experimental data requirements.

9.4 Conclusions and future perspectives

A generic model library for nutrient recovery based on detailed chemical solution speciation and reaction kinetics was proposed. Four key unit process models were developed: anaerobic digestion (NRM-AD), precipitation/crystallization (NRM-Prec), stripping (NRM-Strip), and acidic air scrubbing (NRM-Scrub), as well as four ancillary units: chemical dosing (NRM-Chem), heat exchanger (NRM-heat), storage tank (NRM-Store), and solids settler (NRM-Settle). Each dynamic mathematical model was built using: i) the definition of a chemical speciation model using geochemical modelling software (PHREEQC/MINTEQ), ii) the description of a physicochemical and biochemical transformation model tailored to the models developed in the first step, and iii) the selection of a reactor mass balance model to describe the (time-dependent) process conditions.

To facilitate numerical solution, a generic methodology to allow for accurate chemical speciation at minimal computational effort was developed. A reduction of execution time was established at two critical points during model simulations: i) the uploading and reading of database and input files (through PHREEQC model reduction), and ii) the transfer of data between PHREEQC and Tornado (through tight model coupling). In this respect, a generic procedure for PHREEQC model reduction was proposed. An average improvement of model simulation speeds of 64±10 % and 79±7 % was obtained using the developed reduced model as compared to full PHREEQC and MINTEQ databases, respectively. An important discovery involves the lack of fundamental physicochemical components/species/reactions occurring in WRRFs, e.g. potassium struvite and ammonium sulfate precipitation, in the existing generic PHREEQC/MINTEQ databases. Because of these flaws, an extended database with the purpose of nutrient recovery was created, named *'Nutricover.dat'*.

Simulation results using default parameters showed good agreement with experimental results under steady state conditions. However, outputs were very sensitive to the input ionic composition through its direct effect on pH. For optimization of process performance and sustainability, a more detailed input flow characterization than is common for WRRFs today is recommended. Such data are currently being collected under dynamic conditions at full-scale in order to further calibrate and validate the NRM kinetics. Finally, the ability of the models for increased process understanding and optimization was demonstrated.

It can be concluded that the developed NRM library can and should be used by the various stakeholders in the field to facilitate the implementation, operation, and optimization of nutrient recovery technologies. This, in turn, can stimulate the transition from waste(water) treatment plants to more sustainable waste(water) resource recovery facilities.

CHAPTER 10:

GLOBAL SENSITIVITY ANALYSIS OF NUTRIENT RECOVERY MODELS (NRM): FACTOR PRIORITIZATION, TREATMENT TRAIN CONFIGURATION AND OPTIMIZATION

Towards the balancing of benefits and costs

Redrafted from:

Vaneeckhaute, C., Claeys, F.H., Belia, E., Tack, F.M.G., Meers, E., Vanrolleghem, P.A., submitted. Global sensitivity analysis of nutrient recovery models (NRM): Factor prioritization, treatment train configuration and optimization.

Abstract

In order to hasten the implementation of optimal, cost-effective, and sustainable treatment trains for resource recovery, a nutrient recovery model (NRM) library has been developed and validated at steady state. The present chapter describes the use of global sensitivity analysis (GSA) for factor prioritization in NRM applications for (digested) manure and sludge treatment. The aim was to select the most important factors influencing the model outputs among: 1) input waste characteristics, 2) process operational factors, and 3) kinetic parameters incorporated in the NRMs. To this end, linear regression analyses on Monte Carlo simulation outputs were performed, and the impact of the standardized regression coefficients on major performance indicators for each NRM key unit was evaluated.

Next to the relevance of the outcomes in terms of model validation, the GSA results allowed listing generic recommendations for factor prioritiziation in view of future research efforts. Moreover, important generic insights in the interactions between process inputs and outputs were obtained for the three different waste streams under study. For all unit processes, the variation related to the input waste composition resulted in a major effect on the output variation through its direct effect on the operational pH and ionic strength. Major findings involve, among others, the impact of Cl inhibition on ammonia removal in the stripping unit, the impact of Ca, Fe, and Al inhibition on P recovery in the precipitation unit, and the interaction between Fe/Al, S, and CH_4 production in the anaerobic digester. Based on the results, it was possible to construct an optimal treatment train configuration for nutrient recovery aiming at the production of high-quality fertilizers at minimal cost. Next to the input characterization, it was found that also local/regional fertilizer legislations may greatly influence the optimal configuration.

Finally, the use of the NRM library to establish the operational settings of a sustainable and cost-effective treatment scenario with maximal resource recovery and minimal energy and chemical requirements was demonstrated. Under the optimized conditions and assumptions made, potential financial benefits for a large-scale anaerobic digestion and nutrient recovery project were estimated at 2.8-6.5 USD *(3.5-8.1 CAD; € 2.5-5.7)* m^{-3} manure based on net variable cost calculations, or an average of ± 2 USD *(2.5 CAD; € 1.8)* m^{-3} y^{-1}, equivalent with 40 USD *(50 CAD; € 35)* ton^{-1} total solids y^{-1}, over 20 years in the best case when also taking into account capital costs. Hence, it is likely that in practice a full-scale 'ZeroCostWRRF' (waste(water) resource recovery facility at zero cost) can be constructed.

It can be concluded that the GSA strategy and results obtained in this chapter are very valuable to facilitate future implementation and optimization of nutrient recovery practices. Starting from the results outlined in the present chapter, further elaboration on the development of a generic roadmap for setting up nutrient recovery strategies as function of fertilizer markets and input flow characteristics is suggested. This should facilitate communication and nutrient recovery scenario implementation.

Keywords: *cost optimization, waste(water) characterization, linear regression, Monte Carlo, nutrient recovery model validation, unit process interaction.*

Résumé

Pour accélérer la mise en œuvre d'une chaîne de traitement optimale, durable et rentable permettant la récupération des ressources, une librairie de modèles pour la récupération des nutriments (MRN) a récemment été développée et validée en régime permanent. Le présent chapitre décrit l'utilisation de l'analyse de sensibilité globale (ASG) pour identifier les facteurs prioritaires dans l'application des MRN à des lisiers et des boues (digérés). L'objectif était de sélectionner les facteurs les plus importants influençant les sorties des modèles parmi: 1) les caractéristiques des flux de déchets entrants, 2) les facteurs opérationnels des procédés, et 3) les paramètres cinétiques incorporés dans les MRN. À cette fin, des analyses de régression linéaire sur les résultats de simulation Monte Carlo ont été réalisées et l'impact des coefficients de régression standardisés sur les indicateurs de performance clés pour chaque modèle a été évalué.

Suivant à la pertinence des résultats en termes de validation des modèles, les résultats de l'ASG ont permis de créer une liste de recommandations génériques pour la priorisation des facteurs dans les futurs efforts de recherche. En outre, des connaissances génériques importantes sur les interactions entre les entrées et sorties des procédés ont été obtenues pour les trois différents flux de déchets recherchés. Pour chacun des procédés unitaires, la variation relative à la composition des déchets entrants a entraîné un effet majeur sur la variation des sorties par son effet direct sur le pH opérationnel et sur la force ionique. Les principales conclusions portent, entre autres, sur l'impact de l'inhibition du Cl sur l'élimination de l'ammoniac dans l'unité de stripage, l'impact de l'inhibition du Ca, du Fe et de l'Al sur la récupération de P dans l'unité de précipitation et l'interaction entre Fe/Al, S et la production de CH_4 dans le digesteur anaérobie. Basé sur les résultats, il était possible de proposer une configuration optimale de chaîne de traitement pour la récupération des nutriments visant à la production d'engrais de haute qualité à un coût minimal. En plus de la caractérisation des entrants, il a été constaté que les législations d'engrais locales/régionales peuvent aussi grandement influencer la configuration optimale.

Enfin, l'utilisation de la librairie des MRN a été démontrée pour établir les paramètres opérationnels d'un scénario de traitement durable et rentable avec une récupération maximale des ressources et des exigences minimales d'énergie et de produits chimiques. Sous les conditions optimisées et des hypothèses faites, les avantages financiers potentiels d'un projet à grande échelle de digestion anaérobie et récupération des nutriments ont été estimés à 2.8-6.5 USD *(3.5-8.1 CAD; € 2.5-5.7)* m^{-3} lisier sur la base des calculs de coûts variables nets, soit une moyenne de ± 2 USD *(2.5 CAD; € 1.8)* m^{-3} an^{-1}, équivalent avec 40 USD *(50 CAD; € 35)* $tonne^{-1}$ solides totaux an^{-1}, dans le meilleur cas prenant également en compte les coûts d'investissement amortisés sur 20 années. Par conséquent, il est très probable que dans la pratique un 'ZeroCostWRRF' (station de récupération des ressources de l'eau et des déchets à coût nul) à pleine échelle peut être construit.

Il peut donc être conclu que la stratégie d'ASG et les résultats obtenus dans ce chapitre sont très utiles pour faciliter la future mise en œuvre et l'optimisation des pratiques de récupération des nutriments. À partir des résultats décrits dans le présent chapitre, l'élaboration d'une feuille de route générique pour la mise en place des stratégies de récupération des nutriments en fonction des marchés d'engrais et des caractéristiques des flux d'entrée est suggérée. Ces résultats devraient faciliter la communication et la mise en œuvre de scénarios de récupération des nutriments.

Mots-clés: *caractérisation des entrants, interaction des processus unitaires, Monte Carlo, optimisation des coûts, régression linéaire, validation des modèles de récupération des nutriments.*

10.1 Introduction

To hasten the implementation and integration of sustainable nutrient recovery strategies and to adequately put together an optimal treatment train of unit processes for resource recovery, a generic nutrient recovery model (NRM) library has recently been developed and validated at steady state (Chapter 9). The proposed models are dynamic mathematical models, based on detailed solution speciation and reaction kinetics. To facilitate numerical solution, a highly efficient PHREEQC-Tornado/(WEST) (Charlton and Parkhurst, 2011; mikebydhi.com; Vanhooren *et al.*, 2003) interface has been established and verified. Model simulation outputs were found very sensitive to input waste stream characteristics through their direct effect on pH, which is adequately determined by means of the integrated chemical speciation calculation. Moreover, new data needs appeared, especially related to the physicochemical kinetic precipitation/dissolution and liquid-gas/gas-liquid transfer coefficients. For optimization of process performance and sustainability, a more detailed physicochemical characterization of the input flows than is common at waste(water) resource recovery facilities (WRRFs) to date has been recommended. In addition, further experimental studies to adequately calibrate physicochemical kinetic parameters in real waste matrices have been advised.

The present chapter describes the next logical step in model development, i.e. the determination of factors that are most influential on model results. To this end, a global sensitivity analysis (GSA) is performed, which provides information on how the model outputs are influenced by factor variation over the whole space of possible input factor values (Homma and Saltelli, 1996; Saltelli *et al.*, 2004). Such model sensitivity analysis is not only critical to model validation, but also serves to guide future research efforts. Indeed, by means of GSA, factors can be ranked according to the relative magnitude of change of the model outputs caused by input factor variation. Following the findings in Chapter 9, the main objective of the GSA is to classify and select the most important factors (factor prioritisation) in terms of their impact on the model outputs, among three factor classes:

1. Input waste characteristics at WRRFs (**Objective 1**);
2. Process operational factors (**Objective 2**);
3. Kinetic rate parameters specific to the NRMs (**Objective 3**).

Among the different sensitivity analysis methods available, Hamby (1994) evaluated regression analysis as the method that provides the most comprehensive sensitivity measure. It is also the common method used to build response surfaces that approximate complex models related to waste(water) treatment and it provides accurate results in terms of factor ranking (Chen *et al.*, 2012a; Cosenza *et al.*, 2013; Saltelli *et al.*, 2008; Sin *et al.*, 2009, 2011; Vanrolleghem *et al.*, 2015). Hence, the standardized regression coefficient (SRC) method will be used for factor prioritization in this research. One limitation of this method is its inability to detect synergistic or cooperative effects among factors, i.e. problems related to multicollinearity (Kutner *et al.*, 2005; Saltelli *et al.*, 2008). Due to the large number of model factors considered in the NRM library and the complex nature of the input waste matrices, i.e. manure and wastewater treatment plant

(WWTP) sludge, the model variance contribution due to multicollinearity may be significant. To overcome this potential problem, model quality was assessed by determination of variance inflation factors (VIFs), a widely accepted detection-tolerance for multicollinearity (Kutner *et al.*, 2005), next to common coefficients for evaluation of model linearity.

Based on the unit process GSA results, input factors that have the highest impact on the output variability and that hence should become standard measurements at WRRFs, at least during start-up, are selected. Secondly, uncertain kinetic parameters that most urgently require additional experimental research for strengthening the knowledge base and for calibration are listed. Thirdly, the most important operational factors requiring optimization are identified. Finally, the use of the NRM library and GSA for treatment train configuration and optimization is demonstrated (**Objective 4**). A conceptual overview of the strategy used is presented in Figure 10.1 and briefly described below.

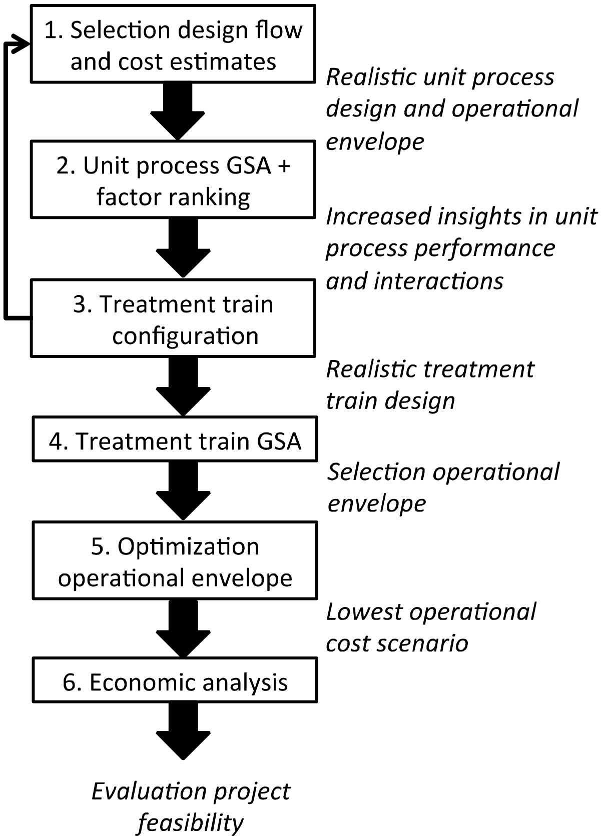


Figure 10.1 Conceptual overview: use of the nutrient recovery model (NRM) library for treatment train configuration and optimization. GSA = global sensitivity analysis.

Starting from the increased insights obtained through unit process GSA (Fig. 10.1: Steps 1-2), an optimal combination of unit processes in a treatment train for nutrient recovery was selected (Fig. 10.1: Step 3). Key technology providers in the field of nutrient recovery were asked to provide designs (and cost estimates) for a given design flow for each of the individual unit processes in the treatment train. Each technology provider applied its in-house design guidelines and safety factors. An operational envelope was compiled based on a treatment train

GSA (Fig. 10.1: Step 4) and the operational settings were optimized aiming at the reduction of net operational costs (Fig. 10.1: Step 5). Finally, an overall economic analysis was conducted for the optimized nutrient recovery scenario (Fig. 10.1: Step 6).

Note that in the future the NRM library may replace the use of the in-house design guidelines applied now by the technology providers for design purposes in a way that is currently being developed for treatment plant design (Talebizadeh *et al.*, 2014). However, such probability-based dynamic design approaches are still under development for the activated sludge process and requires good assessments of the uncertainties in the processes and the waste properties (Talebizadeh *et al.*, 2014). Significant research to reduce these uncertainties and assess them in detail is still required. Hence, at this stage, using the NRM library for sizing of nutrient recovery systems is considered premature.

10.2 Methodology

The overall strategy used for GSA aiming at factor prioritization, treatment train configuration, and optimization is presented in Figure 10.2 and further described in detail in the sections below.

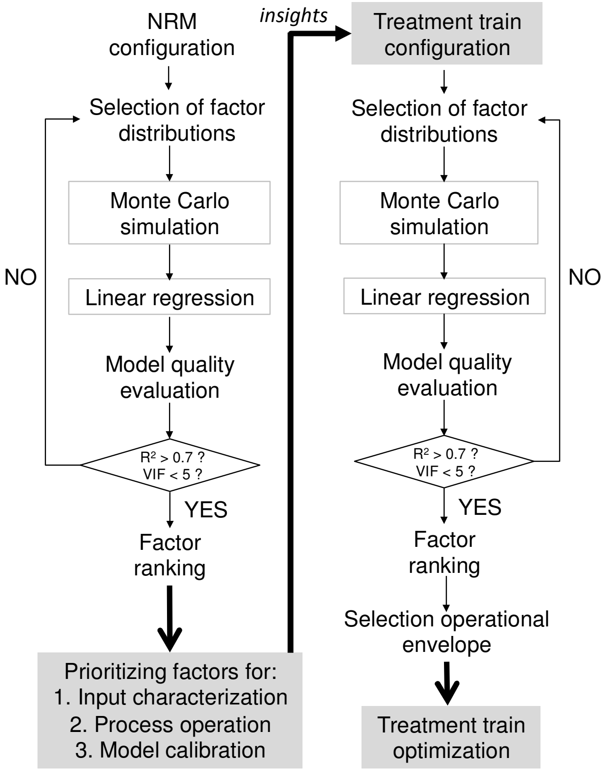


Figure 10.2 Strategy used for global sensitivity analysis. Grey boxes indicate the research objectives. NRM = nutrient recovery model; R^2 = determination coefficient; VIF = variance inflation factor.

First, the NRM configuration and performance indicators under study were selected (Section 10.2.1). Next, the scenarios for sensitivity analysis of each NRM and the corresponding factor distributions were chosen (Section 10.2.2). A Monte Carlo simulation and multivariate linear regression were then performed (Section 10.2.3). When model quality was found to be sufficient, factors were ranked according to predefined selection criteria. Finally, based on the obtained process insights, an optimal treatment train configuration was compiled, a treatment train sensitivity analysis was conducted, and an optimization experiment was performed for the selected treatment train (Section 10.2.4).

10.2.1 NRM configuration and performance indicators

Details of the NRM unit processes are provided in Chapter 9. The GSA was performed for each NRM key unit, i.e. the anaerobic digester (NRM-AD), the precipitation/crystallization unit (NRM-Prec), the stripping unit (NRM-Strip), and the acidic air scrubber (NRM-Scrub). Manure and WWTP sludge were used as input to the NRM-AD, whereas digestate was used as input to the NRM-Prec and NRM-Strip (Fig. 9.1). The output gas flow resulting from the NRM-Strip was used as input to the NRM-Scrub.

For the NRM-AD and NRM-Prec units, a continuously stirred tank reactor (CSTR) design was assumed (Batstone *et al.*, 2002; Crittenden *et al.*, 2012), with continuous biogas and precipitate extraction, respectively (Table 9.6). The NRM-Strip and NRM-Scrub units were modelled using a stirred bubble tank design as in Gujer (2008). A large-scale project was considered, as construction of biogas systems on a large scale (~ 500 kW and more) is becoming increasingly important to meet the global 2020 directives (UNEP, 2013) in terms of energy production, organic matter valorization, and greenhouse gas emission reductions, both at farm, municipality, and regional scale (Thomassen and Zwart, 2008; Zwart *et al.*, 2006).

Realistic design parameters were obtained by distributing a technical questionnaire to key technology suppliers in the field, requesting a cost estimate for a design flow of 2,000 m^3 d^{-1} (input ranges, e.g. for N, P, chemical oxygen demand (COD), volatile suspended solids (VSS), total solids (TS), and alkalinity from Cesur and Albertson (2005)) as input to the anaerobic digester, and the resulting digestate (Cesur and Albertson, 2005) as input to the nutrient recovery units. The results of this questionnaire are provided in Table 10.1. A mesophilic (35 ℃) anaerobic digestion process was assumed, while the design values for the stripper are based on an operational temperature of 50-55 ℃, a pH > 10, and a gas to liquid ratio of ± 800 m^3 m^{-3}.

Table 10.1 Design parameters for each key unit process in the nutrient recovery model (NRM) library. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber.

Key unit	Parameter	Symbol	Design value	Unit
NRM-AD	Liquid volume	V_liq	40,000[a]	m^3
NRM-AD	Gas volume	V_gas	3,000[a]	m^3
NRM-Prec	Liquid volume	V_liq	500[a]	m^3
NRM-Strip / NRM-Scrub[b,c]	Reactor volume	V	80[a]	m^3
NRM-Strip / NRM-Scrub[b,c]	Reactor height	H	12	m

[a] Volume reflects the total capacity. It can be divided over different units, depending on the technology provider, e.g. anaerobic digestion can be performed using four units of 10,000 m^3.

[b] Values indicate reactor dimensions for the individual stripper and scrubber unit. Hence, both units have the same size.

[c] At an operational temperature of 50-55 ℃, pH > 10, and gas to liquid ratio of ± 800 m^3 m^{-3}.

The performance indicators evaluated for each NRM key unit are presented in Table 10.2. The objective functions were selected to evaluate resource recovery and process sustainability in accordance with the observed specifications in Chapters 2-8 and the selected model outputs in Section 9.2.1.2 (Chapter 9) or Table 8.1.

Table 10.2 Performance indicators (+ symbol and unit) used as objective functions in global sensitivity analysis for each key unit in the nutrient recovery model (NRM) library. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber.

NRM-AD	NRM-Prec	NRM-Strip	NRM-Scrub
1. CH_4 production (p_CH$_4$, atm)[a]	1. Effluent soluble P (S_P, kmol m^{-3})	1. NH_4-N removal efficiency (%)	1. NH_3 recovery (= absorption) efficiency (%)
2. Biogas production (p_{biogas}, atm)[a]	2. Fertilizer P (P_P, kmol m^{-3})	2. Effluent soluble NH_4-N (S_N_min3_, kmol m^{-3})	2. Fertilizer soluble NH_4-N (S_N_min3_, kmol m^{-3}),
3. Digestate soluble COD (S_COD, kmol m^{-3})	3. Fertilizer particle diameter (d_p, m)	3. CO_3 precipitation (cfr. scaling) (P_C_4_, kmol m^{-3})	3. Fertilizer pH
4. Digestate particulate COD (X_COD, kmol m^{-3})	4. Fertilizer density (ρ, kg m^{-3})	4. Air requirements (m^3 d^{-1})	4. Acid requirements (m^3 d^{-1})
5. Digestate soluble NH_4-N (S_N_min3_, kmol m^{-3})	5. Struvite purity (%)	5. Overall[b]	5. Overall[b]
6. Digestate soluble P (S_P, kmol m^{-3})	6. Overall[b]		
7. Digestate soluble K (S_K, kmol m^{-3})			
8. Digestate pH			
9. Overall[b]			

[a] Overpressure leads to methane and biogas production (m^3 m^3 d^{-1}; cfr. ADM1; Batstone *et al.*, 2002).

[b] Overall measure of factor sensitivity on all objective functions considered for the unit. Each output was assumed to have an equal weight.

For the NRM-AD unit, it is obvious that CH_4 and biogas production were aimed to be high, in line with the amount of COD removed. Digestate soluble NH_4-N, P, and K were studied in order to evaluate the digestate fertilizer quality and the potential of uncontrolled nutrient precipitation in the digester and subsequent piping. Further, the digestate pH should be neutral or slightly alkaline for fertilizer purposes. The latter also indicates a stable digestion process.

For the NRM-Prec unit, a low effluent P and high fertilizer P concentration was targeted. Moreover, the larger the particle diameter, the higher the revenues, while an increasing fertilizer density reduces the costs for transportation (Chapters 2, 4). As to date struvite precipitation is the most convenient practice used for P recovery, also struvite purity was selected as performance indicator (= mass of N- and K-struvite over total recovered fertilizer mass).

Next, for the NRM-Strip unit, low effluent NH_4-N concentrations and hence high digestate NH_4-N removal efficiencies were targeted at mimimal air consumption. Carbonate precipitation should also be low in order to reduce scaling on the packing material, which may reduce the stripping performance. For the NRM-Scrub unit, a high NH_3 absorption efficiency was intended in line with a high fertilizer N concentration (25-40 % $(NH_4)_2SO_4$ by weight), using a mimimal amount of acid. The interest to evaluate the pH of the recovered ammonium sulfate (AmS) fertilizer is related to the fact that it is often too low (3-4) for direct land application (Chapters 4-5). Hence, process conditions that neutralize the pH at acceptable costs may be favoured.

Finally, for each NRM, also an overall GSA was performed, representing a global measure of factor sensitivity on all objective functions considered for the NRM (i.e. ‘Overall’ in Table 10.2).

10.2.2 Scenarios for sensitivity analysis and factor distributions

To match the purpose of the specific model application (Section 10.1), it was decided to focus the sensitivity analysis on the variation related to the input waste composition (~ objective 1), the operational factors (~ objective 2), and the (new) kinetic parameters incorporated in the NRMs (~ objective 3). The different GSA scenarios, with indication of the varying and fixed factors, are presented in Table 10.3. Varying factors used for GSA were represented using a uniform distribution. The implicit assumption in selecting a uniform distribution is that every value in the provided range has an equal probability of occurrence. As pointed out by Freni and Mannina (2010; Mannina and Viviani, 2009), a uniform distribution of model factors is preferred whenever relevant prior factor information is unavailable, as assuming a non-uniform shape may lead to wrong estimations of uncertainty in modelling results. The other factors in the NRM library were kept fixed at the default value (see below). Their impact on the model outputs was thus not evaluated.

Table 10.3 Scenarios for sensitivity analysis: varying factors (= uniform distribution) and fixed factors (= default value) considered for each key unit in the nutrient recovery model (NRM) library. AD = anaerobic digestion; L-G = liquid-gas; L-S = liquid-solid; Prec = precipitation/ crystallization; Scrub = scrubber; SRB = sulfate reducing bacteria; Strip = stripper.

Key unit	Liquid input	Gas input	Mass transfer (L-G, L-S)	Physicochemical stoichiometry	Bio-kinetics SRBs	Bio-kinetics (other) & stoichiometry	Operation	Design[g]
NRM-AD	A. Uniform (large range): all applications	N/A[a]	Uniform	Default value[b]	Uniform	Default value, except for SRBs	Uniform	Default value
	B. Uniform: manure range[c]	N/A	Uniform	Default value	Uniform		Uniform	Default value
	C. Uniform: sludge range[d]	N/A	Uniform	Default value	Uniform		Uniform	Default value
NRM-Prec	A. Uniform (large range): all applications	N/A	Uniform	Default value	N/A	N/A	Uniform	Default value
	B. Uniform: digestate 1[c,e]	N/A	Uniform	Default value	N/A	N/A	Uniform	Default value
	C. Uniform: digestate 2[f,e]	N/A	Uniform	Default value	N/A	N/A	Uniform	Default value
NRM-Strip	A. Uniform (large range): all applications	Uniform	Uniform	Default value	N/A	N/A	Uniform	Default value
	B. Uniform: digestate 1[c,e]	Uniform	Uniform	Default value	N/A	N/A	Uniform	Default value
	C. Uniform: digestate 2[f,e]	Uniform	Uniform	Default value	N/A	N/A	Uniform	Default value
NRM-Scrub	Uniform (acid)	Uniform	Uniform	Default value	N/A	N/A	Uniform	Default value

[a] N/A = not applicable.
[b] When factors are taken as fixed, they are set to their default values (Tables 10.4-10.7).
[c] Data taken from Cesur and Albertson (2005).
[d] Data taken from Astals *et al.* (2013).
[e] Tested with and without the external addition of base.
[f] Data taken from Vlaco (2012).
[g] Design reactor dimensions based on budget proposals received from technology providers for a specified design flow of 2,000 m^{-3} d^{-1} (Section 10.2.1: Table 10.1).

To cover the high variability of the input waste composition in time and for different locations, for all systems first a wide variation range was applied in order to cover all potential applications and treatment trains (= Scenario A). Secondly, for the NRM-AD, typical pig manure ranges (Cesur and Albertson, 2005; Scenario B) and WWTP sludge ranges (Astals *et al.*, 2013;

Scenario C) were evaluated. For manure, very valuable datasets were provided by Mattocks *et al.* (2002) and Martin (2003), who collected and characterized in detail anaerobic digester input and output variables, and recorded system parameters and operational measurements at 26 sampling points during one year. These datasets were used for ADM1 (Anaerobic Digestion Model No. 1) calibration and validation by Cesur and Albertson (2005), from where the variation ranges in manure composition were taken for this study.

Next, Astals *et al.* (2013) evaluated the characteristics and biodegradability of seven mixed sewage sludges, with different ratios of primary and activated sludge (AS) from different WWTPs that have an anaerobic digester in operation. These data were specifically assessed in order to clarify the literature uncertainty with regard to sludge characteristics and biodegradability in particular. Hence, the dataset was very suitable for the present study. In order to cover high sulfate waste flows (for detection of important kinetic parameters for biochemical sulfate reduction), the sludge range was further adjusted by incorporating data from a full-scale operational anaerobic digester treating S-rich paper mill sludge located at the WRRF Holmen Paper, Madrid, Spain (data obtained by the Center of Studies and Technical Research, CEIT, San Sebastian, Spain; See also Chapter 9).

Next, to cover the uncertainty of digestate characteristics and its variability in time (= input for NRM-Prec and NRM-Strip), data were obtained by Vlaco (2012), who characterized 213 digestates from different (co-)digestion plants in Flanders (Belgium) during four years (2008-2011; Scenario C; see Chapter 2: Section 2.2). Also, the digestate range for manure provided by Cesur and Albertson (2005) was used for the GSA (Scenario B), aiming at the configuration and optimization of a treatment train for resource recovery (Section 10.2.4). Finally, it should be noted that for the NRM-Prec and NRM-Strip, the GSA was performed with and without the possibility of external chemical addition for pH-increase.

For all scenarios, the stoichiometric physicochemical parameters (e.g. Henry coefficients, acid-base equilibrium constants, ion pairing constants, etc.) were determined by the coupled geochemical modelling software tool PHREEQC (Chapter 9: Section 9.2.4). The stoichiometric and kinetic biological parameters used in the NRM-AD were considered sufficiently calibrated by Batstone *et al.* (2002), while the kinetics of the added processes for sulfate reducing bacteria (SRBs) were assumed unknown. Hence, the focus of the analysis was on the extensions included in the NRM-AD as compared to ADM1 (Chapter 9: Section 9.2.2.3). This is reasonable as during validation of the NRM-AD, it was found that especially the calibration of biological S removal deserves further attention (Chapter 9: Section 9.3.2). For the physicochemical kinetics, the following assumptions were made: i) precipitation kinetics are equal to dissolution kinetics (Morse and Arvidson, 2002), ii) the reaction order for all precipitation reactions is 2, indicating surface controlled growth (Mehta and Batstone, 2013; Musvoto *et al.*, 2000a,b), iii) no agglomeration occurs or agglomeration occurs homogeneously, i.e. using the same fixed kinetic rate values for each precipitate (Schneider *et al.*, 2013).

Tables 10.4-10.7 summarise the symbol, description, variation range, default value, and the unit of the variable model factors used in the different sensitivity analysis scenarios for each NRM key unit. The variation ranges provided and default values were taken from literature (see above), existing models, expert-judgement, and contact with technology providers. For more details, reference is made to Chapters 2 and 9. The default values for the input waste characteristics were set at the average values for manure (NRM-AD: Table 10.4) and digested manure (all NRMs following the NRM-AD: Tables 10.5-10.7) provided by Cesur and Albertson (2005), as these values were used in a case study for treatment train optimization (Section 10.2.4).

As mentioned in the introduction of this chapter, the objective of the analysis was to use the NRM library and GSA for the selection (and optimization) of important operational factors for nutrient recovery systems, not for design purposes. In practice, the flow and characteristics of the waste streams available for digestion, and hence the quantity and quality of digestate may vary significantly (see Chapters 3-5). Therefore, flow rates were allowed to change in the GSA and the reactor dimensions were kept at the values of Table 10.1. The aim was to cover the variability in the hydraulic residence time (HRT) and solids retention time (SRT), in accordance with the selected reactor design parameters (Table 10.1). Typical HRTs for NRM-AD range between 10 and 30 d, depending on the nature of the waste material and operational temperature (Fleming and McAlpine, 2008; Tchobanoglous *et al.*, 2003; Wilkie, 2000). HRTs and SRTs for struvite precipitation (NRM-Prec) reported in literature are very variable. The company Ostara (Vancouver, Canada) estimated an average HRT of 25 min (0.0174 d) for digested sludge based on full-scale experiences (Ostara, 2014; Seymour, 2009). However, in literature, HRTs up to 10 h (Schneider *et al.*, 2013) and 1 d (Le Corre *et al.*, 2009) have also been reported. SRTs usually range between 3 and 30 d (Le Corre *et al.*, 2009). Finally, HRTs for the strip-scrub system range between 40 min and 4.8 h (RVTPE, 2014; Tchobanoglous *et al.*, 2003), depending on the ammonium content to be removed, the operational temperature and pH.

Table 10.4 Symbol, description, variation range, default value, and unit for each model factor used in the global sensitivity analysis scenarios for the NRM-AD (anaerobic digestion) key unit. Range A: all applications; Range B: manure (Cesur and Albertson, 2005); Range C: sludge (Astals *et al.*, 2013). L-S = liquid-solid; L-G = liquid-gas.

NRM-AD	Factor symbol	Description	Range A	Range B	Range C	Default[a]	Unit
Input liquid[b]	S_Inert	soluble inerts	0-100	0-1.5	0.1-4.2	0.75	kg COD m^{-3}
	S_fa	soluble long chain fatty acids	0-100	0-1.5	0.1-4.2	0.75	kg COD m^{-3}
	S_su	soluble sugars	0-100	0-1.5	0.1-4.2	0.75	kg COD m^{-3}
	X_Inert	particulate inerts	0-100	28.83-48.92	0-60.04	38.88	kg COD m^{-3}
	X_ch	carbohydrates	0-100	14.95-25.37	0.19-17.22	20.16	kg COD m^{-3}
	X_li	lipids	0-100	0-1.54	0.14-7.96	0.77	kg COD m^{-3}
	X_pr	proteins	0-100	0-1.54	0-13.54	0.77	kg COD m^{-3}
	S_Acetate	soluble acetate	0-100	66.74-103.69	2.89-18.35	85.22	mol m^{-3}
	S_Al	soluble aluminum	0-100	1.48-2.29	0.01-20	1.89	mol m^{-3}
	S_Butyrate	soluble butyrate	0-100	10.68-18.12	1.16-4.03	14.40	mol m^{-3}
	S_C_4_	soluble carbonate (IV)	0-500	115.42-149.24	16.44-72.88	132.33	mol m^{-3}
	S_C_min4_	soluble methane (-IV)	0-10	0-5	0-5	2.50	mol m^{-3}
	S_Ca	soluble calcium	0-100	23.02-61.38	3.85-10.25	42.20	mol m^{-3}
	S_Cl	soluble chloride	0-100	10-40	5.33-15.97	25	mol m^{-3}

NRM-AD (Continuation)	**Factor symbol**	**Description**	**Range A**	**Range B**	**Range C**	**Default**[a]	**Unit**
	S_Fe	soluble iron	0-100	2.91-3.87	0.01-20	3.39	mol m^{-3}
	S_H_0_	soluble hydrogen (0)	0-1	0-1	0-1	0.50	mol m^{-3}
	S_K	soluble potassium	0-100	21.76-30.46	1.82-7.18	26.11	mol m^{-3}
	S_Mg	soluble magnesium	0-100	12.65-29.53	1.52-5.60	21.09	mol m^{-3}
	S_N_0_	soluble nitrogen (0)	0-1	0-1	0-1	0.50	mol m^{-3}
	S_N_5_	soluble nitrogen (V)	0-100	0.13-0.17	0-0.2	0.15	mol m^{-3}
	S_N_min3_	soluble nitrogen (-III)	0-100	176.3-205	10.14-71.07	190.65	mol m^{-3}
	S_Na	soluble sodium	0-100	17.82-35.65	7.48-23.26	26.74	mol m^{-3}
	S_P	soluble phosphorus	0-100	22.38-36.08	0.55-9.26	29.23	mol m^{-3}
	S_Propionate	soluble propionate	0-100	17.54-29.77	1.68-9.2	23.66	mol m^{-3}
	S_S_6_	soluble sulfate (VI)	0-100	9.61-19.25	0.31-6.65	14.43	mol m^{-3}
	S_S_min2_	soluble sulfide (-II)	0-10	0.01-1	0.01-1	0.51	mol m^{-3}
	S_Valerate	soluble valerate	0-100	2.87-4.88	0.85-2.96	3.88	mol m^{-3}
Operation	pH_liq[c]	input pH	5-8.5	7.72-8.3	5.7-7.5	8.01	-
	Temp_liq[d]	liquid temperature	10-55	10-55	10-55	35	°C
	Q_liq	liquid flow rate	1,000-3,000	1,000-3,000	1,000-3,000	2,000	m^3 d^{-1}
L-S kinetics[e]	k_Al_2O_3	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.00E-4	mol m^{-2} d^{-1}
	k_$AlPO_4$	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.00E-4	mol m^{-2} d^{-1}
	k_Anhydrite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.00E-4	mol m^{-2} d^{-1}
	k_Aragonite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.61	mol m^{-2} d^{-1}
	k_Boehmite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	2.80E-4	mol m^{-2} d^{-1}
	k_$Ca_4H(PO_4)_3{:}3H_2O$	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_$CaHPO_4{:}2H_2O$	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	14.64	mol m^{-2} d^{-1}
	k_$CaHPO_4$bis	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Calcite	liquid-solid transfer coefficient	1-5,000	1-5,000	1-5,000	1,080	mol m^{-2} d^{-1}
	k_Diaspore	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Dolomite	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	11.22	mol m^{-2} d^{-1}
	k_FeS_ppt	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.00E-4	mol m^{-2} d^{-1}
	k_Gibbsite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.19E-4	mol m^{-2} d^{-1}
	k_Hercynite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Hydroxyapatite	liquid-solid transfer coefficient	1-5,000	1-5,000	1-5,000	986.65	mol m^{-2} d^{-1}
	k_Kstruvite	liquid-solid transfer coefficient	1E-10-1	1E-10-1	1E-10-1	4.64E-6	mol m^{-2} d^{-1}
	k_Mackinawite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.00E-4	mol m^{-2} d^{-1}
	k_Magnesite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	9.88E-4	mol m^{-2} d^{-1}
	k_$Mg_3(PO_4)_2$	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_$MgHPO_4{:}3H_2O$	liquid-solid transfer coefficient	1E-11-1	1E-11-1	1E-11-1	4.78E-7	mol m^{-2} d^{-1}
	k_Siderite	liquid-solid transfer coefficient	1E-7-10	1E-7-10	1E-7-10	0.0021	mol m^{-2} d^{-1}
	k_Struvite	liquid-solid transfer coefficient	1E-7-10	1E-7-10	1E-7-10	0.0020	mol m^{-2} d^{-1}
	k_Vivianite	liquid-solid transfer coefficient	1E-10-1	1E-10-1	1E-10-1	1.66E-6	mol m^{-2} d^{-1}
L-G kinetics	k_La_H_2	liquid mass transfer coefficient	0-402	0-402	0-402	223	d^{-1}
	D_H_2	liquid-phase diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	1.61E-4	m^{-2} d^{-1}
	theta_CH_4_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_CO_2_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_H_2S_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_H_2_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_N_2_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	k_La_NH_3_[f]/ theta_NH_3_g_[f]	liquid mass transfer coefficient / Arrhenius coefficient	3.2[f] / 1.01-1.05[f]	3.2[f] / 1.01-1.05[f]	3.2[f] / 1.01-1.05[f]	3.2[f] / 1.01-1.05[f]	d^{-1} / -
Bio-kinetics[g]	kdec_xsrb_ac	decay rate of srb_ac	0.005-0.05	0.005-0.05	0.005-0.05	0.02	d^{-1}
	kdec_xsrb_bu	decay rate of srb_bu	0.005-0.05	0.005-0.05	0.005-0.05	0.02	d^{-1}
	kdec_xsrb_h	decay rate of srb_h	0.005-0.05	0.005-0.05	0.005-0.05	0.02	d^{-1}
	kdec_xsrb_pro	decay rate of srb_pro	0.005-0.05	0.005-0.05	0.005-0.05	0.02	d^{-1}
	km_srb_ac	maximum specific growth rate of srb_ac	1-50	1-50	1-50	12.55	d^{-1}
	km_srb_bu	maximum specific growth rate of srb_bu	1-50	1-50	1-50	14.51	d^{-1}
	km_srb_h	maximum specific growth rate of srb_h	1-50	1-50	1-50	20.00	d^{-1}
	km_srb_pro	maximum specific growth rate of srb_pro	1-50	1-50	1-50	20.00	d^{-1}

[a] Initial values used for treatment train optimization.

[b] The solubility of gases was allowed to change with pressure and temperature.

[c] The pH is calculated by PHREEQC at every time step based on the charge balance (Chapter 9).

[d] Temp_liq represents the liquid temperature after the heat exchanger. Default input waste temperature prior to the heat exchanger = 20 °C (cfr. Khiewwijit *et al.*, 2015; Symantec, 2014).

[e] The variation related to the presence of seed material for each precipitate was included in the variation range for the corresponding kinetic liquid-solid transfer coefficient in order to eliminate multicollinearity problems (see Section 10.3.1.2).

[f] All k_La values are derived from k_La_H_2, except for NH_3. For NH_3, the default k_La is set to a very low value (3.2) and the Arrhenius coefficient theta to 0, indicating the very slow stripping of NH_3 in the digester (Chapter 9: Section 9.2.2.2). The effect of calculating the k_La_NH_3 based on the k_La_H_2 (hence a varying kLa instead of a fixed one) is tested here by allowing theta > 0.

[g] srb_ac = sulfate reducing bacteria using acetate; srb_bu = sulfate reducing bacteria using butyrate; srb_pro = sulfate reducing bacteria using propionate; srb_va = sulfate reducing bacteria using valerate.

Table 10.5 Symbol, description, variation range, default value, and unit for each model factor used in the global sensitivity analysis scenarios for the NRM-Prec (precipitation/crystallization) key unit. Range A: all applications; Range B: digestate from manure (Cesur and Albertson, 2005); Range C: (co-)digestate (Vlaco, 2012). L-S = liquid-solid; L-G = liquid-gas.

NRM-Prec	Factor symbol	Description	Range A	Range B	Range C	Default[a]	Unit
Input liquid[b]	S_Acetate	soluble acetate	0-100	0.24-0.53	0-1	0.39	mol m^{-3}
	S_Al	soluble aluminum	0-100	1.45-2.24	1.45-100	1.85	mol m^{-3}
	S_Butyrate	soluble butyrate	0-100	0.17-0.36	0-1	0.27	mol m^{-3}
	S_C_4_	soluble carbonate (IV)	0-500	144.0-152.9	8-109	148.45	mol m^{-3}
	S_C_min4_	soluble methane (-IV)	0-10	0-1	0-1	0.50	mol m^{-3}
	S_Ca	soluble calcium	0-500	17.47-22.46[c]	28.57-98.21[c]	19.97	mol m^{-3}
	S_Cl	soluble chloride	0-100	10-40	2.5-24	25	mol m^{-3}
	S_DOM	dissolved organic matter	0-100	40.10-48.84	0-40	20	mol m^{-3}
	S_Fe	soluble iron	0-100	2.10-2.61	1.45-170	2.36	mol m^{-3}
	S_K	soluble potassium	0-100	25.48-29.72	21.27-37.23	27.60	mol m^{-3}
	S_Mg	soluble magnesium	0-500	4.11-8.23[c]	7.44-49.62[c]	6.17	mol m^{-3}
	S_N_5_	soluble nitrogen (V)	0-100	0.10-0.13	0.22-0.71	0.115	mol m^{-3}
	S_N_min3_	soluble nitrogen (-III)	0-500	166.7-205.6	36-243.86	186.15	mol m^{-3}
	S_Na	soluble sodium	0-500	26.09-39.13[c]	3.74-34.89[c]	32.64	mol m^{-3}
	S_P	soluble phosphorus	0-100	14.79-19.01	9.85-213[d]	16.90	mol m^{-3}
	S_Propionate	soluble propionate	0-100	0.16-0.35	0-1	0.26	mol m^{-3}
	S_S_6_	soluble sulfate (VI)	0-100	9.38-12.5	0.15-9.975	10.94	mol m^{-3}
	S_S_min2_	soluble sulfide (-II)	0-10	0-1	0-5	0.50	mol m^{-3}
	S_Valerate	soluble valerate	0-100	0.07-0.14	0-1	0.11	mol m^{-3}
	S_seed[i][e,f]	concentration of seed material for precipitate i	0.0001-6	0.0001-6	0.0001-6	0.001	g m^{-3}
Operation	pH_liq[g]	operational pH	7-11	7-11	7-11	8.5[h]	-
	Temp_liq	operational temperature	20-50	20-50	20-50	20	℃
	Q_liq	liquid flow rate	40-2,300	40-2,300	40-2,300	2,000	m^3 d^{-1}
	Q_prec	precipitate flow rate	1-300	1-300	1-300	30	m^3 d^{-1}
L-S kinetics	k_AlPO$_4$	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.00E-4	mol m^{-2} d^{-1}
	k_Aragonite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	6.12	mol m^{-2} d^{-1}
	k_Artinite	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_Boehmite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	2.80E-4	mol m^{-2} d^{-1}
	k_Brucite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Ca$_3$(PO$_4$)$_2$_am1	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_Ca$_3$(PO$_4$)$_2$_am3	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_Ca$_3$(PO$_4$)$_2$_beta	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_Ca$_4$H(PO$_4$)$_3$:3H$_2$O	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_CaHPO$_4$:2H$_2$O	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	14.64	mol m^{-2} d^{-1}
	k_CaHPO$_4$bis	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Calcite	liquid-solid transfer coefficient	1-5,000	1-5,000	1-5,000	1,080	mol m^{-2} d^{-1}
	k_Diaspore	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Dolomite	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	11.22	mol m^{-2} d^{-1}
	k_Dolomite_dis	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Fe(OH)$_2$_s	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Gibbsite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	1.19E-4	mol m^{-2} d^{-1}
	k_Hercynite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Hydroxyapatite	liquid-solid transfer coefficient	1-5,000	1-5,000	1-5,000	986.65	mol m^{-2} d^{-1}
	k_Kstruvite	liquid-solid transfer coefficient	1E-10-1	1E-10-1	1E-10-1	4.64E-6	mol m^{-2} d^{-1}
	k_Magnesite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	9.88E-4	mol m^{-2} d^{-1}
	k_Mg$_3$(PO$_4$)$_2$	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_MgHPO$_4$:3H$_2$O	liquid-solid transfer coefficient	1E-11-1	1E-11-1	1E-11-1	4.78E-7	mol m^{-2} d^{-1}
	k_Mg(OH)$_2$_act	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Siderite	liquid-solid transfer coefficient	1E-7-100	1E-7-100	1E-7-100	0.0020	mol m^{-2} d^{-1}
	k_Struvite	liquid-solid transfer coefficient	1E-7-100	1E-7-100	1E-7-100	0.0021	mol m^{-2} d^{-1}
	k_Vaterite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Vivianite	liquid-solid transfer coefficient	1E-10-1	1E-10-1	1E-10-1	1.66E-6	mol m^{-2} d^{-1}

[a] Initial values used for treatment train optimization.

[b] The solubility of gases was allowed to change with pressure and temperature.

[c] Tested with and without an external dose (0-500 mol m^{-3}) .

[d] 9.85-45.77 mol m^{-3} for digested primary and waste activated sludge, 187-213 mol m^{-3} for digested sludge from enhanced biological P removal (EBPR).

[e] i refers to each precipitate included in the NRM-Prec as presented in Appendix 5 (Table A5.5).

[f] The default specific surface area of seed material is 600 m^2 g^{-1} (Charlton and Parkhurst, 2011).

[g] The pH is calculated by PHREEQC at every time step based on the charge balance (Chapter 9).

[h] Without any chemical addition.

Table 10.6 Symbol, description, variation range, default value, and unit for each model factor used in the global sensitivity analysis scenarios for the NRM-Strip (stripper) key unit. Range A: all applications; Range B: digestate from manure (Cesur and Albertson, 2005); Range C: (co-)digestate (Vlaco, 2012). L-S = liquid-solid; L-G = liquid-gas.

NRM-Strip	Factor symbol	Description	Range A	Range B	Range C	Default[a]	Unit
Input liquid[b]	S_Acetate	soluble acetate	0-100	0.24-0.53	0-1	0.39	mol m^{-3}
	S_Al	soluble aluminum	0-100	1.45-2.24	1.45-100	1.85	mol m^{-3}
	S_Butyrate	soluble butyrate	0-100	0.17-0.36	0-1	0.27	mol m^{-3}
	S_C_4_	soluble carbonate (IV)	0-500	144-152.9	8-109	148.45	mol m^{-3}
	S_C_min4_	soluble methane (-IV)	0-10	0-1	0-1	0.50	mol m^{-3}
	S_Ca	soluble calcium	0-500	17.47-22.46[c]	28.57-98.21[c]	19.97	mol m^{-3}
	S_Cl	soluble chloride	0-100	10-40	2.5-24	25	mol m^{-3}
	S_DOM	dissolved organic matter	0-100	40.10-48.84	0-40	20	mol m^{-3}
	S_Fe	soluble iron	0-100	2.10-2.61	1.45-170	2.36	mol m^{-3}
	S_H_0_	soluble hydrogen (0)	0-1	0-1	0-1	0-1	mol m^{-3}
	S_K	soluble potassium	0-100	25.48-29.72	21.27-37.23	27.60	mol m^{-3}
	S_Mg	soluble magnesium	0-500	4.11-8.23[c]	7.44-49.62[c]	6.17	mol m^{-3}
	S_N_0_	soluble nitrogen (0)	0-1	0-1	0-1	0-1	mol m^{-3}
	S_N_5_	soluble nitrogen (V)	0-100	0.10-0.13	0.22-0.71	0.115	mol m^{-3}
	S_N_min3_	soluble nitrogen (-III)	0-500	166.7-205.6	36-243.86	186.15	mol m^{-3}
	S_Na	soluble sodium	0-500	26.09-39.13[c]	3.74-34.89[c]	32.64	mol m^{-3}
	S_O_0_	soluble oxygen (0)	0-1	0-1	0-1	0.50	mol m^{-3}
	S_P	soluble phosphorus	0-100	14.79-19.01	9.85-213[d]	16.90	mol m^{-3}
	S_Propionate	soluble propionate	0-100	0.16-0.35	0-1	0.26	mol m^{-3}
	S_S_6_	soluble sulfate (VI)	0-100	9.38-12.5	0.15-9.975	10.94	mol m^{-3}
	S_S_min2_	soluble sulfide (-II)	0-10	0-1	0-5	0.50	mol m^{-3}
	S_Valerate	soluble valerate	0-100	0.07-0.14	0-1	0.11	mol m^{-3}
Input gas[e]	CH_4_g_	methane gas	0-0.001	0-0.001	0-0.001	4.84E-6	atm
	CO_2_g_	carbon dioxide gas	0-0.01	0-0.01	0-0.01	7.60E-4	atm
	H_2O_g_	water vapour	0-0.001	0-0.001	0-0.001	0	atm
	H_2S_g_	hydrogen sulfide gas	0-0.001	0-0.001	0-0.001	0	atm
	H_2_g_	hydrogen gas	0-0.001	0-0.001	0-0.001	1.21E-6	atm
	N_2_g_	nitrogen gas	0-5	0-5	0-5	1.89	atm
	NH_3_g_	ammonia gas	0-0.001	0-0.001	0-0.001	0	atm
	O_2_g_	oxygen gas	0-5	0-5	0-5	0.51	atm
Operation	d_gas	diameter of the gas bubbles	0.001-0.01	0.001-0.01	0.001-0.01	0.003	m
	P_gas_in	gas pressure	1-7	1-7	1-7	2.42	atm
	Temp_gas_in	gas temperature	20-70	20-70	20-70	25	℃
	pH_liq[f]	liquid pH	7-11	7-11	7-11	10.3	-
	Temp_liq[g]	liquid temperature	20-70	20-70	20-70	55	℃
	Q_gas_in	gas flow rate	1E6-2E6	1E6-2E6	1E6-2E6	1.56E6	m^3 d^{-1}
	Q_liq_in	liquid flow rate	1,000-3,000	1,000-3,000	1,000-3,000	2,000	m^3 d^{-1}
	u	upflow velocity of gas bubbles	2E4-3E4	2E4-3E4	2E4-3E4	2.59E4	m d^{-1}
L-S kinetics[h]	k_Aragonite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	6.12	mol m^{-2} d^{-1}
	k_Artinite	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_Brucite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_$Ca_3(PO_4)_2$_am1	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_$Ca_3(PO_4)_2$_am2	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_$Ca_3(PO_4)_2$_beta	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_$Ca_4H(PO_4)_3{:}3H_2O$	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_$CaHPO_4{:}2H_2O$	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	14.64	mol m^{-2} d^{-1}
	k_$CaHPO_4$bis	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Calcite	liquid-solid transfer coefficient	1-5,000	1-5,000	1-5,000	1,080	mol m^{-2} d^{-1}
	k_Diaspore	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Dolomite	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	11.22	mol m^{-2} d^{-1}
	k_Dolomite_dis	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_$Fe(OH)_2$	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Hercynite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Huntite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Hydromagnesite	liquid-solid transfer coefficient	0.1-1,000	0.1-1,000	0.1-1,000	50	mol m^{-2} d^{-1}
	k_Hydroxyapatite	liquid-solid transfer coefficient	1-5,000	1-5,000	1-5,000	986.65	mol m^{-2} d^{-1}
	k_Kstruvite	liquid-solid transfer coefficient	1E-10-1	1E-10-1	1E-10-1	4.64E-6	mol m^{-2} d^{-1}
	k_Magnesite	liquid-solid transfer coefficient	1E-8-1	1E-8-1	1E-8-1	9.88E-4	mol m^{-2} d^{-1}
	k_$Mg_3(PO_4)_2$	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_$MgHPO_4{:}3H_2O$	liquid-solid transfer coefficient	1E-11-1	1E-11-1	1E-11-1	4.78E-7	mol m^{-2} d^{-1}
	k_$Mg(OH)_2$_act	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Periclase	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Portlandite	liquid-solid transfer coefficient	1E-5-100	1E-5-100	1E-5-100	0.10	mol m^{-2} d^{-1}
	k_Siderite	liquid-solid transfer coefficient	1E-7-100	1E-7-100	1E-7-100	0.0021	mol m^{-2} d^{-1}

NRM-Strip (Continuation)	Factor symbol	Description	Range A	Range B	Range C	Default[a]	Unit
	k_Spinel	liquid-solid transfer coefficient	1E-5-100	1E-7-100	1E-7-100	0.10	mol m^{-2} d^{-1}
	k_Struvite	liquid-solid transfer coefficient	1E-7-100	1E-7-100	1E-7-100	0.0020	mol m^{-2} d^{-1}
	k_Vivianite	liquid-solid transfer coefficient	1E-10-1	1E-10-1	1E-10-1	1.67E-6	mol m^{-2} d^{-1}
L-G kinetics	D_CH_4_g_	liquid diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	3.77E-5	m^{-2} d^{-1}
	D_CO_2_g_	liquid diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	1.56E-4	m^{-2} d^{-1}
	D_H_2S_g_	liquid diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	2.20E-5	m^{-2} d^{-1}
	D_H_2_g_	liquid diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	1.65E-4	m^{-2} d^{-1}
	D_N_2_g_	liquid diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	1.54E-4	m^{-2} d^{-1}
	D_NH_3_g_	gas diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	1.69E-4	m^{-2} d^{-1}
	D_O_2_g_	liquid diffusion coefficient	1E-6-0.001	1E-6-0.001	1E-6-0.001	1.61E-4	m^{-2} d^{-1}
	theta_CH_4_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_CO_2_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_H_2S_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_H_2_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_N_2_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_NH_3_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-
	theta_O_2_g_	Arrhenius coefficient	1.01-1.05	1.01-1.05	1.01-1.05	1.024	-

[a] Initial values used for treatment train optimization.

[b] The solubility of gases was allowed to change with pressure and temperature.

[c] Tested with and without an external dose (0-500 mol m^{-3}).

[d] 9.85-45.77 mol m^{-3} for digested primary and waste activated sludge, 187-213 mol m^{-3} for digested sludge from enhanced biological P removal (EBPR).

[e] Partial pressures at the default gas pressure (P_gas_in) and temperature (Temp_gas_in). Note that these values are adjusted by PHREEQC according to the actual total gas pressure and temperature (Charlton and Parkhurst, 2011).

[f] The pH is calculated by PHREEQC at every time step based on the charge balance (Chapter 9).

[h] Temp_liq represents the liquid temperature after the heat exchanger. Default input waste temperature prior to the heat exchanger = 20 °C (cfr. Khiewwijit *et al.*, 2015; Symantec, 2014).

[g] The variation related to the presence of seed material for each precipitate was included in the variation range for the corresponding kinetic liquid-solid transfer coefficient in order to eliminate multicollinearity problems (see Section 10.3.1.2).

Table 10.7 Symbol, description, variation range, default value, and unit for each model factor used in the global sensitivity analysis scenarios for the NRM-Scrub (acidic air scrubber) key unit. L-S = liquid-solid; L-G = liquid-gas.

NRM_Scrub	Factor symbol	Description	Range	Default[a]	Unit
Input gas[b]	CH_4_g_	methane gas	0-0.5	0.0024	atm
	CO_2_g_	carbon dioxide gas	0-3	0.015	atm
	H_2O_g_	water vapour	0-0.1	0.00024	atm
	H_2S_g_	hydrogen sulfide gas	0-0.5	0.0024	atm
	H_2_g_	hydrogen gas	0-0.5	0.0024	atm
	N_2_g_	nitrogen gas	0-1	0.24	atm
	NH_3_g_	ammonia gas	0-6	1.94	atm
	O_2_g_	oxygen gas	0-1	0.22	atm
Input liquid[c]	S_S_6_	soluble sulfate	5-20	10	mol m^{-3}
Operation	pH_liq[d]	liquid pH	1-4	1.3	-
	Temp_liq	liquid temperature	15-25	20	°C
	d_gas	diameter of the gas bubbles	0.001-0.01	0.003	m
	P_gas_in	gas pressure	1-7	2.42	atm
	Temp_gas_in	gas temperature	20-50	25	°C
	u	upflow velocity of gas bubbles	2E4-3E4	2.59E4	m d^{-1}
	Q_liq_in	liquid flow rate	5-30	11.2	m^3 d^{-1}
	Q_gas_in	gas flow rate	1E6-2E6	1.95E6	m^3 d^{-1}
L-S kinetics[e]	k_$(NH_4)_2SO_4$_s	liquid-solid transfer coefficient	1E-6-10	0.001	mol m^{-2} d^{-1}
L-G kinetics	D_CH_4_g_	liquid diffusion coefficient	1E-6-0.001	3.77E-5	m^{-2} d^{-1}
	D_CO_2_g_	liquid diffusion coefficient	1E-6-0.001	1.56E-4	m^{-2} d^{-1}
	D_H_2S_g_	liquid diffusion coefficient	1E-6-0.001	2.20E-5	m^{-2} d^{-1}
	D_H_2_g_	liquid diffusion coefficient	1E-6-0.001	1.65E-4	m^{-2} d^{-1}
	D_N_2_g_	liquid diffusion coefficient	1E-6-0.001	1.54E-4	m^{-2} d^{-1}
	D_NH_3_g_	gas diffusion coefficient	1E-6-0.001	1.69E-4	m^{-2} d^{-1}
	D_O_2_g_	liquid diffusion coefficient	1E-6-0.001	1.61E-4	m^{-2} d^{-1}
	theta_CH_4_g_	Arrhenius coefficient	1.01-1.05	1.024	-
	theta_CO_2_g_	Arrhenius coefficient	1.01-1.05	1.024	-
	theta_H_2S_g_	Arrhenius coefficient	1.01-1.05	1.024	-
	theta_H_2_g_	Arrhenius coefficient	1.01-1.05	1.024	-
	theta_N_2_g_	Arrhenius coefficient	1.01-1.05	1.024	-
	theta_NH_3_g_	Arrhenius coefficient	1.01-1.05	1.024	-
	theta_O_2_g_	Arrhenius coefficient	1.01-1.05	1.024	-

[a] Initial values used for treatment train optimization.

[b] Gas phase coming from the stripper. Values represent partial pressures at the default gas pressure (P_gas_in) and temperature (Temp_gas_in). Note that these values are adjusted by PHREEQC according to the actual total gas pressure and temperature

(Charlton and Parkhurst, 2011).
[c] H_2SO_4-solution to capture ammonia as ammonium sulfate (AmS).
[d] The pH is calculated by PHREEQC at every time step based on the charge balance (Chapter 9).
[e] The variation related to the presence of seed material was included in the variation range for the corresponding kinetic liquid-solid transfer coefficient in order to eliminate multicollinearity problems (see Section 10.3.1.2).

10.2.3 Monte Carlo simulation and linear regression

The method used for global sensitivity analysis involves fitting a linear regression to Monte Carlo (MC) simulation outputs, also known as the standardized regression coefficient (SRC) method (Saltelli *et al.*, 2008). Both MC and linear regression tools are available in the Tornado(/WEST) software package (mikebydhi.com; Vanhooren *et al.*, 2003).

The aim of the MC simulation is to propagate variation from model factors to outputs. The model factor domains used were as specified in Section 10.2.2. The Latin hypercube sampling (LHS) method of Iman and Conover (1982) was used for sampling the inputs, by drawing 4,000 shots from a uniform distribution. All GSAs were performed in duplicate and replicability of simulation outputs was found to be high. This can be confirmed by the fact that the number of shots (or simulations) was chosen so as to respect the typically required range for LHS, i.e. 40-150 times the number of input factors (Benedetti at al., 2011). For the most complex scenarios, replicability was also tested by comparison with GSA results obtained using 10,000 shots (Vanrolleghem *et al.*, 2015).

Next, the linear regression performed on the MC results describes each model output of interest (Table 10.2) as a multivariate linear function of the model factors. In order to use the SRC as a valid measurement of sensitivity, model linearity should be high, while multicollinearity should be low. The following criteria were used for quality assessment of the linear regression model:

i. The **model determination coefficient**, R^2: A value of $R^2 > 0.7$ is generally used for acceptance of a linear model (Cosenza *et al.*, 2013; Saltelli *et al.*, 2006; Sin *et al.*, 2011). Also the adjusted coefficient of multiple determination, R^2_{adj}, was evaluated, which corrects for the number of explanatory terms in the model relative to the number of data points (Kutner *et al.*, 2005).
ii. The **F-statistic**: The obtained F-statistic (= explained variance/unexplained variance or regression mean square (MSR)/mean square error (MSE)) was compared to $F^*_{(p-1,n-p),0.95}$, where p is the number of factors and n the number of samples. If $F > F^*$, the null hypothesis that the model factors have no significant effect on the objective value (i.e. the performance indicator) at the 5 % confidence level can be rejected (Kutner *et al.*, 2005).
iii. The **variance inflation factor** (VIF_j):

$$VIF_j = (1 - R_j^2)^{-1} \qquad \boldsymbol{Eq.(10.1)}$$

where R_j^2 is the coefficient of determination of a regression of factor j on all the other factors. It measures how much the variances of the estimated regression coefficients are inflated as compared to when the predictor variables are not linearly related (Kutner *et al.*, 2005). Large VIF values denote high collinearity, with a common cut-off threshold being a VIF value above 10 (Chen and Lu, 2014; Kutner *et al.*, 2005; Tabachnick and Fidell, 2001). A more conservative value of 5 has also been suggested (Menard, 1995; Rogerson, 2001) and was adapted in this research.

iv. The **correlation coefficient**, r: The correlation of all factors with the objective value should be high. However, the correlation between the predictors should be close to 0.

If multicollinearity was high, the linear models were reduced by eliminating overlapping factors until acceptable VIF and R^2_{adj} values were obtained (Kutner *et al.*, 2005; PSU, 2014). When the quality of the linear model was found to be sufficient, model factors were ranked according to the significance of their effect on the different performance indicators. To provide an accurate factor selection, four different cut-off tresholds (CFT) were assumed, resulting in five classes of factor importance (Table 10.8).

Table 10.8 Class, cut-off treshold (CFT), description, and level of importance used for factor ranking. SRC = standardized regression coefficient; tSRC = t-statistic of the SRC; n-p = degrees of freedom; n = number of samples; p = number of factors.

Class	Cut-off treshold	Description	Importance
1	$\lvert SRC \rvert > 0.1$	± 1 % fraction of total variance	Very high
2	$\lvert tSRC \rvert > t_{n-p,0.95}$	Significant at the 5 % confidence level	High
3	$\lvert tSRC \rvert > t_{n-p,0.90}$	Significant at the 10 % confidence level	Moderate
4	$\lvert tSRC \rvert > t_{n-p,0.85}$	Significant at the 15 % confidence level	Low
5	$\lvert tSRC \rvert \leq t_{n-p,0.85}$	Not significant	Very low

A very high importance was attributed to factors with an |SRC| higher than 0.1, as most often found in literature (e.g. Cosenza *et al.*, 2013; Mannina *et al.*, 2012; Sin *et al.*, 2011). This CFT is, however, not based on statistical reasoning. Therefore, the tSRC was also evaluated, which refers to the t-statistic of the SRC found. If the obtained t-statistic is higher than $t_{n-p,1-\alpha}$, then the null hypothesis that the factor has no significant effect on the objective value, i.e. SRC = 0, can be rejected at the α % significance level (Kutner *et al.*, 2005).

If R^2_{adj} was low (= poor model quality), but VIF values were low as well (= low inter-factor correlation), still the same ranking methodology was applied as presented in Table 10.8. Cosenza *et al.* (2013) and Mannina *et al.* (2012) indeed found that, even though the SRC method was applied outside its range of applicability ($R^2 < 0.7$), the ranking of important model factors (factor prioritisation) was very similar to the results obtained with other GSA methods, such as Extended-FAST. Hence, within the objectives of this study, i.e. factor ranking, the methodology presented above was deemed to be suitable. Nevertheless, one should bear in mind that quantitative estimates of the variance contributions are only valid when $R^2 > 0.7$.

10.2.4 Treatment train configuration and optimization

Based on the increased insights in the interactions between process inputs and outputs obtained from the GSA results for each NRM key unit, an optimal sequence of unit processes in a treatment train for resource recovery was sought (Fig. 10.1: Step 3). To this end, also ancillary units from the NRM library were selected, i.e. a heating unit (NRM-Heat), chemical dosing unit

(NRM-Chem), and solid-liquid phase separation unit (NRM-Settle) (see Chapter 9). The treatment train was configured in Tornado(/WEST) and a treatment train GSA (Fig. 10.1: Step 4) was performed using the strategy described in Figure 10.2. The most important operational factors were then optimized by means of an optimization experiment (Fig. 10.1: Step 5) in Tornado(/WEST) using pig manure (Scenario B) as a case study. The GN_Direct algorithm (= DIviding RECTangles algorithm for global optimization; Gablonsky and Kelley, 2001; Jones *et al.*, 1993), available from the NLOpt solver package (Johnson, 2008) included in Tornado(/WEST), was used, with a tolerance of 10^{-8} and a maximum of 10,000 evaluations.

The reactor dimensions of the various unit processes in the treatment train were set at the design values (including safety factors) provided by technology providers for the expected flows and composition (based on Cesur and Albertson (2005) and calculated mass balances) arriving at each individual unit process (Table 10.1). Based on the data obtained from the budget proposals, the operational envelope for optimization was compiled. The operational settings of the configured treatment train were optimized in order to maximize resource recovery and minimize energy and chemical requirements in a cost-effective way. The operational envelope involves (Table 10.9): i) the operational temperature, liquid flow rate, and amount of base/alkalinity dosing for the anaerobic digester, ii) the fraction of non-settleable precipitates and particulate COD for the phase separation unit, iii) the amount of base dosing, the concentration of seed material in the input flow, and precipitate extraction rate for the precipitation unit, iv) the operational temperature and gas flow rate for the stripping unit, and v) the acid dose and liquid recycle flow rate for the scrubbing unit.

Table 10.9 Lower and upper limit and initial value used for each factor in the treatment train optimization experiment. For factor descriptions, see Tables 10.4-10.7. For model descriptions, see Section 10.2.1. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber. f_ns_P = fraction of non-settleable precipitates; f_ns_X = fraction of non-settleable biological particulate solids.

Model	Symbol	Lower	Upper	Initial	Unit
NRM-Heat 1	Temp_target_AD	20	55	35	°C
NRM-AD	Q_liq_in	1,000	3,000	2,000	m^{-3} d^{-1}
NRM-AD	S_Ca	42	300	92	mol m^{-3}
NRM-Settle	f_ns_P	0	0.5	0.1	-
NRM-Settle	f_ns_X	0	0.1	0.005	-
NRM-Dose	$Mg(OH)_2$ dose	0	3,000	1,500	kg d^{-1}
NRM-Prec	S_Seed_KStruvite	0.000125	6.25	0.001	g m^{-3}
NRM-Prec	S_Seed_Struvite	0.000125	6.25	0.001	g m^{-3}
NRM-Prec	Q_prec	1	300	30	m^3 d^{-1}
NRM-Strip	Q_gas_in	1,000,000	2,000,000	1,600,000	m^3 d^{-1}
NRM-Strip	P_gas_in	1	7	2.4	atm
NRM-Heat 2	Temp_target_Strip	40	70	55	°C
NRM-Scrub	Q_liq_in (acid)	5	30	11	m^3 d^{-1}
NRM-Scrub	Q_recycle	0	5	2	m^3 d^{-1}

The initial values (Table 10.9) for the optimization experiment were set at the design values given in the budget proposals of the technology providers. The lower and upper limits were the same as for the unit process GSAs described above (Section 10.2.2).

The key performance indicators evaluated in the optimization experiment were:

i. **Net costs = chemical costs + energy costs – revenues** (objective = minimize), where:
    a. energy cost items are related to raising the liquid temperature for anaerobic digestion and stripping (with potential for heat exchange, see below), as well as to air pumping for stripping;
    b. chemical cost items refer to the addition of alkalinity or base to the digester, of acid for N absorption in the scrubber, and of base for pH-increase prior to precipitation and stripping;
    c. revenues are related to CH_4 production (energy recovery was assumed, see below), the marketing of mineral fertilizer N, P, and K, and the potential marketing of organic fertilizer.

ii. **Resource recovery** (objective = maximize), which includes:
    a. methane recovery in NRM-AD;
    b. mineral N/P/K recovery in NRM-Prec;
    c. mineral N/S recovery in NRM-Strip/NRM-Scrub;
    d. organic (+ N/P/K) fertilizer recovery (settled solids) in NRM-Settle.

iii. **Use of consumables** (objective = minimize), involving:
    a. net thermal energy use = heat required for stripping + heat required for digestion – heat recovered from CH_4 production – potential heat recovered in heat exchangers (see below);
    b. net electricity use = blower energy (air) – electricity recovered from CH_4 production;
    c. chemical use = acid use + base/alkalinity use.

An overview of the parameters used in the energy and cost calculations is given in Table 10.10. Costs are expressed in USD (1 USD = 1.14 CAD; 1 USD = € 0.80; November 2014).

Biogas CH_4 was assumed to be valorized as energy in a combined heat and power generation (CHP) unit, with a conversion efficiency of 40 % as heat, 38 % as electricity, and with 22 % losses (Verstraete and Vlaeminck, 2011). In terms of heat requirements, both a worst and best-case scenario was considered. In the best case, 10 % heat losses in the digester (Wu and Bibeau, 2010; Zupancic and Ros, 2003) and 50 % internal heat recovery in the stripping system were assumed (Colsen, 2014; RVTPE, 2014). In the worst case, the heat requirements in the digester were 1.9 times higher than the theoretical heat required to heat the input flow (CDM, 2009; Symantec, 2014; Tchobanoglous *et al.*, 2003; Vaneeckhaute, 2009). Also, in this case, no internal heat recovery in the stripping system was considered.

Table 10.10 Parameters used to calculate energy and cost functions in the virtual optimization experiment. $ = USD; 1 USD = 1.14 CAD = € 0.80 (November 2014).

Category	Item	Value	Unit	Reference
Chemical cost	H_2SO_4 (98 %)	0.087	$\$ kg^{-1}$	Icis (2014)
	$Mg(OH)_2$	0.204	$\$ kg^{-1}$	Icis (2014)
	$MgCl_2$:$6H_2O$ (99%)	0.066	$\$ kg^{-1}$	Icis (2014)
	$Ca(OH)_2$	0.070	$\$ kg^{-1}$	Icis (2014)
	NaOH (100 %)	0.635	$\$ kg^{-1}$	Icis (2014)
Energy cost	Electricity	0.076	$\$ kWh^{-1}$	USEPA (2013)
Energetic value	Air (strip)[a]	0.00195	kWh m^{-3} air	RVTPE (2014)
	CH_4[b]	13.9	kWh kg^{-1}	Tchobanoglous *et al.* (2003)
	Heat capacity sludge/manure	4.2	kJ kg^{-1} $℃^{-1}$	Tchobanoglous *et al.* (2003)
Nutrient value	N	1.411	$\$ kg^{-1}$	USEPA (2013)
	P	2.984	$\$ kg^{-1}$	USEPA (2013)
	K	0.960	$\$ kg^{-1}$	USEPA (2013)

[a] Internal air recycling between the stripper and scrubber system is assumed (RVTPE, 2014).
[b] Density CH_4 at 25 ℃ = 0.656 kg m^{-3} (Tchobanoglous *et al.*, 2003).

It should be noted that only the major factors for the NRM key units were included in the cost and energy calculations for the optimization presented above. Nevertheless, using the optimized treatment train settings, an overall economic analysis (Fig. 10.1: Step 6) was also performed, including additional operational costs, labor, material and maintenance costs, revenues from CO_2-emission reduction credits, as well as capital costs (see Section 10.3.4.2).

10.3 Results and discussion

Results for the individual GSAs per NRM key unit process (Fig. 10.1: Step 2) and overall recommendations for factor prioritization are provided and discussed in Section 10.3.1. Based on the findings, Section 10.3.2 discusses the configuration (Fig. 10.1: Step 3) of an optimal treatment train of unit processes for nutrient recovery. The results of the whole treatment train sensitivity analysis (Fig. 10.1: Step 4) are presented in Section 10.3.3, while results of the optimization case study (Fig. 10.1: Step 5), including the economic analysis (Fig. 10.1: Step 6), are presented in Section 10.3.4. Finally, the main limitations of the applied methodology in this research are listed in Section 10.3.5.

10.3.1 Global sensitivity analysis of unit processes

Detailed results of the GSAs including the model quality evaluation are provided in Appendix 10 (Tables A10.1-A10.10). In this section, only the ten major factors are presented per performance indicator for each scenario analyzed and for each NRM key unit (Sections 10.3.1.1-10.3.1.4). Based on the discussions, recommendations for factor prioritization per key unit are compiled in Section 10.3.1.5. Note that all results should be interpreted within the scope of the analysis, as outlined above (Section 10.2).

10.3.1.1 NRM-AD: Factor ranking and interpretation

Results from the GSA for the NRM-AD unit are shown in Table 10.11 (Appendix 10: Tables A10.1-10.3). For all cases, the R^2 and R^2_{adj} values were higher than 0.7, except for X_COD

Table 10.11 Global sensitivity analyses for the NRM-AD unit: ten prioritized factors with standardized regression coefficient (SRC) per performance indicator for each scenario. Scenario A: all applications; Scenario B: manure (Cesur and Albertson, 2005); Scenario C: sludge (Astals *et al.*, 2013). Dark grey = very high importance (CFT1); grey = high importance (CFT2); light grey = moderate importance (CFT3). CFT = cut-off threshold. * indicates R^2_{adj} value below 0.7. Description of factor symbols can be found in Table 10.4.

A	CH$_4$ production		Biogas production		Digestate S_COD		Digestate X_COD *		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall *	
	S_C_min4_	0.924	S_C_4_	0.704	Q_liq_in	0.851	k_Aragonite	-0.061	S_N_min3_	0.913	S_P	0.938	S_K	0.999	S_S_6_	-0.355	Q_liq_in	0.070
	Temp_liq	0.307	Temp_liq	0.487	S_Ca	0.130	S_Butyrate	-0.060	Temp_liq	-0.172	S_Na	0.244	S_Al	-0.020	S_Mg	0.348	k_Aragonite	-0.062
	S_Al	0.024	S_C_min4_	0.364	S_Valerate	0.118	km_srb_bu	0.060	S_C_4_	0.159	S_Fe	0.034	S_S_6_	-0.011	S_Ca	0.338	km_srb_bu	0.060
	S_Propionate	0.018	S_Ca	-0.127	S_Al	0.114	S_H_0_	0.059	S_Al	0.097	S_Al	0.026	S_Ca	-0.009	S_Fe	0.299	S_Butyrate	-0.059
	S_N_5_	0.018	S_S_6_	0.116	S_Mg	0.113	S_Propionate	-0.056	S_Ca	0.093	S_Ca	0.024	S_N_5_	-0.008	S_Al	0.291	S_H_0_	0.059
	D_H$_2$	0.017	S_Fe	-0.113	S_S_6_	-0.102	km_srb_h	0.057	S_S_6_	-0.063	Temp_liq	-0.023	S_N_min3_	-0.007	S_C_4_	-0.221	S_Propionate	-0.056
	S_Cl	0.016	S_Mg	-0.079	S_Butyrate	0.100	S_Na	0.051	S_Fe	0.061	pH_liq	-0.016	S_Valerate	-0.007	S_P	-0.192	km_srb_h	0.056
	S_S_min2_	-0.014	S_N_5_	0.069	S_Fe	0.071	k_Magnesite	-0.048	S_Mg	-0.051	S_su	0.015	Temp_liq	-0.006	S_Na	0.189	S_Na	0.052
	S_N_0_	0.012	S_Al	-0.065	S_Na	0.067	k_Ca$_4$H(PO$_4$)$_3$:3H$_2$O	-0.046	S_K	0.039	theta_CH$_4$_g_	-0.015	S_C_4_	-0.005	S_K	0.177	k_Magnesite	-0.049
	k_Struvite	-0.012	S_Na	-0.063	S_fa	0.063	theta_NH$_3$_g_	0.045	S_P	-0.037	X_Inert	0.014	S_Fe	-0.005	S_N_5_	-0.164	S_Inert	0.047
B	**CH$_4$ production**		**Biogas production**		**Digestate S_COD**		**Digestate X_COD**		**Digestate S_N_min3_**		**Digestate S_P**		**Digestate S_K**		**Digestate pH**		**Overall**	
	S_C_min4_	0.928	Temp_liq	0.677	Q_liq_in	0.941	Q_liq_in	0.956	S_N_min3_	0.820	S_P	0.898	S_K	0.984	Temp_liq	-0.834	Q_liq_in	0.959
	Temp_liq	0.309	S_C_min4_	0.615	X_ch	0.138	X_Inert	0.151	S_Mg	-0.534	S_Na	0.395	Temp_liq	-0.086	S_Ca	0.410	X_Inert	0.105
	S_Ca	0.011	S_C_4_	0.184	S_su	0.033	k_CaHPO$_4$bis	-0.020	Temp_liq	-0.159	S_Ca	0.041	S_Ca	-0.068	S_N_5_	-0.202	X_ch	0.046
	k_Mg$_3$(PO$_4$)$_2$	0.010	S_Ca	-0.175	X_li	0.027	S_S_min2_	-0.018	S_N_5_	-0.100	Temp_liq	-0.028	S_N_5_	-0.019	S_Cl	-0.164	X_li	0.019
	Q_liq_in	0.010	S_N_0_	0.129	S_fa	0.025	S_Propionate	0.016	S_Cl	-0.078	X_li	0.015	S_Mg	-0.018	S_C_4_	-0.108	S_su	0.019
	k_Ca$_4$H(PO$_4$)$_3$:3H$_2$O	0.010	S_N_5_	0.100	S_Inert	0.019	k_Calcite	0.015	S_Ca	0.043	S_Cl	0.014	S_N_min3_	-0.015	S_S_6_	-0.099	k_CaHPO$_4$bis	-0.016
	S_Fe	-0.010	S_H_0_	0.097	theta_N$_2$_g_	-0.017	X_li	0.015	S_S_6_	-0.041	kdec_xsrb_h	0.011	S_S_6_	-0.006	S_Na	0.091	S_S_min2_	-0.015
	k_CaHPO$_4$:2H$_2$O	0.009	S_Cl	0.079	X_pr	0.016	k_Mackinawite	0.014	S_Na	0.027	S_Al	0.010	S_Na	-0.004	S_Mg	0.088	k_Calcite	0.015
	k_Al$_2$O$_3$	-0.009	S_N_min3_	-0.076	k_Calcite	0.014	S_Al	0.013	S_P	-0.020	S_Acetate	-0.010	S_Cl	-0.004	S_N_min3_	0.083	S_Propionate	0.015
	S_Mg	0.008	S_S_6_	0.046	Temp_liq	-0.014	S_S_6_	-0.013	S_K	0.010	k_MgHPO$_4$:3H$_2$O	-0.009	S_P	0.003	S_P	-0.072	k_Mackinawite	0.014
C	**CH$_4$ production**		**Biogas production**		**Digestate S_COD**		**Digestate X_COD**		**Digestate S_N_min3_**		**Digestate S_P**		**Digestate S_K**		**Digestate pH**		**Overall**	
	S_C_min4_	0.935	S_C_min4_	0.795	Q_liq_in	0.921	Q_liq_in	0.779	S_N_min3_	0.996	S_P	1.000	S_K	1.001	S_C_4_	-0.451	Q_liq_in	0.881
	Temp_liq	0.305	Temp_liq	0.448	X_ch	0.191	X_Inert	0.456	S_Mg	-0.058	S_Al	0.005	S_N_5_	-0.030	S_N_5_	-0.411	X_Inert	0.319
	km_srb_pro	0.016	S_C_4_	0.270	X_pr	0.148	theta_CO$_2$_g_	0.036	S_N_5_	-0.039	S_N_5_	0.005	S_Al	-0.028	S_Fe	0.375	X_ch	0.094
	k_Boehmite	-0.013	S_N_min3_	-0.173	X_li	0.089	X_ch	0.034	Temp_liq	-0.028	S_N_min3_	0.004	S_N_min3_	-0.024	S_Al	0.331	X_pr	0.071
	kGibbsite	0.013	S_N_0_	0.172	S_fa	0.052	S_C_min4_	-0.030	S_Cl	-0.011	S_C_4_	0.003	S_C_4_	-0.016	Temp_liq	-0.196	X_li	0.050
	S_Propionate	-0.011	S_H_0_	0.125	S_su	0.048	S_S_6_	0.028	S_Acetate	-0.011	S_Fe	0.002	S_Fe	-0.015	S_Na	0.171	theta_CO$_2$_g_	0.028
	k_Al$_2$O$_3$	0.010	S_Al	-0.073	S_Inert	0.043	X_li	0.025	S_S_6_	-0.011	Temp_liq	-0.002	S_S_6_	-0.009	S_Ca	0.153	S_S_6_	0.021
	S_N_min3_	0.009	S_N_5_	0.070	km_srb_h	-0.018	kdec_xsrb_ac	0.025	S_C_4_	0.010	S_Na	0.002	Temp_liq	-0.008	S_Acetate	-0.107	S_C_min4_	-0.021
	k_CaHPO$_4$:2H$_2$O	0.009	S_Fe	0.070	S_Al	-0.016	pH_liq	0.025	S_Al	-0.006	S_S_6_	0.001	S_Acetate	-0.006	S_S_6_	-0.105	S_Fe	-0.021
	k_Vivianite	0.009	S_Na	0.070	k_Anhydrite	0.015	S_Butyrate	-0.024	S_Na	0.006	S_Cl	0.001	S_Cl	-0.006	S_Cl	-0.090	pH_liq	0.020

(effluent particulate COD) and the overall sensitivity measure in Scenario A (Appendix 10: Table A10.1). Hence, overall GSA quality was high. Major factors selected (based on CFT1) were reasonably similar for all scenarios, but the order of importance was not always the same. Some fundamental differences between the substrates were also observed (see below).

First, it should be pointed out that the bio-kinetic parameters (except for SRBs) were assumed to be known (Table 10.3), so these parameters were fixed and not included in the GSA. Among the factors studied, the variation in **CH_4 and biogas production** was mainly attributed to the input soluble CH_4 concentration (from storing, piping, pits, etc.), reactor temperature, and carbonate alkalinity (S_C_4). Noteworthy is that the sign of the SRCs is meaningful, i.e. all three factors are positively correlated with biogas production, which is in agreement with prior knowledge (Tchobanoglous *et al.*, 2003).

Moreover, looking at the results of **S_COD and X_COD**, clearly degradation of particulate to soluble COD takes place, except for the non-biodegradable X_Inert, as expected. Nevertheless, it should be noted that, because of the large variation ranges possible for the input waste composition in combination with the operational variability considered, the reactor pH (a major operating factor for anaerobic digestion) became regularly too low (< 5) for good methanogenesis to occur. This was especially the case for manure (Scenario B). Therefore, according to the analysis, adding additional COD did not always result in a higher CH_4 production because of volatile fatty acid (VFA) and/or long chain fatty acid (LCFA) accumulation in the digester. As a consequence, longer HRTs (reduced Q_liq_in) for manure were not beneficial.

Similar findings of input stream composition on anaerobic digestion were reported by Ossiansson and Lidholm (2008) using the Siegrist (2002) model. Moreover, Jhong-Hwa *et al.* (2006) experimentally found that the external addition of an optimal Ca dose is essential for anaerobic mono-digestion of swine manure so as to overcome acid accumulation, mainly by improving propionate and valerate degradation and their conversion to CH_4. This can explain the importance of Ca on CH_4 production observed in the GSA for Scenario B.

To further identify the most important model factors, a **second analysis** was performed for Scenarios B and C, using a low fixed input CH_4 concentration of 0.0001 mol m^{-3} and a mesophilic temperature of 35 °C (Fig. 10.3). For manure, an external Ca dose (range S_Ca: 42-220 mol m^{-3}) was allowed to be applied, in line with the findings of Jhong-Hwa *et al.* (2006).

Results for this second analysis clearly show that the amount of Ca added plays an important role for CH_4 production from manure (Scenario B; Fig. 10.3A), which is in agreement with observations of Jhong-Hwa *et al.* (2006) and the findings above. Among the organics, mainly the input butyrate, propionate, valerate, and carbohydrates positively influence CH_4 production, indicating that no (hindering) VFA accumulation is present now. The main precipitate negatively impacting CH_4 production seems to be struvite. Remarkable is also the stimulating effect of nitrate (within the provided range) on CH_4 production for both manure and sludge, similar as experimentally observed by Sheng *et al.* (2013) for digester NO_3-N concentrations up to 335 mg

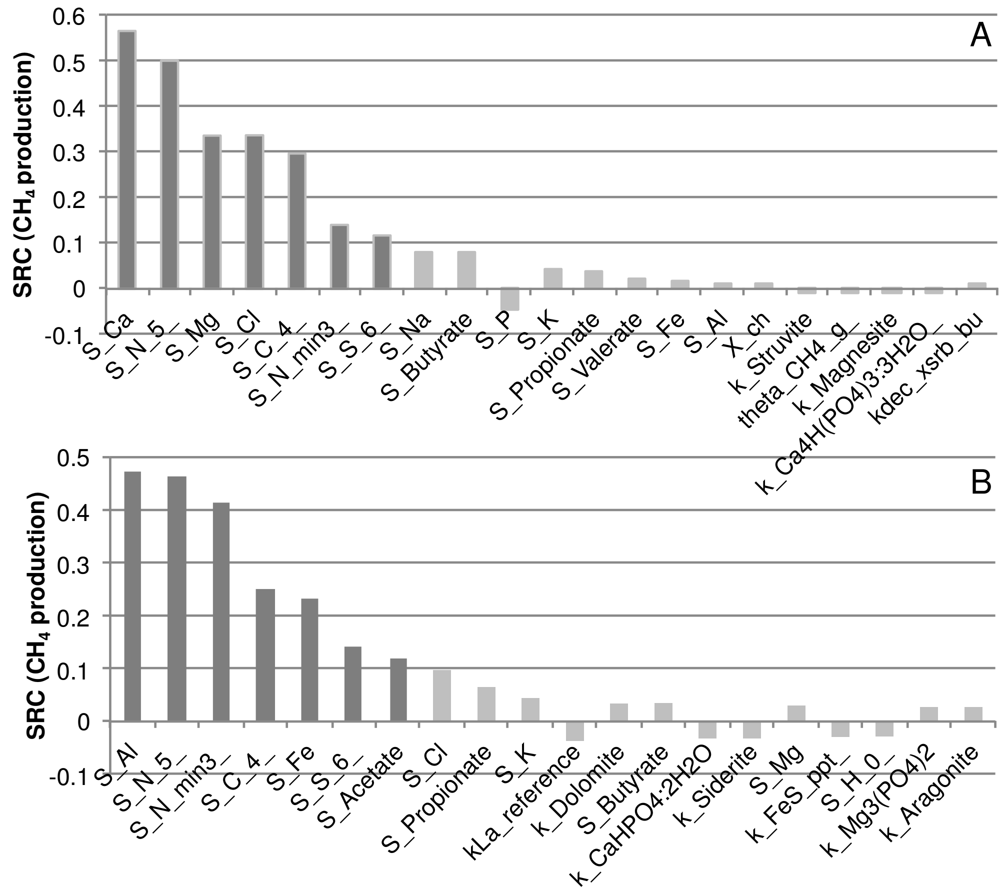


Figure 10.3 Standardized regression coefficient (SRC) for CH_4 production resulting from global sensitivity analyses at fixed input CH_4 concentration (0.0001 mol m^{-3}) and temperature (35 °C) for Scenario B (A; $R^2 = 0.83$, $R^2_{adj} = 0.83$) and C (B; $R^2 = 0.83$, $R^2_{adj} = 0.82$). Scenario B: manure (Cesur and Albertson, 2005); Scenario C: sludge (Astals *et al.*, 2013). Dark grey = very high importance (CFT1); grey = high importance (CFT2). CFT = cut-off threshold.

L^{-1}. During denitrification H^+ ions are consumed, leading to a significant pH increase in the digester, which is favorable for methanogenic bacteria. However, too high NO_3-N concentrations provoque NO_2 accumulation in the digester and inhibition of methanogenics.

For sludge (Scenario C; Fig. 10.3B), an important observation is the beneficial effect of Fe and Al on CH_4 production. Indeed, in agreement with literature observations (Hoban and van den Berg, 1979; Jackson-Moss and Dunkan, 1991; Parc and Novak, 2013; Preeti and Seenayya, 1994; Raju *et al.*, 1991; Suarez *et al.*, 2014), both Fe and Al can positively influence CH_4 production (although total biogas production may decrease). These trace metals would cause an increased conversion from acetate to CH_4, meanwhile interacting with sulfate and sulfide. As such, acetate was found to be the most important input COD component to be determined for sludge digestion. Moreover, sulfide precipitation as amorphous FeS(ppt) and Mackinawite (FeS) were highly present in the reactor, thereby reducing the inhibitory effect of the presence of SRBs and sulfides on CH_4 production. Indeed, a decrease in biogas H_2S content and increase in CH_4 content was found at increasing Fe concentrations (Fig. 10.4), although in the provided range the input sulfate concentration was not supposed to cause a net negative impact on CH_4 production (< 5 g SO_4 L^{-1}; Isa *et al.*, 1986).

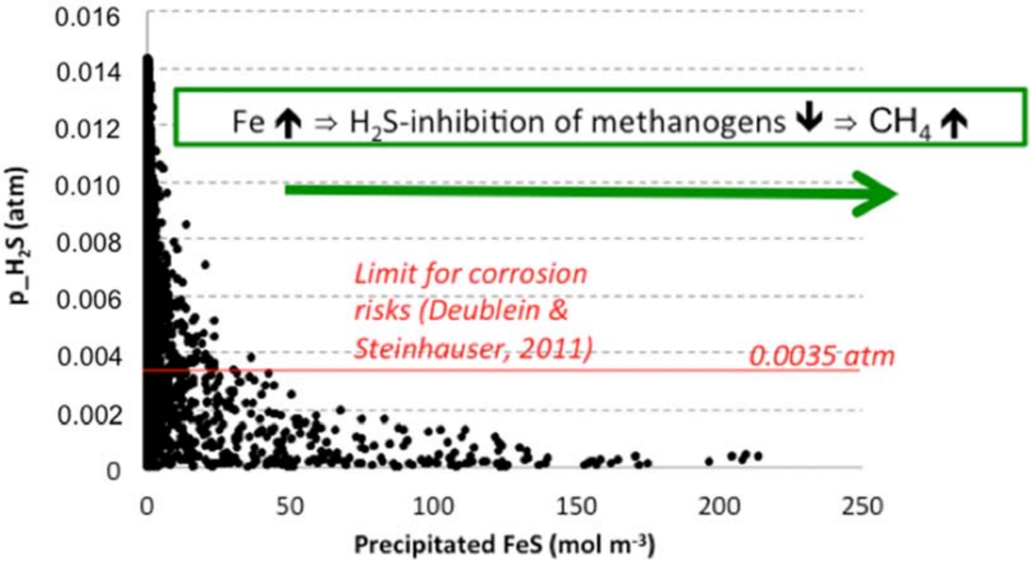


Figure 10.4 Detail Monte Carlo simulation results: biogas H_2S partial pressure (atm) as function of precipitated FeS (mol m^{-3}) for Scenario C (sludge; Astals *et al.*, 2013). Red non-dashed line indicates the limit for corrosion risks (0.0035 atm; Deublein and Steinhauser, 2011).

Note that this effect also has practical implications in terms of corrosion risks in subsequent biogas piping and equipment (see Fig. 10.4: limit for corrosion risks = 0.0035 atm; Deublein and Steinhauser, 2011). Hence, it impacts on costs related to biogas purification. This finding also strengthens the hypothesis made in Chapter 9 (Section 9.3.2), where the lower SO_4 removal found with model simulations compared to experimental results was attibuted to the omission of interactions with Fe/Al in the model (due to the lack of Fe/Al input characterizations). Finally, Isa *et al.* (1986) observed that intensive H_2S formation mainly occurs when H_2 gas or a H_2 precursor is supplied. This can explain the negative influence of S_H_0_ on CH_4 production found in the GSA for sludge (Fig. 10.3B). **All these results confirm the importance of an accurate input characterization and chemical speciation, as well as the relevance of treatment train simulations** in order to couple unit process interactions throughout the WRRF. For example, the relationship between Fe/Al dosing for sludge conditioning upstream and subsequent biogas production must be accounted for in the overall process/treatment train optimization.

The **main precipitates** that require kinetic rate calibration (based on CFT2) during manure digestion following the GSA results (Table 10.11; Fig. 10.3) are k_Calcite ($CaCO_3$), k_$CaHPO_4$:$2H_2O$, k_$CaHPO_4$bis, k_$Ca_4H(PO_4)_3$:$3H_2O$, k_$MgHPO_4$:$3H_2O$ (newberyite), k_Mackinawite (FeS), k_Magnesite ($MgCO_3$), and k_Struvite ($MgNH_4PO_4$:$6H_2O$), while for sludge this would be k_Anhydrite ($CaSO_4$), k_Aragonite ($CaCO_3$), k_Boehmite (AlOOH), k_$CaHPO_4$:$2H_2O$, k_Dolomite ($CaMg(CO_3)_2$), k_FeS_ppt, k_Siderite ($FeCO_3$), k_Vivianite ($Fe_3(PO_4)_2$:$8H_2O$), and k_$Mg_3(PO_4)_2$. Note that Fe and Al precipitation seems more important for sludge than for manure. The detected species of Fe and Al precipitates are in agreement with the findings of Mamais *et al.* (1994) and Ofverstrom *et al.* (2011) for digestion of Fe/Al-rich sludge. It should be noted that for sludge from enhanced biological P removal (EBPR), containing both high Mg and P contents, and usually low Fe and Al concentrations, Mg precipitates are expected to be more important than Fe/Al precipitates (supersaturation depends on ion concentrations). Modelling of EBPR sludge was out of scope of the present study, but looking at Scenario A, where higher input concentrations of Mg were allowed, it can be seen that the main precipitate impacting CH_4 production was struvite (~ importance of k_struvite; Table 10.11). This is in agreement with what has often been observed during digestion of EBPR sludge (Marti *et al.*, 2008; Ofverstrom *et al.*, 2011).

Regarding the **digestate quality**, it can be seen that the amount of soluble mineral N is highly dependent on the input NH_4 concentration (which is obvious) and the temperature. Higher temperatures cause lower soluble digestate NH_4 concentrations, which can be attributed to the increased transfer of NH_3 into the biogas. Furthermore, it should be noted that for both manure and sludge, higher amounts of Mg and P seem to lower the amount of digestate soluble NH_4, which may be attributed to struvite formation. This can be confirmed by the observed increment in the amount of soluble N at increasing concentration of other components that may compete for P complexation and/or precipitation, such as Ca and Na. Also newberyite ($MgHPO_4$:$3H_2O$) seems to be a principal competitor (Scenario B) (cfr. Marti *et al.*, 2008; Musvoto *et al.*, 2000a,b). An important observation is the significant effect of Na on P solubility (Scenarios A and B). Indeed, as observed in Chapter 9 (Section 9.3.3.1), Na binds with soluble P to form NaH_2PO_4, making it less available for precipitation. This effect was found to be negligible for WWTP sludge due to the generally lower Na:P-ratio observed in the analysis for this waste source.

Overall, it can be stated that the variation related to the physicochemical input waste stream characteristics for the anaerobic digester is more important than that of the kinetic parameters considered in the GSA. The reason is that small changes in input factors (mainly those selected by CFT1) have a high effect on the digester pH and/or alkalinity, which are, next to the temperature and liquid flow rate, the most important operational factors for digestion. In this context, the importance of the correct representation of the charge balance for determination of the digestate pH is again underlined (Table 10.11: performance indicator ‘pH’).

10.3.1.2 NRM-Prec: Factor ranking and interpretation

For the NRM-Prec unit, GSAs using all the factors provided in Table 10.5 resulted in high VIF values (~ 5-10) for all performance indicators, showing high multicollinearity. The most important correlation was found between the concentration of seed material (S_seed) and the kinetic solid-liquid transfer coefficients (k). To overcome this problem, the GSA was reduced by incorporating the variation of S_seed into the variation range of the corresponding kinetic transfer coefficient, which is reasonable when looking at the precipitation reaction used (Nielsen, 1984; Chapter 9: Eq. 9.8). As k and S_seed are multiplied in the equation, their impact is perfectly correlated, and hence the overall range of variation can be attributed to k only. Implementing this measure resulted in VIFs below 1.06, while the R^2_{adj} value for the effluent S_P was higher than 0.7. Hence, the reduced GSA was valid for evaluation of P recovery based on the effluent S_P. However, R^2_{adj} values for the other fertilizer quality performance indicators became lower than 0.7 due to the elimination of seed material. This effect is logical as seed material is a major factor determining the particle diameter, density, and purity (Le Corre *et al.*, 2007a). As such, it should be understood that the importance of the precipitation/dissolution kinetics presented refers to both the kinetic transfer coefficient and seed material. Despite the relatively low GSA quality, the SRC may still be assumed valid for factor ranking (Section 10.2.3; Cosenza *et al.*, 2013).

Results of the reduced GSA for the different scenarios can be found in Table 10.12 (Appendix 10: Tables A10.4-10.6). For Scenarios B and C, first the sensitivity was tested within the range of daily input Mg variability, whereafter an external Mg dose was allowed to be applied up to 200 and 500 mol m^{-3} for Scenario B and C, respectively (difference due to lower P and Ca contents in the input waste flow for Scenario B). When **no external Mg** was added, Scenario B showed no uncontrolled P precipitation in the NRM-Prec, due to the low digestate Mg:P-ratio and relatively low pH for precipitation. Note that Mg-P nucleation and/or precipitation was to be expected in the digester (Section 10.3.1.1) and that the range of Mg and P in the digestate was much lower than in the digester input (Section 10.2.2; Cesur and Albertson, 2005). Hence, it is likely that Mg-P precipitates were retained in the digester and/or piping prior to the digestate sampling location (cfr. Marti *et al.*, 2008).

Due to the generally higher Ca and P concentrations in Scenario C, Ca-P precipitation can be expected (Song *et al.*, 2001). The observed variation in the amount of Ca-P precipitates was mainly caused by the liquid temperature, the input Ca concentration, and the $Ca_3(PO_4)_2$:beta precipitation/dissolution kinetics. However, as the input Ca concentration was also positively correlated with the effluent soluble P concentration, Ca-P complex formation and/or redissolution seem to occur in concurrence with precipitation. This is reasonable since no base was added for pH-increase.

When allowing the **external addition of Mg**, P precipitation occurred and the Mg dose became an important factor influencing all performance indicators, next to the amount of input S_P, S_Ca, and S_Na. The latter inhibits P precipitation (cfr. NRM-AD and Chapter 9: Section 9.3.3.1). According to the hypothesis of Schulze-Rettmer (1991), the Mg:P-ratio should be higher than 1:1 to promote struvite precipitation. However, the amount of Mg required further increases with the amount of complexing agents that can bind to Mg, which is generally high in a digestate waste matrix (Burns *et al.*, 2003; Moody *et al.*, 2009; Nelson *et al.*, 2000). As such, the inhibitory and competitive effect of Ca on struvite precipitation at increasing pH is clear from the results, as a major factor for all scenarios is the precipitation/dissolution rate of $Ca_3(PO_4)_2$:beta. This finding is in agreement with the observations of Le Corre *et al.* (2005) that at molar ratios of Ca:Mg ~ 1:1 and above no more crystalline struvite compound is formed, but a substance identified as an amorphous calcium phosphate ($Ca_3(PO_4)_2$). Noteworthy is the fact that the mean molecular weight (MW) found for Scenario C was in more than 50 % of the cases around 310 g mol^{-1}, which is the MW of $Ca_3(PO_4)_2$.

Table 10.12 Global sensitivity analyses for the NRM-Prec unit: ten prioritized factors and standardized regression coefficient (SRC) per performance indicator for each scenario. Scenario A: all applications; Scenario B: digestate from manure (Cesur and Albertson, 2005); Scenario C: (co-)digestate (Vlaco, 2012). Dark grey = very high importance (CFT1); grey = high importance (CFT2); light grey = moderate importance (CFT3). CFT = cut-off threshold. * indicates R^2_{adj} value below 0.7. Description of factor symbols can be found in Table 10.5.

A	**Effluent S_P**		**Fertilizer P_P ***		**Particle diameter**		**Fertilizer density ***		**Struvite purity ***		**Overall ***					
	S_P	0.934	Temp_liq	-0.267	S_Na	-0.572	S_Na	-0.484	S_C_4_	-0.050	Temp_liq	-0.267				
	S_Na	0.274	S_Ca	0.259	S_P	0.552	S_P	0.448	k_Ca$_4$H(PO$_4$)$_3$:3H$_2$O	-0.051	S_Ca	0.259				
	S_Fe	0.037	S_Na	-0.242	k_Gibbsite	0.051	pH_liq	0.054	S_S_6_	0.050	S_Na	-0.242				
	S_Al	0.038	S_P	0.207	S_Ca	0.039	k_Gibbsite	0.053	k_Gibbsite	-0.049	S_P	0.207				
	S_S_6_	0.034	k_Ca$_3$(PO$_4$)$_2$_beta	0.192	k_Aragonite	0.036	k_Siderite	0.051	k_Calcite	-0.048	k_Ca$_3$(PO$_4$)$_2$_beta	0.192				
	S_N_min3_	0.028	S_Mg	0.086	k_Ca$_3$(PO$_4$)$_2$_am3	-0.035	k_Aragonite	0.050	S_Ca	-0.047	S_Mg	0.086				
	S_Cl	0.024	k_Mg$_3$(PO$_4$)$_2$	-0.069	S_Mg	0.035	k_Calcite	0.045	k_Dolomite	0.047	k_Mg$_3$(PO$_4$)$_2$	-0.069				
	S_Ca	0.022	k_Struvite	-0.059	pH_liq	0.030	k_Ca$_3$(PO$_4$)$_2$_am3	-0.044	S_Fe	0.044	k_Struvite	-0.059				
	S_N_5_	0.020	S_S_6_	-0.059	k_MgHPO$_4$:3H$_2$O	0.029	k_Artinite	0.040	k_MgHPO$_4$:3H$_2$O	0.043	S_S_6_	-0.059				
	S_K	0.017	S_C_4_	-0.057	S_N_min3_	-0.029	k_Fe(OH)$_2$_s	-0.040	k_Hydroxyapatite	0.043	S_C_4_	-0.057				
B	**No external Mg-addition**				**External Mg-Addition**											
	Effluent S_P		**Fertilizer P_P**		**Effluent S_P**		**Fertilizer P_P ***		**Particle diameter ***		**Fertilizer density ***		**Struvite purity ***		**Overall ***	
	S_P	0.993	No P precipitation		S_P	0.984	Temp_liq	-0.368	S_P	0.615	S_P	0.255	Temp_liq	0.072	Temp_liq	-0.368
	S_Mg	0.091			S_Mg	0.074	S_Mg	0.267	S_Mg	0.091	S_Mg	0.177	S_Ca	-0.069	S_Mg	0.267
	S_N_min3_	0.017			S_Na	0.060	S_P	0.249	S_Na	-0.090	S_Valerate	0.083	S_N_min3_	0.056	S_P	0.249
	S_Cl	0.015			S_Cl	-0.009	k_Ca$_3$(PO$_4$)$_2$_beta	0.208	S_S_min2_	-0.040	k_Magnesite	0.073	S_Mg	0.051	k_Ca$_3$(PO$_4$)$_2$_beta	0.208
	S_Ca	0.006			k_Aragonite	-0.008	S_K	-0.046	k_Artinite	-0.038	S_S_min2_	-0.063	k_AlPO$_4$	0.047	S_K	-0.046
	S_Na	0.005			S_S_6_	-0.008	S_S_min2_	-0.039	S_Acetate	-0.038	S_Na	-0.063	k_Magnesite	-0.046	S_S_min2_	-0.039
	S_S_6_	0.004			k_Mg$_3$(PO$_4$)$_2$	-0.008	S_Ca	0.039	k_CaHPO$_4$:2H$_2$O	0.037	S_Acetate	-0.050	k_Mg$_3$(PO$_4$)$_2$	-0.042	S_Ca	0.039
	Temp_liq	-0.004			k_Vaterite	-0.008	S_C_min4_	-0.037	k_Calcite	0.035	S_Al	-0.047	k_Dolomite	0.042	S_C_min4_	-0.037
	S_N_5_	0.002			k_Gibbsite	0.008	S_Na	-0.036	S_Ca	0.033	S_Butyrate	-0.047	pH_op	-0.040	S_Na	-0.036
	S_C_min4_	-0.001			Q_Prec	-0.007	S_N_min3_	0.034	k_Dolomite	0.031	S_Cl	-0.047	k_CaHPO$_4$bis	-0.038	S_N_min3_	0.034
C	**No external Mg-addition**				**External Mg-Addition**											
	Effluent S_P		**Fertilizer P_P ***		**Effluent S_P**		**Fertilizer P_P ***		**Particle diameter ***		**Fertilizer density ***		**Struvite purity ***		**Overall ***	
	S_P	0.959	Temp_liq	-0.384	S_P	0.991	Temp_liq	-0.551	S_P	0.370	S_P	0.367	k_Ca$_3$(PO$_4$)$_2$_beta	-0.160	Temp_liq	-0.551
	S_Fe	0.125	S_Ca	0.252	S_Na	0.090	k_Ca$_3$(PO$_4$)$_2$_beta	0.372	S_Na	-0.164	S_Na	-0.159	Temp_liq	0.089	k_Ca$_3$(PO$_4$)$_2$_beta	0.372
	S_Na	0.089	k_Ca$_3$(PO$_4$)$_2$_beta	0.247	S_Mg	-0.023	S_Ca	0.254	k_Gibbsite	0.072	k_Gibbsite	0.071	S_Ca	-0.088	S_P	0.254
	S_Ca	0.070	S_P	-0.188	Temp_liq	-0.009	S_P	0.234	k_CaHPO$_4$:2H$_2$O	0.063	k_CaHPO$_4$:2H2O	0.066	k_Kstruvite	0.072	S_Ca	0.234
	S_N_min3_	-0.040	S_C_4_	-0.164	S_C_4_	0.009	S_C_4_	-0.099	k_Kstruvite	-0.053	k_Magnesite	0.048	S_Na	-0.066	S_C_4_	-0.099
	Temp_liq	-0.022	S_N_min3_	0.110	S_N_min3_	-0.008	S_Na	-0.052	Calcite	0.052	S_Fe	-0.044	k_CaHPO$_4$:2H$_2$O	0.063	S_Na	-0.052
	S_C_4_	0.020	S_Al	-0.096	S_Ca	-0.008	S_Mg	-0.038	k_Dolomite_dis	-0.046	k_Dolomite_dis	-0.044	S_P	0.061	S_Mg	-0.038
	S_S_6_	-0.018	S_Fe	0.065	S_Al	0.005	S_Propionate	-0.035	S_C_4_	-0.041	k_Artinite	0.043	k_Vivianite	-0.058	S_Propionate	-0.035
	S_Mg	0.016	k_Ca$_3$(PO$_4$)$_2$_am3	-0.063	Q_liq_in	-0.003	k_Aragonite	0.032	S_Propionate	0.036	k_Kstruvite	-0.041	k_Ca$_3$(PO$_4$)$_2$_am3	-0.047	k_Aragonite	0.032
	k_Magnesite	-0.015	S_Na	0.049	k_CaHPO$_4$bis	-0.003	k_Calcite	0.031	S_C_min4_	0.036	k_Calcite	0.036	k_Mg(OH)$_2$_act	-0.042	k_Calcite	0.031

Furthermore, also the variation related to the input soluble organic (S_ac, S_bu, S_pro, S_va) and inorganic (S_C_4) carbon concentrations significantly affected (based on CFT2) the fertilizer quality through complexation with Ca and Mg. Nevertheless, it was observed that an overdose of Mg did not aid in P recovery (see e.g. Scenario B: positive impact of Mg on effluent S_P). The reason is that at high Mg-dose the pH may increase to values (> 10) for which precipitation of carbonates, such as artinite ($MgCO_3$:$Mg(OH)_2$:$3H_2O$) and dolomite ($CaMg(CO_3)_2$), are known to be favoured (Mamais *et al.*, 1994). Similar observations were made during the lab-scale experiments for validation of the NRM-Prec model (Chapter 9: Section 9.3.3.2; De Corte, 2013). Moreover, this effect is in line with the findings of Jarosinski and Madejska (2010) who recovered these crystals from wastewater by increasing the pH. Indeed, struvite precipitation is known to be favoured at neutral to slightly alkaline pH (up to 9; Musvoto *et al.*, 2000a), which can also be seen at the higher struvite purity found for lower operational pH's within the context of the analysis (Table 10.12).

Next to the pH, the main operational factor seems to be the liquid temperature, where P precipitation was found to be lower at higher temperatures, especially for Scenario C (Fig. 10.5).

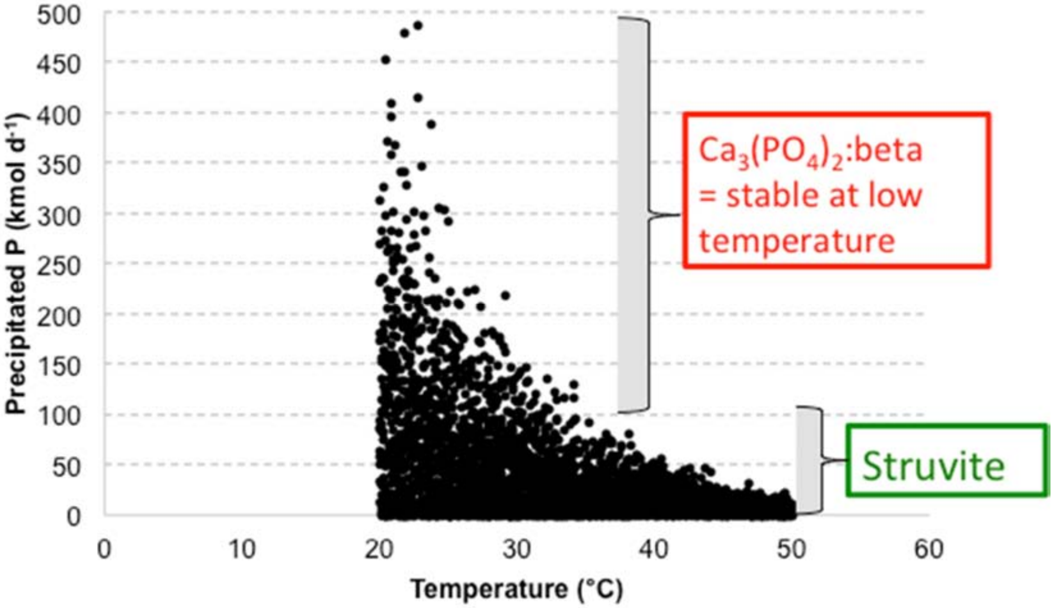


Figure 10.5 Detail Monte Carlo simulation results: P precipitation (kmol d^{-1}) as function of temperature (°C) for Scenario C (Co-digestate; Vlaco, 2012).

Interestingly, rather a logarithmic than a linear effect was found due to the combination of the Arrhenius temperature correction used for the kinetic rates and the Van't Hoff correction used for the solubility products (Chapter 9: Section 9.2.2.1). The decreasing effect in this case can be explained by the fact that $Ca_3(PO_4)_2$:beta (the main precipitate in Scenario C) is the main stable calcium phosphate that forms at lower temperatures (Mirhadi *et al.*, 2011; Moghimian *et al.*, 2012). Nevertheless, a temperature increment positively influenced struvite purity in the GSA. Looking at the decreasing struvite solubility product with increasing temperature (Hanhoun *et al.*, 2011), this finding seems realistic. Hence, **if the aim would be to produce high purity**

struvite, it can be recommended to work at relatively high operational temperature (e.g. after mesophilic digestion) and rather low pH within the considered ranges (Table 10.5). Knowing that high concentrations of Ca ions can reduce the yield of struvite crystals formed to around 15 % in full-scale operational systems for struvite recovery, thereby making the plant economically unfeasable (Dangaran, 2013), **the reduction of Ca inhibition creates an important optimization challenge in nutrient recovery systems**.

According to the GSA results for all scenarios, input factors that should become standard measurements at WRRFs aiming at P recovery through precipitation, next to of course S_P, are S_Al, S_Ca, S_C_4_, S_Fe, S_Mg, S_Na, and S_N_min3_, because of their direct effect on pH and/or ion pair formation/precipitation with P. Precipitation kinetics that should be prioritized for calibration (based on CFT2), next to k_Struvite, are: k_AlPO$_4$, k_Aragonite (CaCO$_3$), k_Artinite (MgCO$_3$:Mg(OH)$_2$:3H$_2$O), k_Calcite (CaCO$_3$), k_CaHPO$_4$:2H$_2$O, k_Ca$_3$(PO$_4$)$_2$_am3, k_Dolomite_dis (CaMg(CO$_3$)$_2$), k_Gibbsite (Al(OH)$_3$), k_Kstruvite (MgKPO$_4$:6H$_2$O), k_Magnesite (MgCO$_3$), k_Mg$_3$(PO$_4$)$_2$, k_Vaterite (CaCO$_3$), and k_Vivianite (Fe$_3$(PO$_4$)$_2$:8H$_2$O). For Scenario A, also k_Ca$_4$H(PO$_4$)$_3$:3H$_2$O, k_Fe(OH)$_2$_s, k_Hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_5$), k_Newberyite (MgHPO$_4$:3H$_2$O), and k_Siderite (FeCO$_3$) were found to be important. Consequently, **if pure struvite is aimed for, the removal of Ca prior to the precipitation reactor, as well as the implementation of struvite precipitation prior to or instead of Fe/Al dosing, is recommended**. Noteworthy is that similar conclusions were made in Chapter 9: Section 9.3.3.2.

10.3.1.3 NRM-Strip: Factor ranking and interpretation

GSA results for the NRM-Strip unit are provided in Table 10.13 (Appendix 10: Tables A10.7-10.9). All R^2_{adj} values were higher than 0.7, except for S_C_4_ precipitation in Scenarios A and C.

The most important input characteristics determining NH$_3$ removal were S_Ca, S_Cl, S_C_4_, S_Mg, S_Na, S_N_min3_, S_P, and S_S_6_. Indeed, these are major input characteristics determining the pH and ionic strength of the solution, which impact on the Henry coefficient of NH$_3$ (DOE, 2014; Wickramanyake, 2009). In this respect, an important observation is that especially high Cl contents negatively influenced the NH$_3$ removal efficiency in each scenario by decreasing the pH, while increasing the ionic strength of the solution (cfr. Yuwza, 1982). A detail of the MC results showing the effect of this anion for Scenario B is provided in Figure 10.6. Also the higher effluent NH$_4^+$ concentration found for higher input Cl contents, and the higher air requirements to obtain efficient NH$_3$ removal, provide evidence for chloride interference.

Indeed, an increase in the ionic strength of the solution results in a decrease of the activity coefficients (< 1 ~ less active), which on its turn results in a decrease of the partial pressure of NH$_3$ in the gas phase (Zumdahl, 2005). Moreover, higher Cl concentrations will increase the amount of chemicals (often caustic soda, NaOH) and/or CO$_2$ stripping needed to increase the pH prior to stripping (DOE, 2014). As such, without chemical pH-increment (hence only pH-

Table 10.13 Global sensitivity analyses for the NRM-Strip unit: ten prioritized factors and standardized regression coefficient (SRC) per performance indicator for each scenario. Scenario A: all applications; Scenario B: digestate from manure (Cesur and Albertson, 2005); Scenario C: (co-)digestate (Vlaco, 2012). Dark grey = very high importance (CFT1); grey = high importance (CFT2); light grey = moderate importance (CFT3). CFT = cut-off threshold. * indicates R^2_{adj} value below 0.7. Description of factor symbols can be found in Table 10.6.

A	NH$_4$-N removal efficiency		Effluent NH$_4$-N		Precipitation CO$_3$*		Air requirement[a]		Overall	
	S_Cl	-0.930	S_Cl	0.935	Temp_liq	-0.174	Temp_liq	-0.711	Temp_liq	-0.733
	S_N_min3_	0.508	S_Mg	-0.156	S_Mg	0.171	P_gas_in	0.430	P_gas_in	0.423
	S_Mg	0.136	S_N_min3_	0.106	S_Ca	0.136	Q_liq_in	0.358	Q_liq_in	0.364
	S_C_4_	0.084	S_C_4_	-0.061	S_P	-0.119	S_Cl	0.046	S_Cl	0.031
	CO$_2$_g_	-0.046	S_Ca	-0.033	k_Magnesite	0.114	k_Ca$_3$(PO$_4$)$_2$_am1	-0.030	k_Mg$_3$(PO$_4$)$_2$	-0.021
	k_Ca$_3$(PO$_4$)$_2$_am1	0.044	S_Al	-0.028	S_S_6_	-0.103	S_K	0.025	k_Mg(OH)$_2$_act	-0.022
	D_CH$_4$_g_	-0.041	S_H_0_	-0.028	S_Cl	-0.102	k_Aragonite	-0.024	D_NH$_3$_g_	0.021
	S_H_0_	0.038	S_S_6_	0.027	N$_2$_g_	0.088	k_Hercynite	0.024	theta_CH$_4$_g_	-0.021
	k_Ca$_3$(PO$_4$)$_2$_beta	-0.038	k_Struvite	0.026	S_Fe	-0.081	Temp_gas_in	0.023	k_Kstruvite	0.020
	S_N_0_	-0.036	S_P	0.022	Q_liq_in	-0.071	S_Butyrate	-0.022	CO$_2$_g_	0.020
B	**NH$_4$-N removal efficiency**		**Effluent NH$_4$-N**		**Precipitation CO$_3$**		**Air requirement[a]**		**Overall**	
	S_Cl	-0.922	S_Cl	0.860	Q_liq_in	0.963	Temp_liq	-0.711	Temp_liq	-0.711
	S_N_min3_	0.244	S_N_min3_	0.350	D_N$_2$_g_	-0.021	P_gas_in	0.440	P_gas_in	0.440
	S_Mg	0.175	S_Mg	-0.164	S_K	0.017	Q_liq_in	0.354	Q_liq_in	0.354
	Temp_liq	0.153	Temp_liq	-0.144	theta_CH$_4$_g_	-0.015	S_Cl	0.121	S_Cl	0.121
	S_Na	0.139	S_Na	-0.130	k_Dolomite	-0.016	S_Na	-0.048	S_Na	-0.048
	S_Ca	0.110	S_Ca	-0.104	S_N_min3_	-0.014	S_N_min3_	-0.027	S_N_min3_	-0.027
	S_S_6_	-0.058	S_S_6_	0.054	S_C_min4_	0.014	S_C_4_	-0.026	S_C_4_	-0.026
	S_K	0.047	S_P	0.043	S_Na	0.012	u	-0.024	u	-0.025
	S_P	-0.045	S_K	-0.042	S_Propionate	-0.013	S_Ca	-0.024	S_Ca	-0.024
	S_N_5_	-0.038	S_N_5_	0.034	S_Al	-0.013	k_Diaspore	-0.021	k_Diaspore	-0.022
C	**NH$_4$-N removal efficiency**		**Effluent NH$_4$-N**		**Precipitation CO$_3$***		**Air requirement[a]**		**Overall**	
	S_C_4_	0.513	S_N_min3_	0.730	S_P	-0.212	Temp_liq	-0.630	Temp_liq	-0.735
	S_N_min3_	-0.467	S_C_4_	-0.382	S_N_min3_	-0.157	P_gas_in	0.376	P_gas_in	0.423
	S_Mg	0.365	S_Mg	-0.261	S_Ca	0.107	Q_liq_in	0.312	Q_liq_in	0.362
	S_Cl	-0.230	S_P	-0.114	S_Mg	0.096	S_C_4_	-0.171	k_Mg$_3$(PO$_4$)$_2$	-0.031
	S_P	0.131	S_Cl	0.104	S_DOM	-0.081	S_N_min3_	0.153	K_Kstruvite	0.020
	S_Al	0.046	S_DOM	-0.042	S_Na	0.072	S_Mg	-0.115	D_NH$_3$_g_	0.020
	S_DOM	0.042	S_Al	-0.036	k_Calcite	0.068	S_P	0.082	k_Dolomite	-0.018
	S_Fe	0.040	theta_CO$_2$_g_	0.034	S_Fe	-0.064	S_Cl	0.052	theta_H$_2$_g	-0.018
	S_Na	-0.036	S_Fe	-0.029	theta_O$_2$_g_	0.062	D_NH$_3$_g_	0.035	k_Portlandite	-0.017
	O$_2$_g_	0.035	k_Dolomite	-0.028	d_gas	-0.060	k_Mg$_3$(PO$_4$)$_2$	-0.034	D_H$_2$_g_	-0.017

[a] Air needed to obtain 90 % NH_3 removal.

increase through CO_2 removal in the stripper), the average NH_3 removal efficiency for Scenario B (with high Cl content) was only 48.8±5.0 %, whereas it amounted to 75.4±16.2 % for Scenario C. This phenomenom may impact on the treatment train configuration, as often $MgCl_2{:}6H_2O$ is used for P recovery through precipitation. **Hence, if P recovery is to be implemented prior to stripping, the addition of $Mg(OH)_2$ or MgO instead of $MgCl_2{:}6H_2O$ may be more feasible** (although more expensive; Table 10.10). Note that the above also underlines the fundamental importance of the accurate pH calculation and ion activity corrections provided by the NRMs (Chapter 9).

Furthermore, it is important to notice that the input P content negatively influenced NH_3 stripping in Scenarios A and B. This is likely due to Na-P, Ca-P, and/or Mg-P ion pair formation/ precipitation, thereby reducing the positive effect (basicity) of these cations on NH_3 removal. However, in Scenario C, where much higher P concentrations were allowed (Table 10.6), the increasing P concentration (N:P-ratios ~ 1) seems to positively influence NH_3 removal, likely due to the formation of struvite (see also the importance of struvite kinetics for Scenario C in the

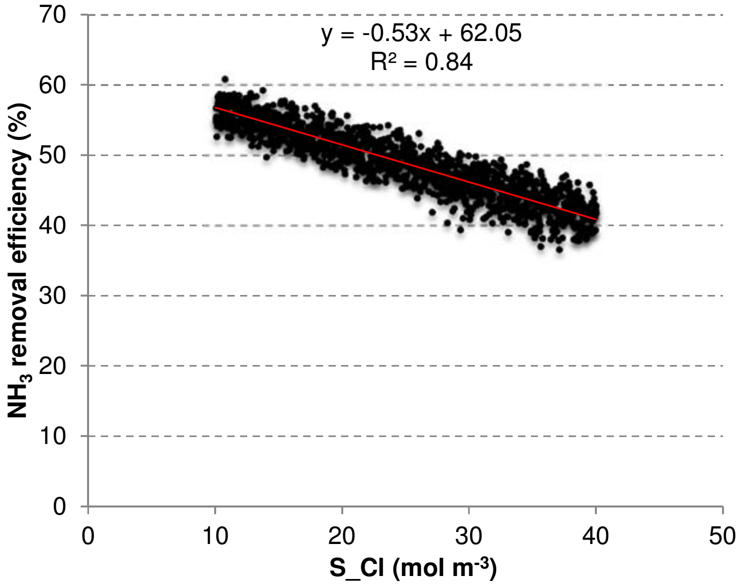


Figure 10.6 Detail Monte Carlo simulation results: NH_3 removal efficiency (%) as function of input chloride concentration (S_Cl; mol m^{-3}) for Scenario B (Cesur and Albertson, 2005).

stripping column; Appendix 10: Table A10.9). Besides, this can explain why Na negatively impacts on NH_3 removal for this scenario (cfr. Na-P ion pair formation in NRM-AD and NRM-Prec). Hence, **the interest of removing P prior to stripping is clear for all scenarios, so as to avoid ion pairing and/or uncontrolled precipitation (scaling) of P in piping/equipment**.

The most important operational factors for process optimization based on CFT1 are the liquid temperature (Temp_liq), liquid flow rate (Q_liq_in) and pH (determined by the charge balance), as well as the gas pressure (P_gas_in). All effects (including the sign) are in agreement with operational practice (Wang *et al.*, 2007). An interesting observation is that an increment in the operational temperature (Temp_liq) not only significantly improved NH_3 removal (in line with prior knowledge), but also reduced air requirements. Hence, a cost optimization problem arises.

Overall, the most important kinetic factor for calibration following CFT1 is k_Magnesite ($MgCO_3$), which contributes to carbonate scaling on the packing material. The NH_3 diffusion coefficient (D_NH_3_g_) and calcite precipitation kinetics (k_Calcite) are only of secondary importance (CFT2) according to the GSA.

10.3.1.4 NRM-Scrub: Factor ranking and interpretation

The GSA results for the NRM-Scrub unit are provided in Table 10.14 (Appendix 10: Table A10.10). The R^2_{adj} values for the NH_3 recovery efficiency and the acid requirements were slightly below 0.7 (0.68 and 0.67, respectively), but still acceptable for factor ranking (Cosenza *et al.*, 2013). The GSA quality for fertilizer N, pH, and the overall sensitivity measure was high.

Table 10.14 Global sensitivity analyses for the NRM-Scrub unit: ten prioritized factors and standardized regression coefficient (SRC) per performance indicator. Dark grey = very high importance (CFT1); grey = high importance (CFT2); light grey = moderate importance (CFT3); salmon = low importance. CFT = cut-off threshold. * indicates R^2_{adj} value below 0.7. Description of factor symbols can be found in Table 10.7.

NH_3 recovery efficiency *		**Fertilizer S_N_min3_**		**Fertilizer pH**		**Acid requirement ***		**Overall**	
NH_3_g_	-0.590	NH_3_g_	0.900	NH_3_g_	0.814	NH_3_g_	-0.623	NH_3_g_	0.860
CO_2_g_	0.390	O_2_g_	-0.309	CO_2_g_	-0.310	CO_2_g_	0.398	CO_2_g_	-0.299
O_2_g_	0.278	S_S_6_	-0.154	O_2_g_	-0.231	S_S_6_	0.255	O_2_g_	-0.271
S_S_6_	0.240	H_2_g_	0.072	S_S_6_	-0.175	O_2_g_	0.248	S_S_6_	-0.170
Temp_liq	-0.074	CH_4_g_	0.059	H_2_g_	0.056	H_2_g_	-0.064	H_2_g_	0.069
H_2_g_	-0.073	Temp_gas_in	-0.046	CH_4_g_	0.033	theta_H_2_g_	-0.035	P_gas_in	-0.033
CH_4_g_	-0.043	P_gas_in	0.021	Temp_liq	-0.025	pH_liq	0.032	Temp_gas_in	-0.027
u	-0.029	D_CH_4_g_	-0.020	D_N_2_g_	0.018	theta_N_2_g_	-0.029	Temp_liq	-0.021
D_O_2_g_	-0.025	theta_H_2_g_	0.016	D_CO_2_g_	-0.015	Temp_gas_in	0.025	Q_liq_in	-0.017
D_CH_4_g_	-0.025	Temp_liq	-0.015	theta_NH_3_g_	-0.014	D_CO_2_g_	0.025	H_2O_g_	0.016

All performance indicators were mainly sensitive to variations in the partial pressure of NH_3, O_2, and CO_2 in the gas phase (coming from the stripper), as well as to the acid concentration (represented by input sulfate, S_S_6_). Logically, the higher the acid dose, the higher the N recovery efficiency. However, when sulfate concentrations are so high that ammonium sulfate (AmS) supersaturation occurs, then crystallization will take place and further ammonia absorption will be inhibited. This may explain the negative effect of input sulfate (S_S_6_) on the fertilizer soluble ammonium (S_N_min3_) concentration. On the other hand, upconcentration of AmS (usually up to 25-40 % AmS) by use of a recycle flow (Q_rec) is interesting so as to reduce acid requirements and transportation costs, as well as to meet fertilizer quality specifications. Hence, again **an optimization problem arises: a fertilizer recycle flow should be used and retention times should be adjusted to obtain the targeted product quality, while avoiding AmS precipitation.**

The other operational factors and kinetic parameters tested seem to have a lower impact on the scrubber performance than the above-mentioned input variables. Next to the acid dose, important operational factors (based on CFT2) seem to be the liquid temperature (Temp_liq, i.e. more N absorption at lower temperature) and gas temperature (Temp_gas_in, i.e. more N volatilization at higher temperature), as well as the gas phase pressure (P_gas_in, i.e. more N absorption at higher pressure). All these effects are in agreement with prior knowledge (Crisalle, 2013; Manuzon *et al.*, 2007; Powers *et al.*, 1987). Moreover, based on CFT2, the most important kinetic parameters for calibration are the Arrhenius temperature dependency coefficient theta for H_2 and the diffusion coefficient of CH_4.

10.3.1.5 Overview of generic recommendations for factor prioritization

From the unit process GSAs above, it can be stated that major effects of the selected factors on the model outputs are representative for the three different input waste substrates under study (Scenarios A, B, and C; Table 10.3). For example, the presence of Ca inhibits struvite purity, whereas the presence of Cl inhibits NH_3 stripping. Based on the generic observations, an overview of recommended factors to be prioritized based on CFT1 is given in Table 10.15.

Table 10.15 Generic recommendations in terms of 1) input characterization at resource recovery facilities, 2) operational factors that should be prioritized for process optimization and control, and 3) kinetic model parameters that most urgently require calibration, for each key unit in the nutrient recovery model (NRM) library based on cut-off treshold 1 (CFT1 = very high importance). AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber.

Key unit	1. Input factors	2. Operational factors	3. Kinetic parameters
NRM-AD	Inorganic: S_Al, S_C_min4_, S_C_4_, S_Ca, S_Cl, S_Fe, S_Mg, S_Na, S_N_0_, S_N_5_, S_N_min3_, S_P, S_S_6_ + S_Fe and S_Al (if dosing upstream) Organic: S_acetate, S_butyrate, S_propionate[a], S_valerate, X_ch, X_inert, X_pr	Temp_liq, Alkalinity (S_C_4_) / pH, Q_liq_in (~ HRT)	no major importance based on CFT1
NRM-Prec	S_Al[a], S_Ca, S_C_4_, S_Fe, S_Mg, S_Na, S_N_min3_, S_P	Temp_liq, Mg-dose (~ pH)	k_$Ca_3(PO_4)_2$:beta
NRM-Strip	S_Ca, S_Cl, S_C_4_, S_Mg, S_Na, S_N_min3_, S_P, S_S_6_	Temp_liq, pH_liq (~ base dose), P_gas_in, Q_liq_in	k_Magnesite
NRM-Scrub	CO_2_g_, NH_3_g_, O_2_g_, S_S_6_	Acid dose (S_S_6) / pH	no major importance based on CFT1

[a] Note that this component was only selected based on CFT2, but due to the frequency of its selection, measurement of this component is also recommended.

In line with the overall objectives of the GSA (Section 10.1), recommendations are given in terms of:

1) Input factors that should become standard measurements at WRRFs, at least during the start-up phase;
2) Operational factors that should be prioritized for process optimization and control;
3) Kinetic parameters that most urgently require calibration.

It should be remarked that, especially for the NRM-AD and NRM-Scrub units, the impact of the kinetic parameters under study was minor compared to the daily variability in waste input composition and the operational decisions. Overall, it can be concluded that **the input flow characteristics play a major role in nutrient recovery, as they directly impact on the operational pH and ionic strength of the solution.** These findings are in line with activated sludge modelling, in which input characterization was also evaluated as an essential step (Rieger *et al.*, 2012).

10.3.2 Treatment train configuration

Based on the generic insights obtained from the unit process GSA results presented in Section 10.3.1, an optimal combination of unit processes in a treatment train for nutrient recovery can be derived. First, it was observed that Ca has a negative influence on both the struvite purity and the stripping performance (scaling on the packing column). Moreover, the occurrence of calcite precipitation, as well as Fe and Al precipitation, during digestion was found to be very probable. Hence, it is expected that the implementation of a phase separation unit after the digester may separate the Ca, Fe, and Al precipitates from the liquid digestate, thereby improving the performance of the subsequent technologies for nutrient recovery from the liquid digestate. The settled solids, rich in Ca and organic matter (COD), may then be valorized as a soil conditioner if fertilizer quality requirements (e.g. in terms of pasteurization) can be met (Vaneeckhaute *et al.*, 2012). Note that this is in agreement with the current common practice for digestate treatment (Chapter 2).

Next, it was observed that Cl and P have a negative effect on the stripping performance, while the amount of soluble ammonium influences struvite purity in a positive way. Hence, if the aim would be to produce both high purity struvite and concentrated AmS, the precipitation unit should preferably be added prior to the stripping unit, while the use of $Mg(OH)_2$ or MgO should be preferred for P precipitation instead of $MgCl_2:6H_2O$. Although these products are less soluble, they have the additional benefit of increasing the pH, whereas $MgCl_2$ slightly decreases the pH (Burns and Moody, 2002). As such, depending on the waste stream to be treated, it may be possible to obtain high struvite recovery without the addition of base (NaOH) for pH-increase. Indeed, struvite recovery is favoured at neutral to slightly alkaline pH (Section 10.3.1.2). Hence, the combination of a phase separation unit for Ca removal and an optimized dose of $Mg(OH)_2$/MgO (without addition of NaOH) may be sufficient for optimal P recovery as struvite. As such, Westerman *et al.* (2010) found high P recovery efficiencies with addition of $Mg(OH)_2$ only, or with only a small addition of NaOH, i.e. raising the pH from 7.3 to 7.8, while digestate pH's are generally around 8.

Moreover, by implementing the precipitation unit prior to the stripper, it is possible that no additional base has to be added for stripping. Indeed, the Mg dose for precipitation in combination with the pH-increase obtained through CO_2 stripping from the remaining digestate alkalinity is usually sufficient (Anaergia, 2014; Colsen, 2014). Finally, if struvite is to be recovered, the implementation of the precipitation unit after digestion is also beneficial as higher temperatures increase struvite purity (Fig. 10.5).

The proposed treatment train configuration targeting struvite and AmS recovery is presented in Figure 10.7. Note that extraction of the precipitated fertilizer is included in the NRM-Prec, so no additional settling tank is required. Moreover, in order to save energy, a closed air loop between stripper and scrubber is considered, where the 'clean' air from the scrubber is recycled back to the stripper (BEC, 2014).

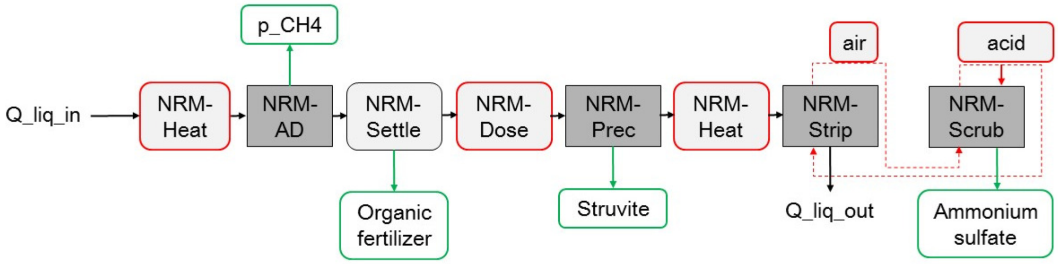


Figure 10.7 Proposed treatment train configuration targeting struvite and ammonium sulfate fertilizer. Red = consumable (= cost). Green = recovered resource (= revenue). AD = anaerobic digestion; Dose = chemical dosing; Heat = heat exchanger; Prec = precipitation/crystallization; p = partial pressure in the biogas; Q_liq = liquid flow rate; Scrub = scrubber; Strip = stripper.

Also, depending on the input P concentration, local fertilizer legislations, and operational conditions in the digester, pre-treatment (e.g. acidification + mechanical treatment; Chapter 7) of the digestate prior to solid-liquid separation may be considered in order to increase the amount of P in the liquid fraction (for subsequent recovery as struvite, Ca/Mg-P precipitate, or concentrated P-solution), as well as the local marketing potential of the (P-poor) organic thick fraction. However, the use of HCl for acidification is discouraged if subsequent stripping is supposed to occur (see above).

If the market for calcium phosphate fertilizers would be more advantageous than the struvite fertilizer market, then the use of $Ca(OH)_2$/CaO may be considered instead of $Mg(OH)_2$/MgO for P precipitation, while the phase separation unit may not be needed (depending on the required product quality). Moreover, due to legislative constraints in some regions, it may be more interesting to separate N from P in order to obtain both a pure N and P fertilizer. In this case, NH_3 stripping prior to Mg-P or Ca-P precipitation may be beneficial so as to reduce N losses through precipitation (and volatilization) in the precipitation unit. However, in that case P precipitation on the stripping column may occur (depending on the technology provider). Hence, a new optimization problem arises.

It can be concluded that the unit process GSA results are very useful for configuration of an optimal treatment train for nutrient recovery. However, the optimal configuration also depends on local/regional fertilizer legislations and markets, next to the input flow characteristics, and should therefore be evaluated in function of these. As an example, a treatment train GSA and optimization experiment is presented below for pig manure (Scenario B) as a case study, supposing that there is a (local) market for struvite and AmS fertilizer. A generic algorithm for configuration of nutrient recovery facilities as function of input flow characteristics and fertilizer markets/legislations is presented in Chapter 11.

10.3.3 Treatment train GSA: Case study pig manure

First, a GSA was conducted for the treatment train presented in Figure 10.7 using the pig manure input range for the NRM-AD (Scenario B, Table 10.4) and the same factor variation ranges as for the individual process GSAs (Scenario B, Tables 10.4-10.7). Compared to the GSA on the individual unit processes, only the concentration of seed material was eliminated as factor (see Section 10.3.1.2). As mentioned before, a request for proposals was distributed to key technology providers in the field of nutrient recovery in order to obtain reactor dimensions (and capital costs) for each unit process (Table 10.1) in the treatment train presented above (Fig. 10.7). Flow rates were subject to change in order to cover the impact of a typical HRT range on the performance indicators. For this treatment train GSA, the model output evaluated was the net treatment train cost, as defined in Section 10.2.4.

As one could expect, due to the large number of factors considered, high VIF values were obtained indicating a multicollinearity problem, although the R^2_{adj} value was higher than 0.7. To overcome this issue, the input manure characteristics to the NRM-AD were fixed at the default values (= average values for Scenario B; Table 10.4). Only the input Ca content and alkalinity (S_C_4_) to the digester were allowed to change, as these components are often added during pig manure digestion in order to control the digester pH and so augment process stability (see Section 10.3.1.1). The results of this second analysis showed low VIF values (< 1.06), but now the R^2_{adj} was out of the range of a qualitative linear model (< 0.7). Nevertheless, as mentioned before, within the scope of this study, the obtained SRCs and tSRCs may still be used for factor prioritization. The value of the SRC itself should, however, be interpreted carefully in terms of quantitative estimates of the variance contributions.

The selected factors which have an important impact on the net treatment train cost according to the different CFTs are shown in Table 10.16 (Details: Appendix 10: Table A10.11) and described below per unit process.

Table 10.16 Prioritized factors for the net operational cost of the nutrient recovery treatment train (Fig. 10.7), including operational factors and kinetics. Grey = high importance (CFT2); light grey = moderate importance (CFT3); salmon = low importance (CFT 4). CFT = cut-off threshold.

Factor	SRC	Factor	SRC
NRM_Strip.k_Hydroxyapatite	0.080	NRM_AD.S_C_4_	-0.042
NRM_Strip.k_$Mg_3(PO_4)_2$	0.075	NRM_Prec.k_Calcite	-0.041
NRM_Strip.k_Calcite	0.071	NRM_Prec.k_Vaterite	-0.040
NRM_Strip1.k_$Fe(OH)_2$	-0.070	NRM_Prec.k_Dolomite	0.039
NRM_Strip.D_CO_2_g_	-0.068	NRM_AD.kdec_xsrb_pro	0.039
NRM_Strip.D_N_2_g_	-0.066	NRM_Strip.k_Dolomite	-0.039
NRM_Scrub.Q_liq_in (acid)	0.063	NRM_Prec.k_$CaHPO_4{:}2H_2O$	0.038
NRM_Prec.k_Aragonite	0.062	NRM_Prec.k_$Ca_3(PO_4)_2$_beta	0.038
NRM_AD.k_$CaHPO_4{:}2H_2O$	0.059	NRM_AD.k_FeS_ppt_	0.038
NRM_Prec.k_Vivianite	0.057	NRM_Heat_Strip.T_target	-0.037
NRM_AD.k_Mackinawite	0.057	NRM_AD.Q_liq_in	-0.036
NRM_Strip.k_Magnesite	-0.056	NRM_Prec.k_Gibbsite	0.034
NRM_Strip.k_$CaHPO_4{:}2H_2O$	-0.055	NRM_AD.km_srb_ac	-0.034
NRM_AD.k_$MgHPO_4{:}3H_2O$	-0.052	NRM_AD.kLa_H_2	0.033
NRM_Prec.k_Hercynite	-0.048	NRM_AD.k_$AlPO_4$	0.030
NRM_Strip.D_NH_3_g_	-0.046	NRM_Prec.k_Hydroxyapatite	0.029
NRM_AD.k_Siderite	-0.043	NRM_AD.kdec_xsrb_h	0.030
NRM_AD.S_Ca	-0.043	NRM_Scrub.D_CH_4_gas	0.029

From the treatment train GSA, it can be seen that, except for the stripping unit, in majority the same factors were selected as for the unit process GSAs above, strengthening the validity of the individual analyses.

Overall, the most important factors determining the net treatment train cost seem to be related to the **stripping unit** (NRM-Strip), i.e. the precipitation/dissolution rate of hydroxyapatite ($Ca_5(PO_4)_3OH$), $Mg_3(PO_4)_2$, and calcite ($CaCO_3$). When precipitation occurs in the stripper, these precipitates may cause scaling on the packing material, thereby increasing the air and chemical requirements for effective NH_3 stripping and hence the overall net costs (cfr. Section 10.3.1.3). The fact that the selected Ca-P and Mg-P precipitates are different than those found with the individual stripping unit GSA (Section 10.3.1.3) is related to the Mg dose added for P precipitation prior to stripping and to the fact that part of the Ca, Mg, and P is already removed prior to the stripper (depending on the MC scenario). As also diffusion coefficients in the stripper and the stripping temperature are among the most important factors, it is likely that the heat requirements and possibly the air requirements in the stripper are of principal importance for determination of the net treatment train cost.

Next, for the **acidic air scrubber** (NRM-Scrub), especially the acid dose influenced the net treatment cost, as it impacts both the chemical costs and the revenues obtained form ammonium sulfate recovery. Also the diffusion coefficient of CH_4 was influential, similar as was observed for the unit process GSA (Table 10.14). Note that the stripping temperature (which is an important factor, see above) also determines the temperature of the gas flow in the scrubber, while the gas flow leaving the stripper determines the flow rate into the scrubber.

For the **anaerobic digester** (NRM-AD), the main factors influencing the net treatment train cost are the amount of available Ca and the input alkalinity (= chemical cost and/or impact on CH_4 production), the precipitation/dissolution rate of P precipitates (= impact on Ca availability in the digester and on P recovery), and of Fe precipitates (= impact on P recovery and S removal by SRBs). Also, some SRB kinetic parameters were important (= competition with CH_4 producers). An interesting observation is that the digester temperature had only a minor effect on the overall net treatment train cost. Hence, the increasing biogas production (and so revenues) at higher temperatures seems in this case not worth the increasing cost of raising the temperature of the large waste flow. A detail of the MC results showing the revenues obtained from CH_4 production as function of the costs related to digester heating is shown in Figure 10.8.

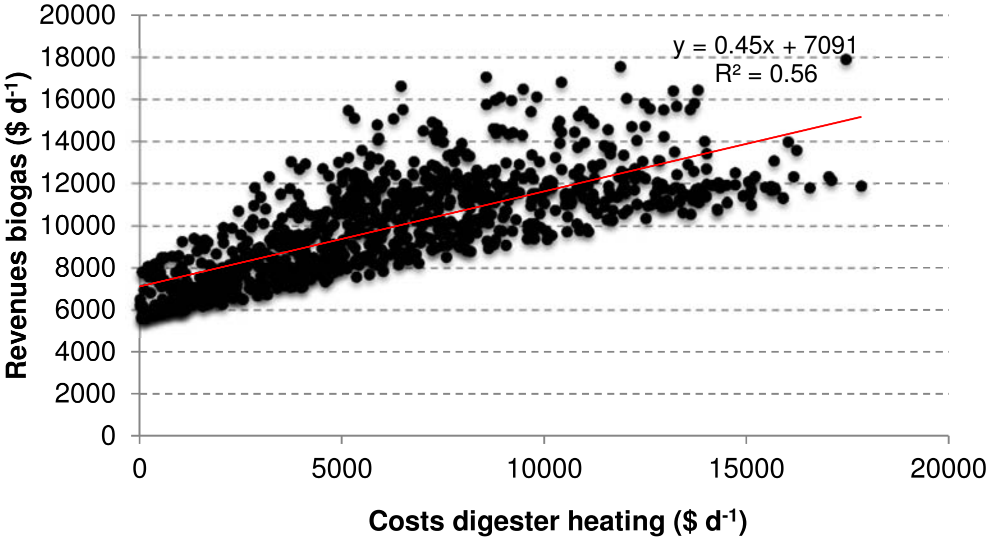


Figure 10.8 Monte Carlo simulation results for the pig manure treatment train (Fig. 10.7): revenues ($ d^{-1}) from CH_4 production (considering 22 % losses) as function of digester heating costs ($ d^{-1}), considering that the actual digester heat requirement (including losses) is about 1.9 times higher than the theoretical heat required for manure heating (CDM, 2009; Tchobanoglous *et al.*, 2003; USEPA, 1981; Vaneeckhaute, 2009). Reference temperature = 20 °C. $ = USD; 1 USD = 1.14 CAD = € 0.80 (November 2014).

The presented situation accounts for an actual digester heat requirement (including losses) that is about 1.9 times higher than the theoretical heat required for manure heating, as e.g. observed in CDM (2009), Tchobanoglous *et al.* (2003), and Vaneeckhaute (2009). Also 22 % CH_4 losses were assumed during anaerobic digestion and its conversion into energy (Section 10.2.4). The fact that the slope of the linear regression on the MC output is lower than 1 confirms the statement above, that the increasing revenues from biogas production at higher temperature are not worth the higher heating costs. Nevertheless, it can be seen on the basis of the variation of the revenues for a particular heating cost that calibration of the prioritized factors will be important for process and treatment train optimization.

Finally, as expected, for the **precipitation unit** (NRM-Prec), mainly factors that may interfere with P and struvite precipitation are important, i.e. Ca, Mg, Fe, and Al precipitation/dissolution kinetics.

10.3.4 Treatment train optimization: Case study pig manure

The aim of this optimization experiment was to use the NRM library for optimization of the operational settings of the various unit processes in the proposed nutrient recovery treatment train (Fig. 10.7), designed using the (unknown) guidelines of the technology providers. Hence, as mentioned before, the reactor dimensions were fixed to the design values for each unit in the treatment train obtained from the various technology providers (Table 10.1), whereas the operational envelope (including flow rates; Table 10.9) was optimized in order to reduce net operational costs and to identify the true capacity of the system. The optimized scenario obtained is discussed in Section 10.3.4.1. The resulting economic analysis is presented in Section 10.3.4.2.

10.3.4.1 Optimized factors and performance indicators

The optimized values of the operational factors considered in the optimization experiment are compiled in Table 10.17. Key performance indicators that were calculated from the optimized factors are also provided.

A first important remark is that the obtained optimal digester HRT (15 d) is low, definitely for an operational digester temperature of 28 ℃ (= lower end of the mesophilic range). It could even be questioned if such a scenario is realistic. A literature survey provided evidence that anaerobic digestion of swine manure at only 20 ℃ for 15-20 d can be considered promising for reducing indigenous performance indicators and pathogenic microorganism populations, while providing sufficient waste stabilization at relatively low costs (Côté *et al.*, 2006; Kearny *et al.*, Masse *et al.*, 2004; Nasir *et al.*, 2012). Wilkie (2000) evaluated 15 d as the lower acceptable limit for pig manure monodigestion in a CSTR to guarantee a stable process, especially at low temperature. However, optimal ranges of 5-20 d have also been reported for various operational temperatures (USDA, 2007). Manure has a relatively low biodegradability (see also Chapter 7)

Table 10.17 Value of the optimized factors in the treatment train optimization experiment and of the resulting performance indicators. Red = impact on costs. Green = impact on revenues. COD = chemical oxygen demand; f_ns_P = fraction of non-settleable precipitates; f_ns_X = fraction of non-settleable biological particulate solids.

	OPTIMIZATION		PERFORMANCE	
Unit process	**Optimized factor**	**Value**	**Indicator**	**Value**
Anaerobic digester	Temperature (°C)	28	Heat input (best/worst case; MWh$_{th}$ d^{-1})[a]	24-41
	Flow rate (m^3 d^{-1})	2,700	HRT (d)	15
	Ca-dose (kg d^{-1})	0	COD degradation (%)	55
			VSS degradation (%)	45
			CH_4 production (m^3 m^{-3} manure)	5.8-7.4[b]
			Heat recovery (MWh$_{th}$ d^{-1})[c]	72
			Electricity recovery (MWh$_{el}$ d^{-1})[c]	68
Phase separation	f_ns_P	0.25	Organic fertilizer production (ton X_COD d^{-1})[d]	15
	f_ns_X	0.05		
Precipitation unit	$Mg(OH)_2$ dose (ton d^{-1})	1.5	Mineral fertilizer production (ton P d^{-1})[e]	1.5
	Seeding Kstruvite (g m^{-3})	3.1	P recovery (%)[e]	99
	Seeding Struvite (g m^{-3})	3.1		
	Precipitate flow rate (m^3 d^{-1})	150		
Stripper	Temperature (°C)	55	Heat input (best/worst case; MWh$_{th}$ d^{-1})[f]	42-85
	Gas flow rate (Mm^3 d^{-1})	1.5	Electricity input (MWh$_{el}$ d^{-1})	2.9
	Gas pressure (atm)	4		
Scrubber	Acid flow rate (m^3 d^{-1})	17.5[g]	Mineral fertilizer production (ton N d^{-1})[h]	5.0
	Liquid recycle rate (m^3 d^{-1})	2.5	NH_4-N recovery (%)[h]	84

[a] Best case: 10 % heat losses (Wu and Bibeau, 2010; Zupancic and Ros, 2003). Worst case: heat requirement that is 1.9 times higher than the theoretical heat required for manure heating (CDM, 2009; Tchobanoglous *et al.*, 2003; USEPA, 1981; Vaneeckhaute, 2009). Waste input temperature: 20 °C (Khiewwijit *et al.*, 2015; USEPA, 1981).

[b] First number: considering 22 % CH_4 losses (see below); second number: not accounting for CH_4 losses.

[c] Conversion of CH_4 in conventional heat and power system: 40 % thermal energy, 38 % electricity, 22 % losses (Verstraete and Vlaeminck, 2011).

[d] Recovered as digested solids (= particulate COD + Ca, Fe, and Al precipitates) in NRM-Settle.

[e] Recovered as Mg/P fertilizer. % recovery was calculated from soluble P that enters the NRM-Prec unit. The same maximal % recovery was found by Ye *et al.* (2010).

[f] Best case: 50 % internal heat recovery in the stripping system. Worst case: no heat recovery.

[g] Equal to 31.5 ton d^{-1} of H_2SO_4 at a density of 1,800 kg m^{-3}.

[h] Recovered as a 28 % ammonium sulfate (AmS) solution containing 6 % N in the NRM-Strip/NRM-Scrub units. % N recovery was calculated from soluble N that enters the stripper.

and high acidification and NH_3 inhibition potential compared to other organic waste sources (Jhong-Hwa *et al.,* 2006; Ossiansson and Lidholm, 2008; Section 10.3.1.1). Hence, in order to improve the feasibility of manure digestion, operation at low temperature and high rate is of increasing interest, especially in cold regions (Jhong-Hwa *et al.,* 2006; Ossiansson and Lidholm, 2008). Hence, the obtained lowest-cost scenario was found to be acceptable, although to date rather uncommon. It should be remarked that the more conventional scenario with a residence time of 15 d at 50 °C was competitive with the optimal scenario found above. However, in this case a $Ca(OH)_2$ dose of about 21 ton d^{-1} was required.

Although the **optimal digester HRT** was low, the optimal loading rate to the digester was about 2.2 kg VSS m^{-3} d^{-1} (± 65 % VSS on TS content), which is an average value for an anaerobic CSTR (Tchobanoglous *et al.*, 2003). The value obtained for **energy recovery** (≈ 52 kWh m^{-3} manure ≈ 5.8 m^3 CH_4 m^{-3} or 7.4 m^3 CH_4 m^{-3} without energy losses) is at the lower end of the experimental range obtained by Cesur and Albertson (2005) from which the input data were used, i.e. 5.6-10 m^3 CH_4 m^{-3}. This is evidently due to the lower residence time (15 d vs. 33-45 d) and reactor temperature (28 vs. 35 °C) in the simulated system. As such, ± 55 % COD and ± 45 % VSS removal were obtained in the simulated system, while at full-scale an actual average removal of 71 % COD and 65 % VSS was observed. The obtained % COD and VSS destruction are in line with the experimental findings of Elbeshbishy *et al.* (2010) for mesophilic anaerobic digestion of hog manure at a HRT of 15 d, i.e. 55-60 % and 45-50 %, respectively. Also the obtained CH_4 production is in good agreement with full-scale values for large-scale mesophilic monodigestion of pig manure obtained by Lithania (2006), i.e. 7.6 m^3 CH_4 m^{-3} at a HRT of 15 d, and by Kasper and Peters (2012), i.e. 5.2-13 m^3 CH_4 m^{-3} pig manure. Due to the high acidification and NH_3 inhibition potential during monodigestion of pig manure (Section 10.3.1.1), a higher liquid flow rate was in this case more beneficial than the addition of a high Ca dose (optimum = no external Ca addition).

The reason for the relatively low digester temperature could be attributed to the fact that the additional gas that can be produced at higher temperature is in this case not worth the energy needed to raise the digester temperature (Section 10.3.3). Although the average trend of the MC output confirms this statement, Figure 10.8 shows that a more optimal scenario may be possible (only looking at the digester unit), resulting in an income of about 16,000 \$ d^{-1} (present case: ± 10,500 \$ d^{-1}; see Section 10.3.4.2) at a heating cost of 6,000 \$ d^{-1} (present case: ± 3,500 \$ d^{-1}; Section 10.3.4.2). One explanation for this observation may be that in the MC analysis all operational and kinetic factors were considered variable, whereas in the optimization experiment, the default values were used for all factors other than the operational items mentioned in Table 10.17. This again underlines the importance of an accurate calibration of the prioritized kinetics.

Another possible reason for both the rather low HRT and temperature is related to the interactions of the digester's operating conditions with the economics of nutrient recovery downstream in the treatment train. As such, total revenues from mineral fertilizer production were in this case higher than the revenues obtained through biogas production. On top of that, the digested separated solids obtained may be reused as an organic fertilizer containing N, P, and K (from bacterial cells), as well as Ca and Mg. Depending on local legislations, important revenues can be obtained from organic fertilizer marketing. However, in other (often nutrient-rich) regions, a cost is attached to the disposal of this product. Depending on the situation, additional costs and energy requirements may also be attributed to solids drying and/or pasteurization. Moreover, in regions with P saturated soils, a pre-treatment prior to solid-liquid separation may be implemented in order to stimulate the release of P in the liquid fraction for subsequent recovery as struvite, Ca/Mg-P precipitate, or concentrated P-solution, while increasing the local valorization potential of the (P-poor) organic thick fraction (Chapter 7).

Furthermore, an interesting observation is that under the optimal conditions obtained an important amount of Ca (± 64 % of the daily digester input) was removed as **$CaCO_3$ precipitate** with the separated solids. Hence, as expected, liquid-solid separation of digestate prior to struvite precipitation and NH_3 stripping may provide an interesting measure to reduce Ca inhibition in the downstream processes. Indeed, no Ca precipitation was detected in the stripping column or in the precipitation unit. However, the fraction of non-settleable precipitates (f_ns_P) was found to be an important factor, for which an optimal value of 25 % was found. In practice this value may be hard to reach without the addition of coagulants, such as lime ($Ca(OH)_2$ or CaO). Excess lime may also cause Ca/P precipitation at pH > 10. Depending on local fertilizer markets, the latter may be interesting or not. Further research is required to experimentally determine the f_ns_P in the phase separation unit under different operating conditions and input waste flow compositions.

Also interesting is the fact that the use of **$Mg(OH)_2$ as the only base** for both P precipitation and N stripping (+ CO_2 stripping) resulted in high recovery efficiencies for both N and P at low costs. As such, the inhibitory effect of Cl (from $MgCl_2$:$6H_2O$ dosing) on N stripping and of Na (from NaOH dosing) on P precipitation can be reduced. The obtained electricity need for air pumping is relatively low, as it was assumed that air is continuously recycled between the stripper and scrubber unit (RVTPE, 2014). This electricity need can be completely covered by the recovered electricity in the conventional heat and power (CHP) system. Note that the heat needed for stripping was higher than that for digestion. However, internal heat recovery in the strip-scrub system can be achieved (recuperation from the stripped flow), resulting in total energy savings of more than 50 % (Colsen, 2014; RVTPE, 2014). The heat recovery potential in the strip-scrub system will determine whether all heat requirements can be covered by the heat produced by the CHP system or whether external heat has to be supplied.

No **effluent quality** criteria were set for the present case as the focus was on nutrient and energy recovery. The final effluent resulting from the stripping unit contains very low soluble P concentrations (< detection limits of analytical instruments, i.e. 0.05 mg L^{-1} for a continuous flow analyzer; Chapter 6), and relatively low N concentrations, i.e. ± 350 mg L^{-1}. This N content is generally too high for disposal, however, the water may be recycled as process water in the plant, e.g. for cleaning of the phase separation unit. If specific effluent quality criteria for N need to be achieved, the treatment train may be further optimized to reach these specifications. A low-cost final effluent treatment may also be considered (Chapter 2) or the water may be recycled to a nearby wastewater treatment plant (usually onsite in case of sludge digestion).

11.3.4.2 Economic analysis

An overview of the annual treatment train operational costs and revenues, as well as the capital costs for each unit process is presented in Table 10.18. The estimation is based on an operational basis of 8,000 hours per year, which is a common figure (ECN, 2014; Vaneeckhaute, 2009). For convenience of discussion, all costs are expressed in US dollars (1 USD = 1.14 CAD = € 0.80; November 2014).

Table 10.18 Costs and revenues ($\mathrm{k\$\ y^{-1}}$) for the optimized nutrient recovery treatment train. $ = USD; 1 USD = 1.14 CAD = € 0.80 (November 2014). AD = anaerobic digester; CHP = conventional heat and power system; CAPEX = capital expenditures; OPEX = operational expenditures.

COSTS ($\mathrm{k\$\ y^{-1}}$)	**FIXED COSTS**	**VARIABLE COSTS**					**REVENUES RESOURCE RECOVERY**		
		OPEX				**Maintenance, material & labor**[h]	**Biogas + fertilizer**	**Biogas + fertilizer**	**CO_2 credits**[k]
UNIT	**CAPEX**	**Heat (best)**[f]	**Heat (worst)**[g]	**Electricity**	**Chemicals**		**best**[i]	**worst**[j]	
AD + CHP[a]	22,500	694	1,198	621	-	977	3,547	3,547	1,334
Phase separation[b]	1,250	-	-	2.5	to be evaluated	226	1,741	0	-
Precipitation[c]	4,750	-	-	6.3	102	48	1,468	1,468	-
Strip/Scrub[d]	680	1,034	2,069	74	913	6.8	2,365	2,365	-
Other[e]	2,000	-	-	-	-	-	-	-	-
Rounded total	**31,000**	**1,750**	**3,250**	**700**	**1,000**	**1,250**	**9,100**	**7,400**	**1,350**

[a] Unit process construction + equipment costs: eight digester tanks of 5,000 m^3 with floating cover, gas circulation unit, heating unit, gas safety equipment, sludge pump, and conventional heat and power system (ECN, 2014; Symantec, 2014; USEPA, 1981).

[b] Unit process construction + equipment costs: standard gravity thickener (Symantec, 2014; USEPA, 1981).

[c] Unit process construction + equipment costs: precipitation/crystallization unit and sludge pump (Technology provider X, 2014).

[d] Unit process construction + equipment costs: feed pump, stripper column, stripper discharge pump, ventilator, absorption column, circulation pump, sulfuric acid dosing pump, feed heat exchanger, secondary heat exchanger, piping and fittings (Technology provider Y, 2014).

[e] Other construction costs, such as land costs (agricultural land is assumed), legal costs, inspection costs, costs for lab and administration buildings, and miscellaneous costs (Symantec, 2014; USEPA, 1981).

[f] Best case: 10 % heat losses (Wu and Bibeau, 2010; Zupancic and Ros, 2003). Waste input temperature: 20 °C (Symantec, 2014; USEPA, 1981).

[g] Worst case: heat requirement that is 1.9 times higher than the theoretical heat required for manure heating (CDM, 2009; Tchobanoglous *et al.*, 2003; USEPA, 1981; Vaneeckhaute, 2009).

[h] Operator labor rate: 51.5 $\$\ h^{-1}$ (Symantec, 2014; USEPA, 1981). Maintenance labor rate: 43.5 $\$\ h^{-1}$ (Symantec, 2014; USEPA, 1981).

[i] Best case: 50 % internal heat recovery in the stripping system.

[j] Worst case: no heat recovery.

[k] Net CO_2-equivalent emission savings through manure digestion compared to manure spreading: 0.1 ton m^{-3} manure (Zwart *et al.*, 2006).
Revenues CO_2 emission reduction credits: 15 $\$\ ton^{-1}$ CO_2-equivalents (IPCC, 2007; LLC, 2012).

First, it should be remarked that fixed and variable costs are highly influenced by the specifications of the applied technology (i.e. the design, the material used for construction, isolation, etc.), the options for recovered product valorization (e.g. biogas conversion into electricity, heat, fuel, or other), as well as the location (climate, market prices, land costs, regulations, etc.). Hence, it should be emphasized that various assumptions (see below) had to be made to obtain the values represented in Table 10.18. The aim of the economic analysis was merely to give an idea (order of magnitude) of the economic feasibility of installing a nutrient recovery treatment train, rather than to provide exact values.

In this case study, the **capital costs** (including equipment and construction costs) for each unit process were obtained from the same technology providers who delivered the design reactor dimensions for the treatment train set-up (Table 10.1). When possible, the values were compared with values obtained from simulations with the CAPDET (Computer Assisted Procedure for the Design and Evaluation of Wastewater Treatment Systems; Symantec, 2014; USEPA, 1981) software to ensure that the obtained costs are realistic. The complete treatment train was also implemented in CAPDET in order to estimate other important direct and indirect construction costs, not included in the unit process cost estimations, such as land costs (agricultural land was assumed), legal costs, inspection costs, costs for lab and administration buildings, and miscellaneous costs (Symantec, 2014; USEPA, 1981). For the nutrient recovery systems not yet available in CAPDET, user-defined unit processes were implemented, using the specifications (capital costs, dimensions, etc.) obtained by the technology providers.

Operational costs in terms of **heat and chemical consumption** were calculated from the derived data provided in Table 10.17 (red values). For the heat requirements, both a worst and best-case scenario were considered. In the worst case, an above-ground digester was assumed, with heat requirements of about 1.9 times the theoretical heat required for manure heating, similar as observed in CDM (2009) and Tchobanoglous *et al.* (2003), and assumed by the CAPDET software. Also, in this case, no heat recovery in the strip-scrub system was supposed. In the best-case scenario, a belowground anaerobic digester was assumed with heat losses of about 10 % of the heat required for manure heating (Wu and Bibeau, 2010; Zupancic and Ros, 2003). In this case, 50 % internal heat recovery in the strip-scrub system was considered, as is in practice most often the case (Colsen, 2014; RVTPE, 2014). In each scenario, an average input manure temperature of 20 °C was supposed, as e.g. in the CAPDET software and in Khiewwijit *et al.* (2015). The final effluent leaves the stripper at 25 °C (Technology provider Y, 2014). Hence, the temperature difference between the final effluent and the input manure to the digester is in this case too small for heat recovery between these flows (Technology provider Y, 2015).

The estimated operational costs for air pumping were also directly calculated from the air requirements provided in Table 10.17. **Electricity consumption** related to the digester can be estimated at ± 24.5 MWh_{el} d^{-1} or 33 MJ ton^{-1} manure, resulting in a cost of ± 1,850 \$ d^{-1} (Zwart *et al.*, 2006) for a farm-scale digester of similar capacity as in the present study. Electricity use for the phase separation unit (gravity thickener) can be estimated at ± 100 kWh d^{-1} or 0.037 kWh ton^{-1}, resulting in a cost of about 7.5 \$ d^{-1} (USEPA, 1981; Zwart *et al.*, 2006). For the struvite precipitation unit, electricity use would be ± 250 kWh d^{-1} or 0.094 kWh m^3, which results in another 19 \$ d^{-1} (Seymour, 2009).

Maintenance, material, and labor costs for the precipitation unit and the strip/scrub unit were obtained from the technology providers who delivered a proposal for this case. For the anaerobic digester and phase separation unit, these data were obtained by running simulations with the CAPDET software (Symantec, 2014; USEPA, 1981), with user-defined input of the design data, operational conditions, and waste flow characteristics. Maintenance costs for the CHP unit were also included, calculated at 0.3 \$ kWh^{-1} produced at an operational basis of 8,000 h y^{-1} (ECN, 2014).

Revenues from biogas production and fertilizer marketing were assumed. The methane produced was supposed to be valorized using a conventional heat and power (CHP) system with a conversion efficiency of 40 % as thermal energy, 38 % as electricity, and with 22 % losses (Verstraete and Vlaeminck, 2011). It was supposed that a market exists for the produced ammonium sulfate fertilizer and Mg-P fertilizer, and that the products can be valued according to the current marketing value for N and P (Table 10.10). No incomes were currently considered for S, but in the future this macronutrient may also be of value (± € 0.75 kg^{-1} S; Triferto, Ghent, Belgium, personal communication 2014), depending on the S need of the agricultural crop (Chapter 2: Section 2.4.3). In the best-case scenario, also a market for the produced organic fertilizer was supposed according to its nutrient content, in contrast to the worst-case scenario.

Furthermore, when digesting animal manure, a significant reduction in CO_2 emissions can be expected. For pig manure, Zwart *et al.* (2006) quantified that 0.1 net tons of CO_2 equivalents can be saved per m^3 of manure when treated by anaerobic digestion as compared to land spreading. In the economic analysis, it was assumed that an income of 15 \$ ton^{-1} saved CO_2 equivalents can be obtained from **CO_2 emission reduction credits** for anaerobic digestion under the Clean Development Mechanism defined in the Kyoto Protocol (Ciborowski, 2001; IPCC, 2007; LLC, 2012). Note that this assumption is based on current (conservative) US carbon prices. World carbon prices today are roughly 40 \$ ton^{-1} CO_2 equivalent (LLC, 2012). Other potential subsidies and fees, for example, for accepting animal manure in high-nutrient regions (Chapter 4), were not included in the analysis.

As depreciation costs and loan service costs vary depending on when and where the money is borrowed, companies are most often interested in the **yearly net cash flows** determined by the variable costs and revenues. On the basis of the optimized values obtained and all assumptions made in this case study, the yearly net variable cost balance can be positive. Financial benefits could even be obtained, estimated at about 2.8-6.5 \$ m^{-3} manure y^{-1} (55-130 \$ $tonne^{-1}$ TS^{-1} y^{-1}) for the large-scale project and associated assumptions in this case study. Hence, in terms of net variable cash flows, it is likely that in practice **a ZeroCostWRRF (water resource recovery facility at zero cost) could be achieved**. As one could be critical on the optimized digester temperature and residence time used in this study (Section 10.3.4.1), the economic analysis was also performed for a digester operated at a temperature of 50 °C with a HRT of 15 d and a $Ca(OH)_2$ dose of 21 ton d^{-1} (see above). The financial benefits in this scenario amounted to 2-6 \$ m^{-3} manure y^{-1}, which is as stated above very competitive with the optimal scenario. Hence, if a high-temperature treatment is required for product hygienisation, the latter scenario may be targeted, though it is less sustainable in terms of consumables (heat and chemical use). At a HRT of 30 days, the financial benefits amounted to about 3 \$ m^{-3} y^{-1} in the best case, but a loss of 1.5 \$ m^{-3} y^{-1} was obtained in the worst case. The most important factor impacting the operational cost balance, next to the HRT, is the potential for heat recovery. Hence, process and design engineers should focus on the optimization of heat balances in the configuration of future nutrient recovery facilities.

Furthermore, when considering the capital costs, one may be interested in the net present value (NPV), which is the sum of the present values of incoming and outgoing cash flows over a period of time, including the investment cost at time 0 (Eq. 10.2; Charles *et al.*, 2014):

$$NPV(i,N) = \sum_{t=0}^{N} \frac{R_T}{(1+i)^t} - NINV \qquad \boldsymbol{Eq. (10.2)}$$

in which R_T represents the net cash flow, i.e. cash inflow – cash outflow, at time t, N is the total number of periods (y), t is the time of the cash flow, i is the discount rate, i.e. the rate of return that could be earned on an investment in the financial markets with similar risk, and $NINV$ is the net investment. The purpose of the NPV is to help analysts and managers decide whether or not new projects are financially viable. Essentially, the NPV measures the total amount of gain or loss that a project will produce compared to the amount that could be earned simply by saving the money in a bank or investing it in some other opportunity that generates a return equal to the discount rate. If a long-term project has a positive NPV, then it is expected to produce more income than what could be gained by earning the discount rate, which means the company should go ahead with the project.

Assuming an average discount rate of 6 % (Harrison, 2010) and a depreciation period of 20 years for all unit processes (Technology provider X, 2014; Symantec, 2014; USEPA, 1981), except for the stripping unit, for which a depreciation period of eight years was assumed (Technology provider Y, 2014), the nutrient recovery project presented above would have a positive NPV in year 7 of operation in the best case. This value is at the lower end of the range of payback times for existing anaerobic digestion plants without a nutrient recovery treatment train in the US, i.e. 6.9-8.9 years based on a survey of 24 plants (Vik, 2003). **The NPV after 20 years amounted to about 3.5 M \$, resulting in average net financial benefits of ± 2 \$ m^{-3} manure y^{-1} (40 \$ ton^{-1} TS y^{-1}) over 20 years**.

The internal rate of return (IRR), i.e. the discount rate that makes the NPV equal to zero, after 20 years in this case was 18 %, which is about the same as the estimated best-case IRR (including subsidies) after 20 years for an operational full-scale WRRF in the Netherlands, i.e.

19-21 % (Gebrezgabher *et al.*, 2010). In the worst-case scenario, the IRR after 20 years was only 5 %. Generally, the project should only be accepted if the IRR is higher than the firm's cost of capital. Hence, based on the analysis (worst vs. best case), it can be stated that the feasibility of implementing a resource recovery project will depend a lot on the heat recovery potential, the marketing potential of the fertilizers, as well as the subsidies obtained. For instance, when accounting for an income of 40 \$ ton^{-1} net saved CO_2-equivalents (= current global market price of carbon; LLC, 2012) instead of the conservative US carbon prices, the IRR would be around 26 % and 14 % in the best and worst case, respectively, resulting in a revenue of 1.3-3.4 \$ m^{-3} manure y^{-1} (25-70 \$ ton^{-1} TS y^{-1}) averaged over 20 years.

Finally, it should be remarked that the **benefits of nutrient recovery over the whole nutrient value chain** may be much higher than presented above, taking into account, for instance, the saved nutrient emissions to air and water bodies due to spreading and storing of animal manure, and the saved energy and costs for mineral fertilizer production. For example, only the production of mineral N through the Haber Bosch process consumes 35.2-40.5 GJ ton^{-1} NH_4, which is equal to about 750-850 \$ ton^{-1} NH_4 (Chapter 4; EFMA, 2014; Foged, 2011; Vaneeckhaute *et al.*, 2013b). Moreover, Zwart *et al.* (2006) estimated that anaerobic digestion of animal manure could result in an overall nutrient emission (e.g. greenhouse gases, leaching, etc.) reduction of 95 % compared to manure spreading. Holistic life cycle analyses should be aspect of further research, aiming at the evaluation of the overall environmental impact of anaerobic digestion and nutrient recovery treatment trains for bio-based fertilizer production, as presented above. Such studies are currently being conducted by the Luxembourg Institute of Science and Technology (LIST, Esch-sur-Alzette, Luxembourg; Vázquez-Rowe *et al.*, submitted), Bangor University (Gwynedd, UK; Vaneeckhaute *et al.*, in preparation), and the University of Bath (Bath, UK; Adams and Vaneeckhaute, in preparation) using the data collected in this dissertation (see Chapter 12). Moreover, in a next stage, the NRM treatment train could be coupled to soil nutrient balance models, e.g. the NDICEA modelling tool (Chapter 5), and agro-economic tools (e.g. Chapter 4) in order to optimize nutrient recovery strategies throughout the whole waste-nutrient-soil-plant system. The obtained information could then be used for further policy-making in terms of subsidies, thereby stimulating the full-scale implementation of nutrient recovery projects.

10.3.5 Research strategy limitations

The main limitations of the above strategy used for GSA and treatment train optimization that modellers should be aware of for future applications are listed below:

- For determination of the overall sensitivity measure in the unit process GSAs, each performance indicator was supposed to have an equal weight. However, depending on the application, one may be interested in allocating specific weights to each targeted model output;

- The use of uniform distributions. It was accepted that every value in the provided variation ranges has an equal probability of occurrence;
- Some factor variation ranges for GSA were estimated based on expert knowledge, since quantitative experimental data is lacking to date, e.g. for precipitation/dissolution kinetics;
- Sometimes, the obtained R^2 values for linear regression were lower than 0.7, though the results were assumed to be acceptable for factor ranking (Cosenza *et al*., 2013; Mannina *et al.,* 2012). Nevertheless, in these cases, the resulting standardized regression coefficients can not be interpreted in terms of their quantitative contribution to the variance of the model outputs. Future modellers may want to use an alternative GSA strategy for these cases, such as variance-based sensitivity analysis methods, e.g. the Extended Fourier Amplitude Sensitivity Testing (Extended-FAST) method (Cosenza *et al.,* 2014), in order to adequately quantify the effects of non-linearity. The increased computational load of these methods has to be considered though.
- The operational settings of the treatment train were optimized using a default (constant) input flow composition for pig manure as a case study. However, the composition of manure and other organic waste flows is very variable in time and between different installations (Chapters 4-5). Moreover, the GSA results showed that key performance indicators are highly influenced by the input waste flow composition. Hence, the use of other default values may result in a different optimal scenario. This means that in practice model-based optimization should be performed for each specific case using the average waste flow composition for that case. It is also recommended to frequently monitor the input waste composition, and, if required, to use the NRM library to adjust (i.e. optimize) the operational settings;
- A list of assumptions had to be made in order to perform the economic analysis. Hence, also the feasibility of a nutrient recovery project should be evaluated for each specific case. The present study only provides an order of magnitude. Aspects as, for example, local legislations and subsidies will play a major role in the evaluation;
- The NRM library itself still contains uncertainties, especially in terms of the precipitation/dissolution kinetics (Chapter 9);
- Design reactor dimensions for the different unit processes were obtained from technology providers using their in-house design guidelines for a nominal waste flow. Unit sizing is usually done according to a set of experience-based rules, using safety factors to cope with the uncertainty related to the input waste flow composition, flow rates, and other factors such as equipment failures, etc. Hence, the dimensions of the various unit processes are likely not optimally coordinated. Application of the probabilistic model-based design procedure of Talebizadeh *et al.* (2014) using the existing NMR library would be the next step if the analysis presented in this chapter is to be used for design.

10.4 Conclusions and perspectives

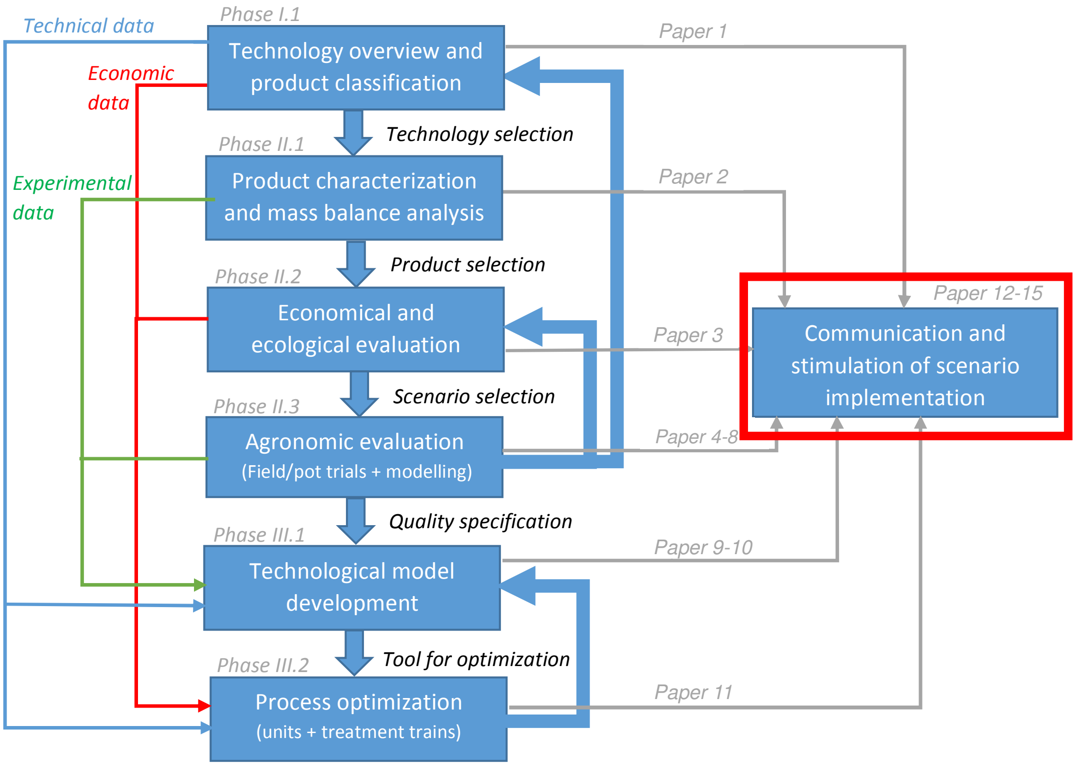
Global sensitivity analysis (GSA) using linear regression on Monte Carlo simulation outputs was found to be an appropriate tool for factor prioritization in nutrient recovery model (NRM) applications. In addition, for the adopted GSA method based on standardized regression coefficients (SRC), the use of variance inflation factors (VIF) is recommended to detect and resolve problems related to multicollinearity of factors in complex models.

Using GSA for each individual NRM unit process, factor ranking was performed for: 1) input waste flow characteristics, 2) process operational factors, and 3) NRM kinetics. For all unit processes, the variation related to the variable input waste composition resulted in a major effect on the output variation through its direct effect on the operational pH and ionic strength. GSA provided valuable insights in the interactions between unit process inputs and outputs. Major findings involve, among others, the impact of Cl inhibition on NH_3 removal in the stripping unit, the impact of Ca, Fe, and Al inhibition on P recovery in the precipitation unit, and the interaction between Fe/Al, S, and CH_4 production in the anaerobic digester.

Starting from the single process GSA results, an optimal nutrient recovery treatment train configuration was derived. Design reactor dimensions for each unit process in the treatment train (including capital cost prediction) were obtained from technology providers, given an expected nominal flow and composition arriving at each individual unit. The potential of the NRM library for optimization of the operational settings of the selected treatment train was presented by means of a case study for pig manure. An economic analysis indicated that in the best-case scenario a ZeroCostWRRF could be constructed. Under the optimized conditions and assumptions made, financial benefits could even be achieved. The net present value (NPV) after 20 years amounted to about 3.5 M USD *(4.4 M CAD; 3.1 M €)*, resulting in average net financial benefits of ± 2 USD *(2.5 CAD; € 1.8)* m^{-3} manure y^{-1} or 40 USD *(50 CAD; € 35)* ton^{-1} total solids y^{-1}, over 20 years. The internal rate of return (IRR) after 20 years was 18 %.

Nevertheless, subsidies and heat balances were found to play a crucial role in determining the feasibility of resource recovery projects. Moreover, the optimal treatment train configuration and operating conditions were also found to be dependent on local legislations and fertilizer markets. Further model-based optimization studies using the NRM library based on real cases for various waste flow compositions are required in order to confirm the above statements. Experimental research to confirm new generic observations made using GSA, for example, Cl inhibition during NH_3 stripping, is also recommended.

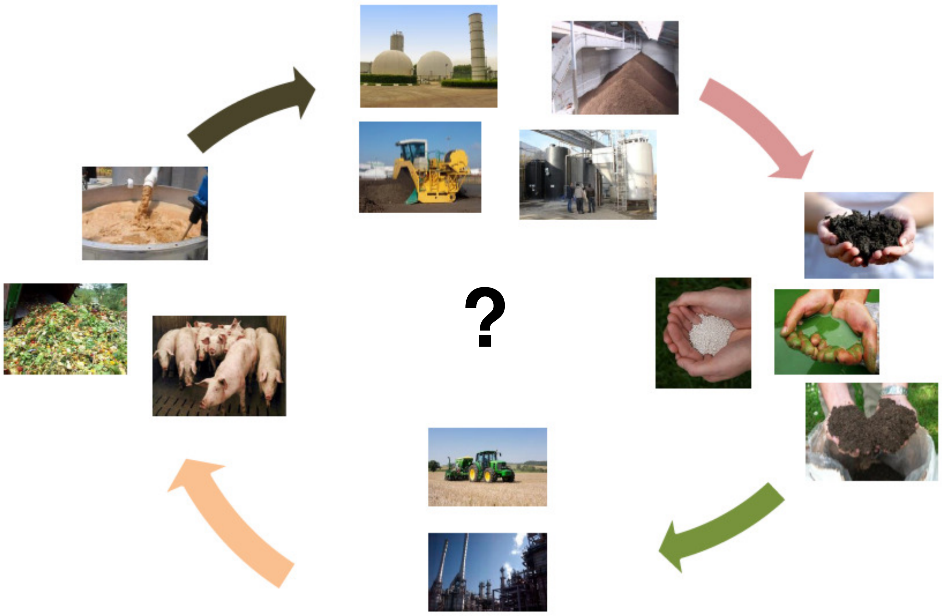
Overall, it can be concluded that the NRM library and GSA strategy developed in the present chapter provide a valuable and cost-effective framework for increased process understanding, treatment train configuration, and optimization of region-specific nutrient recovery model applications. Based on the findings, the development of a generic algorithm for configuration of nutrient recovery treatment trains as function of fertilizer markets and input waste flow characteristics is suggested (see Chapter 11). This should facilitate communication and nutrient recovery scenario implementation.



COMMUNICATION AND STIMULATION OF SCENARIO IMPLEMENTATION

CHAPTER 11:

ROADMAP FOR SETTING UP NUTRIENT RECOVERY STRATEGIES



Closing the nutrient cycle: Which way to go?
(Picture: Flemish Knowledge Center Water, Vlakwa, Kortrijk, Belgium)

Redrafted from:

Vaneeckhaute, C., Belia, E., Tack, F.M.G., Meers, E., Vanrolleghem, P.A., in preparation. Roadmap for setting up nutrient recovery strategies.

Abstract

This PhD research has revealed important insights in the agronomic, economic, and ecological value of recovered fertilizer products, in the process technological performance and operation, as well as in the unit process interactions that may occur in nutrient recovery treatment trains. Based on the results, this chapter aimed at the development of a generic roadmap for setting up strategies for nutrient recovery from digestate. First, guidelines were presented to set up an optimal bio-based fertilization strategy as function of local/region-specific fertilizer legislations. Next, instructions were provided to evaluate the feasibility of bio-based fertilizer production as function of input waste characterizations. Finally, an algorithm was developed aiming at the configuration and optimization of nutrient recovery treatment trains. Important input waste characteristics to measure and essential factors for monitoring and control were identified. As such, this chapter should provide useful and comprehensive guidance for waste(water) processing utilities aiming to implement nutrient recovery strategies. This, in turn, may stimulate and hasten the global transition from waste(water) treatment plants to waste(water) resource recovery facilities. On top of that, the proposed roadmap may aid in the economic valorization of bio-based recovered products, thereby speeding up the transition from a fossil-reserve based to a bio-based nutrient economy.

Keywords: *anaerobic digestion, environmental management, renewable fertilizers, resource recovery, sustainable agriculture, waste valorization.*

Résumé

Cette thèse de doctorat a révélé des informations importantes sur la valeur agronomique, économique et écologique des produits fertilisants récupérés, sur l'exécution et l'exploitation technologique des processus et sur les interactions entre les procédés unitaires qui peuvent survenir dans les chaînes de traitement pour la récupération des nutriments. Basé sur ces résultats, ce chapitre vise le développement d'une feuille de route générique pour la mise en place des stratégies pour la récupération des nutriments à partir des digestats. Tout d'abord, les lignes directrices sont présentées pour mettre en place une stratégie de bio-fertilisation en fonction des législations d'engrais locales ou spécifiques à la région. Ensuite, des instructions ont été fournies pour la détermination du potentiel de production des bio-engrais en fonction de la caractérisation des déchets entrants. Enfin, un algorithme a été développé visant à la configuration et l'optimisation des chaînes de traitement pour la récupération des nutriments. Les caractéristiques importantes à mesurer sur les déchets entrants et les facteurs essentiels pour le suivi et le contrôle ont été identifiés. En tant que tel, ce chapitre devrait guider les usines de traitement des déchets et eaux usées à mettre en œuvre des stratégies pour la récupération des nutriments. Cela peut stimuler et accélérer la transition mondiale des stations de traitement des déchets et eaux usées en installations de récupération des ressources en eaux et en déchets. En fin de compte, la feuille de route proposée peut livrer les instructions fondamentales pour accélérer la transition à partir d'une économie axée sur des réserves fossiles vers une économie axée sur l'utilisation des ressources biologiques comme source de nutriments.

Mots-clés: *agriculture durable, digestion anaérobie, engrais renouvelables, gestion de l'environnement, récupération des ressources, valorisation des déchets.*

11.1 Introduction

A review of nutrient recovery technologies for digestate treatment (Chapter 2) has highlighted the potential for nitrogen (N) recovery as ammonium sulfate (AmS) fertilizer, as well as for phosphorus (P) recovery as struvite, $MgNH_4PO_4{:}6H_2O$ (and/or calcium (Ca) / magnesium (Mg)-P precipitates). Through a field trial (Chapter 5) and greenhouse experiment (Chapter 6), the agronomic potential of these fertilizers has been demonstrated. The economic and ecological benefits of bio-based fertilization scenarios have also been confirmed (Chapters 4-5). Nevertheless, implementation of nutrient recovery strategies is still limited due to legislative constraints, (operational) problems associated to the (variability of the) quality and quantity of the fertilizers produced, as well as the persisting uncertainty of fertilizer sales and inconsistency of marketing prices in regions where commercialization is possible (Seymour, 2009).

To facilitate nutrient recovery process and treatment train configuration and optimization, a nutrient recovery model (NRM) library has been developed (Chapters 8-9). Essential insights in unit process interactions acquired from global sensitivity analyses allowed the set-up of an optimal treatment train configuration (Chapter 10). It was revealed that the optimal configuration and associated operational conditions also depend on local legislations and fertilizer markets, next to the high influence of the input waste flow characteristics. Hence, the development of an algorithm for configuration of nutrient recovery facilities as function of these influencing factors was proposed.

Based on all results, insights, and understanding obtained throughout this PhD research, the present chapter aims at providing a roadmap for **setting up nutrient recovery strategies as function of local/regional fertilizer legislations and markets, as well as waste stream (digestate) properties.** The scope of the study includes anaerobic digestion and the selected best available technologies (and resulting bio-based products) applied at full-scale for the recovery of nutrients as marketable fertilizer commodities (Chapter 2), i.e. P precipitation/crystallization (struvite, Ca/Mg-P precipitates), NH_3 stripping/absorption (AmS fertilizer), and acidic air scrubbing (AmS fertilizer). The selection of these technologies (and products) was made on the basis of the stage of implementation, the technical performance, and financial aspects, next to the fertilizer marketing potential (Chapter 2). Besides the information acquired in this dissertation, additional data were obtained through contact with technology providers. Hence, the roadmap is (partially) based on full-scale operational experience. Important factors for input characterization, monitoring, and control are identified. As such, the roadmap provided in this chapter may function as a helpful tool for waste(water) processing utilities considering the implementation of anaerobic digestion and subsequent recovery and recycling of nutrients as marketable agricultural commodities.

11.2 Three-step roadmap

Two important factors determining the optimal treatment train configuration for nutrient recovery are i) (local/regional) fertilizer legislations and markets, and ii) input characteristics of the waste flow (digestate in this case) to be treated. A three-step roadmap for setting up nutrient recovery strategies as function of these determining factors is presented and discussed below.

Step I: ***Set-up bio-based fertilization strategy as function of fertilizer legislations***

If one wants to install a nutrient recovery treatment train, first contact should be sought with local/regional agronomic agencies and/or consultants in order to obtain insights in fertilizer related legislation and the corresponding market demand. If no local market would exist, interest can be sought abroad. Depending on the targeted region, N or P can be the limiting factor for manure (and digestate) application as (organic/organo-mineral) base fertilizer. The latter determines for which fertilizers the market demand is the highest in the particular region. Figure 11.1 gives a conceptual overview of bio-based fertilization recommendations as function of legislation. As is usually the case to date (e.g. MAP4, 2011), a maximum allowable fertilization standard is assumed for N application from organic (or organo-mineral) ‘manure’ products (= base fertilizer) and for N application from mineral fertilizers. Another standard is set for total P. Note that K application was not included in the recommendations, as currently no legislative standards exist for K.

If N is the limiting factor for fertilizer application, which is the case in P-poor regions, e.g. Brazil, Russia, Argentina, Western Africa, Northern Germany, etc. (MacDonald *et al.*, 2011), digestate may be applied to the field in its crude form (or mixed with some liquid fraction if solid-liquid separation would take place) up to the maximum allowable N level for base fertilizer application. Additional bio-based N fertilization up to the level for mineral fertilizers can and will to date most likely occur using AmS (high immediate N use efficiency), but struvite may also be applied for this purpose. The choice will depend on the crop’s nutrient demand (in time), the soil type, and the (local) product availability: the application of AmS is thus interesting as starter fertilizer or for additional fertilization of direct available N during spring or summer (Chapter 5), whereas struvite may provide a source of slow-release N and P (Chapter 6). If the availability of both products would be restricted and/or transportation costs unacceptably high, it may be required to additionally apply chemical N. Nevertheless, as to date air scrubbers are required at most farms, anaerobic digestion plants, and manure/digestate processing facilities in order to avoid NH_3 emissions to air, future practice should focus on the maximal recovery of the resulting AmS. Note that the use of N/K-rich membrane filtration concentrates were not included in the presented fertilization recommendations (Fig. 11.1), as to date membrane filtration has not yet proven to be a viable technology for digestate processing (Chapters 2-3). However, in the near future, these products may also provide a solution (De Hoop *et al.*, 2011; Velthof, 2011).

In addition, Ca/Mg-P precipitates could be applied up to the maximum allowable level for P fertilization. Also P-rich thick fractions (locally available or imported from P-rich regions) could be used for this purpose. However, in this case, the N content of the thick fraction also has to be taken in account when setting up the fertilization strategy.

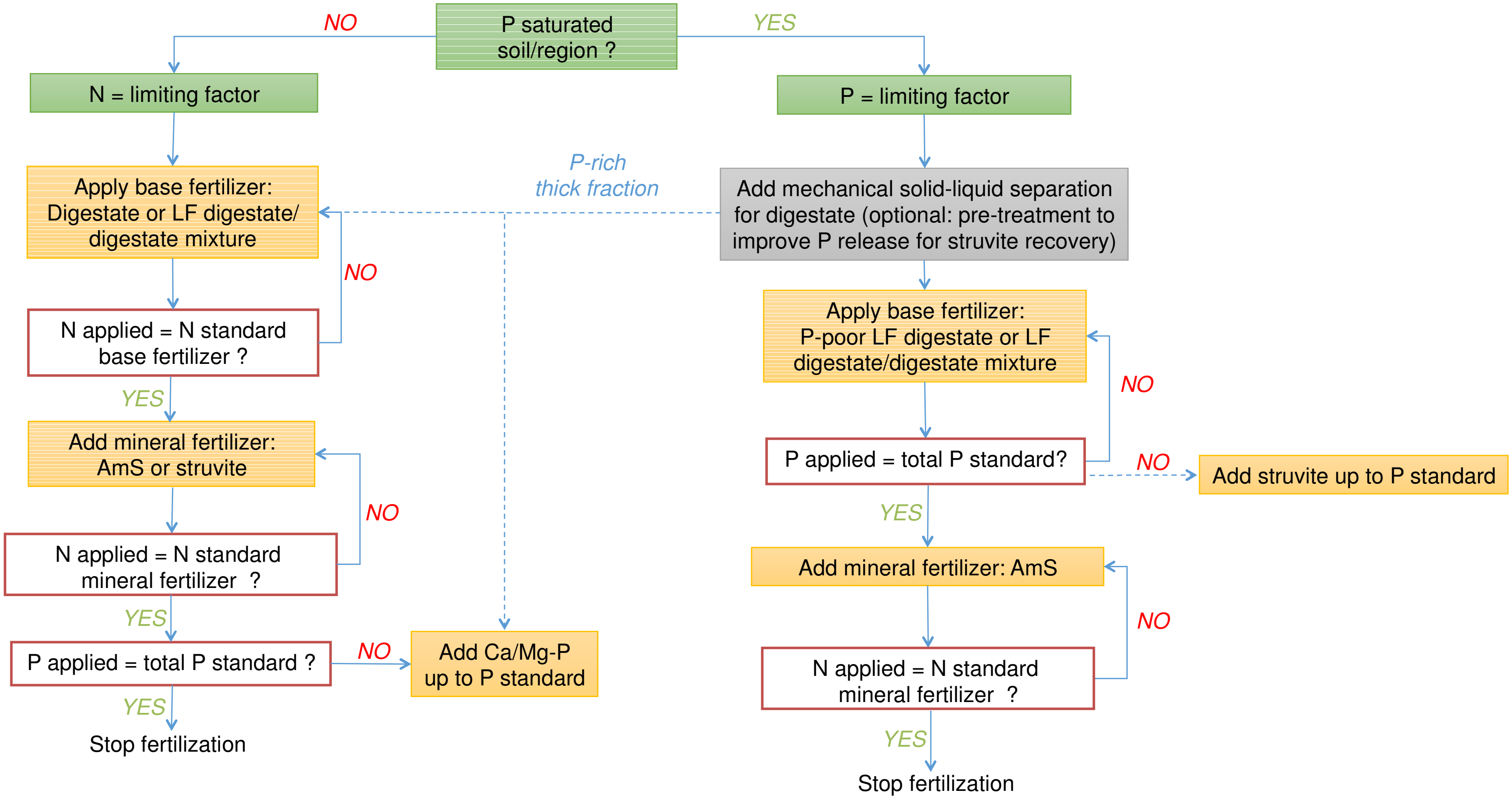


Figure 11.1 Bio-based fertilization recommendations as function of local/regional fertilizer legislations. AmS = ammonium sulfate; LF = liquid fraction.

In summary, in P-poor regions, among the considered best available bio-based products to date, the agricultural demand for digestate (base fertilizer), recovered AmS and/or struvite, and Ca/Mg-P fertilizers is expected to be high.

In P saturated regions, e.g. Flanders, Quebec, Eastern China, Italy, Northern Spain, etc. (MacDonald *et al.*, 2011), standards for P application are (or will become) increasingly strict due to historical manure and/or chemical fertilizer surpluses on the soil balance and the resulting environmental pollution. This means that the P supply via manure and/or mineral fertilizers (whether chemical or bio-based) is under pressure and that as much P as possible should be extracted from the soil complex. Previous chapters have shown the interest of mechanically separating the digestate in order to obtain a P-poor liquid fraction, so as to apply more available N as base fertilizer for the same amount of P. Moreover, it was observed that mixtures of digestate and its liquid fraction may increase the use efficiency of soil P (Chapters 5-6). Additional mineral fertilization up to the maximum allowable N level could then occur using AmS. **Hence, overall, in P saturated regions, among the considered recycled products, the most interesting fertilizers for agricultural purposes are likely the liquid fraction of digestate (as base fertilizer, whether or not mixed with raw digestate) and AmS.**

Note that in this case, most of the P ends up in the organic thick fraction after solid-liquid separation, which is usually exported to P-poor regions because local markets are restricted (Chapter 2). However, in light of the depleting natural P resources and soil organic carbon contents, the interest is growing to maximally recover P from the liquid fraction of digestate as struvite, Ca/Mg-P fertilizer, or P-rich solution, meanwhile increasing the local valorization potential of the valuable organic matter that ends up in the thick fraction (improved C:P-ratio). The recovered mineral P fertilizers could also be recycled locally, e.g. for horticultural purposes or for specific crops that require lots of P, such as potatoes, beets, and maize. As such, pre-treatments that stimulate P release in the liquid fraction during solid-liquid separation are gaining importance in P saturated regions (e.g. Chapter 7: acidification + mechanical pre-treatment).

Step 2: Evaluate feasibility of bio-based fertilizer production as function of input waste characterization

An important point to consider when aiming at the implementation of nutrient recovery is the physicochemical characterization of the input waste stream to be treated (Chapter 10). Obviously, first the macronutrients, especially N and P, of the waste flow have to be measured in order to check whether there is effectively an interest for N and P recovery. As such, technology providers confirmed that P recovery is only of interest if the P-load is higher than 80 kg d^{-1}, whereas N recovery using air stripping and scrubbing only becomes economically feasible at concentrations in the range of 400-500 mg N L^{-1}. Moreover, struvite production is only of interest if the waste flow has an N:P molar ratio above 1. The optimal N:P-ratio to maximize struvite recovery and purity would be higher than 6 (Ostara, 2014).

If, based on the above measurements, the recovery of N and P seems feasible, additional physicochemical analyses will have to be conducted in order to set up an optimal nutrient recovery treatment train configuration (see Step 3).

Step 3: Use of conceptual algorithm for treatment train configuration and optimization

Figure 11.2 provides a conceptual algorithm developed on the basis of the findings in this PhD dissertation and contact with technology providers. It gives an overview of guidelines for configuration of nutrient recovery treatment trains, taking in account input waste characteristics and fertilizer market demands. The various treatment train configurations per feasibility scenario (Step 2) are described below. Note that for privacy reasons, no company names will be given.

a) N and P recovery not feasible

Clearly, if there is **no interest in N and P recovery** (Step 2: waste input concentrations too low to be economically feasible), then no action should be taken, unless discharge regulations are to be met. Minor contents of N and P can be removed and recovered using a low-cost final effluent treatment. Ion exchange and sorption processes are of increased interest for this purpose (Chapter 2). Further treatment in lagoons prior to discharge may also provide a solution (Chapter 3). However, in this case, large areas of land can be required. Alternatively, the water could be reused, e.g. as irrigation water if quality requirements are met (Vaneeckhaute, 2010), or the water can be recycled to a nearby wastewater treatment plant (usually onsite in case of sludge digestion).

b) P recovery not feasible, N recovery feasible

If there is **only interest in N recovery** (Step 2: P-load too low), the recommended treatment train configuration concerns NH_3 stripping and acidic air scrubbing (after anaerobic digestion), with optional pre- and post-treatments, depending on the nature of the waste material (Fig. 11.2: Configuration 1).

Important input waste flow characteristics that may influence the configuration and capital/operating costs and that thus should be monitored, next to the N content, are the total suspended solids (TSS) and chloride (Cl) contents, as well as the input alkalinity. In general, the lower the input TSS and Cl contents, the better the ammonia stripping performance (Chapter 10). Excess TSS (> 2 %; RVTPE, 2014) must usually be removed using a solid-liquid phase separation unit prior to stripping. However, the company Anaergia recently developed a strip/scrub system (without packing) that allows stripping of the raw digestate with high TSS content. Its performance was demonstrated at full-scale for TSS contents up to 8-9 % (Chapter 2). Excess Cl (> 20 mol m^{-3} ~ 50 % NH_3 removal; Fig. 10.6) removal is more complicated. It could potentially be achieved through ion exchange or sorption (Chapter 2), though the feasibility of implementing such treatments remains to be evaluated along with the impact of the

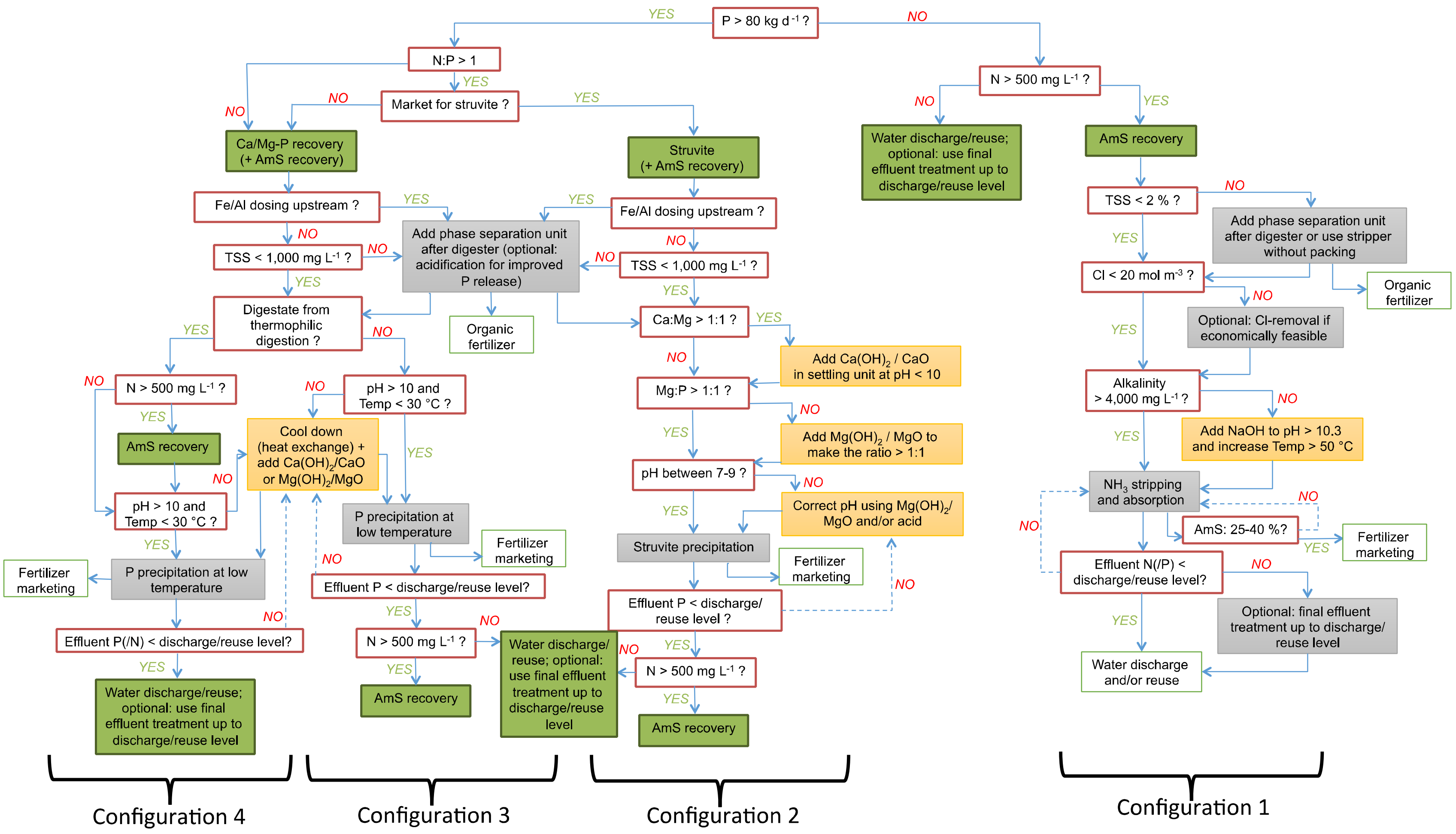


Figure 11.2 Conceptual algorithm for configuration and optimization of nutrient recovery treatment trains. Dashed lines indicate recycle flows. AmS = ammonium sulfate; TSS = total suspended solids.

present chlorides on the stripping performance. Input alkalinity should be checked to determine whether or not the addition of base (mostly NaOH in order to minimize scaling) is required for pH increase in the stripper (Chapter 9). Usually the digestate alkalinity (4,000-6,000 mg L^{-1} as $CaCO_3$) is sufficient to satisfy the pH requirements by stripping out CO_2, without the use of chemicals. In this case, it is interesting to select a stripping process without packing column in order to avoid $CaCO_3$ precipitation on the packing (Chapter 2). Overall, depending on the input characteristics of the waste flow (mainly TSS content and alkalinity) and market requirements (e.g. fertilizer pH), the most suitable stripping technology should be selected for each specific case. Indeed, to date, the operating conditions of the strip-scrub process and the composition of the recovered AmS-solution are highly dependent on the technology provider (Chapter 2).

Next to the above (optional) pre-treatments, the main operational factors to control in the stripping process itself are the temperature and pH. In the scrubbing column, the AmS-solution can be recycled up to the preferred AmS concentration, which should be in the range of 25-40 % (Chapter 2). Higher concentrations are not recommended because they may cause unwanted AmS precipitation on the stripping column (Chapter 10), whereas lower concentrations provoke high transportation costs (Chapter 4). Therefore, the system is usually operated in semi-continuous mode, where the AmS concentration is monitored (usually pH measurements are sufficient) and the solution is discharged when product specifications are met. The effluent N (and P) concentration, as well as other qualitative parameters, should then be checked against discharge regulations or recommended quality levels for water reuse (which depend on the application; Vaneeckhaute, 2010). In most cases, it will economically be more attractive to recover only 80-90 % of the N using the air stripping technology, and to add a more low-cost alternative for the final effluent treatment up to discharge/reuse levels. Reuse as irrigation water may provide an interesting solution. Alternatively, the water could be recycled to a nearby wastewater treatment plant (see above).

c) P recovery feasible, N recovery feasible or not feasible

If **P recovery is of interest** (Step 2: P-load of the waste stream = sufficient), one should first check whether there exists a market for struvite at acceptable transportation costs (see Step 1) and whether the N:P molar ratio is suitable for struvite precipitation (see Step 2). Hence, two scenarios are possible: i) struvite and AmS recovery (depending on the N content) are targeted (Fig. 11.2: Configuration 2), or ii) the N:P-ratio and/or fertilizer markets are not favourable for struvite recovery and Ca/Mg-P precipitation is targeted, whether or not in combination with AmS recovery (depending on the N content) (Fig. 11.2: Configurations 3-4).

In the first case (Fig. 11.2: Configuration 2), it is recommended to implement struvite precipitation prior to stripping so as to avoid unwanted precipitation in the stripping unit (Chapter 10). However, in this case, $Mg(OH)_2$/MgO should be used as Mg source for struvite precipitation instead of $MgCl_2$ in order to avoid Cl inhibition in the subsequent stripper (Chapter 10). Note that this configuration has as additional advantage that often no more base is required for pH increase in the stripper (Chapter 10). Indeed, the pH increase through Mg addition and CO_2

stripping is usually sufficient to achieve high NH_3 removal efficiencies. Prior to implementation, one should check whether iron (Fe) or aluminium (Al) dosing occurred upstream (e.g. for sludge conditioning), as these components may influence the struvite recovery potential and product quality (Chapters 6, 9, 10). In Chapter 6, for example, it was revealed that $FePO_4$ sludge is not interesting as P fertilizer from an agronomic point of view because of Fe-P fixation. This is likely also the case for Al because of the comparable P binding properties of trivalent Fe and Al. Hence, for waste flows containing high Fe and/or Al contents, the implementation of a phase separation unit for precipitate removal after digestion is recommended. Indeed, it was observed in Chapter 10 that Fe and Al precipitation could already start in the digester. Obviously, also the TSS content of the waste flow (limit: 1,000 mg L^{-1}; Ostara, 2014) will determine whether or not a solid-liquid separation unit has to be installed. Note that, if there is an interest in applying acidification as pre-treatment for improved P release during solid-liquid separation (Chapter 7), attention should also be paid to the impact of salts (mainly chlorides, see above) on the stripping performance when selecting the chemical (e.g. HCl) to be used.

In addition, important factors to monitor are the molar N:P-, Ca:P-, and Mg:P-ratios of the input waste flow. Ca may seriously hinder struvite precipitation and product purity (Chapters 9-10). In case of high Ca contents relative to N and Mg, the addition of $Ca(OH)_2$ in the phase separation unit is recommended to induce precipitation and removal of $CaCO_3$. However, the pH should then be controlled at a value lower than 10 to avoid P losses through Ca-P precipitation (Chapter 10), unless there would be a market for the resulting separated Ca-P rich thick fractions (see Step 1). Next, the Mg:P-ratio should be adjusted and the pH controlled according to Figure 11.2 so as to obtain optimal struvite recovery. Usually the process is operated such that it reaches the discharge levels for P. Subsequently, AmS recovery can take place (if N levels are sufficiently high) as described above (Fig. 11.2: Configuration 1).

In the second case (Fig. 11.2: Configurations 3-4), i.e. the N:P-ratio is **not favourable for struvite recovery** or local legislations do not stimulate struvite application, excess P can be recovered through Ca/Mg-P precipitation, whether or not in combination with AmS production (depending on the N content). In this case, the temperature used in the anaerobic digestion process may influence the overall digestate treatment train configuration. Indeed, in Chapter 10 it was revealed that P recovery through Ca-P precipitation is maximal at low temperatures and high pH. Hence, if the digestate would be produced using thermophilic digestion (optimal temperature: 50-57 °C; Tchobanoglous *et al.*, 2003), it is likely more feasible to implement AmS recovery prior to Ca-P precipitation in order to save heat requirements (Fig. 11.2: Configuration 4). The heat can then be recovered from the effluent, thereby cooling down the input flow for the subsequent precipitation of P. Moreover, if the stripper is operated to achieve N:P molar ratios below 1, then the absence of N in the recovered P fertilizer product can somehow be guaranteed.

On the other hand, if a mesophilic (optimal temperature: 30-38 °C; Tchobanoglous *et al.*, 2003) or psychrophilic (optimal temperature: 12-18 °C; Tchobanoglous *et al.*, 2003) digestion takes place, then Ca-P production should preferably take place prior to stripping in order to avoid precipitation in the stripping unit and reduce/eliminate chemical requirements for stripping (Fig. 11.2: Configuration 3).

In any case, the most important operational factors for monitoring and control are the pH and temperature. This again underlines the fundamental importance of accurate pH and temperature calculations in nutrient recovery models (Chapters 8-10).

Finally, if there is no market for neither struvite nor Ca/Mg-P precipitates, but precipitation is required to reach the discharge/reuse levels for P, then these mineral fertilizers can be mixed with the separated organic thick fraction and exported to P-poor regions after pasteurization (= common practice in high-nutrient regions). It should also be noted that in each of the above cases, the installation of an acidic air scrubber is recommended (and often obliged) in order to capture NH_3 losses during digestate processing. The captured NH_3 can then again be recovered as AmS solution (Chapter 2).

An important remark for the decision tree above is that other potential recovered products (apart from those selected in Chapter 2, see above), such as concentrates from membrane filtration (Chapter 2), were not yet considered. Nevertheless, if the production of new bio-based fertilizers from digestate proves to be viable at a large scale, then the roadmap will have to be extended by inclusion of these nutrient products. Model-based optimization of promising nutrient recovery processes may help speeding up the implementation of new technologies for bio-based fertilizer production. Another remark is that in the above roadmap no particular attention was given to K and S fertilization. Nevertheless, the crop demand for these nutrients may additionally influence the optimal fertilizer choice and nutrient recovery strategy. Hence, if more bio-based products become available, the roadmap should also be further diversified in terms of macronutrients, other than N and P.

11.3 Conclusions and perspectives

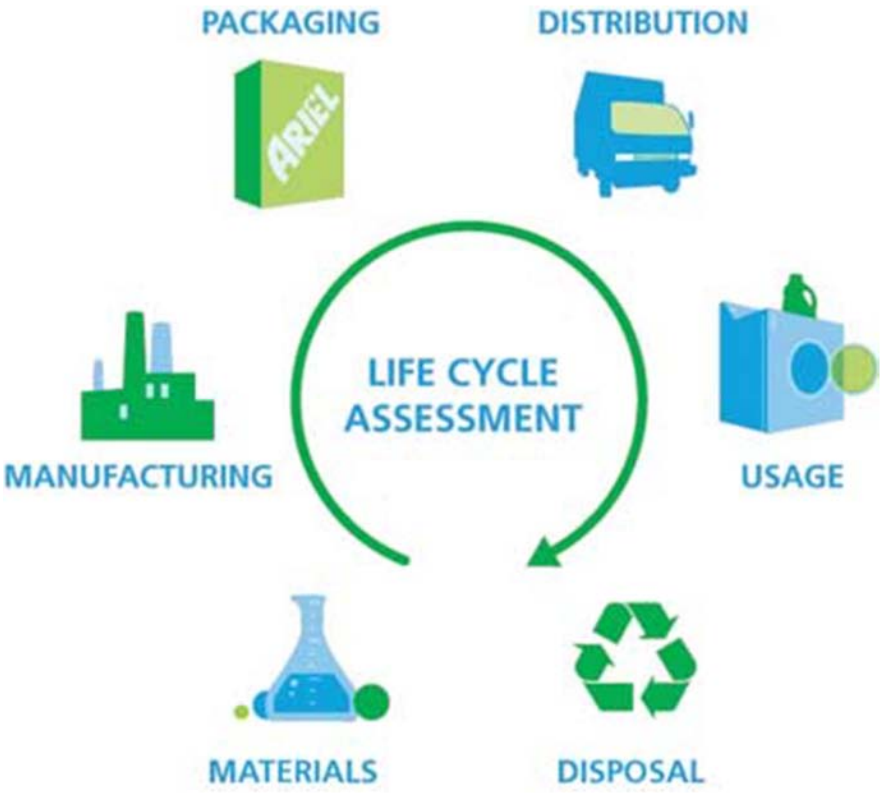
A generic three-step roadmap for setting up strategies for nutrient recovery from digestate was presented. It involves:

1. An overview of bio-based fertilization recommendations as function of fertilizer legislations;
2. Guidelines for determining the feasibility of nutrient recovery based on operational experience;
3. An algorithm for configuration and optimization of nutrient recovery treatment trains as function of input waste characterization and fertilizer markets.

As such, this chapter provides useful guidance for waste(water) processing utilities considering the implementation of nutrient recovery practices. If the production of new bio-based fertilizers at a large scale proves to be feasible, the roadmap should be further extended to allow for the integration of these products and technologies. In that case, it can also be important to further diversify the recommendations in terms of macronutrients, other than N and P.

CHAPTER 12:

LIFE CYCLE ASSESSMENT OF DIGESTATE PROCESSING AND NUTRIENT RECOVERY STRATEGIES: SUMMARY AND PERSPECTIVES



Picture: P&G Beauty & Grooming, USA

Summarized from:

Vázquez-Rowe, I., Golkowska, K., Lebuf, V., Vaneeckhaute, C., Michels, E., Meers, E., Benetto, E., Koster, D., submitted. Environmental assessment of digestate treatment technologies using LCA methodology.

Vaneeckhaute, C., Adams, P., Rodhe, L., Thelin, G., Styles, D., Ödman, A., D'Hertefeldt, T., in preparation. Wide-scale use of recycled nutrients: Bottlenecks or opportunities ?

Adams, P., Vaneeckhaute, C., in preparation. Life cycle analysis of on-farm anaerobic digestion and digestate reuse: A case-study.

Abstract

The present PhD dissertation has provided important evidence of the agronomic, economic, and ecological benefits of the application of bio-based fertilization scenarios as compared to conventional fertilization using animal manure and chemical fertilizers. Hence, it was concluded that the use of bio-based recovered products should be stimulated in environmental legislations. Nevertheless, one of the most important topics in global policy making, communication, and stimulation of recovery scenario implementation is the overall improvement of process sustainability. This leads to the proposition to further investigate the overall environmental impact of the nutrient recovery technologies and treatment trains for bio-based fertilizer production themselves. For this reason, the data obtained in this PhD dissertation have been used by the Luxembourg Institute of Science and Technology (LIST, Esch-sur-Alzette, Luxembourg; Vázquez-Rowe *et al.*, submitted), Bangor University (Gwynedd, United Kingdom, UK; Vaneeckhaute *et al.*, in preparation) and the University of Bath (Bath, UK; Adams and Vaneeckhaute, in preparation) to conduct holistic life cycle assessments (LCA).

In Vázquez-Rowe *et al.* (submitted), the environmental impacts of spreading digestate directly to agricultural land as compared to five different treatment trains were assessed. For this purpose, the data resulting from the mass balance analyses in Chapter 3 were used, as well as the field-scale observations (Chapter 5). Results suggest relevant environmental gains when the digestate is treated using the examined conversion technologies prior to spreading, although important trade-offs between impact categories were observed and discussed.

In Vaneeckhaute *et al.* (in preparation), first the fertilizer replacement value of digestates using the MANNER-NPK (MANure Nitrogen Evaluation Routine) tool was assessed. It concerns a practical software tool that provides a quick estimate of crop available nitrogen, phosphate, and potash supply from applications of organic/organo-mineral fertilizers. Next, LCA's were performed comparing conventional fertilizer production with digestate and bio-based fertilizer production. Herewith, the effective fertilizer value of recovered products (as determined in the first step) was taken in account. Also innovative as compared to other LCA studies, in this assessment the effect of different organic residues (digestates, liquid fractions, and mixtures of these) on the soil organic carbon (SOC) content under different crop rotations has been investigated using the Introductory Soil Carbon Balance Model (ISCBM) and the field-scale data collected in this dissertation (Appendix 3). The obtained results represent a better picture of greenhouse gas (GHG) emissions compared to not including an assessment of SOC effects at all in LCA studies. A techno-economic and socio-economic study was also performed aiming to evaluate stakeholder perception and societal acceptance.

Finally, in Adams and Vaneeckhaute (in preparation), an LCA was undertaken for the implementation of a 1.4 MW full-scale anaerobic digestion plant on farm land at Down Ampney Estate (Gloucestershire, UK). Substrates proposed for the digestion system consist predominantly of crops (both food and fodder) grown on-site (maize and grass), underpinned by grass silage and chicken manure imported to the site. The overall aim of the study was to quantify the energy, GHG emission, and resource changes compared to the existing conventional farm management using an LCA approach. This study uses actual farm data to compare LCA results on-farm both prior to and after the implementation of the anaerobic digestion facilities. Results are currently being collected.

Overall, an important bottleneck observed in existing LCA studies is that the they do not account for the effective fertilizer value of recovered products (replacement of chemical mineral fertilizer production and use) and their impact on soil organic carbon. Moreover, current databases underestimate the depletion of natural mineral resources. Hence, the information obtained from the three innovative and more advanced LCA studies above may and should be used as basis to stimulate the use of recovered products in environmental legislations, next to all other results obtained in this dissertation. Moreover, the work provides fundamental

guidelines for improvement of LCA modelling tools for future studies. Indeed, further assessments will be required in order to provide sufficient quantitative evidence of the global environmental benefits when implementing resource recovery facilities for bio-based fertilizer production as compared to traditional practices for waste processing (i.e. nutrient removal), chemical fertilizer production, and manure spreading. Further work is also suggested on the coupling of the nutrient recovery model library (Chapters 9-10) to LCA modelling tools, agro-economic tools (e.g. Chapter 4), and/or agronomic soil nutrient balance models (e.g. the NDICEA model used in Chapter 5). This may allow for environmental and economic optimization of nutrient recovery strategies throughout the entire value chain.

Résumé

La présente thèse de doctorat a fourni des preuves importantes des avantages agronomiques, économiques et écologiques de l'application de scénarios de bio-fertilisation par rapport à une fertilisation conventionnelle utilisant du lisier et des engrais chimiques. Par conséquent, il a été conclu que l'utilisation des bio-produits récupérés devrait être stimulée dans les législations environnementales. Néanmoins, l'amélioration globale de la durabilité des processus reste l'un des sujets les plus importants dans l'élaboration de la politique mondiale, la communication et la stimulation de l'implantation des scénarios de récupération. Cela conduit à proposer d'étudier plus en détail l'impact global sur l'environnement des technologies de récupération des nutriments et des chaînes de traitement pour la production des bio-engrais. Pour cette raison, les données obtenues dans cette thèse de doctorat ont été utilisées par l'Institut Luxembourgeois de la Science et de la Technologie (LIST, Esch-sur-Alzette, Luxembourg) (Vázquez-Rowe *et al.*, soumis), l'Université de Bangor (Gwynedd, Royaume-Uni, RU) (Vaneeckhaute *et al.*, en préparation) et l'Université de Bath (Bath, RU) (Adams et Vaneeckhaute, en préparation) pour effectuer des analyses holistiques du cycle de vie (ACV).

Dans Vázquez-Rowe *et al.* (soumis), les impacts environnementaux de l'application du digestat directement aux terres agricoles ont été comparés aux cinq chaînes de traitement différentes. À cet effet, les données résultant de l'analyse des bilans de masse dans le Chapitre 3 ont été utilisées, ainsi que les observations sur le terrain (Chapitre 5). Les résultats suggèrent des avantages environnementaux mesurables lorsque le digestat est traité par les technologies de conversion examinées avant l'épandage, bien que d'importants arbitrages entre les catégories d'impact ont été observés et discutés.

Dans Vaneeckhaute *et al.* (en préparation), la valeur de remplacement des lisiers par des digestats à l'aide de l'outil MANURE-NPK (MANure Nitrogen Evaluation Routine) a d'abord été évaluée. Il s'agit d'un outil logiciel pratique qui permet d'obtenir une estimation rapide d'azote, de phosphate et de potasse disponible pour les plantes provenant d'applications d'engrais organiques/organo-minéraux. Ensuite, des ACV ont été effectuées afin de comparer la production d'engrais conventionnel avec la production du digestat et des bio-engrais. Ici, la valeur fertilisante réelle des produits récupérés (tel que déterminé dans la première étape) a été prise en compte. Aussi innovateur par rapport à d'autres études d'ACV, l'effet de différents résidus organiques (digestats, fractions liquides et mélanges de ceux-ci) sur la teneur en carbone organique du sol (COS) sous différentes rotations de cultures a également été étudié en utilisant le 'Introductory Soil Carbon Balance Model' (ISCBM) et les données recueillies sur le terrain dans cette these (Annexe 3). Les résultats obtenus offrent une meilleure mesure des gaz à effet de serre (GES), lorsque comparés aux ACV n'incluant pas d'évaluation du COS. Une étude technico-économique et socio-économique a également été effectuée, visant à évaluer la perception des parties prenantes et l'acceptation sociale.

Finalement, dans Adams et Vaneeckhaute (en préparation), une ACV a été réalisée pour la mise en œuvre d'une usine de digestion anaérobie de 1.4 MW à pleine échelle sur les terres agricoles à Down Ampney Estate (Gloucestershire, RU). Les substrats proposés pour le système de digestion se composent principalement des cultures (à la fois alimentaires et fourragères) cultivées sur place (maïs et herbe), soutenues par l'ensilage d'herbe et de lisier de poulet importé sur le site. L'objectif général de l'étude était de quantifier les changements dans la consommation d'énergie, les émissions de GES, et l'utilisation des ressources par rapport à la gestion agricole conventionnelle existante en utilisant une approche d'ACV. Cette étude utilise des données agricoles réelles pour comparer les résultats d'ACV à la ferme à la fois avant et après la mise en œuvre des équipements de digestion anaérobie. Les résultats sont actuellement en production.

Dans l'ensemble, une faille importante observée dans les études actuelles d'ACV est la non-prise en compte de la valeur fertilisante réelle des produits récupérés (remplacement de la production et l'utilisation d'engrais minéraux chimiques) et leur teneur en carbone organique. En outre, les bases de données actuelles sous-estiment l'épuisement des ressources minérales naturelles. Par conséquent, l’information obtenue à partir des trois études novatrices et plus poussées ci-dessus peut et doit être utilisée comme point de départ pour stimuler l'utilisation des produits récupérés dans les législations environnementales, en plus de tous les autres résultats obtenus dans cette thèse. En outre, le travail fournit des lignes directrices fondamentales pour l'amélioration des outils de modélisation d'ACV pour les études futures. En effet, d'autres ACV seront nécessaires pour fournir suffisamment de preuves quantitatives des avantages environnementaux globaux de la mise en œuvre des installations de récupération des ressources pour la production des bio-engrais par rapport aux pratiques traditionnelles pour le traitement des déchets (l'élimination des nutriments), la production d'engrais chimiques et l'épandage de lisier. Des travaux complémentaires sont aussi suggérés sur le couplage de la librairie de modèles de récupération des nutriments (Chapitres 9-10) à des outils de modélisation d'ACV, des outils agro-économiques (par exemple, le Chapitre 4) et/ou des modèles agronomiques de bilan des nutriments du sol (tel que le modèle NDICEA utilisé aux Chapitre 5). Ceci peut permettre l'optimisation environnementale et économique des stratégies de récupération des nutriments à travers la chaîne de valeur.

CHAPTER 13:

GENERAL CONCLUSIONS AND RECOMMENDATIONS

13.1 General conclusions

Unless action is taken, increases in population and per capita consumption of energy and animal products will exacerbate nutrient losses and resource depletion, pollution levels and land degradation, further threatening the quality of our water, air, and soils, affecting climate and biodiversity. A new global effort is needed to address 'The Nutrient Nexus', where reduced nutrient losses and improved nutrient use efficiencies across all sectors simultaneously provide the foundation for a greener economy to produce more food and energy while reducing environmental pollution.

The aim of this PhD dissertation was to stimulate the transition from a fossil reserve-based to a bio-based economy by providing (tools to develop) sustainable strategies for nutrient recovery from digestate, the remaining product after bio-energy production through anaerobic digestion of organic biodegradable wastes. The focus was on the valorization of the recovered products as sustainable and marketable fertilizers, which may even (partially) replace the use of chemical fertilizers in agriculture. Three complementary research phases were conducted: 1) technology inventory and product classification (Chapter 2), 2) product value evaluation (Chapters 3-7), and 3) process modelling and optimization (Chapters 8-10). The fundamental knowledge obtained throughout this PhD has led to the proposal of a generic roadmap for setting up nutrient recovery strategies (Chapter 11) and can be used as information base for life cycle assessments (LCAs; Chapter 12). All of this should greatly enhance communication and nutrient recovery scenario implementation. The main conclusions from this dissertation are summarized below:

PHASE I: Technology inventory and product classification

From the technology inventory (Chapter 2; Fig. 1.6: Objective I.1), **phosphorus (P) precipitation/crystallization, nitrogen (N) stripping/absorption, and acidic air scrubbing were found to be the best available technologies for nutrient recovery from digestate applied to date at full-scale**. The resulting fertilizer products, i.e. struvite and ammonium sulfate (AmS) wastewater, can and should be classified as recovered N/P-precipitates and N/S-solutions, respectively, in environmental and fertilizer legislations. Membrane filtration also showed promise. However, traditional membrane filtration systems often suffer technical problems in wastewater treatment, making them economically not yet viable for digestate treatment. All available technologies require further technical fine-tuning in order to minimize operational costs, produce high-quality fertilizers, and economically valorize the recovered nutrients. In phase III of this dissertation, first attempts were made to meet these needs by the use of models.

PHASE II: Product value evaluation

In order to obtain insights regarding the fate of macronutrients in digestate processing, a mass balance study at a full-scale digestate treatment and nutrient recovery facility was performed

(Chapter 3: Vaneeckhaute *et al.*, 2012; Fig. 1.6: Objective II.1). In this case study, a potentially interesting alternative for traditional membrane filtration, i.e. the vibratory shear enhanced processing (VSEP) technology, was tested as final effluent treatment to produce both N/K-concentrates and reusable water. The performance of **the VSEP filtration system proved, however, not yet satisfactory from a technical and mechanical point of view to allow for reliable, continuous operation.** Nevertheless, concentrates produced by the first VSEP filtration step were rich in macronutrients and could potentially be reused as sustainable substitute for fossil reserve-based mineral N/K fertilizers.

Detailed physicochemical characterizations of the various derivatives produced during digestate processing provided insights in the composition and properties of these products, as well as in their potential bottlenecks for agricultural reuse (Chapters 3-4, 6: Vaneeckhaute *et al.*, 2012, 2013b, 2015a,b; Fig. 1.6: Objective II.1). As such, the potential of the above-mentioned recovered AmS-solutions, N/K-concentrates, and struvite as sustainable chemical fertilizer substitutes was confirmed. Important bottlenecks for agricultural reuse of concentrates could be the salt content, the sodium adsorption ratio, and the potassium (K) content, especially for cattle farmers. Potential bottlenecks for agricultural reuse of acidic air scrubber water concern the pH, the salt content, and its corrosive properties. An important challenge in the production of struvite is the guarantee of the product's purity. Moreover, the struvite recovery potential was found to be limited, since current practice of digestate processing (in P saturated regions) mostly involves the elimination (through export) of P-rich organic thick fractions from the local agricultural cycle.

Based on the product characterizations, different fertilization scenarios were set up for use of recovered products in agriculture, in compliance with the Flemish manure regulation for the cultivation of maize on non-sandy soils (MAP4, 2011). The economic and ecological benefits of substituting conventional fertilization practices, using animal manure and chemical fertilizers (N, K), by bio-based alternative scenarios were quantified and evaluated (Chapter 4; Fig. 1.6: Objective II.2). The costs/benefits, energy use, and associated greenhouse gas emissions of fertilizer production, packing, transport, and application were taken in account. **On the basis of the assumptions made, the substitution of chemical fertilizers by N/S-solutions and N/K-concentrates always resulted in significant economic and ecological benefits for the crop farmer**. The highest combined environmental and economic benefits were obtained through an optimal (in terms of effective N:P-ratio) combination of digestate and its liquid fraction, meanwhile substituting chemical N by air scrubber wastewater or membrane filtration concentrates. Based on the analyses, to maintain overall costs for the crop farmer, a marketing value of ± € 0.93 *(1.31 CAD)* kg^{-1} N and ± € 0.60 *(0.85 CAD)* kg^{-1} N, equivalent to the chemical fertilizer cost, could be imposed for the production of acidic air scrubber water and membrane filtration concentrates, respectively.

Starting from the theoretical cultivation scenarios outlined in Chapter 4, field test validation of the most beneficial scenarios was performed in order to confirm the potential substitution of conventional fertilizers by bio-based alternatives (Chapter 5: Vaneeckhaute *et al.*, 2013c, 2014; Fig. 1.6: Objective II.3). The products under study were AmS wastewater from an acidic air scrubber, liquid fractions of digestate, and optimized mixtures of raw digestate and its liquid fraction. Based on a two-year field trial, it was revealed and confirmed that nutrient recovery and cradle-to-cradle reuse of these bio-digestion waste derivatives can: i) create valuable substitutes for chemical fertilizers with high nutrient use efficiencies (no reduction in crop yield!), ii) reduce nitrate (NO_3) leaching and increase soil P_2O_5 and K_2O recovery (to be confirmed on the long term), iii) result in economic and ecological benefits (confirmation of the findings in Chapter 4). No detoriating impact on soil quality was observed during the experimental period. As added advantages to the generation of sustainable bio-fertilizers from waste via anaerobic (co-)digestion, renewable energy is produced and negative environmental impacts (e.g. methane and odor emissions, pathogen distribution, eutrophication, and soil nutrient accumulation) of untreated wastes (animal manure, sludges, etc.) are reduced. Moreover, the use of bio-based fertilizers can result in added supply of (effective) organic carbon (next to various essential macro- and micronutrients) to agricultural land, thereby contributing to the struggle against organic carbon depletion in many soils worldwide. **We therefore conclude that the use of bio-based fertilizers has a positive impact on the economy, agronomy, and ecology of intensive plant production.** Best management practices for agricultural implementation of these products were provided.

Interesting observations made during the field trial were further studied in detail at greenhouse scale. As such, the P use efficiency and bio-availability in soils, as well as the underlying mechanisms, were studied in depth by land-application of recovered bio-based P fertilizers, including struvite, iron phosphate ($FePO_4$) sludge, digestate, and animal manure, as compared to fossil reserve-based mineral P fertilizer (Chapter 6: Vaneeckhaute *et al.*, 2014b; Fig. 1.6: Objective II.3). **Struvite was found to be interesting as starter and slow release fertilizer, whereas $FePO_4$-sludge proved not useful in terms of P release** for agricultural crop production due to its strong P binding capacity. **The benefits of converting animal manure into digestate through anaerobic (co-)digestion in terms of nutrient use efficiency and environmental impact were confirmed.** The additional use of Rhizon soil moisture samplers, next to the existing methodologies for measurement of bio-available P, is recommended for determination of both organic and inorganic P in the framework of environmental and fertilizer legislations, and the associated fertilizer application recommendations.

Finally, if struvite or a concentrated P-solution is targeted, then a pre-treatment of the digestate prior to solid-liquid separation can be considered in order to increase the P release in the liquid fraction and hence its recovery potential as mineral fertilizer (Chapter 7). This can also improve the local reuse potential of the remaining organic thick fraction as valuable soil conditioner in the case of P saturated regions. Based on the costs and the efficiency of various potential mechanical and chemical pre-treatments, the combined use of acidification with hydrogen chloride (HCl) and orbital shaking (i.e. mixing in industrial practice) seems to be most feasible. If pasteurization is required for effective product marketing, then microwave treatment in combination with HCl may provide a solution. However, the chemical choice can also influence processes downstream in the treatment train. Hence, the technically and economically most effective pre-treatment will have to be identified for each specific case.

All the above-mentioned agronomic experimental results can and should be used as a source of valuable information to describe fertilizer quality specifications, to prove the effectiveness of recovered fertilizers in the context of environmental and fertilizer legislations, as well as to stimulate their acceptability in the farming community.

PHASE III: Process modelling and optimization

Based on the obtained insights in the technological performance, the value of recovered products, and their bottlenecks for agricultural reuse, **a generic nutrient recovery model (NRM) library was developed aiming at fertilizer quality and quantity as model outputs** (Chapters 8-9; Fig. 1.6: Objective III.1). It is one of the first implementations of a set of waste(water) models in the widely used Modelica language. This generic framework for modelling of nutrient recovery systems should greatly enhance the cost-effective implementation, optimization, and useful application of sustainable treatment trains for resource recovery. Dynamic physicochemical three-phase mathematical process models were developed for the nutrient recovery systems selected in Chapter 2 (see above). In addition, a compatible combined biological-physicochemical anaerobic digester model was constructed, including sulfurgenesis, biological N/P/K/S release/uptake, interactions with organics, next to other relevant processes, such as precipitation, ion pairing, and liquid-gas transfer.

Each dynamic mathematical model was built using: 1) the definition of a chemical speciation model using geochemical modelling software (PHREEQC/MINTEQ), 2) the description of a physicochemical and biochemical transformation model tailored to the models developed in the first step, and 3) the selection of a reactor mass balance model to describe the (time-dependent) process conditions. In order to account for accurate chemical solution speciation and reaction kinetics at minimal computational effort, **an efficient PHREEQC-Tornado interface was developed.** The correctness of the programming of the models was verified by comparison with simulation results from the stand-alone PHREEQC geochemical modelling software. A reduction of execution time was established at two critical points during model simulations: i) the uploading and reading of database and input files (through PHREEQC model reduction), and ii) the transfer of data between PHREEQC and Tornado/(WEST) (through tight model coupling). On average, **a three-to-five fold improvement of model simulation speeds was obtained** using the developed reduced models as compared to full PHREEQC and MINTEQ geochemical databases, respectively. Fundamental physicochemical components/ species/reactions occurring in resource recovery facilities, e.g. potassium struvite and ammonium sulfate precipitation, were found to be lacking in the existing standard geochemical PHREEQC/MINTEQ databases. Because of these constraints, a generic extended database in view of nutrient recovery was created for future applications.

After implementation, the models were subjected to a battery of tests to ensure implementation correctness, also referred to as **model verification**. As such, for example, two implementations of each model were set up and the outcomes compared: one based on all separate individual equations and one compact matrix-based implementation. As such, typing errors, inconsistencies, gaps, and conceptual errors were eliminated, while software bugs were discovered and dealt with. Next to verification, also **model validation** was performed by comparison of the model outcomes with experimental data. Validation is often neglected in mathematical modelling but is a key component of Good Modelling Practice. **Simulation results using default parameters showed good agreement with experimental results under steady state conditions,** providing a first sense of validity of the implemented model library. Moreover, **the ability of the models as a tool for increased process understanding and optimization was successfully demonstrated** (Fig. 1.6: Objective III.2). Detailed chemical input characterization and chemical solution speciation were found to be of prime importance for modelling of nutrient recovery systems. Further research in terms of determination of precipitation/dissolution and gas transfer kinetics in real waste matrices is required to accurately calibrate and validate the models under dynamic conditions.

Following the general findings above, global sensitivity analyses (GSAs) were performed in order to identify the factors with the highest impact on the fundamental model outputs, i.e. the factors that should be prioritized in further experimental studies and for future input characterization at waste(water) resource recovery facilities (WRRFs; Chapter 10). GSA using linear regression on Monte Carlo simulation outputs was found to be an appropriate strategy for factor prioritization in NRM applications. For the adopted GSA method based on standardized regression coefficients (SRCs), the use of variance inflation factors (VIFs) is recommended to detect and resolve problems related to multicollinearity of factors in complex models. Factor ranking was performed for: 1) input waste flow characteristics at WRRFs, 2) process operational factors, and 3) model kinetics, within the context of the analysis.

For all models, **the variation in input waste composition resulted in major output variation through its direct effect on the operational pH and ionic strength.** This underlines the fundamental importance of the accurate chemical solution speciation provided by the NRMs. Main impacts were found to be generalizable for different substrates, showing the wide relevance of the study. Moreover, valuable insights in the interactions between unit process inputs and outputs were obtained through the GSAs. Major findings involve, among others, the impact of chloride (Cl) inhibition on ammonia removal in the stripping unit, the impact of calcium (Ca), iron (Fe), and aluminium (Al) inhibition on P recovery in the precipitation unit, and the interaction between Fe/Al, S, and methane (CH_4) production in the anaerobic digester. Based on the results, **it was possible to set up an optimal treatment train configuration for nutrient recovery that maximizes resource recovery at minimal cost** (Fig. 1.6: Objective III.2).

Finally, **the valuable use of the models to select optimal operational conditions in the treatment train that maximize resource recovery at minimal costs and use of consumables was demonstrated** for pig manure as a case study (Fig. 1.6: Objective III.2). Under the optimized conditions and assumptions made, potential financial benefits for a large-scale anaerobic digestion and nutrient recovery project were estimated at 2.8-6.5 USD *(3.5-8.1 CAD; € 2.5-5.7)* m^{-3} manure based on net variable cost calculations, or an average of ± 2 USD *(2.5 CAD; € 1.8)* m^{-3} y^{-1}, equivalent with 40 USD *(50 CAD; € 35)* ton^{-1} total solids y^{-1}, over 20 years when also taking into account capital costs. Hence, it is very likely that in practice a full-scale ZeroCostWRRF (waste(water) resource recovery facility at zero cost) can be constructed. Nevertheless, it was found that local legislations and fertilizer markets also play an important role in determining the optimal treatment train configuration and operational conditions. **In summary, it is concluded that the NRM library and GSA strategy developed in this dissertation provide a valuable and cost-effective framework for increased process understanding, treatment train configuration, and optimization of region-specific nutrient recovery applications.**

Communication and stimulation of scenario implementation

Based on all results, knowledge, and insights obtained throughout the PhD research, **a roadmap for setting up strategies for nutrient recovery from digestate was established** (Chapter 11). The focus was on the technologies and bio-based products selected in Chapter 2 (see above). The roadmap involves: i) an overview of bio-based fertilization recommendations as function of fertilizer legislations, ii) guidelines for determining the feasibility of nutrient recovery based on operational experience, and iii) an algorithm for configuration and optimization of nutrient recovery treatment trains as function of input waste characterization and fertilizer markets. As such, the roadmap provides useful guidance for waste(water) processing utilities considering the implementation of nutrient recovery practices. This, in turn, should stimulate and hasten the global transition from traditional waste(water) treatment plants (WWTPs) to WRRFs.

Finally, it is believed that holistic LCA studies aiming at the evaluation of the overall environmental impact of anaerobic digestion and nutrient recovery scenarios can provide important evidence for further policy making, communication, and stimulation of nutrient recovery scenario implementation. Contact has been sought by/with various research institutions working on this topic. As such, **the results obtained in this dissertation have been and are currently being used for LCA studies** (Chapter 12) by the Luxembourg Institute of Science and Technology (LIST, Esch-sur-Alzette, Luxembourg; Vázquez-Rowe *et al.*, submitted), the University of Bath (Bath, UK; Adams and Vaneeckhaute, in preparation), and Bangor University (Gwynedd, UK; Vaneeckhaute *et al.*, in preparation). Although preliminary outcomes are promising in view of anaerobic digestion and nutrient recovery, flaws in LCA model libraries were discovered and are currently dealt with.

13.2 Scientific contributions and impact

The scientific contributions resulting from this dissertation are: i) a technology inventory (Fig. 1.6: Paper 1), ii) a product classification (Fig. 1.6: Paper 1), iii) full-scale mass balance analyses and product characterizations (Fig. 1.6: Paper 2), iv) an economic and ecological nutrient recovery scenario evaluation (Fig. 1.6: Paper 3), v) a two-year field trial and greenhouse experiment for agronomic fertilizer value evaluation, as well as associated lab study on P recovery (Fig. 1.6: Papers 4-8), vi) a generic model library for nutrient recovery and associated GSA analyses (Fig. 1.6: Papers 9-11), vii) a roadmap for setting up nutrient recovery strategies (Fig. 1.6: Paper 12), and viii) an objective base for LCA studies (Fig. 1.6: Papers 13-15). As such, this PhD dissertation provides fundamental information and tools to aid and guide decision making, configuration, operation, and optimization of (and research into) sustainable nutrient recovery strategies.

The results obtained in this dissertation should be widely spread as **the expected impact is multi-sectorial and addresses the three pillars of sustainable development: environment, society, and economics.** First, this research may help to better classify recovered products in environmental and fertilizer legislations and serve as a support to stimulate their use, meanwhile fostering nutrient recovery technology and scenario implementation. This, in turn, may improve the competitiveness of recovered products as compared to conventional fertilizers, thereby promoting their use and acceptability in the farming community. By providing sustainable and effective recovered fertilizers, the agricultural sector can reduce its environmental impact caused by nutrients, can become less dependent on the use of chemical fertilizers, and improve its social acceptance, while developing a sustainable and profitable agriculture.

Over the medium to long term, there are also opportunities for the private sector to capitalize on this research in view of the required improvement of existing waste(water) treatment practices to turn them into innovative resource recovery facilities. This can lead to important economic benefits to companies developing and manufacturing waste(water) treatment and advanced treatment technologies, biogas generation technologies, and mathematical models for designing and optimizing recovery plants. Moreover, the governmental institutions involved, e.g. Agriculture and Agri-Food Canada and the European Commission, can directly profit from the additional knowledge provided in this dissertation regarding the efficiency of renewable fertilizers.

Underlying benefits that can arise from this work over the long term are the obvious health and environmental benefits associated with improved agricultural practice and food supply thanks to resource recovery from biodegradable wastes. This may open up new opportunities for sustainable and more bio-based economic growth and thus create a win-win situation for both the environment, the society, and the economy in Belgium, Canada, and beyond.

13.3 Recommendations

Based on all experiences, observations, and communications made during the PhD research period, the present section provides key recommendations towards the different stakeholders in the field of nutrient recovery.

➢ Researchers:

- *Technological perspective:*
    1. Further technical fine-tuning of nutrient recovery technologies in order to minimize operational costs, produce high-quality fertilizers, and economically valorize the recovered nutrients;
    2. Further technical/mechanical optimization of the VSEP process in order to implement the system at full-scale;
    3. Further development of novel nutrient recovery technologies with minimal energy and chemical consumption;
    4. Study on the crystallization or granulation of AmS-solutions in order to increase their marketing value. Integration of the crystallization process in the scrubbing unit may provide an economic solution, though it remains questionable if this is technically feasible;
    5. Further substantive case studies on the economic feasibility of implementing pre-treatments for P release from digestate at full-scale. Aspects such as improved COD (chemical oxygen demand) degradation and biogas production, chemical fertilizer replacement, local fertilizer markets, the fertilizer value of the produced organic thick fractions, transport costs, and pasteurization will have to be considered in the evaluation.

- *Agronomic perspective:*
    1. Evaluation of field trials in the longer term, for different soil types, and for different cropping systems;
    2. Assessment of field trials using other original combinations of recovered products;
    3. Development of effective and sustainable fertilizer application methods for recovered products;
    4. Study of the microbiological quality of recovered products and their impact on soil organisms. It is expected that the pathogen content after digestion is lower as compared to animal manure, though a thorough quantification could greatly stimulate the acceptance of bio-based products in environmental legislations and their use in the farming community. Also the degree of contamination with organic substances in the various bio-based products needs to be investigated;
    5. Accurate determination of the humification coefficient for the various bio-based fertilizers. This is required to better assess the impact on soil organic carbon (by

use of models or by experiments) when applying bio-based fertilization scenarios instead of conventional practices using animal manure and chemical fertilizers.

- *Modelling perspective:*
    1. Increased use of models for process understanding, treatment train configuration and optimization, study of 'what-if' options, improved technology transfer to industry, and set-up of research objectives;
    2. Development of a generic chemical analysis procedure for precipitate identification in order to facilitate the experiments required for kinetic model calibration and validation;
    3. Further data collection for accurate calibration of the NRM kinetics, focusing on real waste matrices instead of synthetic solutions (on-going);
    4. Accurate calibration and validation of the developed models under dynamic conditions;
    5. Improvement of the physicochemical submodel reduction procedure with a more time-efficient (but still adequate) method to go through a multidimensional set of input scenarios for selection of species and reactions to be included in new nutrient recovery models;
    6. Model development of new promising nutrient recovery technologies in order to hasten their implementation and optimization, e.g. ion exchange, sorption, and alternative membrane filtration technologies;
    7. Further extension of the model library. According to the specific model application, the proposed extensions involve the inclusion of:
        - Lactate as specific substrate for biological sulfate removal in the NRM-AD, e.g. as in UCT (2007);
        - A transformer tool in the NRM-AD to allow for co-digestion of multiple input streams, e.g. the general integrated solid waste co-digestion (GISCOD) modelling tool (Zaher *et al.*, 2009b);
        - Biochemical transformations of sludge from enhanced biological P removal in the NRM-AD, e.g. as in Ikumi (2011);
        - Sludge retention in the NRM-AD, e.g. as in Cesur and Albertson (2005);
        - Microscale flocculation in the NRM-Prec, e.g. as in Crittenden *et al.* (2012);
        - Particle size distributions in the NRM-Prec, e.g. as in Perez *et al.* (2008);
        - Differential settling in the NRM-Settle and (if relevant) in the NRM-Prec, e.g. using the Stokes equation (Crittenden *et al.*, 2012);
        - Heavy metals and other contaminants in all NRM models.
    8. Coupling of the NRM library to soil nutrient balance models, e.g. the NDICEA (Nitrogen Dynamics In Crops rotation in Ecological Agriculture) modelling tool (Chapter 5), agro-economic tools (e.g. Chapter 4), and/or life cycle assessment (LCA) tools (Chapter 12) in order to optimize nutrient recovery strategies over the whole waste-nutrient-soil-plant system;

ix. Application of the probabilistic model-based design procedure of Talebizadeh *et al.* (2014) using the existing NMR library as an alternative to classical design guidelines;
x. Further performance of holistic life cycle assessments of nutrient recovery strategies, which may aid in effective policy making for recovered fertilizers and product marketing. The existing databases will have to be updated to allow for all aspects of nutrient recovery, including, for example, nutrient scarcity and organic carbon recycling.

- **Policy makers:**
  i. Use of the experimental results obtained in this PhD (among others) to establish a clearly defined and homogenized legislative framework for application of recovered bio-based products in agriculture, for product registration in fertilizer regulations, and/or for (inter)national product marketing. The legislative revisions should involve:
    - A reconsideration of the regulatory status of digestate and its derivatives (different than 'animal manure') based on their effective fertilizer properties. The introduction of a new category of 'renewable' organo-mineral and mineral fertilizers may be indispensable to stimulate the efficient use of these products for agricultural purposes;
    - Use of test data provided in this dissertation for registration of novel fertilizer products;
    - Improved differentiation between soils, crops, and fertilizer types in the recommendations given on N, P, and K fertilizer requirements, thereby stimulating the efficient and sustainable use of these essential nutrients in agriculture;
    - Additional use of Rhizon soil moisture samplers for determination of total direct available P, which should lead to better understanding and categorization of different inorganic and organic P fertilizers in environmental and fertilizer legislations;
    - Subsidisies for farmers for using bio-based products in agriculture;
    - Subsidisies for the conversion of animal manure, sludge, and other organic biodegradable waste flows through anaerobic (co-)digestion.

- **Agriculturists:**
  i. Increased use of bio-based recovered fertilizers as sustainable substitutes for chemical fertilizers. The developed roadmap (Chapter 11) provides guidance for successful implementation of (completely) bio-based fertilization scenarios;
  ii. Valorization of (excessive) animal manure, crop residues, and/or other agricultural biodegradable wastes through anaerobic (co-)digestion, and application of

digestate (mixtures) to the field as base fertilizer in order to improve nutrient use efficiencies;

iii. Increased collaboration among farmers for effective manure, digestate, and recovered product valorizarion at a regional scale.

- **Technology developers:**

  i. Development of new nutrient recovery technologies with minimal energy and chemical requirements, and maximal product valorization potential. The focus should not only be on N and P recovery, but also on other essential macro- and micronutrients, such as K, S, Ca, Mg, and Zn, as well as organic carbon;

  ii. Increased attention to the value of the recovered end products in order to meet the specifications required for agricultural and/or industrial end-use;

  iii. Increased use of models for process understanding, technology development, and optimization.

- **Operators:**

  i. Increased thinking in terms of product marketing and process sustainability prior to decision-making on operational strategies;

  ii. More detailed and accurate measurement of recommended input factors, as specified in Chapters 10 and 11;

  iii. Increased use of models to specify operating conditions, optimize process performance, for study of ‘what if’ conditions, and training of operators;

  iv. Use of the generic guidelines provided in Chapter 11 for nutrient recovery treatment train configuration and optimization.

- **Consultants (towards agriculture and waste processing facilities):**

  i. Stimulation of the acceptability of recovered products in the farming community;

  ii. Increased use of bio-based products in the set-up of agronomic recommendations for fertilizer application;

  iii. Encouragement of the implementation of nutrient recovery strategies instead of nutrient removal technologies at various waste(water) processing facilities;

  iv. Use of the developed roadmap (Chapter 11) for setting up nutrient recovery strategies, both in terms of bio-based fertilization recommendations and nutrient recovery treatment train configuration;

  v. Use of models to select optimal treatment train configurations and operating conditions;

  vi. Dissemination towards the general public in order to increase the social acceptance of nutrient recovery strategies and the efficient application of recovered products.

- **General public:**
  i. Increased open-mindedness and willingness towards innovation;
  ii. Minimization of nutrient wasting, e.g. through:
    - Better collection and separation of organic biodegradable household waste;
    - Use of bio-based fertilizers for home-gardening;
    - Reduction of meat consumption.

All of the above should foster the development and implementation of more sustainable, effective, and environmentally friendly practices for farming, waste(water) treatment, and food production. As such, this dissertation may contribute to the challenge of producing more food and energy with less environmental pollution, thereby meeting renewable energy and waste(water) directives across the world.

‘It is our nutrient world. We turned it into a nutrient chaos.

Time has come to restructure.

Solutions are there. Urgent action is required.’

Céline Vaneeckhaute, February 2015.

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APPENDIX

Picture: Arbor (2013)

APPENDIX 1:

Fate of micronutrients and heavy metals in water treatment of digestate using vibrating reversed osmosis

Table A1.1 Concentrations (g kg^{-1} FW) of aluminium (Al), cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) in the characterized process flows (mean ± standard deviation; n = 4). Numbers 1-11 correspond with the sample locations in Chapter 3: Figure 3.1. FW = fresh weight; LF = liquid fraction; TF = thick fraction.

	Al	**Cd**	**Cu**	**Fe**
Process flow	**mg kg^{-1} FW**	**mg kg^{-1} FW**	**mg kg^{-1} FW**	**mg kg^{-1} FW**
1. Digestate	285 ± 132	0.013 ± 0.019	6.4 ± 3.7	1,102 ± 128
2. TF Rotating drum	490 ± 107	0.025 ± 0.035	21 ± 4	1,977 ± 362
3. LF Rotating drum	<0.05 ± -	<0.004 ± -	0.029 ± 0.032	6.0 ± 7.0
4. Polymer solution	0.23 ± 0.33	<0.004 ± -	0.039 ± 0.012	0.64 ± 0.37
5. TF Screw press	715 ± 6	0.038 ± 0.053	22 ± 2	2,675 ± 764
6. LF Screw press	188 ± 240	0.27 ± 0.38	5.4 ± 5.9	553 ± 686
7. VSEP-permeate 1st filtration	0.046 ± 0.064	<0.004 ± -	<0.01 ± -	0.18 ± 0.05
8. VSEP-concentrate 1st filtration	1.8 ± 2.5	0.007 ± 0.011	0.26 ± 0.37	32 ± 42
9. VSEP-permeate 2nd filtration	<0.05 ± -	<0.004 ± -	0.0058 ± 0.0082	0.12 ± 0.13
10. VSEP-concentrate 2nd filtration	0.056 ± 0.079	<0.004 ± -	0.012 ± 0.007	3.3 ± 3.1
11. Dry end product	2,368 ± 195	1.3 ± 1.5	73 ± 9	8,652 ± 1,584

	Mn	**Ni**	**Pb**	**Zn**
Process flow	**mg kg^{-1} FW**	**mg kg^{-1} FW**	**mg kg^{-1} FW**	**mg kg^{-1} FW**
1. Digestate	28 ± 21	0.60 ± 0.85	0.46 ± -	16 ± 16
2. TF Rotating drum	68 ± 14	1.0 ± 1.4	0.93 ± -	31 ± 31
3. LF Rotating drum	0.64 ± 0.80	0.10 ± 0.07	<0.04 ± -	0.23 ± 0.23
4. Polymer solution	<0.005 ± -	<0.012 ± -	0.038 ± -	5.5 ± 5.5
5. TF Screw press	97 ± 22	1.3 ± 1.9	1.44 ± -	45 ± 45
6. LF Screw press	22 ± 28	0.52 ± 0.74	0.29 ± -	13 ± 13
7. VSEP-permeate 1st filtration	<0.005 ± -	0.020 ± 0.028	<0.04 ± -	0.06 ± 0.06
8. VSEP-concentrate 1st filtration	2.3 ± 2.4	0.22 ± 0.31	0.036 ± -	5.6 ± 8.0
9. VSEP-permeate 2nd filtration	<0.005 ± -	<0.012 ± -	<0.04 ± -	<0.02 ± 0.00
10. VSEP-concentrate 2nd filtration	0.24 ± 0.23	0.016 ± 0.023	<0.04 ± -	0.42 ± 0.40
11. Dry end product	438 ± 29	44 ± 11	4.9 ± -	463 ± 118

APPENDIX 2:

Total soil macronutrient amounts during the field trial in 2011-2012, and total micronutrient and heavy metal concentrations in soil and plant during the field trial in 2011

Table A2.1 Total soil nutrient amounts (N, P_2O_5, K_2O, S, Ca, Mg, Na; kg or ton ha^{-1}) in time for the eight different fertilization scenarios (mean ± standard deviation; n = 4). p-values and small letters refer to statistical analyses using one-way ANOVA and post-hoc pair-wise comparisons. * = significant difference at the 5 % level.

Scenario	**Jul/11**	**Sep/11**	**Oct/11**	**Aug/12**	**Nov/12**
N (ton ha^{-1})	**p = 0.97**	**p = 0.89**	**p = 0.99**	**p = 0.85**	**p = 0.11**
1	7.2 ± 0.6	7.2 ± 0.6	7.2 ± 0.6	7.4 ± 0.9	7.3 ± 1.8
2	7.2 ± 0.6	7.2 ± 0.6	7.4 ± 0.7	7.9 ± 0.9	6.4 ± 2.6
3	7.0 ± 0.2	7.2 ± 0.4	7.3 ± 0.5	8.1 ± 0.8	9.5 ± 0.8
4	7.2 ± 0.4	7.2 ± 0.6	7.3 ± 0.6	7.9 ± 1.6	9.0 ± 1.9
5	7.0 ± 0.9	7.3 ± 0.6	7.4 ± 0.7	8.1 ± 0.9	8.8 ± 1.0
6	7.3 ± 0.7	7.4 ± 0.2	7.5 ± 0.4	8.4 ± 0.1	9.3 ± 1.1
7	7.1 ± 0.6	7.5 ± 0.1	7.4 ± 0.5	8.4 ± 0.4	9.7 ± 0.2
8	6.7 ± 0.5	7.1 ± 0.5	7.2 ± 0.3	7.9 ± 0.3	9.7 ± 0.9
P_2O_5 (ton ha^{-1})	**p = 0.78**	**p = 0.89**	**p = 0.99**	**p = 0.57**	**p = 0.33**
1	14 ± 2	12 ± 1	12 ± 1	12 ± 1	7.7 ± 5.3
2	14 ± 1	11 ± 1	12 ± 1	11 ± 1	7.4 ± 5.7
3	14 ± 2	12 ± 1	12 ± 1	12 ± 1	12 ± 2
4	14 ± 1	12 ± 1	12 ± 1	12 ± 1	11 ± 1
5	14 ± 1	12 ± 1	12 ± 1	12 ± 0	11 ± 2
6	14 ± 2	11 ± 1	13 ± 1	12 ± 1	12 ± 1
7	13 ± 1	12 ± 1	12 ± 1	12 ± 1	12 ± 1
8	13 ± 2	12 ± 1	12 ± 1	12 ± 0	11 ± 1
K_2O (ton ha^{-1})	**p = 0.37**	**p = 0.10**	**p = 0.56**	**p = 1.0**	**p = 0.44**
1	1.7 ± 0.1	1.9 ± 0.3	2.0 ± 0.2	1.5 ± 0.6	1.6 ± 0.3
2	1.6 ± 0.1	1.5 ± 0.1	1.9 ± 0.3	1.4 ± 0.3	1.5 ± 0.2
3	1.8 ± 0.1	1.6 ± 0.4	2.0 ± 0.1	1.4 ± 0.1	1.7 ± 0.1
4	1.8 ± 0.2	1.5 ± 0.3	2.1 ± 0.3	1.4 ± 0.2	1.8 ± 0.2
5	1.8 ± 0.0	1.9 ± 0.2	1.9 ± 0.1	1.3 ± 0.4	1.7 ± 0.1
6	1.8 ± 0.2	2.0 ± 0.3	2.2 ± 0.5	1.5 ± 0.4	1.9 ± 0.2
7	1.8 ± 0.1	2.0 ± 0.3	2.1 ± 0.3	1.5 ± 0.2	1.8 ± 0.3
8	1.7 ± 0.1	1.7 ± 0.4	2.1 ± 0.1	1.4 ± 0.3	1.7 ± 0.2
S (ton ha^{-1})	**p = 0.87**	**p = 0.71**	**p = 0.70**	**p = 0.99**	**p = 0.10**
1	1.2 ± 0.1	1.2 ± 0.2	1.3 ± 0.1	1.5 ± 0.3	0.9 ± 0.2
2	1.2 ± 0.1	1.3 ± 0.1	1.3 ± 0.1	1.5 ± 0.3	0.9 ± 0.2
3	1.2 ± 0.0	1.3 ± 0.1	1.3 ± 0.1	1.7 ± 0.3	1.2 ± 0.0
4	1.2 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	1.5 ± 0.4	1.1 ± 0.2
5	1.2 ± 0.2	1.2 ± 0.1	1.3 ± 0.2	1.6 ± 0.4	1.2 ± 0.2
6	1.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.6 ± 0.3	1.2 ± 0.1
7	1.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.5 ± 0.2	1.2 ± 0.0
8	1.1 ± 0.1	1.2 ± 0.0	1.3 ± 0.1	1.5 ± 0.3	1.1 ± 0.1
Ca (ton ha^{-1})	**p = 0.72**	**p = 0.98**	**p = 0.96**	**p = 0.63**	**p = 0.18**
1	8.7 ± 1.9	8.5 ± 1.3	8.1 ± 1.3	9.6 ± 2.6	8.6 ± 2.2
2	8.5 ± 1.2	8.1 ± 1.1	8.3 ± 1.2	9.3 ± 1.5	9.1 ± 1.7
3	8.6 ± 1.0	8.6 ± 0.7	8.3 ± 0.9	11 ± 1	12 ± 2
4	8.0 ± 1.3	8.4 ± 1.5	7.9 ± 1.5	9.5 ± 2.5	9.5 ± 2.0
5	8.6 ± 0.6	8.4 ± 1.0	8.1 ± 1.3	11 ± 2	11 ± 2
6	8.4 ± 0.9	8.1 ± 0.6	8.5 ± 0.3	11 ± 1	11 ± 0
7	8.5 ± 0.9	8.5 ± 1.0	8.1 ± 0.7	11 ± 1	11 ± 1
8	7.3 ± 0.4	7.9 ± 0.8	7.6 ± 0.5	9.5 ± 0.4	10 ± 1
Mg (ton ha^{-1})	**p = 0.54**	**p = 0.38**	**p = 0.63**	**p = 0.15**	**p = 0.10**
1	1.7 ± 0.2	1.7 ± 0.1	1.6 ± 0.2	1.4 ± 0.2	1.5 ± 0.0
2	1.6 ± 0.2	1.6 ± 0.1	1.5 ± 0.1	1.6 ± 0.1	1.5 ± 0.2
3	1.7 ± 0.0	1.7 ± 0.1	1.6 ± 0.1	1.7 ± 0.1	1.7 ± 0.1
4	1.6 ± 0.1	1.6 ± 0.2	1.6 ± 0.2	1.3 ± 0.2	1.6 ± 0.2
5	1.6 ± 0.1	1.6 ± 0.0	1.5 ± 0.1	1.4 ± 0.1	1.6 ± 0.2
6	1.7 ± 0.1	1.6 ± 0.0	1.7 ± 0.1	1.6 ± 0.1	1.8 ± 0.1
7	1.7 ± 0.1	1.7 ± 0.1	1.7 ± 0.1	1.8 ± 0.1	1.8 ± 0.2
8	1.6 ± 0.1	1.7 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	1.6 ± 0.1
Na (kg ha^{-1})	**p = 0.030***	**p = 0.11**	**p = 0.38**	**p = 0.99**	**p = 0.29**
1	263 ± 72ab	214 ± 32	267 ± 20	212 ± 115	178 ± 29
2	227 ± 41b	209 ± 56	297 ± 62	217 ± 41	187 ± 26
3	246 ± 18b	200 ± 31	292 ± 79	211 ± 19	217 ± 26
4	225 ± 19b	188 ± 25	287 ± 22	227 ± 66	251 ± 8
5	335 ± 37a	264 ± 37	232 ± 31	234 ± 40	219 ± 82
6	264 ± 39ab	233 ± 23	298 ± 28	233 ± 35	271 ± 49
7	320 ± 76ab	225 ± 21	264 ± 10	209 ± 48	257 ± 52
8	266 ± 36ab	238 ± 42	317 ± 46	204 ± 38	237 ± 74

Table A2.2 Soil concentrations (g or mg kg^{-1} DW) of aluminium (Al), cadmium (Cd), chrome (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) for the eight different fertilization scenarios during the growing season (5/07/2011, 5/09/2011) and after the harvest (13/10/2011) (mean ± standard deviation; n = 4). Contents of arsenic (As) and mercury (Hg) were always below the detection limit of 25 mg kg^{-1} DW. '<' indicates that the value of one or more of the repetitions was below the detection limit; in this case the maximum value obtained is presented.

Metal	Unit	Date	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6	Scenario 7	Scenario 8
Al	g kg^{-1} DW	5/07/2011	5.1 ± 1.0	4.1 ± 0.0	5.0 ± 0.1	5.1 ± 1.0	5.2 ± 0.0	5.1 ± 1.0	5.2 ± 0.1	5.0 ± 0.1
		5/09/2011	4.0 ± 0.0	4.1 ± 0.1	4.1 ± 0.0	4.0 ± 0.0	4.1 ± 0.1	4.0 ± 0.1	5.0 ± 0.2	5.1 ± 0.2
		13/10/2011	4.0 ± 0.1	4.0 ± 0.0	4.0 ± 0.1	5.0 ± 0.1	4.0 ± 0.0	5.1 ± 0.2	5.1 ± 0.1	5.0 ± 0.1
Cd	mg kg^{-1} DW	5/07/2011	<0.40	<0.39	<0.40	<0.39	<0.39	<0.39	<0.39	<0.40
		5/09/2011	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.39
		13/10/2011	<0.64	0.53 ± 0.07	0.50 ± 0.09	<0.60	<0.40	0.43 ± 0.04	<0.43	<0.49
Cr	mg kg^{-1} DW	5/07/2011	11 ± 1	11 ± 0	11 ± 0	<12	11 ± 1	11 ± 1	11 ± 1	11 ± 1
		5/09/2011	11 ± 1	11 ± 1	11 ± 1	10 ± 1	11 ± 0	11 ± 1	11 ± 0	11 ± 0
		13/10/2011	11 ± 1	10 ± 1	11 ± 2	10 ± 1	10 ± 0	11 ± 0	10 ± 1	10 ± 0
Cu	mg kg^{-1} DW	5/07/2011	35 ± 3	33 ± 3	35 ± 1	<36	33 ± 3	35 ± 2	35 ± 2	32 ± 1
		5/09/2011	34 ± 1	32 ± 2	33 ± 2	32 ± 2	33 ± 2	33 ± 1	34 ± 2	33 ± 1
		13/10/2011	34 ± 2	33 ± 3	34 ± 2	33 ± 3	34 ± 3	33 ± 2	34 ± 2	31 ± 2
Fe	g kg^{-1} DW	5/07/2011	4.1 ± 1.0	3.0 ± 0.0	3.0 ± 0.0	4 ± 0	3.0 ± 0.0	3.0 ± 0.1	3.0 ± 0.1	3.2 ± 0.0
		5/09/2011	3.1 ± 0.1	3.0 ± 0.0	3.0 ± 0.0	3 ± 0	3.1 ± 0.2	3.0 ± 0.2	3.1 ± 0.2	3.1 ± 0.1
		13/10/2011	3.0 ± 0.1	3.0 ± 0.0	3.1 ± 0.1	3 ± 0	3.0 ± 0.1	3.1 ± 0.1	3.0 ± 0.1	3.0 ± 0.2
Mn	g kg^{-1} DW	5/07/2011	0.17 ± 0.01	0.16 ± 0.01	0.17 ± 0.01	<0.18	0.17 ± 0.02	0.17 ± 0.01	0.16 ± 0.01	0.15 ± 0.01
		5/09/2011	0.17 ± 0.00	0.16 ± 0.01	0.17 ± 0.01	0.15 ± 0.01	0.17 ± 0.01	0.17 ± 0.00	0.16 ± 0.01	0.15 ± 0.01
		13/10/2011	0.17 ± 0.02	0.17 ± 0.01	0.17 ± 0.01	0.16 ± 0.01	0.17 ± 0.01	0.18 ± 0.01	0.16 ± 0.02	0.16 ± 0.01
Ni	mg kg^{-1} DW	5/07/2011	3.8 ± 0.1	3.5 ± 0.3	3.7 ± 0.5	<4.0	3.2 ± 0.3	3.4 ± 0.2	3.4 ± 0.1	3.4 ± 0.3
		5/09/2011	2.6 ± 0.5	2.6 ± 0.2	3.0 ± 0.4	2.3 ± 0.4	3.1 ± 0.1	3.0 ± 0.2	3.0 ± 0.4	3.3 ± 0.4
		13/10/2011	4.0 ± 0.3	4.0 ± 0.5	4.6 ± 0.9	4.2 ± 0.6	2.7 ± 0.5	2.3 ± 0.2	2.3 ± 0.2	2.4 ± 0.5
Pb	mg kg^{-1} DW	5/07/2011	16 ± 1	15 ± 1	17 ± 2	<17	31 ± 30	16 ± 0	17 ± 1	15 ± 1
		5/09/2011	16 ± 1	16 ± 1	15 ± 1	16 ± 1	19 ± 8	15 ± 1	15 ± 0	16 ± 1
		13/10/2011	17 ± 1	16 ± 0	18 ± 1	15 ± 2	15 ± 1	16 ± 1	15 ± 1	16 ± 2
Zn	mg kg^{-1} DW	5/07/2011	58 ± 4	54 ± 5	57 ± 2	<59	57 ± 3	58 ± 1	56 ± 3	53 ± 2
		5/09/2011	56 ± 2	51 ± 3	54 ± 3	51 ± 5	54 ± 3	54 ± 1	54 ± 3	53 ± 2
		13/10/2011	58 ± 4	57 ± 4	61 ± 6	56 ± 7	52 ± 5	58 ± 10	52 ± 3	47 ± 2

Table A2.3 Biomass concentrations (g or mg kg^{-1} DW) of aluminium (Al), cadmium (Cd), chrome (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) for the eight different fertilization scenarios during the growing season (6/07/2011, 6/09/2011) and at the harvest (7/10/2011) (mean ± standard deviation; n = 4). Contents of arsenic (As) and mercury (Hg) were always below the detection limit of 25 mg kg^{-1} DW. '<' indicates that the value of one or more of the repetitions was below the detection limit; in this case the maximum value obtained is represented.

Metal	Unit	Date	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6	Scenario 7	Scenario 8
Al	mg kg^{-1} DW	6/07/2011	<80	61 ± 60	48 ± 36	37 ± 14	32 ± 16	31 ± 6	31 ± 7	<24
		6/09/2011	27 ± 3	26 ± 5	31 ± 16	26 ± 6	32 ± 15	26 ± 5	23 ± 7	34 ± 12
		7/10/2011	58 ± 13	63 ± 20	74 ± 24	68 ± 29	59 ± 8	52 ± 11	70 ± 8	73 ± 21
Cd	mg kg^{-1} DW	6/07/2011	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
		6/09/2011	<0.35	<0.20	<0.21	<0.20	<0.20	<0.20	<0.20	<0.23
		7/10/2011	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Cr	mg kg^{-1} DW	6/07/2011	<0.73	0.76 ± 0.41	0.59 ± 0.09	0.66 ± 0.04	0.51 ± 0.07	0.42 ± 0.07	0.55 ± 0.03	<1.28
		6/09/2011	1.4 ± 0.6	1.0 ± 0.1	1.7 ± 1.3	2.6 ± 1.0	4.3 ± 3.7	2.5 ± 1.7	1.1 ± 0.4	2.4 ± 2.3
		7/10/2011	6.9 ± 5.0	4.3 ± 1.6	3.7 ± 0.3	5.2 ± 1.3	4.5 ± 1.1	3.5 ± 0.4	11.3 ± 5.3	7.4 ± 8.7
Cu	mg kg^{-1} DW	6/07/2011	<7.1	7.7 ± 1.5	6.1 ± 0.7	6.5 ± 1.7	6.6 ± 1.8	5.8 ± 0.4	7.2 ± 0.5	<5.7
		6/09/2011	4.1 ± 0.4	4.1 ± 0.2	6.8 ± 3.6	3.9 ± 0.5	5.5 ± 1.4	5.2 ± 0.8	4.8 ± 1.2	4.3 ± 0.4
		7/10/2011	4.0 ± 0.8	4.0 ± 0.8	3.6 ± 0.4	3.9 ± 0.5	3.5 ± 1.0	2.9 ± 0.4	3.2 ± 0.3	3.7 ± 0.6
Fe	mg kg^{-1} DW	6/07/2011	<69	63 ± 7	61 ± 6	62 ± 4	58 ± 7	55 ± 4	60 ± 9	<55
		6/09/2011	46 ± 6	41 ± 5	44 ± 7	48 ± 6	65 ± 18	50 ± 11	41 ± 9	50 ± 11
		7/10/2011	171 ± 77	191 ± 113	196 ± 80	176 ± 9	183 ± 59	158 ± 54	236 ± 101	222 ± 80
Mn	mg kg^{-1} DW	6/07/2011	<31	29 ± 5	30 ± 9	28 ± 6	29 ± 6	24 ± 4	28 ± 1	<21
		6/09/2011	16 ± 3	15 ± 2	17 ± 5	13 ± 1	17 ± 1	15 ± 3	16 ± 3	13 ± 2
		7/10/2011	15 ± 3	403 ± 123	385 ± 77	338 ± 55	348 ± 22	284 ± 40	360 ± 9	318 ± 45
Ni	mg kg^{-1} DW	6/07/2011	<0.60	<0.82	<0.60	<0.87	<0.60	<0.60	<0.60	<0.60
		6/09/2011	1.0 ± 0.6	1.0 ± 0.5	1.8 ± 1.0	2.1 ± 0.4	3.2 ± 3.0	2.1 ± 1.3	1.3 ± 0.6	1.7 ± 1.3
		7/10/2011	2.9 ± 2.1	2.0 ± 0.6	1.6 ± 0.2	2.0 ± 0.7	2.0 ± 0.5	1.5 ± 0.2	4.7 ± 2.2	3.1 ± 3.6
Pb	mg kg^{-1} DW	6/07/2011	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
		6/09/2011	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
		7/10/2011	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Zn	mg kg^{-1} DW	6/07/2011	<70	64 ± 7	70 ± 13	65 ± 12	66 ± 5	63 ± 14	70 ± 4	<66
		6/09/2011	40 ± 8	41 ± 5	60 ± 29	35 ± 5	55 ± 26	41 ± 10	50 ± 16	33 ± 2
		7/10/2011	32 ± 8	27 ± 2	30 ± 5	27 ± 4	31 ± 2	27 ± 4	30 ± 3	26 ± 2

APPENDIX 3:

Soil organic carbon (SOC) effect of different bio-based fertilizers used as soil amendment

Materials and methods

Based on the data from Vaneeckhaute *et al.* (2014; Chapter 5), the effect of different organic residue amendments on the soil organic carbon (SOC) content has been investigated. In order to calculate changes in the soil carbon content as influenced by the choice of crop rotation, the Introductory Soil Carbon Balance Model (ICBM) was used (Andrén and Kätterer, 1997; Kätterer and Andrén, 2001). The model was applied to calculate the soil carbon content according to carbon inputs and mineralization rates.

All carbon from organic residue amendments enters the young carbon pool (Y). This pool has an outflow of carbon with a relatively high reaction coefficient of k_Y=0.8 (i.e. within one year 1-exp(-0.8)=55% of the carbon leaves the young carbon pool again; Andrén and Kätterer, 1997). From here, only a fraction described by a humification coefficient (h) enters the old carbon pool, which has a much lower reaction coefficient (k_O) than the young carbon pool. The humification coefficient describes the amount that stays in the soil in the longer term, i.e. the amount that is not mineralised and released as the greenhouse gas (GHG) CO_2 in the first year. The humification coefficients used in this study are shown in Table A3.1.

Table A3.1 Organic residues and the corresponding humification coefficients (h) used.

Type of material	Amendments	Base case h	Alternative case h	Reference
Manures	Pig manure	0.27	0.34	(Kätterer *et al.*, 2011)
Digestates	Raw digestate	0.41	0.34	(Kätterer *et al.*, 2011)
	Liquid fraction digestate			
	Digestate mixture			

In order to adapt the ICBM to Nordic conditions (cold climate regions; Peel *et al.*, 2007), the model was calibrated against data derived from the long-term soil carbon field experiment in Ekebo, Sweden (Kirchmann *et al.*, 1999). The Ekebo SOC field experiment includes two different crop rotations (with/without fodder production)[1] on a clay-rich soil. For each rotation 16 different fertilization regimes (all combinations of four nitrogen and four phosphorus/potassium fertilization levels) were tested. The experiment started in 1957 and is ongoing with regular soil carbon content analyses[2].

The model was calibrated by using the reaction coefficient of the old carbon pool (k_O) as a variable to fit model soil carbon predictions to the measured soil carbon data. This was done using crop residue data computed by the Nordic calculation method for comparison (Björnsson *et al.*, 2013).

The amount of carbon added to the soil in the different scenarios is given in Table A3.2.

Table A3.2 Amount of carbon added in Scenarios 1-8 and used for modelling the soil organic carbon effect.

Scenario	Carbon (kg ha^{-1})	Organic residue	Carbon (kg ha^{-1})
	2011 / 2012		**2011 / 2012**
1	807 / 220	Pig manure	1,235 / 568
2	807 / 220	Raw digestate	- / 1,514
3	807 / 220	Liquid fraction	538 / 509
4	847 / 963	Digestate mixture	1,187 / 1,078
5	831 / 1,029		
6	831 / 1,029		
7	837 / 329		
8	874 / 329		

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[1] The first crop rotation was designed for an animal production farm, with all cereal, straw, and sugar beet tops removed as bedding/fodder. The other crop rotation was designed for a pure plant production farm, with all straw and sugar beet tops left in the field.

[2] At an interval of approximately four years.

For modelling the SOC effect, it was assumed that each amendment was repeated for 20 years. The **SOC effect of the different fertilization strategies (Scenarios 1-8) was calculated as the annual change of the total amendment-derived SOC pools averaged over the first 20 years** (IPCC, 2006). The SOC effect presented is thus the amount of carbon that is sequestered (or released, if negative) on average going from one system to another, i.e. going from a system with no soil amendments to a system with soil amendments (digestate, manure, etc.). For direct comparison of the different residues, the SOC effect of each residue was modelled for an effective nitrogen application of 150 kg ha^{-1}.

Results

Of the eight different scenarios, Scenarios 4-6 result in SOC additions of between 0.34 and 0.43 Mg ha^{-1} (Fig. A3.1). In Scenarios 1-3, 7, and 8, a large difference exist between years. For Scenarios 1-3, the SOC addition was 0.25 and 0.07 Mg ha^{-1} in 2011 and 2012, respectively. For Scenarios 7 and 8, the SOC addition was 0.27-0.29 and 0.11 Mg ha^{-1} in 2011 and 2012, respectively. This large variation was due to large differences in composition of the pig manure and the resulting liquid fraction of digestate.

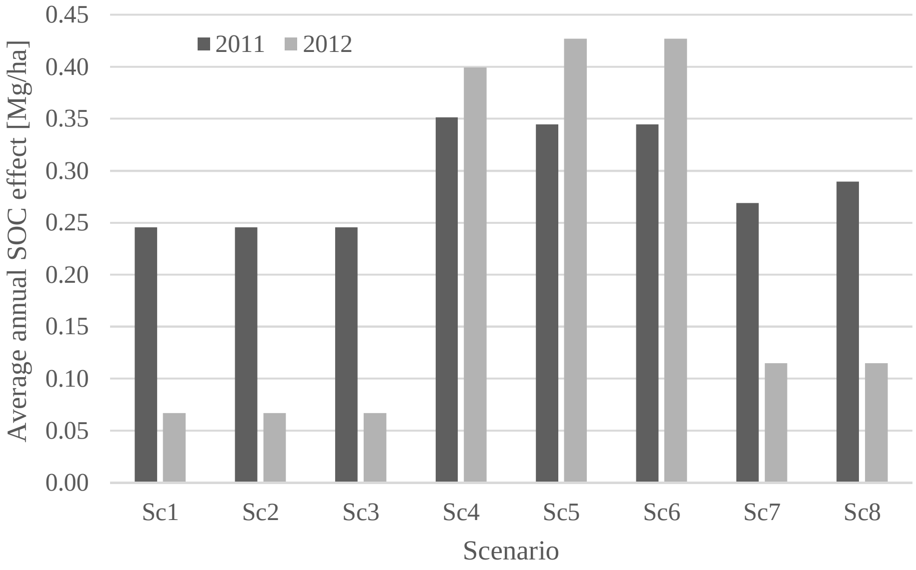

Figure A3.1 Effect of the different scenarios´ fertilization strategies on the soil organic carbon content (base case).

When comparing each of the organic residues on an exclusive use basis at an effective nitrogen level of 150 kg ha^{-1}, the raw digestate results in the highest (0.63 Mg ha^{-1}) SOC addition (Fig. A3.2, left). The digestate mix optimized for a high effective N content and low P content, resulted in SOC additions between 0.45 and 0.49 Mg ha^{-1}. Pig manure showed large differences in composition between years. When equal amounts of dry matter of the organic residues are applied, differences in SOC effect are less dramatic (Fig. A3.2, right).

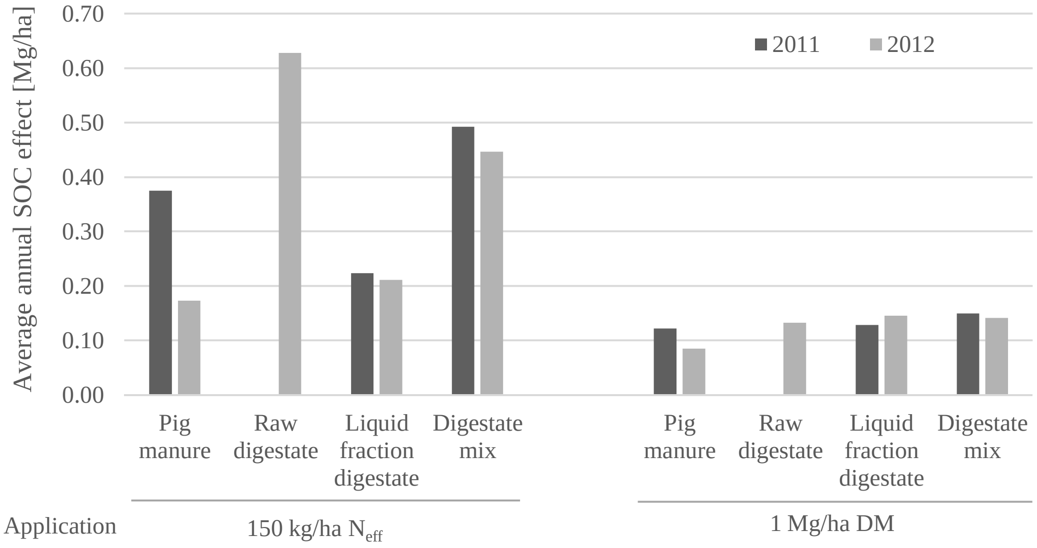

Figure A3.2 Effect of the different organic residues on soil organic carbon content (base case) after application of an amount corresponding to 150 kg ha^{-1} effective N (left) and to 1 Mg ha^{-1} dry matter (right), respectively.

Sensitivity analysis

There is a low sensitivity to changes in the humification factor for the SOC effect of the different organic residues (Fig. A3.3).

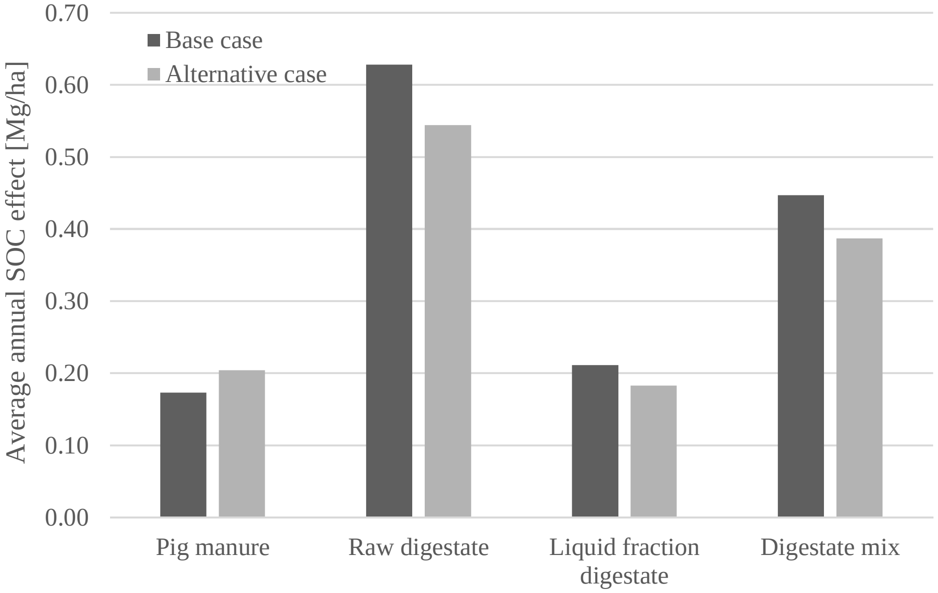

Figure A3.3 Effect of the different organic residues on soil organic carbon content based on the 2012 data.

Due to an additive effect, the differences between the scenarios disappear in the alternative case, in which equal humification factors for manure and digestate-based amendments were assumed (Fig. A3.4).

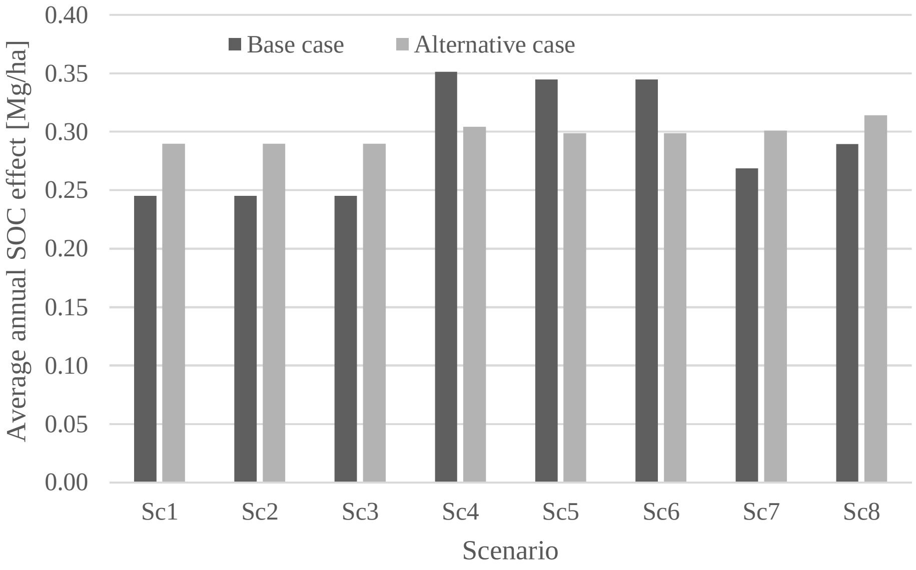

Figure A3.4 Effect of the different scenarios´ amendment strategies on the soil organic carbon content based on the 2011 data.

Discussion

Soil organic carbon (SOC) effect

The SOC effect shown in this study relates only to the effect of the organic residue amendments and excludes SOC changes due to existing SOC pools and the addition from other sources, e.g. crop residues. Although the model was calibrated for specific conditions such as Nordic climate and clay soil, this does not affect the relative differences between the scenarios and between the organic residues. The absolute level of SOC effect is, however, dependent on the calibration, i.e. the mineralisation rate of the more stable SOC fraction. Therefore, reliability of the absolute levels of SOC effect could be improved by choosing calibration data from the same climate zone and similar soil conditions.

Humification coefficient

Besides the actual amount of residue applied to a soil, the humification coefficient is the main parameter affecting the SOC effect. The humification coefficient is an indicator for the quality of the added carbon and is therefore residue-specific. Choosing the appropriate humification coefficient is therefore crucial when comparing different amendments.

Humification coefficients are usually derived from litter bag or ^{14}C experiments (Andrén and Kätterer, 1997). Earlier studies suggested that the fraction of carbon remaining after one year represents the humification coefficient (Janssen, 1984), but later studies suggest a longer initial degradation phase of 5-10 years (Andrén and Kätterer, 1997). A more detailed analysis of the estimation of humification coefficients can be found in Kätterer *et al.* (2011).

Often values for the humification coefficient are given for types of soil amendments such as straw, manure, digestate, etc. (e.g. Kätterer *et al.*, 2011). For comparing similar organic residues (raw digestate, liquid fractions digestate, mixtures, etc.), this poses an oversimplification, but more specific data are lacking.

Conclusions

Based on the preliminary results obtained in the present study comparing digestate derivatives and pig manure, raw digestates showed the most beneficial SOC effect, i.e. Scenarios 4-6 in Vaneeckhaute *et al.* (2014) (Chapter 5). It should, however, be noted that the results on the

SOC effect are indications only in respect to their absolute levels. Differences between treatments are dependent on the humification coefficients chosen for the assessment. Here, data supporting comparison of similar organic residues (digestate-based amendments) is lacking. Still, the above results show the importance of including an assessment of SOC effects in studies evaluating the environmental impact of anaerobic digestion, nutrient recovery, and bio-based fertilization scenarios. It is, for example, expected that inclusion of such effects will represent a better picture of greenhouse gas emissions compared to not including an assessment of SOC effects at all in life cycle assessments (see Chapter 12).

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APPENDIX 4:

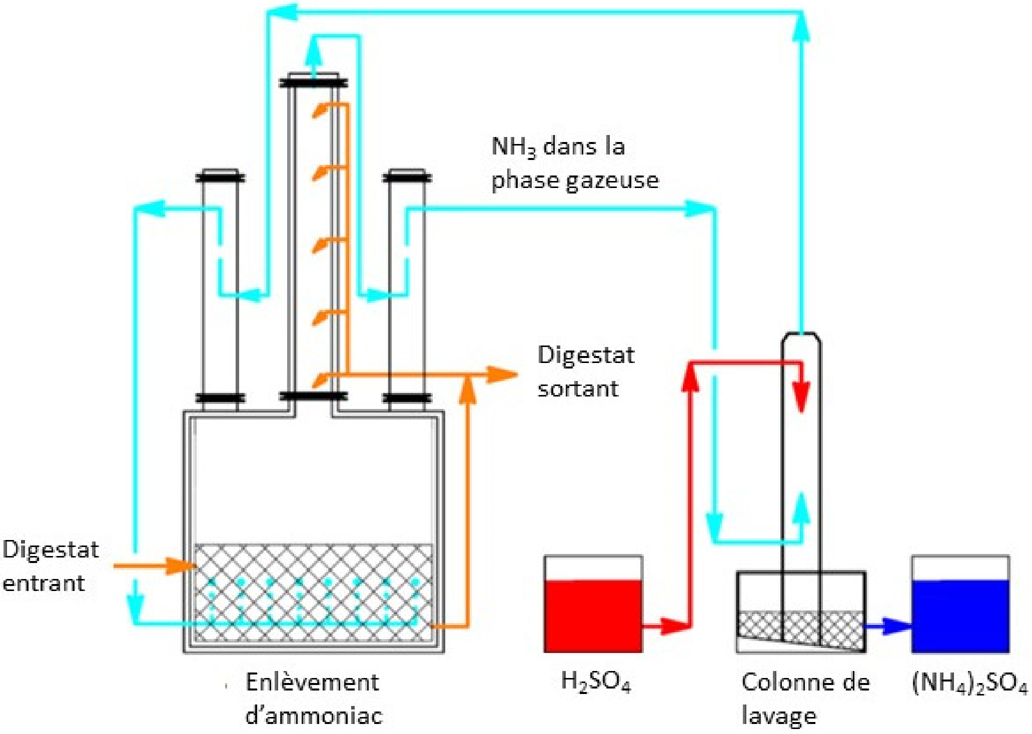
Technical fact sheet air scrubber water for Ville de Québec (in French)

FICHE TECHNIQUE 1

SULFATE D'AMMONIUM (S.A.) PROVENANT DE L'ENLÈVEMENT D'AMMONIAC

ORIGINE ET DÉSCRIPTION DU PRODUIT

Le sulfate d'ammonium (S.A.) est un sous-produit du traitement physicochimique des eaux (digestats liquides) par le procédé de stripage (= élimination) et absorption (= récupération) d'ammoniac. Dans une première colonne, après augmentation du pH (8.5-10) et de la température (55-70 ºC), l'ammonium présent dans l'eau est transformé en ammoniac et capturé par une phase gazeuse. Dans une deuxième colonne, l'ammoniac dans la phase gazeuse est absorbé par l'acide sulfurique. Le produit résultant est une solution liquide contenant du S.A. (25-38 %).



VALEUR AGRONOMIQUE

La valeur agronomique des S.A. (voir tableau ci-dessous) dépend beaucoup du procédé de stripage et du fournisseur. En général, la solution produite contient de 25 à 38 % de S.A. Selon les fournisseurs, le pourcentage restant serait surtout de l'eau et des traces d'acide sulfurique. Ces dernières peuvent influencer le continu en soufre (max.: 10 %).

$(NH_4)_2SO_4$ (%p)	N (%p)	P (%p)	K (%p)	S (%p)	Matière organique (%p)	Teneur en eau (%p)	pH (-)
25-38	5.3-8	0	0	6.1-10	0	62-75	4-7

Source : Fournisseurs des procédés de stripage et d'absorption d'ammoniac.
(%p) = pourcentage de poids.

AVANTAGES	CONTRAINTES
· Source d'azote et de soufre. · Engrais minéral. · Substitut pour les engrais chimiques. · L'azote et le soufre sont immédiatement disponibles pour les plantes = moins de pertes dans l'environnement. · Source indirecte de phosphore: l'ammonium libère le phosphore fixé dans le sol. · Engrais très pur: réaction sélective d'ammoniac gazeux avec l'acide sulfurique.	· Le S.A. ne contient pas de potassium ou d'autres macronutriments à part l'azote et le soufre. · Selon le procédé le pH peut être bas (4-7). · Le contenu en soufre peut être trop élevé pour certaines cultures. · Le S.A. est en forme liquide, donc les frais de transport pourraient être élevés. Cristallisation du produit possible.

VALEUR ÉCONOMIQUE

La valeur économique du produit est estimée à 132 $ par tonne matière humide, basée uniquement sur le contenu en N et en supposant une valeur moyenne de 1.55 \$ kg^{-1} N au Québec en 2014. Néanmoins, il est à noter que la demande de soufre au Québec est en augmentation, donc la valeur de cet élément nutritif pourrait aussi devenir importante dans le futur. En Europe, les S.A. provenant des procédés de stripage d'ammoniac sont présentement vendus sous forme liquide à 139-185 \$ $tonne^{-1}$ humide. Certaines applications produisent les S.A. sous forme cristallisée, ce qui augmente la valeur du produit et réduit les coûts de transportation.

CLASSIFICATION DANS LA RÉGLEMENTATION SUR LES ENGRAIS

Tiré du réglement sur les engrais à l'annexe 1 sous le point 1.2 page 31, le sel d'ammonium de l'acide sulfurique contenant au moins 20 % d'azote peut être reconnu comme engrais minéral (classe 1.2). La cristallisation ou le séchage des S.A. pourrait donc augmenter la valeur du produit.

CLASSIFICATION C-P-O-E DES S.A.

C	P	O	E
1	1	2 ou 3	1

La classification C-P-O-E du MDDEFP (2012) permet de connaître les restrictions d'utilisation des matières résiduelles fertilisantes (MRF) (doses d'épandage, entreposage, types d'usages et de cultures) pour leur recyclage en agriculture, sylviculture, horticulture, etc.

Contaminants chimiques (**C1)**
D'après les fournisseurs d'équipements, le S.A. ne contient aucun contaminant chimique, car le procédé concerne une élimination sélective d'ammoniac vers une phase gazeuse et une absorption sélective de l'ammoniac gazeux par l'acide sulfurique. Néanmoins, si l'acide sulfurique utilisé n'est pas de qualité industrielle à haute grade, il faudrait s'assurer qu'il n'y a pas de contaminants, p.ex. le mercure, dans l'acide.

Pathogènes (**P1)**
D'après les fournisseurs d'équipements, le S.A. ne contient aucun pathogène, car le procédé concerne une élimination sélective d'ammoniac vers une phase gazeuse et une absorption sélective de l'ammoniac gazeux par l'acide sulfurique. De plus, la température de réaction est élevée. Selon le guide MDDEFP (2012) aucune preuve d'absence des pathogènes n'est requise pour les résidus minéraux issus de procédés thermiques.

Odeurs (**O2/O3, à vérifier**)
Aucune caractérisation des odeurs n'est disponible. Car le produit contient l'ammonium et le soufre, ainsi des risques de volatilisation d'ammoniac et de H_2S sont réels. Néanmoins, car le pH du produit est souvent au-dessous de 7, les émissions pourraient être minimales. La classification des S.A. est donc à vérifier. Présentement, il est supposé que le produit ne se trouve pas dans la catégorie O1.

Corps étrangers (**E1)**
D'après les fournisseurs d'équipements, le S.A. ne contient aucun corps étranger, car le procédé concerne une élimination sélective d'ammoniac vers une phase gazeuse et une absorption sélective de l'ammoniac gazeux par l'acide sulfurique.

CONTRAINTES DE VALORISATION, ENTREPOSAGE ET RISQUES ENVIRONNEMENTAUX

CONTRAINTES DE VALORISATION	RISQUES POTENTIELS
• Contraintes O2/O3 (à vérifier): le stockage temporaire et l'épandage des S.A. doivent respecter une distance de 75 m des maisons d'habitation. De plus, les municipalités et les voisins doivent être avisés lors de la livraison et des activités d'épandage. Dans certains cas, la valorisation pour les aménagements en bordure de route est proscrite.	• Risque de volatilisation d'ammoniac et d'odeurs pendant l'épandage/stockage: une injection du produit dans le sol est recommandée. • Risque de corrosion, surtout si le pH du produit est acide (selon le fournisseur). • Risque de brûlure pour les plantes si le produit est appliqué directement sur les plantes + risque d'acidification des sols si le pH n'est pas ajusté avant l'application. • Risques pour la santé reliés au travail avec un produit acide (brûlure, irritation, etc.).

SECTEURS POTENTIELS D'UTILISATION

SECTEURS D'UTILISATION	
AGRICULTURE	
Grandes cultures (alimentation humaine)	√
Grandes cultures (alimentation animale)	√
Prairies (alimentation animale)	√
Pâturages (alimentation animale)	√
Cultures maraîchères et fruitières	√
Cultures énergétiques dédiées	√
HORTICULTURE / USAGE URBAIN	
Horticulture ornementale (plein champ et pépinières)	√
Espaces verts et parcs (aménagements paysagers)	1
FORESTERIE	√
AUTRES USAGES	
Fabrication de terreaux et engrais	√
Distribution aux citoyens	2
Abords d'infrastructures routières	1
Végétalisation de sites dégradés	√
Paillis - cultures alimentaires	n.a.
Paillis - cultures ornementales	n.a.

Légende :

Non
Incertitudes
Oui

1 : Une catégorie O1 est requise pour cette application. La catégorie de S.A. est à vérifier.

2 : Une catégorie O2 est requise pour cette application. La catégorie de S.A. est à vérifier.

n.a. : Non applicable.

<u>Modes d'application</u>

L'injection de S.A. dans les sols est recommandée pour éviter des émissions d'ammoniac.

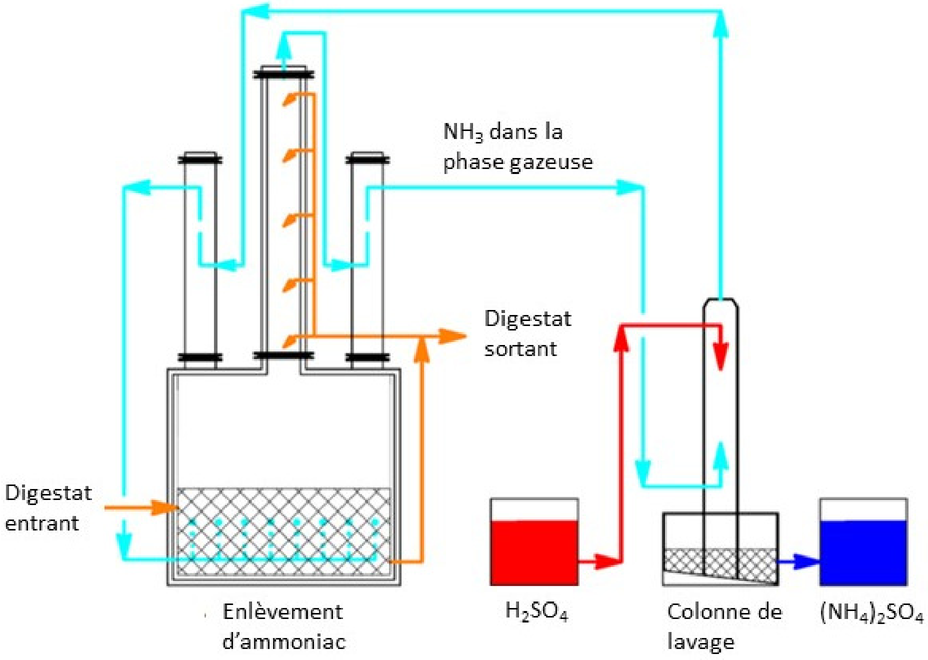
Si le pH est faible (4-5), il est recommandé d'ajuster le pH du produit afin d'éviter la brûlure des plantes et l'acidification du sol. Le pH des S.A. peut être ajusté en ajoutant de l'urée ou de la chaux. Une option économiquement intéressante serait de mélanger les S.A. avec le sous-produit base provenant du traitement d'air. Des tests sur le champs ont démontré que cette option est valable (Vaneeckhaute *et al.*, 2014).

FICHE TECHNIQUE 2

SULFATE D'AMMONIUM (S.A.) À PH ACIDE (3) PROVENANT DE L'ENLÈVEMENT D'AMMONIAC

ORIGINE ET DESCRIPTION DU PRODUIT

Le sulfate d'ammonium (S.A.) est un sous-produit du traitement physicochimique des eaux usées par le procédé de stripage (= élimination) et absorption (= récupération) d'ammoniac. L'opération s'applique à une température élevée (70-80 ºC). Ainsi l'ammonium présent dans l'eau est transformé en ammoniac et capturé par une phase gazeuse. Dans une deuxième colonne, l'ammoniac dans la phase gazeuse est absorbé par l'acide sulfurique, résultant en une solution liquide contenant du S.A. Pour garantir des faibles concentrations de NH_3 dans la décharge d'air et pour réduire les dimensions des unités, certains fournisseurs visent à garder un pH faible (± 3) dans la colonne d'absorption. Ainsi, une solution de S.A. à pH de 3 est obtenue. Cette pratique permet aussi d'obtenir une concentration plus élevée des S.A. de ± 40 %. Généralement, l'alcalinité naturellement disponible dans le digestat est suffisante pour augmenter le pH par stripage de CO_2 pendant l'opération. Ainsi, aucun ajout de produits chimiques n'est requis.



VALEUR AGRONOMIQUE

La valeur agronomique des S.A. à pH 3 est présentée ci-dessous

$(NH_4)_2SO_4$ (%p)	N (%p)	P (%p)	K (%p)	S* (%p)	Matière organique (%p)	pH (-)
40	8.5	0	0	9.7-10	0	3

Source : Fournisseur des procédés de stripage et d'absorption d'ammoniac.
(%p) = pourcentage de poids.
* Note : cette valeur est une estimation basée sur la stoechiométrie. Aucune analyse n'est disponible présentement pour un produit à pH 3.

Il a été approuvé par analyse que le produit ne contient aucun contaminant, tel que des métaux lourds ou des pathogènes. Néanmoins, la contamination potentielle est déterminée par la pureté de l'acide sulfurique utilisé.

AVANTAGES	CONTRAINTES
· Source d'azote et de soufre. · Engrais minéral. · Substitut pour les engrais chimiques. · L'azote et le soufre sont immédiatement disponibles pour les plantes = moins de pertes dans l'environnement. · Source indirecte de phosphore: l'ammonium libère le phosphore fixé dans le sol. · Engrais très pur: réaction sélective d'ammoniac gazeux avec l'acide sulfurique. · Aucune contamination détectée dans le produit (si l'acide sulfurique est de bonne qualité).	· Le S.A. ne contient pas de potassium ou d'autres macronutriments à part l'azote et le soufre. · Le pH est très bas pour application directe sur le champ. Le mélange avec l'urée pourrait améliorer la commercialisation. Autre option: ajout de chaux ou mélange avec le digestat ou des fumiers. · Le contenu en soufre peut être trop élevé pour certaines cultures. · Le S.A. est en forme liquide, donc les frais de transport pourraient être élevés. Cristallisation du produit possible.

VALEUR ÉCONOMIQUE

La valeur économique du produit est estimée à 132 $ par tonne matière humide, basée uniquement sur le contenu en N et en supposant une valeur moyenne de 1,55 $ par kg N au Québec en 2014. Néanmoins, il est à noter que la demande de soufre au Québec est en augmentation, donc la valeur de cet élément nutritif pourrait aussi devenir importante dans le futur. En Europe, les S.A. provenant des procédés de stripage d'ammoniac sont présentement vendus sous forme liquide à 139-185 $ par tonne humide. Certaines applications produisent les S.A. sous forme cristallisée, ce qui augmente la valeur du produit et réduit les coûts de transportation.

CLASSIFICATION DANS LA RÉGLEMENTATION SUR LES ENGRAIS

Tiré du réglement sur les engrais à l'annexe 1 sous le point 1.2 page 31, le sel d'ammonium de l'acide sulfurique contenant au moins 20 % d'azote peut être reconnu comme engrais minéral (classe 1.2). La cristallisation ou le séchage des S.A. pourrait donc augmenter la valeur du produit.

CLASSIFICATION C-P-O-E DES S.A.

C	P	O	E
1	1	1	1

La classification C-P-O-E du MDDEFP (2012) permet de connaître les restrictions d'utilisation des matières résiduelles fertilisantes (MRF) (doses d'épandage, entreposage, types d'usages et de cultures) pour leur recyclage en agriculture, sylviculture, horticulture, etc.

Contaminants chimiques (**C1)**
Des analyses par les fournisseurs ont démontré que le S.A. à pH 3 ne contient aucun contaminant chimique, car le procédé concerne une élimination sélective d'ammoniac vers une phase gazeuse et une absorption sélective de l'ammoniac gazeux par l'acide sulfurique. Néanmoins, si l'acide sulfurique utilisé n'est pas de qualité industrielle à haute grade, il faudrait s'assurer qu'il n'y a pas de contaminants, p.ex. le mercure, dans l'acide.

Pathogènes (**P1)**
Des analyses par les fournisseurs ont démontré que le S.A. à pH 3 ne contient aucun pathogène, car le procédé concerne une élimination sélective d'ammoniac vers une phase gazeuse et une absorption sélective de l'ammoniac gazeux par l'acide sulfurique. De plus, la température de réaction est élevée. Selon le guide MDDEFP (2012) aucune preuve d'absence des pathogènes n'est requise pour les résidus minéraux issus de procédés thermiques.

Odeurs (**O1)**
Puisque le pH du produit est très faible, aucune décharge d'odeur (NH_3, amines, H_2S,…) est attendue. D'après l'expérience des fournisseurs, le produit est pratiquement inodore. Toutes les MRF ayant obtenu des cotes d'odeurs moyennes inférieures à celle du fumier solide de bovins laitiers sont considérées O1. Il est donc très raisonnable de classifier les S.A. à faible pH dans la catégorie O1.

Corps étrangers (**E1)**
D'après les fournisseurs d'équipements, le S.A. ne contient aucun corps étranger, car le procédé concerne une élimination sélective d'ammoniac vers une phase gazeuse et une absorption sélective de l'ammoniac gazeux par l'acide sulfurique.

CONTRAINTES DE VALORISATION, ENTREPOSAGE ET RISQUES ENVIRONNEMENTAUX

CONTRAINTES DE VALORISATION	RISQUES POTENTIELS
· Faible pH.	· Risque de corrosion car le pH du produit est acide. · Risque de brûlure pour les plantes si le produit est appliqué directement sur les plantes + risque d'acidification des sols si le pH n'est pas ajusté avant l'application. · Risques pour la santé reliés au travail avec un produit acide (brûlure, irritation, etc.).

SECTEURS POTENTIELS D'UTILISATION

SECTEURS D'UTILISATION	
AGRICULTURE	
Grandes cultures (alimentation humaine)	√
Grandes cultures (alimentation animale)	√
Prairies (alimentation animale)	√
Pâturages (alimentation animale)	√
Cultures maraîchères et fruitières	√
Cultures énergétiques dédiées	√
HORTICULTURE / USAGE URBAIN	
Horticulture ornementale (plein champ et pépinières)	√
Espaces verts et parcs (aménagements paysagers)	√
FORESTERIE	√
AUTRES USAGES	
Fabrication de terreaux et engrais	√
Distribution aux citoyens	1
Abords d'infrastructures routières	√
Végétalisation de sites dégradés	√
Paillis - cultures alimentaires	n.a.
Paillis - cultures ornementales	n.a.

Légende :

Non
Incertitudes
Oui

1 : Incertitude relié au faible pH. Une option serait de mélanger les S.A. avec l'urée avant la commercialisation.
n.a. : Non applicable.

Modes d'application

Pour application comme engrais, il est recommandé d'ajuster le pH du produit afin d'éviter la brûlure des plantes et l'acidification du sol. Le pH des S.A. peut être ajusté en ajoutant de l'urée ou de la chaux. Une option économiquement intéressante serait de mélanger les S.A. avec le sous-produit base provenant du traitement d'air. Des tests sur le champs ont démontré que cette option est valable (Vaneeckhaute *et al.*, 2014).

Le produit pourrait aussi être utilisé comme matière primaire pour la fabrication des engrais chimiques ou pour l'industrie des pâtes et papiers.

APPENDIX 5:

Physicochemical species and reactions included in the nutrient recovery models (NRM)

Table A5.1 Dissolved species included in each nutrient recovery model (NRM) (1: NRM-AD = anaerobic digestion, 2: NRM-Prec = precipitation/crystallization, 3: NRM-Strip = stripper, 4: NRM-Scrub = scrubber) resulting from speciation calculations using PHREEQC (and Visual MINTEQ) modelling software.

Species	1	2	3	4	Species	1	2	3	4	Species	1	2	3	4	Species	1	2	3	4
Acetate$^-$	X	X	X	-	DOM	-	X	X	-	HSO_4-	-	-	-	X	NaCl (aq)	X	X	X	-
Al^{3+}	X	X	X		Fe^{2+}	X	X	X	-	H-Valerate	X	X	X	-	$NaCO_3^-$	-	X	X	-
$Al(OH)_2^+$	X	X	-	-	Fe^{3+}	X	X	X	-	K^+	X	X	X	-	$NaHCO_3$ (aq)	X	X	-	-
$Al(OH)_3$ (aq)	X	X	-	-	$FeCl^+$	-	X	-	-	K-Acetate (aq)	X	X	X	-	$NaHPO_4^-$	X	X	X	-
$Al(OH)_4^-$	X	X	X	-	$FeCO_3$	X	-	-	-	KCl (aq)	X	X	X	-	NaH_2PO_4 (aq)	X	X	-	-
Butyrate$^-$ (aq)	X	X	X	-	$FeHPO_4$ (aq)	X	X	-	-	$KHPO_4^-$	X	X	X	-	$NaNO_3$ (aq)	-	X	X	-
Ca^{2+}	X	X	X	-	$FeHS^+$	X	-	-	-	KH_2PO_4	X	X	-	-	NaOH	-	X	X	-
Ca-Acetate$^+$	X	X	X	-	$Fe(HS)_2$	X	-	-	-	KNO_3 (aq)	-	X	X	-	$NaPO_4^{2-}$	-	X	-	-
Ca-Butyrate$^+$ (aq)	X	X	X	-	$FeH_2PO_4^+$	X	-	-	-	KOH (aq)	-	X	X	-	$NaSO_4^-$	X	X	X	-
$CaCl^+$	X	X	X	-	$FeNH_3^{2+}$	X	X	X	-	KPO_4^{2-}	-	X	-	-	N_2 (aq)[a]	X	(X)	X	X
$CaCO_3$ (aq)	X	X	X	-	$Fe(NH_3)_2^{2+}$	X	X	X	-	KSO_4^-	X	X	X	-	NH_2COO^-	X	-	-	X
Ca-DOM	-	X	X	-	$Fe(NH_3)_3^{2+}$	-	X	-	-	Mg^{2+}	X	X	X	-	NH_3 (aq)	X	X	X	X
$CaHCO_3^+$	X	-	X	-	$FeOH^+$	X	X	X	-	Mg-Acetate$^+$	X	X	X	-	NH_4^+	X	X	X	X
$CaHPO_4$ (aq)	X	X	X	-	$Fe(OH)_2$ (aq)	X	X	X	-	Mg-Butyrate$^+$	X	X	X	-	$NH_4SO_4^-$	X	X	X	X
$CaH_2PO_4^+$	X	-	-	-	$Fe(OH)_3^-$	-	X	X	-	$MgCl^+$	X	X	X	-	NO_3^-	X	X	X	X
$CaNH_3^{2+}$	X	X	X	-	$FeSO_4$ (aq)	-	X	-	-	$MgCO_3$ (aq)	X	X	X	-	OH^-	X	X	X	X
$Ca(NH_3)_2^{2+}$	-	X	-	-	H^+	X	X	X	X	$Mg_2CO_3^{2+}$	-	X	X	-	O_2 (aq)	-	X	X	X
$CaNO_3^+$	-	-	X	-	H_2 (aq)	X	-	X	X	Mg-DOM	-	X	X	-	PO_4^{3-}	X	X	X	-
$CaOH^+$	-	-	X	-	H-Acetate	X	X	X	-	$MgHCO_3^+$	X	X	X	-	Propionate$^-$	X	X	X	-
$CaPO_4^-$	X	X	X	-	H-Butyrate	X	X	X	-	$MgHPO_4$ (aq)	X	X	X	-	SO_4^{2-}	X	X	X	X
Ca-Propionate$^+$	X	X	X	-	H-DOM	-	X	X	-	$Mg(NH_3)_2^{2+}$	X	X	X	-	Valerate$^-$	X	X	X	-
$CaSO_4$ (aq)	X	X	X	-	HCO_3^-	X	X	X	X	$MgOH^+$	X	X	X	-					
Ca-Valerate$^+$ (aq)	X	X	X	-	HPO_4^{2-}	X	X	X	-	$MgPO_4^-$	X	X	X	-					
CH_4	X	X	X	X	$H_2PO_4^-$	X	X	-	-	Mg-Propionate$^+$	X	X	X	-					
Cl^-	X	X	X	-	HS^-	X	-	X	X	$MgSO_4$ (aq)	X	X	X	-					
CO_2	X	X	X	X	H_2S (aq)	X	-	X	X	Na^+	X	X	X	-					
CO_3^{2-}	X	X	X	X	H-Propionate	X	X	X	-	Na-Acetate (aq)	X	X	X	-					

[a] Values between brackets represent the use of air instead of chemicals for pH-adjustment.

Table A5.2 Acid-base systems and reactions (AB) included in each nutrient recovery model (NRM). AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber; Ac = acetate; Bu = butyrate; Pro = propionate; Va = valerate.

Acid-base system	**No.**	**Acid-base reaction**	**AD**	**Prec**	**Strip**	**Scrub**
Acetate	AB1	$Ac^- + H^+ \leftrightarrow HAc$	X	X	X	-
Ammonia	AB2	NH_3 (aq) + $H^+ \leftrightarrow NH_4^+$	X	X	X	X
Butyrate	AB3	$Bu^- + H^+ \leftrightarrow HBu$	X	X	X	-
Carbonate	AB4	$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$	X	X	X	X
	AB5	$HCO_3^- + H^+ \leftrightarrow H_2CO_3$ (aq)	X	X	X	X
Phosphate	AB6	$PO_4^{3-} + H^+ \leftrightarrow HPO_4^{2-}$	X	X	X	-
	AB7	$HPO_4^{2-} + H^+ \leftrightarrow H_2PO_4^-$	X	X	-	-
	AB8	$H_2PO_4^- + H^+ \leftrightarrow H_3PO_4$	X	X	-	-
Propionate	AB9	$Pro^- + H^+ \leftrightarrow HPro$	X	X	X	-
Sulfate	AB10	$SO_4^{-2} + H^+ \leftrightarrow HSO_4^-$	-	-	-	X
Sulfide	AB11	$HS^- + H^+ \leftrightarrow H_2S$	X	-	X	X
Valerate	AB12	$Va^- + H^+ \leftrightarrow HVa$	X	X	X	-
Water	AB13	$H^+ + OH^- \leftrightarrow H_2O$	X	X	X	X

Table A5.3 Redox couples and reactions (R) included in each nutrient recovery model (NRM). AD = AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber; Ac = acetate; Bu = butyrate; Pro = propionate; Va = valerate.

Redox system	**No.**	**Redox reaction**	**AD**	**Prec**	**Strip**	**Scrub**
C(+IV) / C(-IV)	R1	$CO_3^{2-} + 10H^+ + 8e^- \leftrightarrow CH_4 + 3H_2O$	X	X	X	X
Fe(+II) / Fe(+III)	R2	$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	X	X	X	-
H(0) / H(+I)	R3	$2H^+ + 2e^- \leftrightarrow H_2$	X	-	X	X
N(-III) / N(+V)	R4	$NO_3^- + 10H^+ + 8e^- \leftrightarrow NH_4^+ + 3H_2O$	X	X	X	X
N(0) / N(+V)	R5	$2NO_3^- + 12H^+ + 10e^- \leftrightarrow N_2 + 6H_2O$	X	(X)[a]	X	X
O(-II) / O(0)	R6	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	-	X	X	X
S(-II) / S(+VI)	R7	$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O$	X	-	X	X

[a] Values between brackets represent the use of air instead of chemicals for pH-adjustment.

Table A5.4 Ion pairing reactions (IP) included in each nutrient recovery model (NRM). AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber.

No.	Ion pairing reaction	AD	Prec	Strip	Scrub
IP1	$Al^{3+} + 2OH^- \leftrightarrow Al(OH)_2^+$	X	-	-	-
IP2	$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3$	X	X	-	-
IP3	$Al^{3+} + 4OH^- \leftrightarrow Al(OH)_4^-$	X	X	X	-
IP4	$Ca^{2+} + Ac^- \leftrightarrow CaAc^+$	X	X	X	-
IP5	$Ca^{2+} + Bu^- \leftrightarrow CaBu^+$	X	X	X	-
IP6	$Ca^{2+} + Cl^- \leftrightarrow CaCl^+$	X	X	X	-
IP7	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$	X	X	X	-
IP8	$Ca^{2+} + DOM \leftrightarrow Ca\text{-}DOM$	-	X	X	-
IP9	$Ca^{2+} + HCO_3^- \leftrightarrow CaHCO_3^+$	X	-	X	-
IP10	$Ca^{2+} + HPO_4^{2-} \leftrightarrow CaHPO_4$	X	X	X	-
IP11	$Ca^{2+} + H_2PO_4^- \leftrightarrow CaH_2PO_4^+$	X	-	-	-
IP12	$Ca^{2+} + NH_3 \leftrightarrow CaNH_3^{2+}$	X	X	X	-
IP13	$Ca^{2+} + 2NH_3 \leftrightarrow Ca(NH_3)_2^{2+}$	-	X	-	-
IP14	$Ca^{2+} + NO_3^- \leftrightarrow CaNO_3^+$	-	-	X	-
IP15	$Ca^{2+} + OH^- \leftrightarrow CaOH^+$	-	-	X	-
IP16	$Ca^{2+} + PO_4^{3-} \leftrightarrow CaPO_4^-$	X	X	X	-
IP17	$Ca^{2+} + Pro^- \leftrightarrow CaPro^+$	X	X	X	-
IP18	$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4$	X	X	X	-
IP19	$Ca^{2+} + Va^- \leftrightarrow CaVa^+$	X	X	X	-
IP20	$Fe^{2+} + Cl^- \leftrightarrow FeCl^+$	-	X	-	-
IP21	$Fe^{2+} + CO_3^{2-} \leftrightarrow FeCO_3$	X	-	-	-
IP22	$Fe^{2+} + HPO_4^{2-} \leftrightarrow FeHPO_4$	X	X	-	-
IP23	$Fe^{2+} + HS^- \leftrightarrow FeHS^+$	X	-	-	-
IP24	$Fe^{2+} + 2HS^- \leftrightarrow Fe(HS)_2$	X	-	-	-
IP25	$Fe^{2+} + H_2PO_4^- \leftrightarrow FeH_2PO_4^+$	X	-	-	-
IP26	$Fe^{2+} + NH_3 \leftrightarrow FeNH_3^{2+}$	X	X	X	-
IP27	$Fe^{2+} + 2NH_3 \leftrightarrow Fe(NH_3)_2^{2+}$	X	X	X	-
IP28	$Fe^{2+} + 3NH_3 \leftrightarrow Fe(NH_3)_3^{2+}$	-	X	-	-
IP29	$Fe^{2+} + OH^- \leftrightarrow FeOH^+$	X	X	X	-
IP30	$Fe^{2+} + 2OH\text{-} \leftrightarrow Fe(OH)_2$	X	X	X	-
IP31	$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3$	-	X	X	-
IP32	$Fe^{2+} + SO_4^{2-} \leftrightarrow FeSO_4\ (aq)$	-	X	-	-
IP33	$K^+ + Ac^- \leftrightarrow KAc$	X	X	X	-
IP34	$K^+ + Cl^- \leftrightarrow KCl$	X	X	X	-
IP35	$K^+ + HPO_4^{2-} \leftrightarrow KHPO_4^-$	X	X	X	-
IP36	$K^+ + NO_3^- \leftrightarrow KNO_3$	-	X	X	-
IP37	$K^+ + OH^- \leftrightarrow KOH$	-	X	X	-
IP38	$K^+ + PO_4^{3-} \leftrightarrow KPO_4^{2-}$	-	X	-	-
IP39	$K^+ + H_2PO_4^- \leftrightarrow KH_2PO_4$	X	X	-	-
IP40	$K^+ + SO_4^{2-} \leftrightarrow KSO_4^-$	X	X	X	-
IP41	$Mg^{2+} + Ac^- \leftrightarrow MgAc^+$	X	X	X	-
IP42	$Mg^{2+} + Bu^- \leftrightarrow MgBu^+$	X	X	X	-
IP43	$Mg^{2+} + Cl^- \leftrightarrow MgCl^+$	X	X	X	-
IP44	$Mg^{2+} + CO_3^{2-} \leftrightarrow MgCO_3$	X	X	X	-
IP45	$2Mg^{2+} + CO_3^{2-} \leftrightarrow Mg_2CO_3^{2+}$	-	X	X	-
IP46	$Mg^{2+} + DOM \leftrightarrow Mg\text{-}DOM$	-	X	X	-
IP47	$Mg^{2+} + HCO_3^- \leftrightarrow MgHCO_3^+$	X	X	X	-
IP48	$Mg^{2+} + HPO_4^{2-} \leftrightarrow MgHPO_4$	X	X	X	-
IP49	$Mg^{2+} + 2NH_3 \leftrightarrow Mg(NH_3)_2^{2+}$	X	X	X	-
IP50	$Mg^{2+} + OH^- \leftrightarrow MgOH^+$	X	X	X	-
IP51	$Mg^{2+} + PO_4^{3-} \leftrightarrow MgPO_4^-$	X	X	X	-
IP52	$Mg^{2+} + Pro^- \leftrightarrow MgPro^+$	X	X	X	-
IP53	$Mg^{2+} + SO_4^{2-} \leftrightarrow MgSO_4$	X	X	X	-
IP54	$Na^+ + Ac^- \leftrightarrow NaAc$	X	X	X	-
IP55	$Na^+ + Cl^- \leftrightarrow NaCl$	X	X	X	-
IP56	$Na^+ + CO_3^{2-} \leftrightarrow NaCO_3^-$	-	X	X	-
IP57	$Na^+ + HCO_3^- \leftrightarrow NaHCO_3$	X	X	-	-
IP58	$Na^+ + HPO_4^{2-} \leftrightarrow NaHPO_4^-$	X	X	X	-
IP59	$Na^+ + H_2PO_4^- \leftrightarrow NaH_2PO_4\ (aq)$	X	X	-	-
IP60	$Na^+ + NO_3^- \leftrightarrow NaNO_3$	-	X	X	-
IP61	$Na^+ + OH^- \leftrightarrow NaOH$	-	X	X	-
IP62	$Na^+ + PO_4^{3-} \leftrightarrow NaPO_4^{2-}$	-	X	-	-
IP63	$Na^+ + SO_4^{2-} \leftrightarrow NaSO_4^-$	X	X	X	-
IP64	$NH_3 + HCO_3^- \leftrightarrow NH_2COO^- + H_2O$	X	-	-	X
IP65	$NH_4^+ + SO_4^{2-} \leftrightarrow NH_4SO_4^-$	X	X	X	X

Table A5.5 Liquid-solid/solid-liquid transfer reactions (P) included in each nutrient recovery model (NRM). AD = anaerobic digestion; Prec = precipitation/crystallization; P = precipitation; Strip = stripper; Scrub = scrubber.

No.	PHREEQC Phase name	Liquid-solid / solid-liquid transfer reaction	AD	Prec	Strip	Scrub
P1	Al_2O_3 (s)	$Al_2O_3(s) + 6H^+ \leftrightarrow 2Al^{3+} + 3H_2O$	X	-	-	-
P2	$AlPO_4$	$AlPO_4 \leftrightarrow Al^{3+} + PO_4^{3-}$	X	X	-	-
P3	Ammoniumsulfate	$(NH_4)_2SO_4 \leftrightarrow 2NH_4^+ + SO_4^{2-}$	-	-	-	X
P4	Anhydrite	$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-}$	X	-	-	-
P5	Aragonite	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	X	X	X	-
P6	Artinite	$MgCO_3{:}Mg(OH)_2{:}3H_2O + 2H^+ \leftrightarrow 2Mg^{2+} + CO_3^{2-} + 5H_2O$	-	X	X	-
P7	Boehmite	$AlOOH + 3H^+ \leftrightarrow Al^{3+} + 2H_2O$	X	X	-	-
P8	Brucite	$Mg(OH)_2 + 2H^+ \leftrightarrow Mg^{2+} + 2H_2O$	-	X	X	-
P9	$CaHPO_4$ (s)	$CaHPO_4 \leftrightarrow Ca^{2+} + H^+ + PO_4^{3-}$	X	X	X	-
P10	$CaHPO_4{:}2H_2O$ (s)	$CaHPO_4{:}2H_2O \leftrightarrow Ca^{2+} + H^+ + PO_4^{3-} + 2H_2O$	X	X	X	-
P11	$Ca_4H(PO_4)_3{:}3H_2O$ (s)	$Ca_4H(PO_4)_3{:}3H_2O \leftrightarrow 4Ca^{2+} + H^+ + 3PO_4^{3-} + 3H_2O$	X	X	X	-
P12	Calcite	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	X	X	X	-
P13	$Ca_3(PO_4)_2$ (am1)	$Ca_3(PO_4)_2 \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	X	X	X	-
P14	$Ca_3(PO_4)_2$ (am2)	$Ca_3(PO_4)_2 \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	X	X	X	-
P15	$Ca_3(PO_4)_2$ (beta)	$Ca_3(PO_4)_2 \leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	X	X	X	-
P16	Diaspore	$AlOOH + 3H^+ \leftrightarrow Al^{3+} + 2H_2O$	X	X	X	-
P17	Dolomite (ordered)	$CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	X	X	X	-
P18	Dolomite (disordered)	$CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	X	X	X	-
P19	$Fe(OH)_2$ (am)	$Fe(OH)_2 + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O$	-	X	X	-
P20	FeS(ppt)	$FeS + H^+ \leftrightarrow Fe^{2+} + HS^-$	X	-	-	-
P21	Gibbsite	$Al(OH)_3 + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$	X	X	-	-
P22	Hercynite	$FeAl_2O_4 + 8H^+ \leftrightarrow Fe^{2+} + 2Al^{3+} + 4H_2O$	X	X	X	-
P23	Huntite	$CaMg_3(CO_3)_4 \leftrightarrow 3Mg^{2+} + Ca^{2+} + 4CO_3^{2-}$	-	-	X	-
P24	Hydromagnesite	$Mg_5(CO_3)_4(OH)_2{:}4H_2O + 2H^+ \leftrightarrow 5Mg^{2+} + 4CO_3^{2-} + 6H_2O$	-	-	X	-
P25	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_5 + 5H^+ \leftrightarrow 10Ca^{2+} + 6PO_4^{3-} + 5H_2O$	X	X	X	-
P26	K-struvite	$MgKPO_4{:}6H_2O \leftrightarrow Mg^{2+} + K^+ + PO_4^{3-} + 6H_2O$	X	X	X	-
P27	Mackinawite	$FeS + H^+ \leftrightarrow Fe^{2+} + HS^-$	X	-	-	-
P28	Magnesite	$MgCO_3 \leftrightarrow Mg^{2+} + CO_3^{2-}$	X	X	X	-
P29	$Mg(OH)_2$ (active)	$Mg(OH)_2 + 2H^+ \leftrightarrow Mg^{2+} + 2H_2O$	-	X	X	-
P30	$Mg_3(PO_4)_2$ (s)	$Mg_3(PO_4)_2 \leftrightarrow 3Mg^{2+} + 2PO_4^{3-}$	X	X	X	-
P31	Newberyite	$MgHPO_4{:}3H_2O \leftrightarrow Mg^{2+} + H^+ + PO_4^{3-} + 3H_2O$	X	X	X	-
P32	Periclase	$MgO + 2H^+ \leftrightarrow Mg^{2+} + H_2O$	-	-	X	-
P33	Portlandite	$Ca(OH)_2 + 2H^+ \leftrightarrow Ca^{2+} + 2H_2O$	-	-	X	-
P34	Siderite	$FeCO_3 \leftrightarrow Fe^{2+} + CO_3^{2-}$	X	X	X	-
P35	Spinel	$MgAl_2O_4 + 8H^+ \leftrightarrow Mg^{2+} + 2Al^{3+} + 4H_2O$	-	-	X	-
P36	Struvite	$MgNH_4PO_4{:}6H_2O \leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-}$	X	X	X	-
P37	Vaterite	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$	-	X	X	-
P38	Vivianite	$Fe_3(PO_4)_2{:}8H_2O \leftrightarrow 3Fe^{2+} + 2PO_4^{3-} + 8H_2O$	X	X	X	-

Table A5.6 Gas-liquid / liquid-gas exchange reactions (GL) included in each nutrient recovery model (NRM). AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber.

No.	Gas-liquid / liquid-gas exchange reaction	AD	Prec	Strip	Scrub
GL1	CH_4 (aq) → CH_4 (g)	X	-	-	-
GL2	CO_2 (aq) ↔ CO_2 (g)	X	(X)[a]	X	X
GL3	H_2 (aq) ↔ H_2 (g)	X	-	X	X
GL4	H_2O (aq) ↔ H_2O (g)	X	(X)[a]	X	X
GL5	H_2S (aq) ↔ H_2S (g)	X	-	X	X
GL6	N_2 (aq) ↔ N_2 (g)	X	(X)[a]	X	X
GL7	NH_3 (aq) ↔ NH_3 (g)	X	(X)[a]	X	X
GL8	O_2 (aq) ↔ O_2 (g)	-	(X)[a]	X	X

[a] Values between brackets represent the use of air instead of chemicals for pH-adjustment.

APPENDIX 6:

Biochemical processes and Gujer matrix included in the nutrient recovery model for the anaerobic digester (NRM-AD)

Table A6.1 Biochemical (BC) processes included in the nutrient recovery model for anaerobic digestion (NRM-AD) and extensions made as compared to the Anaerobic Digestion Model No. 1 (ADM1). Ac = acetate; Bu = butyrate; EBPR = enhanced biological phosphorus (P) removal; LCFA = long chain fatty acids; PAO = P accumulating organism; PHA = poly-hydroxy-alkanoate; PP = poly-phosphate; Pro = propionate; SRB = sulfate reducing bacteria; Va = valerate.

PHYSICOCHEMICAL PROCESSES	**BIOCHEMICAL PROCESSES**			
ADM1:	**ADM1:**	**NRM-AD Extension 2:**	**NRM-AD Extension 3:**	**NRM-AD Potential extension 4:**
4 Acid-base systems: NH_4^+/NH_3, CO_2/HCO_3^-, VFA/VFA$^-$, $H_2O/OH^-/H^+$ **4 Gas-liquid exchange reactions:** CO_2, CH_4, H_2, H_2O	**Disintegration, hydrolysis, acidogenesis, acetogenesis, methanogenesis (Batstone *et al.*, 2002)**	**Sulfurgenesis (Knobel and Lewis, 2002; Lizarralde *et al.*, 2010)**	**Release/uptake of P, K, S from bacterial cells and other biochemical components**	**EBPR sludge (Ikumi, 2011)**
NRM-AD Extension 1: **Acid-base systems: Table A5.2** **Redox reactions: Table A5.3** **Ion pairing reactions: Table A5.4** **Solid-liquid transfer: Table A5.5** **Gas-liquid exchange: Table A5.6**	BC1. Disintegration of complex particulates BC2. Hydrolysis of carbohydrates BC3. Hydrolysis of proteins BC4. Hydrolysis of lipids BC5. Uptake of monosaccharides BC6. Uptake of aminoacids BC7. Uptake of LCFA BC8. Uptake of Va BC9. Uptake of Bu BC10. Uptake of Pro BC11. Uptake of Ac BC12. Uptake of H_2 BC13. Decay of monosaccharide degraders BC14. Decay of amino acid degraders BC15. Decay of LCFA degraders BC16. Decay of Va and Bu degraders BC17. Decay of Pro degraders BC18. Decay of Ac degraders BC19. Decay of H degraders	BC20. Sulfate reduction on Ac BC21. Sulfate reduction on Bu BC22. Sulfate reduction on H_2 BC23. Sulfate reduction on Pro BC24. Decay of SRBs using Ac BC25. Decay of SRBs using Bu BC26. Decay of SRBs using H_2 BC27. Decay of SRBs using Pro	Inclusion in stoichiometric Gujer matrix (Table A6.2-A6.4)	BC28. Release of PP with uptake of Ac by PAOs BC29. Decay of PAOs BC30. Hydrolysis of PP + release of K, Ca, Mg BC31. Hydrolysis of PHA

Table A6.2 Stoichiometry of the biochemical (BC) Gujer matrix incorporated in the nutrient recovery model for the anaerobic digester (NRM-AD). For process description: see Table A6.1. For nomenclature: see Table A6.4. For state variable description: see Appendix 7.

Component	**S_aa**	**S_CO_2**	**S_HAc**	**S_HBu**
Process	kg COD m^{-3}	kmol m^{-3}	kg COD m^{-3}	kg COD m^{-3}
BC1		C_xc - f_ch_xc.C_ch - f_si_xc.C_si - f_pr_xc.C_pr - f_xi_xc.C_xi - f_li_xc.C_li		
BC2		C_ch-C_su		
BC3	1	C_aa-C_pr		
BC4		(f_fa_li-1).C_su - f_fa_li.C_fa + C_li		
BC5		C_su - (1-Y_su).f_ac_su.C_ac - (1-Y_su).f_pro_su.C_pro - (1-Y_su).f_bu_su.C_bu - Y_su.C_biom	(1-Y_su).f_ac_su	(1-Y_su).f_bu_su
BC6	-1	C_aa - (1-Y_aa).f_ac_aa.C_ac - (1-Y_aa).f_bu_aa.C_bu - (1-Y_aa).f_pro_aa.C_pro - (1-Y_aa).f_va_aa.C_va - Y_aa.C_biom	(1-Y_aa).f_ac_aa	(1-Y_aa).f_bu_aa
BC7		C_fa - (1-Y_fa).0.7.C_ac - Y_fa.C_biom	(1-Y_fa).0.7	
BC8		C_va - (1-Y_c4).0.54.C_pro - Y_c4.C_biom - (1-Y_c4).0.31.C_ac	(1-Y_c4).0.31	
BC9		C_bu - (1-Y_c4).0.8.C_ac - Y_c4.C_biom	(1-Y_c4).0.8	-1
BC10		C_pro - (1-Y_pro).0.57.C_ac - Y_pro.C_biom	(1-Y_pro).0.57	
BC11		C_ac - Y_ac.C_biom - (1-Y_ac).C_ch4	-1	
BC12		-Y_h2.C_biom - (1-Y_h2).C_ch4		
BC13		C_biom - C_xc		
BC14		C_biom - C_xc		
BC15		C_biom - C_xc		
BC16		C_biom - C_xc		
BC17		C_biom - C_xc		
BC18		C_biom - C_xc		
BC19		C_biom - C_xc		
BC20		f_co2_ac	-1	
BC21		f_co2_bu		-1
BC22		f_co2_h		
BC23		f_co2_pro		
BC24		C_biom - C_xc		
BC25		C_biom - C_xc		
BC26		C_biom - C_xc		
BC27		C_biom - C_xc		

Table A6.2 Continuation: Stoichiometry of the biochemical (BC) Gujer matrix incorporated in the nutrient recovery model for the anaerobic digester (NRM-AD). For process description: see Table A6.1. For nomenclature: see Table A6.4. For state variable description: see Appendix 7.

Component **Process**	**S_HPO$_4^{2-}$** kmol m^{-3}	**S_HVa** kg COD m^{-3}	**S_CH$_4$** kg COD m^{-3}	**S_fa** kg COD m^{-3}	**S_H$_2$** kg COD m^{-3}	**S_H$_2$S** kmol m^{-3}	**S_inert** kg COD m^{-3}	**S_K$^+$** kmol m^{-3}
BC1	P_xc - f_xi_xc.P_xi - f_si_xc.P_si - f_li_xc.P_li						f_Si_xc	
BC2								
BC3								
BC4	P_li			f_fa_li				
BC5	-Y_su.P_biom				(1-Y_su).f_h2_su			-Y_su.K_biom
BC6	-Y_aa.P_biom	(1-Y_aa).f_va_aa			(1-Y_aa).f_h2_aa			-Y_aa.K_biom
BC7	P_fa - Y_fa.P_biom			-1	(1-Y_fa).0.3			-Y_fa.K_biom
BC8	-Y_c4.P_biom	-1			(1-Y_c4).0.15			-Y_c4.K_biom
BC9	-Y_c4.P_biom				(1-Y_c4).0.2			-Y_c4.K_biom
BC10	-Y_pro.P_biom				(1-Y_pro).0.43			-Y_pro.K_biom
BC11	-Y_ac.P_biom		1-Y_ac					-Y_ac.K_biom
BC12	-Y_h2.P_biom		1-Y_h2		-1			-Y_h2.K_biom
BC13	P_biom - P_xc							K_biom - K_xc
BC14	P_biom - P_xc							K_biom - K_xc
BC15	P_biom - P_xc							K_biom - K_xc
BC16	P_biom - P_xc							K_biom - K_xc
BC17	P_biom - P_xc							K_biom - K_xc
BC18	P_biom - P_xc							K_biom - K_xc
BC19	P_biom - P_xc							K_biom - K_xc
BC20						f_s_ac		
BC21						f_s_bu		
BC22					-1	f_s_h		
BC23						f_s_pro		
BC24	P_biom - P_xc							K_biom - K_xc
BC25	P_biom - P_xc							K_biom - K_xc
BC26	P_biom - P_xc							K_biom - K_xc
BC27	P_biom - P_xc							K_biom - K_xc

Table A6.2 Continuation: Stoichiometry of the biochemical (BC) Gujer matrix incorporated in the nutrient recovery model for the anaerobic digester (NRM-AD). For process description: see Table A6.1. For nomenclature: see Table A6.4. For state variable description: see Appendix 7.

Component	**$S\_NH_4^+$**	**S_pro**	**$S\_SO_4^{2-}$**	**S_su**	**X_aa**	**X_ac**	**X_c**	**X_c4**	**X_ch**	**X_fa**
Process	kmol m^{-3}	kg COD m^{-3}	kmol m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}
BC1	N_xc - f_xi_xc.N_xi - f_si_xc.N_si - f_pr_xc.N_aa						-1		f_ch_xc	
BC2				1					-1	
BC3										
BC4				1-f_fa_li						
BC5	-N_biom.Y_su	(1-Y_su).f_pro_su	-Y_su.S_biom	-1						
BC6	N_aa - Y_aa.N_biom	(1-Y_aa).f_pro_aa	-Y_aa.S_biom		Y_aa					
BC7	-N_biom.Y_fa		-Y_c4.S_biom							Y_fa
BC8	-N_biom.Y_c4	(1-Y_c4).0.54	-Y_c4.S_biom					Y_c4		
BC9	-N_biom.Y_c4		-Y_ac.S_biom					Y_c4		
BC10	-N_biom.Y_pro	-1	-Y_pro.S_biom							
BC11	-N_biom.Y_ac		-Y_ac.S_biom			Y_ac				
BC12	-N_biom.Y_h2		-Y_h2.S_biom							
BC13	N_biom - N_xc		S_biom - S_xc				1			
BC14	N_biom - N_xc		S_biom - S_xc		-1		1			
BC15	N_biom - N_xc		S_biom - S_xc				1			-1
BC16	N_biom - N_xc		S_biom - S_xc				1	-1		
BC17	N_biom - N_xc		S_biom - S_xc				1			
BC18	N_biom - N_xc		S_biom - S_xc			-1	1			
BC19	N_biom - N_xc		S_biom - S_xc				1			
BC20			-f_s_ac							
BC21			-f_s_bu							
BC22			-f_s_h							
BC23		-1	-f_s_pro							
BC24	N_biom - N_xc		S_biom - S_xc				1			
BC25	N_biom - N_xc		S_biom - S_xc				1			
BC26	N_biom - N_xc		S_biom - S_xc				1			
BC27	N_biom - N_xc		S_biom - S_xc				1			

Table A6.2 Continuation: Stoichiometry of the biochemical (BC) Gujer matrix incorporated in the nutrient recovery model for the anaerobic digester (NRM-AD). For process description: see Table A6.1. For nomenclature: see Table A6.4. For state variable description: see Appendix 7.

Component	**X_h2**	**X_pr**	**X_pro**	**X_su**	**X_inert**	**X_li**	**X_srb_ac**	**X_srb_bu**	**X_srb_h**	**X_srb_pro**
Process	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}	kg COD m^{-3}
BC1		f_pr_xc			f_xi_xc	f_li_xc				
BC2										
BC3		-1								
BC4						-1				
BC5				Y_su						
BC6										
BC7										
BC8										
BC9										
BC10			Y_pro							
BC11										
BC12	Y_h2									
BC13				-1						
BC14										
BC15										
BC16										
BC17			-1							
BC18										
BC19	-1									
BC20							Y_srb_ac			
BC21								Y_srb_bu		
BC22									Y_srb_h	
BC23										Y_srb_pro
BC24							-1			
BC25								-1		
BC26									-1	
BC27										-1

Table A6.3 Biochemical (BC) kinetic equations of the Gujer matrix incorporated in the nutrient recovery model for the anaerobic digester (NRM-AD). For process description: see Table A6.1. For nomenclature: see Table A6.4. For state variable description: see Appendix 7.

Process	Kinetic equation (kg COD m^{-3} d^{-1})
BC1	$k_{dis}.X_c$
BC2	$k_{hyd,X_{ch}}.X_{ch}$
BC3	$k_{hyd,X_{pr}}.X_{pr}$
BC4	$k_{hyd,X_{li}}X_{li}$
BC5	$km_{su}.\frac{X_{su}.S_{su}}{Ks_{su}+S_{su}}.I_{pH,bac}.I_{NH,limit}$
BC6	$km_{aa}.\frac{X_{aa}.S_{aa}}{Ks_{aa}+S_{aa}}.I_{pH,bac}.I_{NH,limit}$
BC7	$km_{fa}.\frac{X_{fa}.S_{fa}}{Ks_{fa}+S_{fa}}.I_{pH,bac}.I_{NH,limit}.I_{h2,fa}$
BC8	$km_{c4}.\frac{X_{c4}.S_{HVa}}{Ks_{c4}+S_{HVa}}.\frac{S_{HVa}}{S_{HVa}+S_{HBu}}.I_{pH,bac}.I_{NH,limit}.I_{h2,c4}$
BC9	$km_{c4}.\frac{X_{c4}.S_{HBu}}{Ks_{c4}+S_{HBu}}.\frac{S_{HBu}}{S_{HBu}+S_{HVa}}.I_{pH,bac}.I_{NH,limit}.I_{h2,c4}$
BC10	$km_{pro}.\frac{X_{pro}.S_{HPro}}{Ks_{pro}+S_{HPro}}.I_{pH,bac}.I_{NH,limit}.I_{h2,pro}$
BC11	$km_{ac}.\frac{X_{ac}.S_{HAc}}{Ks_{ac}+S_{HAc}}.I_{pH,ac}.I_{NH3,ac}.I_{NH,limit}$
BC12	$km_{h2}.\frac{X_{h2}.S_{h2}}{Ks_{h2}+S_{h2}}.I_{pH,h2}.I_{NH,limit}$
BC13	$k_{dec,X_{su}}.X_{su}$
BC14	$k_{dec,X_{aa}}.X_{aa}$
BC15	$k_{dec,X_{fa}}.X_{fa}$
BC16	$k_{dec,X_{c4}}.X_{c4}$
BC17	$k_{dec,X_{pro}}.X_{pro}$
BC18	$k_{dec,X_{ac}}.X_{ac}$
BC19	$k_{dec,X_{h2}}.X_{h2}$
BC20	$km_{srb,ac}.\frac{X_{srb,ac}.S_{HAc}}{Ks_{srb,ac}+S_{HAc}}.\frac{S_{SO_4}}{Ks_{srb,ac}+S_{HAc}}.I_{pH,srb}.I_{H_2S,ac}.X_{srb,ac}$
BC21	$km_{srb,bu}.\frac{X_{srb,bu}.S_{HBu}}{Ks_{srb,bu}+S_{HBu}}.\frac{S_{SO_4}}{Ks_{srb,bu}+S_{HBu}}.I_{pH,srb}.I_{H_2S,bu}.X_{srb,bu}$
BC22	$km_{srb,h2}.\frac{X_{srb,h2}.S_{H2}}{Ks_{srb,h2}+S_{H2}}.\frac{S_{SO_4}}{Ks_{srb,h2}+S_{H2}}.I_{pH,srb}.I_{H_2S,h2}.X_{srb,h2}$
BC23	$km_{srb,pro}.\frac{X_{srb,pro}.S_{HPro}}{Ks_{srb,pro}+S_{HPro}}.\frac{S_{SO_4}}{Ks_{srb,pro}+S_{HPro}}.I_{pH,srb}.I_{H_2S,pro}.X_{srb,pro}$
BC24	$k_{dec,X_{srb,ac}}.X_{srb,ac}$
BC25	$k_{dec,X_{srb,bu}}.X_{srb,bu}$
BC26	$k_{dec,X_{srb,h2}}.X_{srb,h2}$
BC27	$k_{dec,X_{pro}}.X_{pro}$

Table A6.4 Nomenclature for Tables A6.2 and A6.3.

Symbol	Description	Unit
C_i	Carbon content of component i	kmol C kg^{-1} COD
f_product_substrate	Yield (catabolism only) of product on substrate	kg COD kg^{-1} COD
$I_{H_2,substrate}$	Hydrogen inhibition for substrate degradation	-
$I_{H_2S,substrate}$	Hydrogen sulfide inhibition for substrate degradation	-
$I_{NH,limit}$	Inhibition of biomass growth due to lack of inorganic nitrogen	-
$I_{pH,bac}$	pH inhibition of acetogens and acidogens	-
$I_{pH,i}$	pH inhibition of component i	-
$k_{dec,i}$	First order decay rate for biomass death of component i	d^{-1}
$k_{dis,i}$	Complex particulate first order disintegration rate of component i	d^{-1}
$k_{hyd,i}$	First order hydrolysis rate of component i	d^{-1}
K_i	Potassium content of component i	kmol K kg^{-1} COD
$k_{m,i}$	Specific Monod maximum uptake rate of component i	d^{-1}
Ks_i	Monod half saturation constant of component i	kg COD m^{-3}
N_i	Nitrogen content of component i	kmol N kg^{-1} COD
P_i	Phosphorus content of component i	kmol P kg^{-1} COD
S_i	Sulfur content of component i	kmol S kg^{-1} COD
Y_substrate	Yield of biomass on substrate	kg COD X kg^{-1} COD S

APPENDIX 7:

State vectors used in the nutrient recovery model (NRM) library

Table A7.1 Generic state vectors used in the nutrient recovery model (NRM) library, component symbols, and descriptions.

State vector	Component symbol	Description	Component symbol	Description
Components_S1_PC	S_Acetate	soluble acetate	S_Mg	soluble magnesium
	S_Al	soluble aluminium	S_Na	soluble sodium
	S_Butyrate	soluble butyrate	S_N_min3_	soluble ammonia (N, -III)
	S_Ca	soluble calcium	S_N_0_	soluble nitrogen (N, 0)
	S_C_4_	soluble carbonate (C, +IV)	S_N_5_	soluble nitrate (N, +V)
	S_Cl	soluble chloride	S_O_0_	soluble oxygen (O, 0)
	S_C_min4_	soluble methane (C, -IV)	S_P	soluble phosphorus
	S_DOM	soluble dissolved organic matter	S_Propionate	soluble propionate
	S_Fe	soluble iron	S_S_min2_	soluble sulfide (S, -II)
	S_H_0_	soluble hydrogen (H, 0)	S_S_6_	soluble sulfate (S, +VI)
	S_K	soluble potassium	S_Valerate	soluble valerate
Components_S1_Bio	S_aa	soluble aminoacids	S_inert	soluble inerts
	S_fa	soluble long chain fatty acids	S_su	soluble sugars
Components_S2	S_C_4_	soluble carbonate (C, +IV)	S_N_5_	soluble nitrate (N, +V)
	S_C_min4_	soluble methane (C, -IV)	S_O_0_	soluble oxygen (O, 0)
	S_H_0_	soluble hydrogen (H, 0)	S_S_min2_	soluble sulfide (S, -II)
	S_N_min3_	soluble ammonia (N, -III)	S_S_6_	soluble sulfate (S, +VI)
	S_N_0_	soluble nitrogen (N, 0)		
Components_G	G_CH4	methane gas	G_H2S	hydrogen sulfide gas
	G_CO2	carbon dioxide gas	G_NH3	ammonia gas
	G_H2	hydrogen gas	G_N2	nitrogen gas
	G_H2O	water vapour	G_O2	oxygen gas
Components_P	P_Al	precipitated aluminium	P_Mg	precipitated magnesium
	P_Ca	precipitated calcium	P_N_min3_	precipitated ammonia (N, -III)
	P_C_4_	precipitated carbonate (C, +IV)	P_P	precipitated phosphorus
	P_Fe	precipitated iron	P_S_min2_	precipitated sulfide (S, -II)
	P_K	precipitated potassium	P_S_6_	precipitated sulfate (S, +VI)
Components_X	X_aa	aminoacid degraders	X_li	lipids
	X_ac	acetate degraders	X_pr	proteins
	X_c	composites	X_pro	propionate degraders
	X_ch	carbohydrates	X_su	sugar degraders
	X_c4	valerate and butyrate degraders	X_srb_ac	sulfate reducing bacteria using acetate
	X_fa	long chain fatty acid degraders	X_srb_bu	sulfate reducing bacteria using butyrate
	X_h2	hydrogen reducing bacteria	X_srb_h	sulfate reducing bacteria using hydrogen
	X_inert	particulate inerts	X_srb_pro	sulfate reducing bacteria using propionate

APPENDIX 8:

Data requirements and data used for nutrient recovery model (NRM) validation

Table A8.1 Types of data required and datasets available for each key unit in the nutrient recovery model (NRM) library. AD = anaerobic digestion; Prec = precipitation/crystallization; Strip = stripper; Scrub = scrubber; N/A = not applicable.

	NRM-AD	NRM-Prec	NRM-Strip	NRM-Scrub
Input waste characteristics				
Biological components	Sludge: Astals *et al.* (2013), Ikumi (2011), Tchobanoglous *et al.* (2003); Manure: Cesur and Albertson (2005), Martin (2003), Mattocks *et al.* (2002); Co-digestion: Zaher *et al.* (2009) + own data	N/A	N/A	N/A
Physicochemical components		Ali and Schneider (2008), Bhuiyan *et al.* (2007), Harrison *et al.* (2011), Schneider *et al.* (2013) + own data	Bhuiyan *et al.* (2007), Campos *et al.* (2013), Collivignarelli *et al.* (1998), Powers *et al.* (1987), Yu *et al.* (2011) + own data	Campos *et al.* (2013), Collivignarelli *et al.* (1998), Manuzon *et al.* (2007), Powers *et al.* (1987), Yu *et al.* (2011) + own data
Physicochemical stoichiometric parameters				
Acid-base / ion pairing equilibrium constants (K_{ab}, K_{ip})	NIST (2001), PHREEQC	NIST (2001), PHREEQC	NIST (2001), PHREEQC	NIST (2001), PHREEQC
Water dissociation constant (K_w)	NIST (2001), PHREEQC	NIST (2001), PHREEQC	NIST (2001), PHREEQC	NIST (2001), PHREEQC
Solubility products (K_s)	NIST (2001), PHREEQC	NIST (2001), PHREEQC	NIST (2001), PHREEQC	NIST (2001), PHREEQC
Henry's law coefficients (H)	Sander (1999)	Sander (1999)	Sander (1999)	Sander (1999)
Physicochemical kinetic parameters				
Precipitation / dissolution transfer coefficients and reaction order (k, n)	Bénézeth *et al.* (2008), Chauhan *et al.* (2011), Ikumi (2011), Inskeep and Silvertooth (1988), Johnson (1990), Musvoto *et al.* (1997, 2000b), Nielsen (1984), NIST (2001), to mention a few	Ali and Schneider (2008), Bhuiyan *et al.* (2008), Galbraith *et al.* (2014), Harrison *et al.* (2011), NIST (2001), Schneider *et al.* (2013), to mention a few	Bénézeth *et al.* (2008), Chauhan *et al.* (2011), Ikumi (2011), Inskeep and Silvertooth (1988), Johnson (1990), Musvoto *et al.* (1997, 2000b), Nielsen (1984), NIST (2001), to mention a few	Belcu and Turtoi (1986), NIST (2001)
Liquid-gas transfer coefficients ($K_{L/G}a$)	Batstone *et al.* (2002), Chapra (2008), Lizarralde *et al.* (2011), Musvoto *et al.* (1997), Munz and Roberts (1989)	If pH increase with aeration: Batstone *et al.*(2002), Chapra (2008), Lizarralde *et al.* (2011), Musvoto *et al.* (1997), Munz and Roberts (1989)	Collivignarelli *et al.* (1998), Musvoto *et al.* (1997, 2000a), Powers *et al.* (1987), Yu *et al.* (2011)	Collivignarelli *et al.* (1998), Manuzon *et al.* (2007), Yu *et al.* (2011)

Biological stoichiometric parameters				
Biomass composition	Batstone *et al.* (2002), Ikumi (2011), Tchobanoglous *et al.* (2003), Zaher *et al.* (2009)	N/A	N/A	N/A
Pre-set fractions (f_product_substrate)	Batstone *et al.* (2002), Ikumi (2011), Knobel and Lewis (2002), Lizarralde *et al.* (2010)	N/A	N/A	N/A
Biomass substrate yield (Y_substrate)	Batstone *et al.* (2002), Ikumi (2011), Knobel and Lewis (2002), Lizarralde *et al.* (2010)	N/A	N/A	N/A
Biological kinetic parameters				
Uptake rates (k_m), disintegration rates (k_{dis}), decay rates (k_{dec}), etc.	Batstone *et al.* (2002), Ikumi (2011), Knobel and Lewis (2002), Lizarralde *et al.* (2010)	N/A	N/A	N/A
Input/output data + operational factors (temperature, pH, etc.) = calibration/validation data				
	Sludge: Astals *et al.* (2013); Manure: Cesur and Albertson (2005), Martin (2003), Mattocks *et al.* (2002), + own data + data from industry	Ali and Schneider (2008), Bhuiyan *et al.* (2007, 2008), Harrison *et al.* (2011), Schneider *et al.* (2013) + own data + data from industry	Campos *et al.* (2013), Collivignarelli *et al.* (1998), Powers *et al.* (1987), Yu *et al.* (2011) + own data + data from industry	Campos *et al.* (2013), Collivignarelli *et al.* (1998), Koptev (1966), Manuzon *et al.* (2007), Melse and Ogink (2005), Powers *et al.* (1987), Yu *et al.* (2011) + own data + data from industry

Additional references for Table A8.1 not yet included in the generic reference list:

Bénézeth, P., Palmer, D.A, Wesolowski, D.J., 2008. Dissolution/precipitation kinetics of boehmite and gibbsite: Application of a pH-relaxation technique to study near-equilibrium rates. Geochim. Cosmochim. Acta 72, 2429-2453.

Inskeep, W.P., Silvertooth, J.C., 1988. Kinetics of hydroxyapatite precipitation at pH 7.4 to 8.4. Geochim. Cosmochim. Acta 52, 1883-1893.

Johnson, M.L., 1990. Ferrous Carbonate Precipitation Kinetics – A Temperature Ramped Approach. PhD Thesis, Rice University, Houston, Texas, USA.

Koptev, 1966. The solubility of ammonium sulphate and saturator washing conditions. Coke Chem. Works 2, 32-33.

Sander, R., 1999. Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry. Report, Air Chemistry Department, Max-Planck Institute of Chemistry, Mainz, USA.

Table A8.2 Input sludge characteristics, reactor design, initial values, and operating conditions for the anaerobic digester at Holmen Paper Madrid (Spain). Data used for validation of the nutrient recovery model for the anaerobic digester (NRM-AD). COD = chemical oxygen demand. COD input fractionation was conducted following the procedure proposed by Grau *et al.* (2007a). For state variable description: see Appendix 7. COD = chemical oxygen demand; HRT = hydraulic residence time; Q_liq = liquid flow rate; T_liq = liquid temperature; T_operational = operational temperature; V_liq = liquid volume.

INPUT FLOW				**REACTOR (DESIGN + INITIAL VALUES + OPERATION)**			
S_aa (kg COD m^{-3})	0	S_Acetate (mol m^{-3})	2.85	S_aa (kg COD m^{-3})	0.0172	S_Acetate (mol m^{-3})	0.0347
S_fa (kg COD m^{-3})	0.217	S_Al (mol m^{-3})	Unknown	S_fa (kg COD m^{-3})	0.0113	S_Al (mol m^{-3})	unknown
S_inert (kg COD m^{-3})	0.170	S_Butyrate (mol m^{-3})	1.14	S_inert (kg COD m^{-3})	0.480	S_Butyrate (mol m^{-3})	0.322
S_su (kg COD m^{-3})	1.05	S_C_4_ (mol m^{-3})	12.8	S_su (g COD m^{-3})	0.569	S_C_4_ (mol m^{-3})	60.1
X_aa (kg COD m^{-3})	0	S_C_min4_ (mol m^{-3})	0	X_aa (kg COD m^{-3})	0.112	S_C_min4_ (mol m^{-3})	1.23
X_ac (kg COD m^{-3})	0	S_Ca (mol m^{-3})	2.85	X_ac (kg COD m^{-3})	0.0178	S_Ca (mol m^{-3})	7.10
X_c4 (kg COD m^{-3})	0	S_Cl (mol m^{-3})	0.0357	X_c4 (kg COD m^{-3})	1.33	S_Cl (mol m^{-3})	0.0357
X_c (kg COD m^{-3})	0	S_Fe (mol m^{-3})	Unknown	X_c (kg COD m^{-3})	31.3	S_Fe (mol m^{-3})	unknown
X_ch (kg COD m^{-3})	0.187	S_H_0_ (mol m^{-3})	0	X_ch (kg COD m^{-3})	4.03	S_H_0_ (mmol m^{-3})	0.0344
X_fa (kg COD m^{-3})	0	S_K (mol m^{-3})	0.0350	X_fa (kg COD m^{-3})	2.30	S_K (mol m^{-3})	6.39
X_h2 (kg COD m^{-3})	0	S_Mg (mol m^{-3})	2.41	X_h2 (kg COD m^{-3})	0.127	S_Mg (mol m^{-3})	2.69
X_inert (kg COD m^{-3})	0.0936	S_N_0_ (mol m^{-3})	0	X_inert (kg COD m^{-3})	13.8	S_N_0_ (mmol m^{-3})	0.000256
X_li (kg COD m^{-3})	0.140	S_N_5_ (mol m^{-3})	0	X_li (kg COD m^{-3})	6.98	S_N_5_ (mmol m^{-3})	0.00100
X_pr (kg COD m^{-3})	0	S_N_min3_ (mol m^{-3})	7.36	X_pr (kg COD m^{-3})	0.998	S_N_min3_ (mol m^{-3})	4.57
X_pro (kg COD m^{-3})	0	S_Na (mol m^{-3})	0.0357	X_pro (kg COD m^{-3})	0.0178	S_Na (mol m^{-3})	0.0357
X_srb_ac (kg COD m^{-3})	0	S_O_0_ (mmol m^{-3})	3.98	X_srb_ac (kg COD m^{-3})	0.469	S_O_0_ (mol m^{-3})	0
X_srb_bu (kg COD m^{-3})	0	S_P (mol m^{-3})	0.309	X_srb_bu (kg COD m^{-3})	4.99	S_P (mol m^{-3})	0.245
X_srb_h (kg COD m^{-3})	0	S_Propionate (mol m^{-3})	1.63	X_srb_h (kg COD m^{-3})	43.6	S_Propionate (mol m^{-3})	0.0451
X_srb_pro (kg COD m^{-3})	0	S_S_6_ (mol m^{-3})	5.42	X_srb_pro (kg COD m^{-3})	16.6	S_S_6_ (mol m^{-3})	1.16
X_su (kg COD m^{-3})	0	S_S_min2_ (mol m^{-3})	0.0106	X_su (kg COD m^{-3})	7.20	S_S_min2_ (mol m^{-3})	6.35
		S_Valerate (mol m^{-3})	0.878			S_Valerate (mol m^{-3})	0.402
Q_liq (m^3 d^{-1})	15.0	T_liq (K)	28.9	Fraction of solids in effluent	0.002	V_liq (m^3)	2.80
pH (-)	6.66			T_operational (K)	302.15	HRT (h)	4.48

Table A8.3 Input digestate characteristics and operating conditions used for the lab-scale experiments on struvite precipitation. Data used for validation of the nutrient recovery model for the precipitation/crystallization unit (NRM-Prec). For state variable description: see Appendix 7.

Variable	Digestate 1	Digestate 2	Variable	Digestate 1	Digestate 2
S_Acetate[a] (mol m^{-3})	0.100	0.100	S_Mg (mol m^{-3})	26.1	26.4
S_Al (mol m^{-3})	0.0100	1.00	S_N_5_ (mol m^{-3})	98.0	127
S_Butyrate[a] (mol m^{-3})	0.100	0.100	S_N_min3_ (mol m^{-3})	362	346
S_C_4_ (mol m^{-3})	10.0	10.0	S_Na (mol m^{-3})	100	127
S_C_min4_[a] (mmol m^{-3})	0.100	0.100	S_P (mol m^{-3})	38.8	45.5
S_Ca (mol m^{-3})	42.1	57.1	S_Propionate[a] (mol m^{-3})	0.0100	0.0100
S_Cl (mol m^{-3})	73.3	25.0	S_S_6_ (mol m^{-3})	40.0	20.0
S_Fe (mol m^{-3})	170	0.100	S_S_min2_ (mmol m^{-3})	0.100	0.100
S_K (mol m^{-3})	104	122	S_Valerate[a] (mmol m^{-3})	0.100	0.100
pH (-)	8.43	7.83	Temperature (K)	293.15	293.15

[a] Estimated from the soluble chemical oxygen demand (COD) content following the procedure described in Cesur and Albertson (2005).

Table A8.4 Input flow composition and operating conditions used for validation of the treatment train: NRM-Chem / NRM-Strip / NRM-Scrub. Operational data were obtained from a technical inquiry at company X. Chem = chemical dosing unit; Strip = stripper; Scrub = scrubber. For state variable description: see Appendix 7. DOM = dissolved organic matter; P_gas = gas pressure; Q_gas = gas flow rate; Q_liq = liquid flow rate.

Input flow (after NaOH-dose)[a]		**Operation NRM-Strip**		**Operation NRM-Scrub**	
S_Al (mol m^{-3})	20	Q_liq_in (m^3 d^{-1})	2,004	H_2SO_4-dose (m^3 d^{-1})	20.16
S_C_4_ (mol m^{-3})	80	Q_gas_in (m^3 d^{-1})	1,560,000	Q_gas_in (m^3 d^{-1})	= Output NRM-Strip
S_C_min4_ (mol m^{-3})	0.0080	Column height (m)	11.5	Column height (m)	11.5
S_Ca (mol m^{-3})	60	Temperature (ºC)	328.15	Temperature (ºC)	= Output NRM-Strip
S_Cl (mol m^{-3})	80	pH (-)	10.3	pH acid (-)	1.3
S_DOM (mol m^{-3})	10	Vol_liq (m^3)	81.3	Vol_liq (m^3)	20.16
S_Fe (mol m^{-3})	1.2	P_gas_in (atm)	2.42	P_gas_in (atm)	= Output NRM-Strip
S_H_0_ (mol m^{-3})	0.0010				
S_K (mol m^{-3})	33				
S_Mg (mol m^{-3})	43				
S_N_0_ (mol m^{-3})	0.10				
S_N_5_ (mol m^{-3})	59				
S_N_min3_ (mol m^{-3})	199				
S_Na (mol m^{-3})	102				
S_O_0_ (mol m^{-3})	0				
S_P (mol m^{-3})	33				
S_S_6_ (mol m^{-3})	40				
S_S_min2_ (mol m^{-3})	0				
Temperature (K)	293.15				

[a] Dose of 4.1 kg NaOH m^{-3} as specified by company X.

APPENDIX 9:

Model verification/validation examples

Table A9.1 Model verification/validation against prior knowledge: some dynamic simulation tests and effects. All results were found to be realistic. For state variable description: see Appendix 7. AD = anaerobic digestion; Prec = precipitation/crystallization; Scrub = scrubber; SRB = sulfate reducing bacteria; Strip = stripper; VFA = volatile fatty acids.

NRM-AD	NRM-Prec	NRM-Strip	NRM-Scrub
S_C_4_in (alkalinity) ↓ ⇒ (delayed) pH ↓, S_C_4_out ↓, VFA ↑, biogas production ↓	S_P_in ↓ ⇒ struvite precipitation ↓	Reactor height ↓ ⇒ no influence on performance	Reactor height ↓ ⇒ no influence on performance
pH ↑ ⇒ CO_3 precipitation ↑ pH ↓ ⇒ CO_2 stripping ↑ (not biologically mediated)	S_Mg_in ↓ ⇒ pH ↓, S_P_out ↑, phosphorus recovery efficiency ↓	Temperature ↑ ⇒ S_N_min3_out ↓, p_NH_3_out (gas phase partial pressure) ↑, NH_3 recovery efficiency ↑, effluent pH ↓	p_NH_3_in (gas phase partial pressure) ↑ ⇒ fertilizer alkalinity ↓ (NH_2COO^- formation), N % fertilizer ↑
Modification: pH-inhibition level SRBs = 5, other bacteria = 6 ⇒ H_2S production ↑ if pH < 6	S_P_in ↑ ⇒ phosphorus precipitation ↑ (supersaturation ↑)	Q_liq_in ↑ ⇒ residence time ↓, $CaCO_3$ precipitation ↓, scaling potential ↓	
Temperature ↑ ⇒ biogas production ↑	pH ↓ (input nutrient contents ↓) ⇒ fertilizer density ↓ and molecular weight ↓		

NRM-AD:

- Reducing the input alkalinity to the digester results in a (delayed) pH decrease (less carbonate buffer) because of volatile fatty acid accumulation. Methanogenic bacteria are very sensitive to pH decreases (Vanrolleghem and Lee, 2003). Hence, a reduction of the biogas production is observed. Obviously, the output alkalinity decreases as well.
- Increasing the input pH results in an increased formation of carbonate precipitates in the digester, whereas decreasing the pH stimulates the stripping of CO_2 (see carbonate equilibria as function of pH; Zuhmdahl, 2005).
- Setting the pH inhibition level of sulfate reducing bacteria (SRBs) at 5, but for the other bacteria at 6, leads to increased H_2S production if the pH in the digester becomes lower than 6. Hence, the other bacteria are inhibited, whereas the SRBs still work at pH values lower than 6.
- Increasing the temperature in the digester stimulates the production of biogas. The increased temperatures facilitate faster reaction rates, and thus more biogas can be produced from the organic matter in an equal amount of time (Tchobanoglous *et al.*, 2003).

NRM-Prec:

- Decreasing the P concentration in the input waste flow reduces the potential for struvite ($MgNH_4PO_4{:}6H_2O$) precipitation.
- Decreasing the Mg concentration in the input waste flow decreases the pH in the reactor, which is obvious as a Mg source is often added to induce P precipitation (Le Corre *et al.*, 2007b). Hence, less Mg-P precipitates are formed, the effluent P concentration increases, while the P recovery efficiency decreases.
- Increasing the P concentration in the input waste flow at a particular (neutral to high) pH increases the amount of P precipitates formed (precipitation is driven by supersaturation).
- Decreasing the pH by decreasing the concentration of nutrients, such as Mg and Ca, in the input waste flow reduces the resulting fertilizer density and molecular weight (fewer and less heavy P precipitates).

NRM-Strip:

- Decreasing the reactor height has no influence on the N recovery efficiency because the NH_3-NH_4^+ equilibrium between a gas bubble and the surrounding water is reached in a very small time interval (Gujer, 2008).
- Increasing the temperature increases the NH_3 stripping performance (Wang *et al.*, 2007). Hence, lower effluent NH_4-N concentrations and higher NH_3 partial pressures in the gas phase are found. The more NH_3 is stripped out, the lower the effluent pH.

- Increasing the liquid flow rate, reduces the residence time in the system. As such, the (slow) formation of $CaCO_3$ precipitates in the reactor is reduced, and thus also the scaling potential.

NRM-Scrub:

- Decreasing the reactor height has no influence on the N recovery efficiency because the NH_3-NH_4^+ equilibrium between a gas bubble and the surrounding water is reached in a very small time interval (Gujer, 2008).
- Increasing the partial pressure of NH_3 in the incoming gas phase (coming from the stripper) decreases the fertilizer alkalinity (through NH_2COO^- formation) and increases the N concentration in the resulting ammonium sulfate solution. Hence, more N can be recovered in an equal amount of time.

APPENDIX 10:

Results from global sensitivity analyses of nutrient recovery models (NRM)

Table A10.1 Global sensitivity analyses for the nutrient recovery model of the anaerobic digester (NRM-AD): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario A (all applications). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.4.

	CH_4 production		Biogas production		Digestate S_COD		Digestate X_COD		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
S_Inert	0.005	0.715	-0.005	-0.519	0.024	1.715	0.038	1.399	-0.002	-0.182	-0.001	-0.140	-0.002	-2.443	0.027	2.117	0.047	1.746
S_fa	-0.005	-0.823	-0.003	-0.331	0.063	4.403	-0.025	-0.920	0.001	0.057	0.003	0.376	2.16E-04	0.252	-0.006	-0.466	-0.015	-0.557
S_su	0.003	0.467	-4.14E-05	-0.004	0.035	2.467	0.020	0.723	-0.014	-1.333	0.015	1.981	-3.89E-04	-0.452	0.006	0.434	0.030	1.102
X_Inert	0.007	1.068	-0.002	-0.229	-0.007	-0.453	0.033	1.234	-0.014	-1.330	0.014	1.814	-0.001	-0.821	0.020	1.577	0.034	1.249
X_ch	-0.004	-0.584	0.011	1.136	0.039	2.738	0.022	0.798	-0.006	-0.633	0.004	0.454	4.19E-04	0.484	0.018	1.384	0.031	1.134
X_li	0.004	0.680	0.012	1.214	0.025	1.811	0.026	0.944	0.012	1.185	-0.011	-1.438	0.001	0.941	0.005	0.388	0.033	1.215
X_pr	-0.010	-1.604	-0.009	-0.873	0.038	2.617	-0.003	-0.105	-0.017	-1.667	0.006	0.810	4.79E-04	0.551	0.003	0.196	0.005	0.185
S_Acetate	0.008	1.289	0.038	3.782	-0.012	-0.847	0.024	0.888	-0.026	-2.509	0.007	0.905	0.001	0.588	-0.117	-9.080	0.024	0.897
S_Al	0.024	3.690	-0.065	-6.573	0.114	7.985	-0.029	-1.059	0.097	9.492	0.026	3.402	-0.020	-22.818	0.291	22.690	-0.029	-1.057
S_Butyrate	-0.004	-0.649	0.035	3.514	0.100	7.050	-0.060	-2.195	-0.007	-0.714	-0.003	-0.381	-0.004	-4.454	-0.132	-10.224	-0.059	-2.172
S_C_4_	0.001	0.158	0.704	70.913	-0.052	-3.640	-0.044	-1.609	0.159	15.642	-0.014	-1.780	-0.005	-6.224	-0.221	-17.095	-0.044	-1.616
S_C_min4_	0.924	145.001	0.364	36.517	-0.008	-0.565	0.007	0.242	-0.010	-0.969	-0.009	-1.092	4.34E-05	0.050	0.002	0.186	0.007	0.251
S_Ca	0.009	1.414	-0.127	-12.886	0.130	9.260	0.042	1.529	0.093	9.271	0.024	3.174	-0.009	-10.115	0.338	25.987	0.042	1.545
S_Cl	0.016	2.551	0.057	5.789	-0.040	-2.841	-0.025	-0.926	-0.033	-3.269	0.002	0.205	-0.001	-1.010	-0.160	-12.447	-0.024	-0.905
S_Fe	0.0015	0.235	-0.113	-11.518	0.071	5.059	-0.035	-1.289	0.061	6.074	0.034	4.457	-0.005	-5.965	0.299	23.213	-0.034	-1.271
S_H_0_	0.010	1.507	0.039	3.967	-0.019	-1.378	0.059	2.137	4.44E-04	0.044	-0.003	-0.407	4.20E-05	0.049	-0.018	-1.401	0.059	2.162
S_K	-0.004	-0.716	-0.038	-3.837	0.036	2.517	0.040	1.471	0.039	3.816	0.005	0.595	0.999	1163.220	0.177	13.798	0.040	1.465
S_Mg	-0.005	-0.834	-0.079	-7.829	0.113	7.866	0.039	1.436	-0.051	-4.907	-0.009	-1.157	-0.005	-5.190	0.348	26.996	0.039	1.444
S_N_0_	0.012	1.943	0.052	5.229	-0.015	-1.065	0.011	0.399	0.004	0.405	0.003	0.432	-9.17E-06	-0.011	-0.012	-0.966	0.011	0.413
S_N_5_	0.018	2.839	0.069	6.938	-0.054	-3.843	-0.036	-1.297	-0.035	-3.417	4.54E-04	0.059	-0.008	-9.715	-0.164	-12.626	-0.036	-1.313
S_N_min3_	0.006	0.876	-0.044	-4.448	-0.033	-2.345	0.004	0.137	0.913	89.965	0.010	1.309	-0.007	-7.815	-0.056	-4.379	0.004	0.131
S_Na	0.006	0.966	-0.063	-6.394	0.067	4.721	0.051	1.890	0.031	3.045	0.244	31.368	2.13E-05	0.025	0.189	14.680	0.052	1.916
S_P	0.008	1.190	0.062	6.289	-0.059	-4.184	-0.006	-0.236	-0.037	-3.633	0.938	121.059	0.002	2.669	-0.192	-14.959	-0.007	-0.261
S_Propionate	0.018	2.900	0.041	4.107	0.052	3.625	-0.056	-2.072	-0.019	-1.902	0.005	0.692	-0.004	-5.046	-0.108	-8.367	-0.056	-2.069
S_S_6_	0.011	1.818	0.116	11.679	-0.102	-7.143	-0.039	-1.455	-0.063	-6.208	-0.003	-0.342	-0.011	-12.383	-0.355	-27.631	-0.040	-1.472
S_S_min2_	-0.014	-2.242	0.006	0.647	0.005	0.374	-0.012	-0.443	-0.008	-0.799	0.005	0.660	-1.44E-04	-0.166	-0.012	-0.960	-0.012	-0.444
S_Valerate	0.003	0.517	0.061	6.126	0.118	8.262	-0.012	-0.442	-0.031	-3.065	0.006	0.828	-0.007	-7.509	-0.099	-7.700	-0.012	-0.435
pH_liq	-0.004	-0.667	-0.013	-1.345	0.006	0.419	-0.005	-0.183	0.011	1.111	-0.016	-2.039	0.000	-0.533	0.017	1.316	-0.005	-0.198
temp_liq	0.307	49.000	0.487	48.865	-0.021	-1.469	0.022	0.817	-0.172	-16.862	-0.023	-2.919	-0.006	-6.720	-0.103	-7.934	0.023	0.835
Q_liq_in	0.009	1.397	-0.001	-0.147	0.851	60.389	0.020	0.746	0.017	1.682	-0.009	-1.189	0.001	0.670	-0.013	-1.022	0.070	2.572
k_Al_2O_3	-0.006	-0.985	-0.017	-1.723	0.026	1.865	0.004	0.130	-0.019	-1.879	-0.005	-0.628	-0.001	-1.428	-0.013	-1.020	0.004	0.135

(Continuation)	CH_4 production		Biogas production		DIgestate S_COD		Digestate X_COD		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_$AlPO_4$	0.008	1.294	0.019	1.955	0.005	0.336	-0.012	-0.430	0.012	1.189	-0.006	-0.827	0.002	2.210	0.011	0.870	-0.012	-0.429
k_Anhydrite	0.008	1.232	-0.001	-0.097	0.004	0.271	0.011	0.393	0.006	0.625	0.007	0.853	0.001	0.716	0.000	0.016	0.010	0.374
k_Aragonite	-0.021	-0.285	0.004	0.443	-0.008	-0.541	-0.061	-2.220	-0.007	-0.688	-0.001	-0.086	-0.001	-0.745	-0.001	-0.064	-0.062	-2.235
k_Boehmite	0.004	0.559	0.002	0.235	-0.010	-0.693	0.006	0.210	-0.013	-1.301	0.002	0.290	-0.001	-0.782	0.014	1.077	0.006	0.231
k_$Ca_4H(PO_4)_3:3H_2O$	0.011	1.791	-0.002	-0.196	-0.023	-1.609	-0.046	-1.699	-0.012	-1.210	0.006	0.708	0.002	1.983	0.010	0.805	-0.047	-1.720
k_$CaHPO_4:2H_2O$	0.003	0.408	0.003	0.319	0.033	2.330	0.016	0.566	0.008	0.802	0.007	0.884	3.06E-04	0.357	0.009	0.721	0.016	0.567
k_$CaHPO_4$bis	-0.097	-1.056	0.012	1.261	0.030	2.104	-0.041	-1.524	0.003	0.338	0.009	1.175	4.32E-04	0.506	-0.024	-1.826	-0.042	-1.541
k_Calcite	-0.007	-1.131	-0.014	-1.393	-0.019	-1.358	-0.010	-0.377	-0.008	-0.757	-0.003	-0.401	-4.21E-04	-0.492	-0.006	-0.497	-0.009	-0.341
k_Diaspore	-0.004	-0.649	0.004	0.379	-0.002	-0.145	0.025	0.905	0.004	0.366	-0.009	-1.118	-0.002	-1.999	0.000	0.007	0.024	0.890
k_Dolomite	-0.010	-1.606	-0.004	-0.453	-0.014	-0.972	-0.011	-0.420	-0.021	-2.063	0.003	0.367	4.25E-04	0.496	-0.003	-0.230	-0.011	-0.415
k_FeS_ppt	0.003	0.465	-0.007	-0.734	-0.024	-1.658	0.006	0.229	-0.005	-0.494	-0.004	-0.550	0.001	0.855	0.029	2.266	0.006	0.217
k_Gibbsite	0.003	0.449	0.007	0.659	-0.013	-0.890	0.018	0.666	0.021	2.037	0.001	0.126	0.002	1.901	0.004	0.326	0.018	0.647
k_Hercynite	0.002	0.269	-0.016	-1.666	0.008	0.562	-0.009	-0.320	0.024	2.387	-0.001	-0.131	-0.001	-1.192	0.008	0.595	-0.008	-0.312
k_Hydroxyapatite	0.008	1.312	0.003	0.326	-0.002	-0.106	-0.030	-1.102	0.009	0.933	-0.001	-0.142	0.002	1.944	0.011	0.886	-0.029	-1.090
k_Kstruvite	0.009	1.452	0.011	1.090	-0.003	-0.197	0.032	1.180	-0.007	-0.650	-0.002	-0.278	-3.32E-04	-0.384	0.012	0.952	0.031	1.158
k_Mackinawite	-0.004	-0.622	0.002	0.163	0.008	0.559	0.024	0.888	-0.005	-0.517	0.012	1.484	0.001	0.674	0.003	0.248	0.025	0.905
k_Magnesite	0.001	0.186	-0.007	-0.664	0.018	1.289	-0.048	-1.780	0.013	1.274	-0.007	-0.936	-1.63E-04	-0.189	-0.016	-1.208	-0.049	-1.794
k_$Mg_3(PO_4)_2$	-0.003	-0.422	0.003	0.332	-0.039	-2.733	0.008	0.304	0.015	1.437	0.012	1.591	-1.40E-04	-0.164	0.012	0.921	0.009	0.320
k_$MgHPO_4:3H_2O$	-0.010	-1.552	0.007	0.698	0.023	1.576	0.023	0.849	0.010	0.937	-0.012	-1.527	0.001	1.574	0.003	0.208	0.023	0.845
k_Siderite	0.002	0.360	0.018	1.791	-0.009	-0.603	-0.004	-0.140	-0.019	-1.872	-0.013	-1.636	2.50E-04	0.287	-0.001	-0.043	-0.004	-0.164
k_Struvite	-0.012	-1.841	-0.004	-0.353	0.019	1.331	0.036	1.311	0.003	0.336	-0.008	-0.975	-0.002	-2.258	0.005	0.347	0.036	1.318
k_Vivianite	-0.009	-1.472	0.004	0.430	0.007	0.510	-0.003	-0.112	0.000	-0.006	0.002	0.289	-1.72E-04	-0.199	-0.011	-0.852	-0.003	-0.098
kLa_H2	0.006	0.984	-0.007	-0.734	0.020	1.378	0.012	0.441	0.001	0.138	-0.003	-0.441	-0.002	-1.783	-0.003	-0.222	0.012	0.445
D_H2	0.017	2.720	0.015	1.470	0.004	0.296	-0.017	-0.624	-0.020	-1.933	0.008	1.013	0.001	0.914	0.003	0.228	-0.017	-0.625
theta_CH_4_g_	0.001	0.201	-0.019	-1.930	-0.020	-1.382	0.035	1.280	0.002	0.180	-0.015	-1.919	0.001	1.197	0.003	0.224	0.035	1.281
theta_CO_2_g_	0.004	0.717	-0.029	-2.960	-0.019	-1.340	0.026	0.975	0.004	0.397	0.008	0.992	-1.42E-04	-0.167	-0.013	-0.973	0.027	0.987
theta_H_2S_g_	0.004	0.591	0.004	0.394	-0.012	-0.825	-0.036	-1.333	-0.007	-0.646	-0.004	-0.486	-0.001	-1.548	-0.002	-0.140	-0.036	-1.325
theta_H_2_g_	0.005	0.770	0.007	0.657	0.007	0.485	-0.008	-0.309	0.002	0.177	0.006	0.816	-0.001	-0.848	0.001	0.046	-0.008	-0.290
theta_N_2_g_	0.008	1.319	-0.018	-1.775	0.019	1.349	-0.013	-0.461	0.012	1.220	0.004	0.568	-0.001	-0.759	-0.018	-1.397	-0.013	-0.469
theta_NH_3_g_	0.005	0.789	-0.001	-0.112	-0.034	-2.397	0.045	1.629	0.012	1.163	-0.008	-1.063	9.50E-05	0.111	0.010	0.806	0.045	1.647
kdec_Xsrb_ac	0.006	0.914	-0.001	-0.069	-0.005	-0.356	0.016	0.581	0.004	0.424	-0.011	-1.367	0.001	1.462	0.006	0.473	0.016	0.578
kdec_Xsrb_bu	-0.003	-0.553	-0.011	-1.100	-0.004	-0.248	0.018	0.652	0.007	0.647	-0.002	-0.195	0.001	0.733	0.010	0.818	0.018	0.680
kdec_Xsrb_h	-0.011	-1.769	-0.002	-0.231	0.010	0.686	0.009	0.345	0.007	0.680	-0.008	-1.034	0.001	1.109	0.002	0.164	0.009	0.345
kdec_Xsrb_pro	0.005	0.796	-0.008	-0.821	0.005	0.335	-0.044	-1.601	0.016	1.621	-0.004	-0.496	1.39E-04	0.162	-0.010	-0.795	-0.044	-1.602

(Continuation)	CH₄-production		Biogas production		DIgestate S_COD		Digestate X_COD		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
km_srb_ac	0.0003	0.048	-2.62E-04	-0.026	-0.005	-0.325	0.023	0.850	0.002	0.188	-0.005	-0.660	0.001	0.662	0.008	0.608	0.024	0.876
km_srb_bu	0.009	1.360	-0.009	-0.930	-0.028	-1.956	0.060	2.181	0.015	1.426	0.000	0.043	-0.001	-1.515	0.003	0.264	0.060	2.182
km_srb_h	-0.005	-0.868	0.003	0.279	-0.004	-0.249	0.057	2.064	0.003	0.280	-0.003	-0.369	-1.55E-04	-0.179	0.010	0.766	0.056	2.057
km_srb_pro	0.006	0.956	0.014	1.388	0.028	2.005	0.006	0.218	0.022	2.169	-0.001	-0.162	-0.001	-0.850	0.007	0.521	0.006	0.213
$\sum_{j=1}^{p} SRC_j^2$	**0.96**		**0.95**		**0.85**		**0.06**		**0.93**		**0.94**		**1.00**		**0.81**		**0.07**	
R^2	**0.96**		**0.93**		**0.86**		**0.06**		**0.93**		**0.96**		**1.00**		**0.79**		**0.07**	
R^2adj	**0.96**		**0.93**		**0.85**		**0.01**		**0.92**		**0.96**		**1.00**		**0.78**		**0.02**	

Table A10.2 Global sensitivity analyses for the nutrient recovery model of the anaerobic digester (NRM-AD): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario B (manure; Cesur and Albertson, 2005). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.4.

	CH_4 production		Biogas production		Digestate S_COD		Digestate X_COD		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
S_Inert	-0.004	-0.880	-0.003	-0.744	0.019	2.599	-0.009	-1.287	2.39E-04	0.386	-0.008	-1.444	6.16E-05	0.179	0.001	0.427	-0.001	-0.117
S_fa	0.001	0.110	-0.001	-0.226	0.025	3.325	0.001	0.100	-3.17E-04	-0.508	0.004	0.790	5.11E-04	1.466	4.54E-04	0.230	0.008	1.132
S_su	-0.003	-0.522	-2.63E-04	-0.063	0.033	4.501	0.012	1.648	0.001	1.102	-0.001	-0.111	1.31E-04	0.376	-0.001	-0.699	0.019	2.641
X_Inert	0.001	0.169	0.003	0.703	-0.002	-0.287	0.151	20.390	8.53E-05	0.137	-0.006	-0.993	-1.25E-04	-0.361	-0.002	-1.175	0.105	14.857
X_ch	-0.004	0.840	0.002	0.476	0.138	18.892	0.006	0.770	-0.001	-1.629	-0.002	-0.355	-0.001	-1.652	0.002	0.813	0.046	6.579
X_li	-0.001	0.240	-0.001	-0.190	0.027	3.649	0.015	2.043	0.001	1.095	0.015	2.606	1.58E-04	0.459	0.001	0.516	0.019	2.660
X_pr	-0.004	-0.807	-0.001	-0.252	0.016	2.150	0.003	0.371	2.20E-04	0.356	0.005	0.901	1.31E-04	0.382	0.003	1.819	0.007	0.956
S_Acetate	-0.002	-0.336	-4.41E-04	-0.108	0.009	1.264	0.004	0.509	-0.002	-5.734	-0.010	-1.753	9.34E-05	0.272	-0.006	-3.329	0.005	0.775
S_Al	-0.008	-1.566	-0.007	-1.619	0.012	1.638	0.013	1.791	-0.004	-0.420	0.010	1.771	-0.003	-9.231	0.010	5.085	0.013	1.833
S_Butyrate	0.005	0.954	3.59E-04	0.087	0.009	1.204	0.008	1.143	-2.59E-04	-2.759	4.22E-05	0.008	-4.63E-04	-1.344	-0.004	-2.019	0.009	1.221
S_C_4_	4.25E-04	0.088	0.184	44.747	-0.006	-0.858	-0.007	-0.983	-0.002	6.085	-0.004	-0.715	3.73E-04	1.083	-0.108	-56.478	-0.007	-0.957
S_C_min4_	0.928	191.489	0.615	149.820	-0.005	-0.751	0.002	0.205	0.004	-0.989	-0.009	-1.539	-2.82E-04	-0.821	0.003	1.531	2.66E-04	0.038
S_Ca	0.011	2.275	-0.175	-42.678	0.009	1.198	0.007	0.912	-0.001	69.997	0.041	7.271	-0.068	-198.442	0.410	214.466	0.007	1.019
S_Cl	0.005	1.066	0.079	19.118	-0.009	-1.231	4.11E-04	0.056	0.043	-126.094	0.014	2.543	-0.004	-11.317	-0.164	-85.267	-0.002	-0.337
S_Fe	-0.010	-1.973	-0.009	-2.170	-0.007	-0.911	-0.005	-0.689	-0.078	3.367	0.006	1.029	-0.001	-4.014	0.010	5.076	-0.006	-0.797
S_H_0_	0.002	0.363	0.097	23.619	-0.004	-0.492	0.002	0.209	0.002	0.156	-0.002	-0.397	-2.13E-04	-0.617	0.001	0.453	1.18E-04	0.017
S_K	0.006	1.136	-0.017	-4.155	-0.002	-0.216	-0.003	-0.450	9.64E-05	16.007	-0.001	-0.266	0.984	2,860.120	0.049	25.758	-0.003	-0.402
S_Mg	0.008	1.714	0.008	2.024	0.003	0.423	0.006	0.764	0.010	-867.227	0.008	1.482	-0.018	-51.804	0.088	46.392	0.005	0.697
S_N_0_	0.001	0.237	0.129	31.130	-0.001	-0.170	-0.005	-0.723	-0.534	0.597	0.003	0.487	-1.38E-04	-0.397	0.003	1.401	-0.004	-0.557
S_N_5_	0.004	0.746	0.100	24.331	3.76E-05	0.005	-0.003	-0.461	3.71E-04	-161.417	2.19E-05	0.004	-0.019	-55.844	-0.202	-105.801	-0.002	-0.318
S_N_min3_	0.001	0.151	-0.076	-18.581	0.005	0.673	1.64E-04	0.022	-0.100	1,328.990	-2.41E-05	-0.004	-0.015	-43.565	0.083	43.521	0.002	0.216
S_Na	-0.003	-0.703	-0.044	-10.727	-0.008	-1.114	-0.005	-0.712	0.820	43.726	0.395	70.402	-0.004	-11.538	0.091	47.516	-0.006	-0.884
S_P	-0.006	-1.164	0.028	6.711	-0.003	-0.471	0.004	0.542	0.027	-32.956	0.898	160.177	0.003	9.630	-0.072	-37.944	0.002	0.253
S_Propionate	0.005	1.117	0.004	1.044	0.011	1.534	0.016	2.221	-0.020	-1.607	-0.005	-0.932	2.35E-04	0.683	-0.001	-0.684	0.015	2.117
S_S_6_	-0.002	-0.438	0.046	11.217	-0.010	-1.310	-0.013	-1.780	-0.001	-65.549	-0.001	-0.200	-0.006	-16.523	-0.099	-51.666	-0.012	-1.714
S_S_min2_	-0.001	-0.264	0.003	0.743	-0.009	-1.246	-0.018	-2.389	-0.041	-0.314	0.003	0.483	4.64E-04	1.340	-0.002	-1.033	-0.015	-2.147
S_Valerate	-0.006	-1.175	-0.010	-2.394	0.001	0.079	0.002	0.228	-1.95E-04	-0.962	-0.002	-0.361	-0.001	-1.938	0.003	1.446	0.001	0.190
pH_liq	-0.001	-0.301	-0.001	-0.332	0.004	0.556	0.004	0.520	-0.001	0.496	0.008	1.371	-1.18E-04	-0.342	0.001	0.344	0.004	0.558
temp_liq	0.309	63.173	0.677	163.337	-0.014	-1.872	-0.002	-0.297	3.08E-04	-255.771	-0.028	-4.912	-0.086	-248.503	-0.834	-433.202	-0.005	-0.686
Q_liq_in	0.010	2.071	0.008	2.038	0.941	128.639	0.956	129.192	-0.159	-0.295	0.002	0.386	2.54E-07	0.001	-0.001	-0.563	0.959	135.665
k_Al_2O_3	-0.009	-1.874	-0.004	-0.858	5.27E-05	0.007	0.002	0.277	-1.83E-04	-2.199	-0.007	-1.195	3.17E-04	0.913	0.001	0.318	0.001	0.205

(Continuation)	CH_4 production		Biogas production		Digestate S_COD		Digestate X_COD		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_$AlPO_4$	0.003	0.686	0.003	0.679	0.012	1.593	0.010	1.311	-0.001	-0.002	0.001	0.090	3.25E-04	0.945	-0.002	-0.886	0.010	1.469
k_Anhydrite	-0.002	-0.432	-0.002	-0.536	-0.004	-0.534	-0.004	-0.554	-0.001	-0.652	0.006	1.000	-1.50E-04	-0.433	0.001	0.741	-0.004	-0.577
k_Aragonite	-0.002	-0.399	-0.001	-0.237	-0.001	-0.078	-0.004	-0.558	-1.53E-06	-1.050	-0.003	-0.448	6.27E-05	0.181	0.001	0.478	-0.003	-0.434
k_Boehmite	0.003	0.655	0.005	1.254	0.001	0.149	0.002	0.319	-4.05E-04	-1.112	2.42E-04	0.043	4.26E-05	0.124	0.002	1.219	0.002	0.282
k_$Ca_4H(PO_4)_3$:$3H_2O$	0.010	1.981	0.007	1.769	0.011	1.539	0.009	1.183	-0.001	1.111	0.003	0.609	1.39E-04	0.402	-0.001	-0.487	0.010	1.359
k_$CaHPO_4$:$2H_2O$	0.009	1.956	0.006	1.432	-0.005	-0.656	-0.008	-1.150	-0.001	-0.403	-0.005	-0.952	-1.71E-04	-0.499	3.40E-04	0.179	-0.007	-1.051
k_$CaHPO_4$bis	-0.003	-0.521	0.001	0.340	-0.007	-1.015	-0.020	-2.734	0.001	-2.452	0.004	0.776	-2.92E-04	-0.848	0.001	0.736	-0.016	-2.327
k_Calcite	0.007	1.363	0.002	0.541	0.014	1.916	0.015	2.062	-2.47E-04	-0.002	-0.003	-0.580	-2.78E-04	-0.793	0.001	0.429	0.015	2.122
k_Diaspore	0.005	1.062	0.004	0.936	-8.74E-05	-0.012	0.010	1.330	-0.002	1.314	-0.003	-0.544	-1.13E-04	-0.329	-0.002	-0.926	0.007	0.972
k_Dolomite	-0.002	-0.444	-0.007	-1.804	5.50E-05	0.008	9.85E-05	0.013	-1.15E-06	0.110	-0.004	-0.647	3.57E-05	0.103	0.001	0.715	7.51E-05	0.011
k_FeS_ppt	0.004	0.861	0.003	0.765	0.013	1.783	0.006	0.818	0.001	0.034	-0.001	-0.184	-1.99E-04	-0.568	0.001	0.587	0.008	1.168
k_Gibbsite	3.86E-05	0.008	0.002	0.433	0.003	0.373	-0.003	-0.390	6.83E-05	1.177	0.004	0.745	-4.40E-05	-0.127	4.38E-04	0.228	-0.001	-0.167
k_Hercynite	0.002	0.338	0.004	0.883	0.002	0.312	-0.008	-1.140	2.12E-05	0.455	-0.007	-1.296	9.15E-05	0.265	-0.002	-1.289	-0.005	-0.736
k_Hydroxyapatite	0.001	0.171	-4.40E-04	-0.106	0.004	0.541	0.003	0.345	0.001	0.526	-0.004	-0.733	1.66E-05	0.048	1.49E-04	0.078	0.003	0.425
k_Kstruvite	-0.004	-0.744	-0.002	-0.570	-0.003	-0.447	-0.001	-0.129	2.82E-04	0.113	0.005	0.826	3.58E-04	1.039	0.002	1.106	-0.002	-0.237
k_Mackinawite	1.43E-05	0.003	4.22E-05	0.010	0.013	1.797	0.014	1.857	3.27E-04	-0.743	-0.002	-0.312	-3.88E-04	-1.125	0.001	0.401	0.014	1.934
k_Magnesite	0.006	1.330	0.006	1.438	0.001	0.089	-0.002	-0.281	6.95E-05	-0.362	-0.001	-0.137	3.31E-04	0.959	0.004	1.923	-0.001	-0.176
k_$Mg_3(PO_4)_2$	0.010	2.155	0.004	0.999	-0.004	-0.619	-0.006	-0.781	-4.59E-04	0.234	-0.003	-0.490	-1.42E-04	-0.413	-0.001	-0.526	-0.005	-0.768
k_$MgHPO_4$:$3H_2O$	0.007	1.453	0.003	0.697	-0.001	-0.154	-0.003	-0.350	-2.24E-04	1.815	-0.009	-1.629	2.28E-04	0.659	-0.002	-1.194	-0.002	-0.305
k_Siderite	0.008	1.545	0.007	1.671	-0.002	-0.250	2.63E-04	0.036	1.44E-04	0.025	0.002	0.433	-3.01E-04	-0.869	-0.001	-0.683	-3.68E-04	-0.052
k_Struvite	0.007	1.435	0.006	1.438	-0.009	-1.256	-0.002	-0.260	0.001	0.433	0.002	0.364	2.42E-04	0.702	-2.77E-04	-0.145	-0.004	-0.590
k_Vivianite	-0.007	-1.496	-0.002	-0.371	0.007	0.943	0.008	1.138	1.57E-05	0.303	0.004	0.741	2.95E-04	0.856	-0.001	-0.449	0.008	1.134
k_La_H_2	0.004	0.796	-0.002	-0.390	-0.011	-1.479	-0.006	-0.833	2.68E-04	-0.952	-0.009	-1.560	-0.001	-2.041	-0.002	-1.233	-0.008	-1.082
D_H_2	-0.003	-0.607	-4.68E-05	-0.011	5.64E-05	0.008	0.006	0.779	1.87E-04	-2.751	-0.006	-1.069	-2.83E-04	-0.815	0.003	1.730	0.004	0.573
theta_CH_4_g_	-0.005	-0.961	0.001	0.194	-0.001	-0.152	0.006	0.797	3.95E-04	-2.438	-0.004	-0.684	2.95E-04	0.857	-0.001	-0.333	0.004	0.536
theta_CO_2_g_	-0.004	-0.839	-0.001	-0.250	0.004	0.593	0.002	0.303	-7.16E-05	-0.416	0.007	1.190	1.19E-05	0.034	0.002	0.990	0.003	0.411
theta_H_2S_g_	0.008	1.588	0.004	0.886	-0.009	-1.228	-0.005	-0.630	0.001	1.588	0.007	1.267	0.001	1.511	0.001	0.684	-0.006	-0.852
theta_H_2_g_	6.00E-05	0.012	0.003	0.816	-0.010	-1.336	-0.001	-0.118	2.84E-04	-0.699	0.005	0.806	-3.50E-04	-1.019	-0.001	-0.325	-0.004	-0.511
theta_N_2_g_	0.004	0.884	-5.88E-05	-0.014	-0.017	-2.282	-0.010	-1.380	0.001	1.230	0.004	0.798	1.42E-04	0.411	-0.002	-1.002	-0.012	-1.738
theta_NH_3_g_	-0.002	-0.508	0.004	0.852	-0.006	-0.873	-0.008	-1.038	0.001	0.408	0.007	1.205	1.61E-04	0.467	-0.002	-1.298	-0.007	-1.038
kdec_Xsrb_ac	-0.004	-0.899	-0.005	-1.097	-0.003	-0.371	0.001	0.123	2.91E-04	0.641	0.003	0.623	-4.05E-04	-1.175	-0.001	-0.553	-2.05E-04	-0.029
kdec_Xsrb_bu	-0.005	-0.988	-0.002	-0.458	0.007	0.981	-0.002	-0.212	3.85E-04	-0.116	0.002	0.412	1.16E-04	0.338	-0.002	-0.797	0.001	0.156
kdec_Xsrb_h	0.005	0.969	-0.002	-0.401	0.004	0.516	0.003	0.417	-0.002	1.042	0.011	1.883	-4.34E-05	-0.125	-0.002	-1.022	0.003	0.470
kdec_Xsrb_pro	-0.003	-0.714	4.25E-04	0.104	-0.005	-0.724	0.004	0.593	-2.57E-04	0.462	-0.006	-0.997	-1.05E-04	-0.305	-0.002	-1.114	0.001	0.204
km_srb_ac	0.002	0.433	0.006	1.395	0.007	1.022	0.010	1.383	0.001	1.002	0.004	0.758	-1.76E-04	-0.508	0.003	1.368	0.009	1.341

(Continuation)	**CH_4 production**		**Biogas production**		**Digestate S_COD**		**Digestate X_COD**		**Digestate S_N_min3_**		**Digestate S_P**		**Digestate S_K**		**Digestate pH**		**Overall**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
km_srb_bu	-0.007	-1.452	-0.010	-2.462	0.007	0.988	0.009	1.144	-4.31E-04	1.302	0.002	0.301	2.01E-04	0.577	-0.005	-2.550	0.008	1.151
km_srb_h	0.001	0.276	0.001	0.132	2.59E-05	0.004	0.004	0.556	0.001	0.465	0.006	0.995	1.64E-04	0.471	-0.003	-1.512	0.003	0.409
km_srb_pro	0.002	0.387	0.002	0.539	0.001	0.076	0.001	0.145	2.52E-04	0.620	-0.004	-0.620	-8.63E-05	-0.249	-0.001	-0.617	0.001	0.131
$\sum_{j=1}^{p} SRC_j^2$	**0.96**		**0.95**		**0.91**		**0.94**		**1.00**		**0.97**		**0.98**		**0.98**		**0.94**	
R^2	**0.97**		**0.98**		**0.93**		**0.93**		**1.00**		**0.96**		**1.00**		**1.00**		**0.94**	
R^2adj	**0.97**		**0.98**		**0.93**		**0.93**		**1.00**		**0.96**		**1.00**		**1.00**		**0.93**	

Table A10.3 Global sensitivity analyses for the nutrient recovery model of the anaerobic digester (NRM-AD): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario C (sludge; Astals *et al.*, 2013). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.4.

	CH_4 production		Biogas production		Digestate S_COD		Digestate X_COD		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
S_Inert	-0.008	-1.743	-0.005	-0.857	0.043	4.910	-0.008	-0.645	0.002	1.260	-3.60E-04	-1.205	-0.001	-0.984	-0.002	-0.172	0.010	1.030
S_fa	0.003	0.693	0.003	0.512	0.052	5.928	-0.011	-0.891	-1.75E-04	-0.136	1.30E-05	0.043	7.36E-05	0.081	-0.016	-1.159	0.011	1.146
S_su	-0.006	-1.149	0.002	0.368	0.048	5.466	-0.011	-0.865	-0.001	-0.432	-7.56E-05	-0.252	-1.76E-04	-0.194	0.040	2.929	0.010	1.022
X_Inert	0.005	1.083	0.008	1.218	3.24E-04	0.037	0.456	37.222	0.001	0.463	-1.76E-04	-0.584	1.21E-04	0.133	0.004	0.321	0.319	32.087
X_ch	-0.001	-0.153	3.12E-04	0.049	0.191	21.893	0.034	2.783	-9.29E-05	-0.072	1.83E-04	0.607	-3.04E-04	-0.336	0.012	0.913	0.094	9.470
X_li	-0.004	-0.752	-0.005	-0.859	0.089	10.228	0.025	2.084	0.001	1.065	-1.07E-04	-0.357	6.54E-05	0.072	0.002	0.170	0.050	5.099
X_pr	-0.001	-0.121	-0.002	-0.298	0.148	16.934	0.024	1.921	-0.001	-1.153	-2.60E-04	-0.862	-1.21E-04	-0.134	-0.022	-1.630	0.071	7.124
S_Acetate	-0.003	-0.585	0.013	2.038	-0.010	-1.151	-0.006	-0.463	-0.011	-8.428	0.001	4.094	-0.006	-7.126	-0.107	-7.889	-0.008	-0.773
S_Al	-0.003	-0.666	-0.073	-11.505	-0.016	-1.812	0.002	0.176	-0.006	-4.828	0.005	17.416	-0.028	-31.153	0.331	24.242	-0.004	-0.429
S_Butyrate	-0.005	-1.105	-0.006	-0.897	0.001	0.134	-0.024	-1.997	-0.002	-1.340	1.26E-04	0.421	-0.002	-2.627	-0.018	-1.358	-0.017	-1.679
S_C_4_	-0.008	-1.650	0.270	42.398	-0.004	-0.502	-0.002	-0.134	0.010	7.526	0.003	9.101	-0.016	-17.987	-0.451	-33.113	-0.003	-0.265
S_C_min4_	0.935	191.644	0.795	125.253	-0.002	-0.205	-0.030	-2.460	0.001	0.489	-2.66E-04	-0.884	-4.85E-04	-0.536	-0.006	-0.406	-0.021	-2.098
S_Ca	0.001	0.135	-0.017	-2.621	-0.003	-0.383	-0.019	-1.582	0.001	0.992	0.001	1.876	-0.004	-4.555	0.153	11.160	-0.015	-1.483
S_Cl	1.12E-04	0.023	0.026	4.048	0.003	0.398	0.020	1.649	-0.011	-8.476	0.001	4.772	-0.006	-6.790	-0.090	-6.658	0.015	1.549
S_Fe	0.003	0.689	-0.063	-9.910	-0.011	-1.278	-0.024	-1.950	0.003	2.081	0.002	7.706	-0.015	-16.310	0.375	27.697	-0.021	-2.086
S_H_0_	-0.001	-0.182	0.125	19.649	-0.007	-0.807	-0.020	-1.619	4.34E-04	0.339	-2.29E-04	-0.763	2.75E-04	0.304	-0.021	-1.570	-0.016	-1.643
S_K	-0.001	-0.167	-0.001	-0.119	-0.001	-0.124	-0.014	-1.152	0.002	1.612	-9.73E-05	-0.323	1.001	1101.750	0.050	3.653	-0.010	-1.031
S_Mg	-0.003	-0.589	4.75E-04	0.075	0.003	0.401	-0.013	-1.047	-0.058	-45.294	8.79E-05	0.293	-0.002	-1.933	0.072	5.288	-0.008	-0.770
S_N_0_	0.005	0.983	0.172	27.054	0.009	1.072	0.022	1.778	1.99E-04	0.156	-3.88E-05	-0.129	3.71E-04	0.411	0.009	0.631	0.019	1.897
S_N_5_	0.003	0.636	0.070	10.959	-0.005	-0.620	-0.023	-1.862	-0.039	-30.363	0.005	16.987	-0.030	-33.312	-0.411	-30.266	-0.018	-1.812
S_N_min3_	0.009	1.845	-0.173	-27.297	0.001	0.074	0.016	1.280	0.996	779.103	0.004	13.460	-0.024	-26.291	-0.031	-2.295	0.011	1.107
S_Na	0.005	1.075	-0.028	-4.496	-0.006	-0.672	0.005	0.405	0.006	4.567	0.002	5.064	-0.002	-1.939	0.171	12.604	0.001	0.135
S_P	0.002	0.363	0.017	2.638	0.002	0.275	0.011	0.859	-0.001	-1.087	1.000	3,328.820	-0.001	-1.631	-0.086	-6.317	0.008	0.828
S_Propionate	-0.011	-2.216	0.002	0.378	-0.004	-0.427	-0.018	-1.456	-0.001	-0.830	2.55E-04	0.848	-0.003	-3.362	-0.058	-4.292	-0.014	-1.395
S_S_6_	0.002	0.435	0.023	3.639	0.005	0.570	0.028	2.294	-0.011	-8.331	0.001	4.897	-0.009	-9.618	-0.105	-7.806	0.021	2.159
S_S_min2_	-0.002	-0.341	0.004	0.629	0.010	1.167	-0.005	-0.434	-2.02E-04	-0.158	-1.50E-04	-0.502	0.001	1.235	-0.011	-0.783	0.000	0.003
S_Valerate	0.003	0.608	-0.010	-1.587	-0.010	-1.105	1.01E-04	-0.025	0.001	0.606	1.55E-04	0.515	-0.002	-2.151	-0.022	-1.640	-0.004	-0.381
pH_liq	0.001	0.122	1.42E-04	0.022	0.006	0.740	0.025	2.021	-0.002	-1.212	-0.001	-2.055	-4.05E-04	-0.449	-0.001	-0.095	0.020	1.981
temp_liq	0.305	62.604	0.448	70.760	0.010	1.163	-0.002	-0.159	-0.028	-21.730	-0.002	-6.802	-0.008	-9.349	-0.196	-14.424	0.003	0.281
Q_liq_in	-0.003	-0.701	2.29E-05	0.004	0.921	106.024	0.779	63.972	0.001	0.503	1.99E-04	0.667	2.30E-04	0.256	0.001	0.069	0.881	89.372
k_Al_2O_3	-0.002	-0.334	0.003	0.487	-0.001	-0.132	-0.012	-0.994	0.001	0.542	2.58E-04	0.854	0.001	0.807	-0.005	-0.368	-0.009	-0.899
k_$AlPO_4$	0.001	0.294	-0.009	-1.419	0.012	1.374	-0.004	-0.315	0.001	1.117	-2.76E-04	-0.918	4.70E-04	0.519	-0.016	-1.177	0.002	0.171
k_Anhydrite	-0.003	-0.648	-0.004	-0.619	0.015	1.785	0.005	0.430	3.71E-04	0.291	-1.44E-05	-0.048	0.001	1.032	0.009	0.701	0.009	0.947

Factor	CH_4 production		Biogas production		Digestate S_COD		Digestate X_COD		Digestate S_N_min3_		Digestate S_P		Digestate S_K		Digestate pH		Overall	
	SRC	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_Aragonite	-0.013	-2.702	-0.008	-1.265	-0.002	-0.250	-0.007	-0.610	-0.001	-0.883	2.17E-04	0.730	-1.74E-04	-0.195	-0.001	-0.046	-0.006	-0.608
k_Boehmite	0.005	1.026	-0.007	-1.078	-0.015	-1.686	-0.008	-0.677	0.001	0.837	-7.24E-05	-0.241	0.001	0.827	0.006	0.434	-0.011	-1.128
k_$Ca_4H(PO_4)_3:3H_2O$	0.009	1.837	0.002	0.363	0.007	0.849	0.008	0.613	-0.001	-0.687	1.50E-04	0.499	-4.67E-04	-0.515	-0.004	-0.269	0.008	0.802
k_$CaHPO_4:2H_2O$	0.007	1.422	0.007	1.150	0.002	0.192	0.017	1.386	-0.002	-1.754	2.38E-04	0.795	-2.70E-04	-0.299	-0.034	-2.503	0.012	1.256
k_$CaHPO_4$bis	0.007	1.355	0.005	0.742	0.011	1.301	0.013	1.057	0.001	0.441	9.24E-05	0.307	-0.001	-1.360	0.011	0.815	0.013	1.332
k_Calcite	-0.001	-0.302	-0.008	-1.245	-0.001	-0.105	-0.001	-0.102	-0.001	-0.757	3.02E-05	0.101	0.001	1.209	-0.009	-0.686	-0.001	-0.123
k_Diaspore	-0.002	-0.513	0.004	0.662	0.006	0.704	-0.009	-0.733	-0.001	-0.440	-1.47E-05	-0.049	-0.001	-0.861	-0.011	-0.844	-0.004	-0.404
k_Dolomite	-0.008	-1.657	-0.009	-1.499	0.001	0.066	-0.007	-0.610	2.93E-04	0.229	1.30E-04	0.433	-0.002	-1.817	-0.006	-0.475	-0.005	-0.506
k_FeS_ppt	-0.005	-0.969	-0.007	-1.123	-0.008	-0.917	-0.001	-0.092	-0.003	-2.116	4.70E-04	1.559	-0.001	-1.100	-0.017	-1.222	-0.004	-0.377
k_Gibbsite	0.013	2.575	0.016	2.505	0.004	0.458	-0.013	-1.027	2.68E-04	0.208	-4.23E-04	-1.400	0.001	0.907	0.013	0.963	-0.007	-0.735
k_Hercynite	0.003	0.558	0.012	1.945	0.009	1.071	0.007	0.610	-0.001	-0.824	-3.09E-04	-1.025	0.001	0.869	-0.010	-0.714	0.009	0.872
k_Hydroxyapatite	-0.001	-0.266	0.001	0.111	-0.001	-0.083	0.006	0.507	-0.003	-1.971	4.02E-04	1.332	-0.001	-0.972	-0.008	-0.594	0.004	0.410
k_Kstruvite	0.005	1.126	0.004	0.678	0.001	0.066	1.11E-04	0.009	-0.001	-0.610	-1.09E-04	-0.363	0.001	1.270	0.002	0.150	0.000	0.030
k_Mackinawite	0.001	0.257	0.001	0.198	0.008	0.933	-0.005	-0.444	0.001	0.561	2.17E-04	0.722	-0.001	-0.865	-0.001	-0.084	-0.001	-0.081
k_Magnesite	0.006	1.169	0.003	0.443	0.012	1.399	0.005	0.397	0.003	1.988	-1.73E-04	-0.575	4.74E-04	0.521	-0.006	-0.464	0.008	0.794
k_$Mg_3(PO_4)_2$	0.003	0.531	0.006	0.927	0.003	0.364	0.004	0.324	0.002	1.883	-2.81E-05	-0.094	0.001	1.154	0.019	1.385	0.004	0.399
k_$MgHPO_4:3H_2O$	0.005	1.002	0.002	0.292	-0.005	-0.585	-0.008	-0.686	-0.001	-0.412	-7.30E-05	-0.242	1.30E-04	0.143	-0.001	-0.098	-0.008	-0.780
k_Siderite	-0.001	-0.122	0.001	0.130	-0.012	-1.359	-0.014	-1.130	-0.003	-2.368	3.89E-04	1.299	-0.001	-0.983	-0.017	-1.272	-0.014	-1.413
k_Struvite	-0.004	-0.724	-0.004	-0.623	-0.014	-1.552	0.001	0.070	-0.001	-0.832	1.72E-04	0.567	0.001	1.212	0.007	0.485	-0.004	-0.441
k_Vivianite	0.009	1.766	0.003	0.512	-0.008	-0.944	0.005	0.371	0.003	2.087	1.75E-04	0.587	-0.001	-0.855	-0.014	-1.035	0.000	0.014
k_La_H_2	0.010	2.016	-0.012	-1.893	-0.010	-1.093	-0.004	-0.340	-4.23E-04	-0.329	1.38E-05	0.046	-3.41E-04	-0.376	-0.032	-2.363	-0.006	-0.649
D_H_2	-0.005	-0.990	-0.002	-0.289	-0.010	-1.197	-0.006	-0.475	1.07E-04	0.083	4.00E-05	0.133	-0.001	-1.509	0.004	0.270	-0.008	-0.796
theta_CH_4_g_	-0.004	-0.850	-0.003	-0.437	0.004	0.509	0.005	0.416	2.79E-04	0.217	4.49E-04	1.488	2.43E-04	0.268	0.003	0.187	0.005	0.523
theta_CO_2_g_	-4.11E-04	-0.085	3.54E-04	0.056	0.009	1.003	0.036	2.971	0.002	1.818	-3.90E-04	-1.304	-0.001	-0.987	0.015	1.122	0.028	2.885
theta_H_2S_g_	0.004	0.861	3.14E-04	0.049	0.002	0.221	0.008	0.688	-0.001	-1.085	-4.61E-05	-0.153	-0.001	-1.339	0.003	0.226	0.007	0.664
theta_H_2_g_	-0.002	-0.387	0.004	0.591	0.001	0.074	-0.009	-0.741	0.001	1.161	-2.90E-04	-0.972	0.002	2.038	0.028	2.053	-0.006	-0.613
theta_N_2_g_	-0.001	-0.268	0.001	0.174	-0.001	-0.084	-0.013	-1.059	0.001	0.397	-3.07E-04	-1.026	3.00E-04	0.332	0.017	1.254	-0.009	-0.939
kdec_Xsrb_ac	-0.002	-0.316	-0.003	-0.470	1.01E-04	0.012	0.025	2.059	0.001	0.892	9.01E-06	0.030	-2.21E-04	-0.246	-0.019	-1.435	0.017	1.777
kdec_Xsrb_bu	-0.003	-0.662	0.006	0.884	0.003	0.350	-0.005	-0.408	-0.001	-0.496	-9.72E-05	-0.323	4.68E-04	0.516	0.003	0.211	-0.002	-0.238
kdec_Xsrb_h	-0.002	-0.434	-0.001	-0.133	-0.003	-0.375	0.001	0.050	0.001	0.699	-1.05E-04	-0.347	0.001	0.727	0.013	0.935	-0.001	-0.077
kdec_Xsrb_pro	0.004	0.793	0.008	1.285	-0.006	-0.633	0.014	1.169	1.64E-04	0.127	-3.57E-04	-1.179	0.001	1.021	-0.005	-0.393	0.008	0.804
km_srb_ac	-0.002	-0.320	-0.002	-0.282	-0.004	-0.502	0.005	0.431	0.001	0.787	-9.75E-05	-0.323	0.001	0.775	0.012	0.905	0.002	0.209
km_srb_bu	0.004	0.754	0.002	0.357	0.005	0.621	-0.005	-0.430	-0.001	-0.871	3.07E-04	1.024	0.001	0.596	-0.009	-0.637	-0.002	-0.170
km_srb_h	-0.001	-0.103	0.010	1.544	-0.018	-2.005	-0.013	1.040	-7.55E-05	-0.059	7.67E-05	0.255	2.48E-04	0.273	0.025	1.799	-0.015	-1.542
km_srb_pro	0.016	3.344	0.010	1.544	0.014	1.576	-0.005	-0.369	0.001	0.549	-4.19E-04	-1.397	-2.22E-04	-0.246	-0.003	-0.197	0.002	0.192
$\sum_{j=1}^{p} SRC_j^2$	**0.97**		**1.00**		**0.93**		**0.83**		**1.00**		**1.00**		**1.00**		**0.78**		**0.90**	

R^2	**0.97**	**0.95**	**0.90**	**0.81**	**1.00**	**1.00**	**1.00**	**0.75**	**0.87**
R^{2}adj	**0.97**	**0.95**	**0.90**	**0.80**	**1.00**	**1.00**	**1.00**	**0.75**	**0.87**

Table A10.4 Global sensitivity analyses for the nutrient recovery model of the precipitation/crystallization unit (NRM-Prec): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario A (digestate: all applications). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.5.

	Effluent S_P		**Fertilizer P_P**		**Particle diameter**		**Fertilizer density**		**Struvite purity**		**Overall**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
S_Acetate	-0.001	-0.154	-0.039	-1.765	0.014	0.880	0.017	0.852	-0.015	-0.551	-0.039	-1.761
S_Al	0.038	5.216	0.005	0.242	-8.32E-05	-0.005	0.019	0.971	-0.011	-0.389	0.005	0.244
S_Butyrate	-0.011	-1.474	-0.001	-0.057	-0.027	-1.752	0.008	0.410	0.007	0.255	-0.001	-0.053
S_C_4_	0.003	0.459	-0.057	-2.535	-0.025	-1.599	-0.013	-0.639	-0.050	-1.854	-0.057	-2.537
S_C_min4_	-0.012	-1.738	0.035	1.584	-0.026	-1.660	0.012	0.619	0.018	0.668	0.035	1.581
S_DOM	-0.001	-0.154	-0.025	-1.133	0.013	0.879	0.016	0.851	-0.014	-0.550	-0.025	-1.133
S_Ca	0.022	3.124	0.259	11.589	0.039	2.532	0.009	0.469	-0.047	-1.748	0.259	11.588
S_Cl	0.024	3.353	-0.024	-1.081	-0.016	-0.999	0.002	0.094	-0.007	-0.269	-0.024	-1.082
S_Fe	0.037	5.234	-0.006	-0.271	-0.004	-0.269	0.020	1.029	0.044	1.631	-0.006	-0.271
S_K	0.017	2.383	0.045	1.996	-0.003	-0.184	-0.034	-1.691	0.035	1.293	0.045	1.995
S_Mg	0.012	1.646	0.086	3.827	0.035	2.233	0.022	1.106	-0.007	-0.243	0.086	3.824
S_N_5_	0.020	2.734	-0.017	-0.779	-0.016	-1.019	-0.029	-1.443	0.015	0.559	-0.018	-0.782
S_N_min3_	0.028	3.943	0.019	0.866	-0.029	-1.859	-0.035	-1.745	0.042	1.563	0.019	0.868
S_Na	0.274	38.280	-0.242	-10.853	-0.572	-37.099	-0.484	-24.553	-0.040	-1.465	-0.242	-10.851
S_P	0.934	130.334	0.207	9.267	0.552	35.735	0.448	22.653	-0.030	-1.101	0.207	9.266
S_Propionate	-2.50E-04	-0.035	-0.003	-0.143	0.017	1.093	0.021	1.070	-0.018	-0.678	-0.003	-0.143
S_S_6_	0.034	4.728	-0.059	-2.598	-0.006	-0.393	0.020	0.979	0.050	1.828	-0.059	-2.600
S_S_min2_	-3.64E-04	-0.051	-0.014	-0.621	-0.015	-0.973	0.001	0.056	0.020	0.730	-0.014	-0.623
S_Valerate	0.006	0.876	0.014	0.604	0.017	1.085	0.033	1.669	-0.009	-0.318	0.014	0.604
pH_liq	-0.010	-1.343	-0.011	-0.492	0.030	1.928	0.054	2.721	0.020	0.751	-0.011	-0.490
Temp_liq	0.003	0.480	-0.267	-11.925	-0.010	-0.637	-0.030	-1.509	-0.008	-0.308	-0.267	-11.924
Q_liq	0.004	0.517	-0.005	-0.220	0.018	1.163	0.009	0.467	-0.035	-1.278	-0.005	-0.218
Q_prec	0.005	0.706	-0.014	-0.623	-0.014	-0.920	-0.014	-0.730	-0.004	-0.158	-0.014	-0.618
k_$AlPO_4$	0.001	0.189	-0.012	-0.519	-0.023	-1.492	-0.023	-1.166	-0.012	-0.449	-0.012	-0.519
k_Aragonite	0.006	0.822	-0.007	-0.308	0.036	2.312	0.050	2.527	0.024	0.899	-0.007	-0.303
k_Artinite	0.008	1.135	-0.017	-0.752	0.010	0.679	0.040	2.019	-0.004	-0.156	-0.017	-0.752
k_Boehmite	0.004	0.520	0.025	1.133	-0.013	-0.846	-0.035	-1.779	0.042	1.564	0.025	1.132
k_Brucite	0.004	0.493	0.048	2.132	0.002	0.129	0.011	0.569	0.030	1.091	0.048	2.128
k_$Ca_3(PO_4)_2$_am1	-0.001	-0.202	-0.007	-0.291	-0.015	-0.982	-0.017	-0.844	-0.041	-1.524	-0.007	-0.292
k_$Ca_3(PO_4)_2$_am3	-0.009	-1.204	0.004	0.159	-0.035	-2.280	-0.044	-2.203	-0.021	-0.783	0.004	0.157
k_$Ca_3(PO_4)_2$_beta	0.006	0.861	0.192	8.583	0.020	1.299	0.008	0.389	0.011	0.392	0.192	8.581

(Continuation)	Effluent S_P		Fertilizer P_P		Particle diameter		Fertilizer density		Struvite purity		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_$Ca_4H(PO_4)_3$:$3H_2O$	0.007	0.920	-0.014	-0.607	-0.012	-0.747	-0.007	-0.363	-0.051	-1.852	-0.014	-0.603
k_$CaHPO_4$:$2H_2O$	0.008	1.125	0.010	0.451	0.012	0.748	-0.004	-0.193	0.027	0.976	0.010	0.453
k_$CaHPO_4$bis	2.24E-04	0.031	0.003	0.130	-0.002	-0.124	-0.005	-0.253	-0.017	-0.640	0.003	0.128
k_Calcite	0.009	1.199	-0.005	-0.210	0.019	1.219	0.045	2.269	-0.048	-1.762	-0.005	-0.209
k_Diaspore	-0.017	-2.340	0.053	2.385	0.008	0.502	0.012	0.592	-0.033	-1.210	0.053	2.386
k_Dolomite	-0.009	-1.276	0.008	0.338	-0.022	-1.404	-0.027	-1.345	0.047	1.718	0.008	0.339
k_Dolomite_dis	0.002	0.285	-0.025	-1.092	0.004	0.265	-0.002	-0.080	-0.028	-1.018	-0.025	-1.092
k_$Fe(OH)_2$_s	-0.006	-0.842	-0.041	-1.836	-0.004	-0.272	-0.040	-2.006	0.008	0.283	-0.041	-1.837
k_Gibbsite	-0.009	-1.194	0.019	0.857	0.051	3.280	0.053	2.673	-0.049	-1.806	0.019	0.857
k_Hercynite	0.007	0.955	-0.012	-0.537	-0.005	-0.327	-0.026	-1.313	-0.025	-0.928	-0.012	-0.538
k_Hydroxyapatite	-0.004	-0.547	-0.002	-0.070	-0.003	-0.210	-0.030	-1.515	0.043	1.574	-0.002	-0.071
k_Kstruvite	-0.007	-0.921	0.006	0.285	-0.009	-0.552	-0.016	-0.797	0.043	1.568	0.006	0.286
k_Magnesite	0.002	0.275	-0.016	-0.700	-0.002	-0.134	0.009	0.450	0.001	0.054	-0.016	-0.696
k_$Mg_3(PO_4)_2$	9.97E-06	0.001	-0.069	-3.078	-3.24E-04	-0.021	-0.033	-1.646	-0.038	-1.398	-0.069	-3.075
k_$MgHPO_4$:$3H_2O$	-3.90E-04	-0.054	0.013	0.578	0.029	1.876	0.016	0.817	0.043	1.605	0.013	0.578
k_$Mg(OH)_2$_act	0.003	0.476	-0.018	-0.802	-0.007	-0.425	0.003	0.163	-0.008	-0.284	-0.018	-0.805
k_Siderite	0.002	0.220	0.013	0.580	0.028	1.804	0.051	2.586	-0.027	-0.993	0.013	0.578
k_Struvite	0.009	1.237	-0.059	-2.609	-0.002	-0.141	0.018	0.931	0.006	0.217	-0.059	-2.608
k_Vaterite	0.002	0.299	0.047	2.101	-0.021	-1.395	-0.011	-0.558	0.034	1.263	0.047	2.104
k_Vivianite	0.009	1.278	-0.005	-0.230	0.011	0.691	0.004	0.209	0.040	1.471	-0.005	-0.227
$\sum_{j=1}^{p} SRC_j^2$	**0.96**		**0.32**		**0.65**		**0.47**		**0.05**		**0.32**	
R^2	**0.93**		**0.35**		**0.69**		**0.49**		**0.04**		**0.35**	
R^2adj	**0.93**		**0.32**		**0.68**		**0.47**		**0.01**		**0.32**	

Table A10.5 Global sensitivity analyses for the nutrient recovery model of the precipitation/crystallization unit (NRM-Prec): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario B (digested manure; Cesur and Albertson, 2005). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.5.

	Effluent S_P		**Fertilizer P_P**		**Effluent S_P**		**Fertilizer P_P**		**Particle diameter**		**Fertilizer density**		**Struvite purity**		**Overall**	
External Mg yes/no	**No**		**No**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**Factor**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**
S_Acetate	-1.15E-04	-0.190	No precipitation		-0.006	-1.502	-0.004	-0.165	-0.038	-1.783	-0.050	-1.959	0.012	0.445	-0.004	-0.165
S_Al	0.001	1.382			-0.006	-1.451	0.027	1.171	0.003	0.156	-0.047	-1.840	0.011	0.423	0.027	1.171
S_Butyrate	-0.001	-1.366			-0.001	-0.258	-0.024	-1.034	-0.016	-0.732	-0.047	-1.822	0.019	0.716	-0.024	-1.034
S_C_4_	0.001	1.953			-0.002	-0.544	0.003	0.146	0.001	0.068	-0.011	-0.409	-0.032	-1.197	0.003	0.146
S_C_min4_	-0.001	-2.020			0.001	0.151	-0.037	-1.643	0.003	0.150	-0.046	-1.793	-0.005	-0.181	-0.037	-1.643
S_Ca	0.006	10.485			-0.001	-0.242	0.039	1.719	0.033	1.561	0.011	0.424	-0.069	-2.559	0.039	1.719
S_Cl	0.015	25.808			-0.009	-2.124	0.009	0.391	-0.025	-1.159	-0.047	-1.816	0.018	0.662	0.009	0.391
S_DOM	-1.00E-04	-0.188			-0.005	-1.279	-0.004	-0.156	-0.016	-0.732	-0.020	-0.777	0.012	0.445	-0.007	-0.325
S_Fe	4.63E-04	0.770			0.003	0.796	0.025	1.076	0.018	0.836	0.035	1.338	0.027	0.981	0.025	1.076
S_K	0.001	1.481			-0.004	-0.943	-0.046	-2.010	0.001	0.052	0.026	0.985	0.035	1.278	-0.046	-2.010
S_Mg	0.091	151.657			0.074	18.143	0.267	11.743	0.091	4.280	0.177	6.872	0.051	1.907	0.267	11.743
S_N_5_	0.002	3.389			-0.005	-1.279	-0.012	-0.547	-0.031	-1.461	-0.004	-0.154	-0.025	-0.936	-0.012	-0.547
S_N_min3_	0.017	27.593			0.006	1.562	0.034	1.504	0.022	1.044	0.046	1.779	0.056	2.078	0.034	1.504
S_Na	0.005	8.054			0.060	14.532	-0.036	-1.595	-0.090	-4.260	-0.063	-2.446	-0.029	-1.063	-0.036	-1.595
S_P	0.993	1646.550			0.984	240.504	0.249	11.003	0.615	29.086	0.255	9.937	0.032	1.199	0.249	11.003
S_Propionate	0.001	1.511			-0.003	-0.807	-0.009	-0.410	0.001	0.054	-0.017	-0.666	0.026	0.977	-0.009	-0.410
S_S_6_	0.004	6.496			-0.008	-2.002	-0.016	-0.705	-0.022	-1.037	-0.025	-0.981	0.017	0.624	-0.016	-0.705
S_S_min2_	1.19E-04	0.197			-0.003	-0.810	-0.039	-1.722	-0.040	-1.898	-0.063	-2.466	0.008	0.291	-0.039	-1.722
S_Valerate	-6.31E-05	-0.105			-0.002	-0.521	0.001	0.039	0.018	0.839	0.083	3.231	0.008	0.307	0.001	0.039
pH_liq	-0.001	-1.362			0.003	0.811	0.010	0.421	0.008	0.395	-0.003	-0.109	-0.040	-1.487	0.010	0.421
Temp_liq	-0.004	-6.437			-0.006	-1.495	-0.368	-16.143	0.025	1.170	-0.041	-1.600	0.072	2.679	-0.368	-16.143
Q_liq	-0.001	-1.087			4.89E-04	0.119	0.008	0.345	-0.017	-0.794	-0.038	-1.473	-0.023	-0.851	0.008	0.345
Q_prec	-0.001	-0.976			-0.007	-1.696	-0.016	-0.700	0.008	0.374	0.021	0.817	0.032	1.174	-0.016	-0.700
k_$AlPO_4$	0.001	0.972			-0.001	-0.127	-0.020	-0.862	-0.009	-0.404	-0.026	-1.017	0.047	1.754	-0.020	-0.862
k_Aragonite	3.52E-04	0.581			-0.008	-2.029	-0.025	-1.111	-0.015	-0.682	-0.044	-1.706	0.038	1.390	-0.025	-1.111
k_Artinite	5.48E-05	0.091			-0.007	-1.630	0.003	0.149	-0.038	-1.799	0.004	0.160	-0.015	-0.550	0.003	0.149
k_Boehmite	-1.76E-04	-0.292			-0.006	-1.362	0.011	0.483	-0.004	-0.168	-0.039	-1.525	0.013	0.474	0.011	0.483
k_Brucite	-0.001	-1.209			0.006	1.346	0.025	1.113	-0.004	-0.174	0.004	0.152	0.021	0.774	0.025	1.113
k_$Ca_3(PO_4)_2$_am1	-3.75E-04	-0.624			-0.002	-0.548	-0.003	-0.134	0.017	0.781	0.028	1.090	0.016	0.596	-0.003	-0.134

(Continuation)	Effluent S_P		Fertilizer P_P		Effluent S_P		Fertilizer P_P		Particle diameter		Fertilizer density		Struvite purity		Overall	
External Mg yes/no	**No**		**No**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_$Ca_3(PO_4)_2$_am3	0.001	0.871			0.003	0.710	0.030	1.336	0.003	0.140	0.010	0.383	-0.001	-0.021	0.030	1.336
k_$Ca_3(PO_4)_2$_beta	-3.21E-04	-0.534			-0.006	-1.445	0.208	9.114	-0.018	-0.826	0.010	0.400	-0.109	-4.028	0.208	9.114
k_$Ca_4H(PO_4)_3$:$3H_2O$	2.91E-04	0.483			0.004	0.866	0.017	0.741	0.026	1.208	0.021	0.821	0.018	0.681	0.017	0.741
k_$CaHPO_4$:$2H_2O$	-0.001	-1.864			0.001	0.237	-0.018	-0.791	0.037	1.728	0.021	0.815	0.014	0.518	-0.018	-0.791
k_$CaHPO_4$bis	0.001	1.529			0.003	0.738	0.011	0.471	0.010	0.456	0.002	0.070	-0.038	-1.403	0.011	0.471
k_Calcite	1.23E-07	0.000			0.001	0.264	-0.024	-1.037	0.035	1.642	-0.016	-0.609	0.023	0.852	-0.024	-1.037
k_Diaspore	1.24E-06	0.002			-0.004	-0.982	0.007	0.325	0.007	0.323	0.031	1.220	0.015	0.554	0.007	0.325
k_Dolomite	-2.68E-04	-0.447			0.003	0.671	0.004	0.169	0.031	1.478	0.020	0.777	0.042	1.547	0.004	0.169
k_Dolomite_dis	-2.53E-04	-0.422			0.002	0.452	0.001	0.046	0.013	0.597	-0.029	-1.121	-0.013	-0.471	0.001	0.046
k_$Fe(OH)_2$_s	-3.62E-04	-0.595			0.003	0.713	0.015	0.650	0.007	0.310	0.005	0.174	-0.010	-0.349	0.015	0.650
k_Gibbsite	3.58E-04	0.595			0.008	1.835	-0.008	-0.365	0.001	0.052	0.004	0.138	-0.035	-1.301	-0.008	-0.365
k_Hercynite	1.99E-04	0.331			0.003	0.645	0.012	0.532	0.010	0.457	-0.008	-0.312	-3.98E-04	-0.015	0.012	0.532
k_Hydroxyapatite	-5.47E-05	-0.091			-0.003	-0.622	0.006	0.282	-0.025	-1.205	0.002	0.073	-0.020	-0.730	0.006	0.282
k_Kstruvite	-3.27E-04	-0.545			-0.001	-0.237	-3.58E-04	-0.016	-0.014	-0.643	-0.011	-0.417	-0.005	-0.204	-3.58E-04	-0.016
k_Magnesite	-0.001	-0.864			-7.38E-05	-0.018	0.009	0.410	0.013	0.594	0.073	2.832	-0.046	-1.679	0.009	0.410
k_$Mg_3(PO_4)_2$	2.72E-05	0.045			-0.008	-1.872	0.007	0.303	-0.022	-1.050	-0.006	-0.235	-0.042	-1.554	0.007	0.303
k_$MgHPO_4$:$3H_2O$	0.001	1.004			0.006	1.429	-0.026	-1.129	-0.027	-1.281	0.001	0.042	-0.033	-1.211	-0.026	-1.129
k_$Mg(OH)_2$_act	-0.001	-1.255			0.001	0.195	-0.014	-0.595	-0.021	-1.013	0.027	1.050	0.010	0.384	-0.014	-0.595
k_Siderite	6.88E-05	0.114			-0.003	-0.684	-0.025	-1.097	-0.021	-0.988	-0.038	-1.486	0.008	0.306	-0.025	-1.097
k_Struvite	-0.001	-1.187			0.003	0.718	0.001	0.043	0.015	0.682	0.012	0.450	0.027	0.994	0.001	0.043
k_Vaterite	-4.25E-04	-0.710			-0.008	-1.871	0.001	0.037	-0.008	-0.369	0.001	0.058	0.008	0.294	0.001	0.037
k_Vivianite	0.001	1.784			0.003	0.668	0.002	0.103	-0.011	-0.506	0.028	1.086	-0.002	-0.088	0.002	0.103
$\sum_{j=1}^{p} SRC_j^2$	**1.00**				**0.98**		**0.33**		**0.41**		**0.15**		**0.055**		**0.330**	
R^2	**1.00**				**0.98**		**0.33**		**0.39**		**0.14**		**0.050**		**0.330**	
R^2adj	**1.00**				**0.98**		**0.30**		**0.41**		**0.11**		**0.020**		**0.300**	

Table A10.6 Global sensitivity analyses analyses for the nutrient recovery model of the precipitation/crystallization unit (NRM-Prec): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario C (co-digestate; Vlaco, 2012). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.5.

	Effluent S_P		Fertilizer P		Effluent S_P		Fertilizer P_P		Particle diameter		Fertilizer density		Struvite purity		Overall	
External Mg yes/no	No		No		Yes		Yes		Yes		Yes		Yes		Yes	
Factor	SRC	tSRC	SRC	tSRC	SRC	tSRC	SRC	tSRC	SRC	tSRC	SRC	tSRC	SRC	tSRC	SRC	tSRC
S_Acetate	-0.003	-0.571	0.003	0.160	0.002	0.931	-0.010	-0.544	-0.012	-0.467	-0.007	-0.292	0.008	0.290	-0.010	-0.544
S_Al	0.007	1.232	-0.096	-4.393	0.005	2.737	0.008	0.446	-0.013	-0.512	-0.008	-0.304	0.003	0.097	0.008	0.446
S_Butyrate	-0.004	-0.730	0.010	0.476	0.001	0.389	0.011	0.631	0.015	0.615	0.015	0.615	-0.021	-0.808	0.011	0.632
S_C_4_	0.020	3.286	-0.164	-7.535	0.009	4.476	-0.099	-5.575	-0.041	-1.623	-0.021	-0.838	0.018	0.693	-0.099	-5.575
S_C_min4_	-0.001	-0.184	-0.030	-1.401	-7.20E-05	-0.037	0.024	1.350	0.036	1.440	0.026	1.056	-0.033	-1.257	0.024	1.350
S_Ca	0.070	11.611	0.252	11.621	-0.008	-4.158	0.254	14.251	0.015	0.593	0.003	0.132	-0.088	-3.324	0.234	13.131
S_Cl	0.002	0.323	-0.036	-1.646	0.003	1.331	-0.002	-0.133	-0.022	-0.895	-0.023	-0.930	-0.028	-1.052	-0.002	-0.133
S_DOM	-0.003	-0.570	-0.010	-0.476	-0.002	-0.931	-0.010	-0.582	-0.012	-0.467	-0.009	-0.355	-0.006	-0.214	-0.009	-0.529
S_Fe	0.125	20.898	0.065	2.989	2.22E-04	0.115	0.006	0.328	-0.032	-1.302	-0.044	-1.780	0.041	1.571	0.006	0.328
S_K	0.001	0.202	0.020	0.912	-0.001	-0.476	0.027	1.503	-0.001	-0.059	-0.001	-0.049	0.035	1.314	0.027	1.503
S_Mg	0.016	2.657	0.026	1.216	-0.023	-11.887	-0.038	-2.139	0.007	0.281	0.003	0.117	-0.012	-0.468	-0.038	-2.139
S_N_5_	0.005	0.899	0.010	0.447	0.001	0.442	0.003	0.192	-0.021	-0.852	-0.018	-0.716	0.016	0.612	0.003	0.192
S_N_min3_	-0.040	-6.582	0.110	5.047	-0.008	-4.284	-0.010	-0.581	0.004	0.173	0.008	0.306	-0.038	-1.421	-0.010	-0.581
S_Na	0.089	14.812	0.049	2.269	0.090	46.353	-0.052	-2.912	-0.164	-6.617	-0.159	-6.360	-0.066	-2.484	-0.052	-2.912
S_P	0.959	159.534	-0.188	-8.657	0.991	507.138	0.234	13.131	0.370	14.770	0.367	14.594	0.061	2.276	0.254	14.251
S_Propionate	0.005	0.908	-0.001	-0.067	-3.05E-04	-0.156	-0.035	-1.945	0.036	1.446	0.028	1.109	0.023	0.876	-0.035	-1.945
S_S_6_	-0.018	-2.927	0.031	1.399	-0.002	-1.003	-0.013	-0.742	-0.025	-0.994	-0.033	-1.320	-0.019	-0.703	-0.013	-0.742
S_S_min2_	0.004	0.732	0.004	0.195	-0.002	-1.025	-0.018	-1.041	0.011	0.441	0.011	0.444	0.032	1.222	-0.018	-1.041
S_Valerate	0.009	1.480	0.023	1.046	-0.001	-0.711	-0.020	-1.133	-0.001	-0.044	-0.005	-0.218	0.035	1.308	-0.020	-1.133
pH_liq	-0.002	-0.256	0.013	0.604	-0.001	-0.558	-0.006	-0.354	0.007	0.288	0.012	0.487	-0.001	-0.045	-0.006	-0.354
Temp_liq	-0.022	-3.623	-0.384	-17.636	-0.009	-4.645	-0.551	-31.012	0.013	0.532	-0.012	-0.487	0.089	3.362	-0.551	-31.012
Q_liq	0.002	0.360	0.014	0.651	-0.003	-1.642	-3.16E-04	-0.018	-0.014	-0.572	-0.011	-0.424	0.002	0.070	-3.16E-04	-0.018
Q_prec	-0.006	-0.982	0.014	0.622	-2.10E-04	-0.108	-0.003	-0.194	0.020	0.813	0.021	0.847	-0.007	-0.254	-0.003	-0.194
k_AlPO$_4$	0.002	0.357	0.005	0.241	-1.65E-04	-0.085	-0.002	-0.131	0.016	0.650	0.021	0.842	0.021	0.806	-0.002	-0.131
k_Aragonite	0.007	1.231	0.013	0.595	-0.001	-0.260	0.032	1.818	0.003	0.115	0.009	0.355	0.042	1.577	0.032	1.818
k_Artinite	0.009	1.545	0.003	0.148	0.001	0.352	-0.012	-0.685	0.036	1.432	0.043	1.689	-0.031	-1.162	-0.012	-0.685
k_Boehmite	0.008	1.294	0.030	1.376	-4.36E-04	-0.225	0.002	0.100	0.014	0.572	0.011	0.433	-0.037	-1.416	0.002	0.100
k_Brucite	0.001	0.144	0.031	1.422	-0.001	-0.304	-0.008	-0.467	0.010	0.401	0.016	0.617	-0.013	-0.476	-0.008	-0.467
k_Ca$_3$(PO$_4$)$_2$_am1	0.008	1.385	-0.039	-1.779	-0.002	-0.966	0.005	0.272	0.009	0.362	-0.002	-0.084	0.004	0.148	0.005	0.272

(Continuation)	**Effluent S_P**		**Fertilizer P**		**Effluent S_P**		**Fertilizer P_P**		**Particle diameter**		**Fertilizer density**		**Struvite purity**		**Overall**	
External Mg yes/no	**No**		**No**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_$Ca_3(PO_4)_2$_am3	-0.006	-0.940	-0.063	-2.908	1.94E-04	0.099	0.025	1.373	-0.001	-0.040	-0.005	-0.209	-0.047	-1.770	0.025	1.373
k_$Ca_3(PO_4)_2$_beta	-0.011	-1.819	0.247	11.361	0.002	0.852	0.372	20.936	0.036	1.434	0.026	1.046	-0.160	-6.025	0.372	20.936
k_$Ca_4H(PO_4)_3$:$3H_2O$	0.003	0.470	0.025	1.127	0.002	0.904	0.006	0.339	0.018	0.701	0.032	1.268	-0.001	-0.045	0.006	0.339
k_$CaHPO_4$:$2H_2O$	0.003	0.509	0.032	1.487	-0.001	-0.554	0.004	0.245	0.063	2.518	0.066	2.641	0.063	2.394	0.004	0.245
k_$CaHPO_4$bis	-0.004	-0.647	-0.009	-0.422	-0.003	-1.475	0.002	0.085	-0.008	-0.307	-0.003	-0.126	-0.014	-0.521	0.002	0.085
k_Calcite	0.008	1.250	-0.008	-0.362	4,99E-05	0.026	0.031	1.737	0.052	2.071	0.036	1.457	0.021	0.795	0.031	1.737
k_Diaspore	-0.003	-0.554	-0.003	-0.117	-0.001	-0.641	0.005	0.277	0.025	1.024	0.025	1.007	-0.030	-1.131	0.005	0.277
k_Dolomite	-0.001	-0.180	-0.031	-1.406	7.73E-05	0.040	-0.022	-1.233	0.026	1.053	0.030	1.213	-0.022	-0.839	-0.022	-1.233
k_Dolomite_dis	0.005	0.888	-0.033	-1.529	-0.002	-0.866	0.006	0.313	-0.046	-1.856	-0.044	-1.736	-0.004	-0.151	0.006	0.313
k_$Fe(OH)_2$_s	-0.005	-0.854	0.003	0.147	-0.001	-0.709	0.010	0.582	-0.003	-0.109	-0.004	-0.169	-0.011	-0.406	0.010	0.582
k_Gibbsite	-0.003	-0.511	-0.036	-1.662	-0.001	-0.271	-0.028	-1.589	0.072	2.877	0.071	2.816	0.022	0.830	-0.028	-1.589
k_Hercynite	0.010	1.687	0.002	0.094	0.001	0.752	-0.015	-0.828	-0.021	-0.853	-0.003	-0.104	-0.006	-0.214	-0.015	-0.828
k_Hydroxyapatite	0.004	0.608	-0.035	-1.609	-0.001	-0.275	0.023	1.283	0.016	0.655	0.023	0.901	-0.019	-0.721	0.023	1.283
k_Kstruvite	-0.007	-1.091	0.040	1.849	-0.003	-1.467	-0.021	-1.172	-0.053	-2.111	-0.041	-1.656	0.072	2.718	-0.021	-1.172
k_Magnesite	-0.007	-1.083	0.004	0.177	-0.002	-1.119	0.003	0.161	0.021	0.824	0.048	1.928	0.007	0.271	0.003	0.161
k_$Mg_3(PO_4)_2$	-0.015	-2.529	-0.040	-1.858	-0.002	-1.001	0.009	0.529	-0.028	-1.140	-0.025	-1.015	0.014	0.521	0.009	0.529
k_$MgHPO_4$:$3H_2O$	-0.002	-0.293	0.020	0.907	-2.46E-04	-0.126	-0.006	-0.339	0.010	0.409	0.006	0.238	-0.002	-0.078	-0.006	-0.339
k_$Mg(OH)_2$_act	-0.006	-1.073	0.030	1.363	0.002	1.015	4.61E-04	0.026	0.004	0.156	-0.008	-0.336	-0.042	-1.590	4.61E-04	0.026
k_Siderite	0.002	0.318	2.08E-04	0.010	-0.003	-1.408	-0.029	-1.649	0.006	0.247	0.002	0.088	-0.003	-0.120	-0.029	-1.649
k_Struvite	-0.012	-2.004	-0.023	-1.073	-0.002	-0.831	0.005	0.277	0.002	0.060	-0.003	-0.136	-0.008	-0.318	0.005	0.277
k_Vaterite	0.011	1.857	-0.004	-0.200	0.002	0.932	-0.010	-0.545	-0.006	-0.224	-0.001	-0.046	0.018	0.666	-0.010	-0.545
k_Vivianite	0.001	0.194	0.001	0.048	-3.72E-04	-0.190	0.001	0.056	0.006	0.238	0.003	0.118	-0.058	-2.180	0.001	0.056
$\sum_{j=1}^{p} SRC_j^2$	**0.95**		**0.39**		**0.99**		**0.59**		**0.20**		**0.19**		**0.09**		**0.59**	
R^2	**0.95**		**0.38**		**1.00**		**0.59**		**0.19**		**0.18**		**0.08**		**0.59**	
R^2adj	**0.95**		**0.36**		**1.00**		**0.57**		**0.16**		**0.15**		**0.05**		**0.57**	

Table A10.7 Global sensitivity analyses for the nutrient recovery model of the stripping unit (NRM-Strip): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario A (digestate: all applications). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.6.

	NH_3 removal efficiency		**Effluent S_N_min3_**		**Precipitation CO_3**		**Air requirement[a]**		**Overall**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
S_Acetate	-0.012	-0.596	0.003	0.295	-0.002	-0.067	-0.009	-0.614	-0.012	-1.016
S_Al	0.030	1.434	-0.028	-2.605	-0.027	-0.775	0.020	1.336	-0.001	-0.057
S_Butyrate	0.023	1.104	0.019	1.834	-0.046	-1.326	-0.022	-1.503	2.84E-04	0.024
S_C_4_	0.084	4.034	-0.061	-5.732	0.049	1.392	-0.020	-1.342	0.011	0.957
S_C_min4_	0.029	1.366	-0.018	-1.656	0.048	1.387	-0.008	-0.520	-0.005	-0.426
S_Ca	0.003	0.149	-0.033	-3.083	0.136	3.919	-0.010	-0.647	-0.014	-1.207
S_Cl	-0.930	-41.461	0.935	87.415	-0.102	-2.911	-0.025	-1.665	0.011	0.969
S_DOM	0.001	0.036	-0.003	-0.257	-0.002	-0.063	-0.004	-0.271	-0.007	-0.617
S_Fe	-0.005	-0.218	-0.015	-1.354	-0.081	-2.301	-0.004	-0.248	0.019	1.586
S_H_0_	0.038	1.812	-0.028	-2.582	-0.014	-0.392	0.014	0.945	-0.005	-0.440
S_K	0.016	0.754	-0.003	-0.278	0.036	1.009	0.046	3.073	0.005	0.456
S_Mg	0.136	6.427	-0.156	-14.515	0.171	4.870	-0.011	-0.759	0.003	0.296
S_N_0_	-0.036	-1.710	-0.004	-0.334	-0.006	-0.167	0.005	0.304	0.006	0.525
S_N_5_	0.008	0.379	-0.013	-1.263	-0.045	-1.298	-0.020	-1.333	0.002	0.146
S_N_min3_	0.508	23.355	0.106	9.839	0.004	0.112	0.003	0.234	0.013	1.082
S_Na	-0.003	-0.163	0.002	0.144	0.069	1.958	-0.004	-0.241	0.004	0.307
S_O_0_	-0.002	-0.073	-0.011	-1.053	-0.050	-1.437	0.008	0.528	-0.009	-0.741
S_P	0.022	1.062	0.022	2.063	-0.119	-3.409	-0.010	-0.707	4.22E-07	3.61E-05
S_Propionate	-0.008	-0.386	-0.005	-0.483	0.001	0.019	-0.010	-0.690	0.010	0.881
S_S_6_	-0.030	-1.406	0.027	2.532	-0.103	-2.944	0.017	1.141	0.002	0.153
S_S_min2_	-0.020	-0.964	0.009	0.842	-0.003	-0.094	0.009	0.628	0.009	0.776
S_Valerate	0.021	1.004	-0.005	-0.505	0.010	0.298	-0.011	-0.734	-0.003	-0.252
CH_4_g_	-0.012	-0.603	-0.006	-0.596	-0.037	-1.061	-0.012	-0.828	0.017	1.441
CO_2_g_	0.001	0.031	0.006	0.605	0.032	0.924	-0.005	-0.349	0.020	1.735
H_2O_g_	0.024	1.144	-0.015	-1.436	-0.020	-0.556	-0.001	-0.046	-0.015	-1.313
H_2S_g_	0.009	0.440	0.009	0.882	-0.036	-1.025	-0.016	-1.035	0.015	1.268
H_2_g_	0.024	1.147	-0.015	-1.371	0.007	0.200	0.005	0.316	-2.37E-04	-0.020
N_2_g_	0.014	0.637	0.004	0.352	0.088	2.491	0.013	0.856	-0.013	-1.104
NH_3_g_	0.006	0.265	-0.004	-0.373	0.013	0.382	-0.015	-1.014	0.008	0.718
O_2_g_	0.001	0.044	-0.005	-0.439	-0.062	-1.758	0.004	0.288	-0.006	-0.548
d_gas	0.010	0.467	0.012	1.160	-0.020	-0.572	-0.011	-0.741	-0.002	-0.148

(Continuation)	NH_3 removal efficiency		Effluent S_N_min3_		Precipitation CO_3		Air requirement[a]		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
P_gas_in	0.016	0.760	-0.013	-1.169	-0.045	-1.284	0.430	28.442	0.423	36.143
Temp_gas_in	-0.015	-0.745	0.016	1.534	-0.014	-0.415	0.023	1.544	-0.015	-1.328
pH_liq	0.014	0.680	-0.015	-1.435	-0.031	-0.880	0.017	1.118	0.011	0.910
Temp_liq	0.001	0.009	-0.005	-0.464	-0.174	-4.886	-0.711	-47.684	-0.733	-62.531
Q_gas_in	-0.003	-0.120	0.007	0.612	-0.028	-0.804	0.009	0.594	-0.003	-0.286
Q_liq_in	-0.026	-1.240	-0.012	-1.133	-0.071	-2.022	0.358	24.077	0.364	31.016
u	0.020	0.940	-0.005	-0.437	-0.016	-0.461	-0.002	-0.109	0.009	0.785
k_Aragonite	-0.004	-0.205	-0.002	-0.185	-0.051	-1.452	-0.024	-1.613	-0.006	-0.532
k_Artinite	0.023	1.126	0.006	0.611	-0.010	-0.282	-0.008	-0.512	-0.006	-0.549
k_Brucite	-0.012	-0.553	-0.008	-0.771	-0.022	-0.629	-0.013	-0.865	0.006	0.520
k_$Ca_3(PO_4)_2$_am1	0.044	2.099	-0.012	-1.128	-0.062	-1.767	-0.030	-2.027	0.002	0.206
k_$Ca_3(PO_4)_2$_am2	0.006	0.263	-0.010	-0.902	-0.043	-1.241	0.001	0.056	-0.011	-0.920
k_$Ca_3(PO_4)_2$_beta	-0.038	-1.784	0.005	0.449	0.011	0.298	-0.006	-0.429	-0.005	-0.393
k_$Ca_4H(PO_4)_3$:$3H_2O$	0.023	1.074	-0.016	-1.493	-0.038	-1.068	-0.004	-0.245	0.012	1.031
k_$CaHPO_4$:$2H_2O$	-0.014	-0.661	-0.012	-1.085	-0.045	-1.293	-0.007	-0.459	-0.008	-0.665
k_$CaHPO_4$bis	-0.015	-0.726	0.017	1.567	0.022	0.627	-0.009	-0.627	0.016	1.422
k_Calcite	0.024	1.159	-0.005	-0.488	0.037	1.062	-0.009	-0.579	0.008	0.699
k_Diaspore	-0.001	-0.051	0.018	1.640	-0.018	-0.521	-0.008	-0.547	0.008	0.677
k_Dolomite	0.028	1.341	-0.009	-0.793	-0.001	-0.025	-0.010	-0.694	-0.017	-1.454
k_Dolomite_dis	0.021	1.002	-0.012	-1.101	-0.031	-0.889	-0.003	-0.174	-0.012	-1.051
k_$Fe(OH)_2$	0.018	0.868	-0.017	-1.587	-0.002	-0.058	-0.020	-1.345	-0.011	-0.904
k_Hercynite	0.005	0.256	0.005	0.506	0.053	1.515	0.024	1.605	0.005	0.441
k_Huntite	0.015	0.715	-0.015	-1.361	0.021	0.601	-0.011	-0.687	-0.009	-0.789
k_Hydromagnesite	0.005	0.256	0.008	0.715	-0.035	-1.011	-0.005	-0.313	0.001	0.085
k_Hydroxyapatite	-0.013	-0.632	-0.014	-1.350	-0.007	-0.193	-0.012	-0.792	-0.012	-1.030
k_Kstruvite	0.016	0.761	0.008	0.732	0.001	0.035	-0.008	-0.527	0.021	1.796
k_Magnesite	0.023	1.104	-0.014	-1.309	0.114	3.232	-0.014	-0.924	0.009	0.775
k_$Mg_3(PO_4)_2$	-0.015	-0.707	-0.001	-0.082	0.027	0.779	-0.002	-0.166	-0.031	-2.693
k_$MgHPO_4$:$3H_2O$	-0.009	-0.398	0.001	0.083	-0.004	-0.106	0.019	1.253	-0.009	-0.768
k_$Mg(OH)_2$_act	-0.015	-0.715	-0.004	-0.395	-0.070	-2.002	0.001	0.068	-0.021	-1.845
k_Periclase	0.001	0.053	-1.19E-04	-0.011	-0.051	-1.455	-0.015	-0.987	-0.016	-1.411
k_Portlandite	0.002	0.084	-0.003	-0.303	0.040	1.125	-0.019	-1.251	-0.016	-1.385
k_Siderite	-0.002	-0.079	-0.002	-0.148	-0.002	-0.048	0.016	1.041	0.002	0.211
k_Spinel	0.034	1.633	-0.011	-1.027	0.018	0.502	-0.015	-1.023	-0.006	-0.510
k_Struvite	-0.032	-1.514	0.026	2.381	0.014	0.401	-0.021	-1.439	0.013	1.102

(Continuation)	NH_3 removal efficiency		Effluent S_N_min3_		Precipitation CO_3		Air requirement[a]		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_Vivianite	-0.011	-0.538	0.006	0.556	-0.005	-0.137	-0.014	-0.916	0.009	0.755
D_CH_4_g_	-0.041	-1.958	-0.001	-0.134	-3.63E-04	-0.010	0.004	0.283	0.016	1.395
D_CO_2_g_	-0.046	-2.182	0.004	0.389	0.015	0.435	-0.013	-0.838	2.07E-04	0.018
D_H_2S_g_	0.011	0.512	0.008	0.773	0.057	1.627	-0.011	-0.756	-0.007	-0.572
D_H_2_g_	-0.016	-0.764	0.020	1.888	0.003	0.096	-0.001	-0.035	-0.019	-1.594
D_N_2_g_	0.021	0.992	-0.003	-0.251	-0.050	-1.412	0.007	0.442	-0.011	-0.919
D_NH_3_g_	0.019	0.941	-0.009	-0.885	0.016	0.455	-0.016	-1.071	0.022	1.842
D_O_2_g_	-2.28E-04	-0.011	-0.009	-0.806	-0.034	-0.965	0.003	0.177	-0.001	-0.065
theta_CH_4_g_	0.016	0.743	-0.013	-1.181	-3.85E-04	-0.011	-0.015	-1.024	-0.021	-1.834
theta_CO_2_g_	0.016	0.764	-0.017	-1.623	-0.005	-0.155	-0.004	-0.242	0.010	0.876
theta_H_2S_g_	0.015	0.722	0.008	0.793	-0.026	-0.747	-0.007	-0.479	-1.80E-04	-0.015
theta_H_2_g_	0.008	0.355	-0.012	-1.075	-0.005	-0.152	-0.016	-1.078	-0.020	-1.663
theta_N_2_g_	0.025	1.213	0.004	0.423	-0.003	-0.077	0.001	0.089	0.008	0.692
theta_NH_3_g_	-0.033	-1.578	-0.003	-0.246	0.026	0.741	-0.009	-0.637	-0.001	-0.092
theta_O_2_g_	-0.006	-0.314	-0.008	-0.728	-0.018	-0.531	0.018	1.176	-0.004	-0.318
$\sum_{j=1}^{p} SRC_j^2$	**1.17**		**0.93**		**0.22**		**0.83**		**0.86**	
R^2	**0.83**		**0.93**		**0.21**		**0.86**		**0.84**	
R^2adj	**0.80**		**0.92**		**0.12**		**0.84**		**0.83**	

[a] Air needed to obtain 90 % NH_3 removal.

Table A10.8 Global sensitivity analyses for the nutrient recovery model of the stripping unit (NRM-Strip): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario B (digested manure; Cesur and Albertson, 2005). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.6.

	NH_3 removal efficiency		Effluent S_N_min3_		Precipitation CO_3		Air requirement[a]		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
S_Acetate	-7.38E-05	-0.042	0.001	1.383	0.008	1.057	-0.003	-0.287	-0.003	-0.286
S_Al	0.027	15.104	-0.028	-73.932	-0.013	-1.627	0.007	0.637	0.007	0.630
S_Butyrate	-0.002	-1.242	3.42E-04	0.929	-0.006	-0.786	-0.003	-0.261	-0.003	-0.262
S_C_4_	4.63E-04	0.260	3.44E-06	0.009	-0.007	-0.862	-0.026	-2.343	-0.026	-2.339
S_C_min4_	0.001	0.826	-2.63E-04	-0.709	0.014	1.842	-0.001	-0.062	-0.001	-0.067
S_Ca	0.110	63.008	-0.104	-284.349	-0.003	-0.371	-0.024	-2.166	-0.024	-2.163
S_Cl	-0.922	-521.253	0.860	2321.130	0.005	0.706	0.121	10.813	0.121	10.803
S_DOM	-0.014	-7.932	0.013	36.358	0.005	0.594	0.011	1.017	0.011	1.018
S_Fe	0.009	4.821	-0.010	-27.589	0.006	0.799	-0.005	-0.430	-0.005	-0.433
S_H_0_	-0.001	-0.748	-4.08E-04	-1.109	0.002	0.211	0.018	1.638	0.018	1.644
S_K	0.047	26.561	-0.042	-114.953	0.017	2.272	-0.001	-0.076	-0.001	-0.073
S_Mg	0.175	99.680	-0.164	-444.330	0.007	0.958	-0.015	-1.371	-0.015	-1.365
S_N_0_	0.001	0.581	-1.75E-04	-0.475	0.003	0.435	0.002	0.188	0.002	0.188
S_N_5_	-0.038	-21.586	0.034	93.588	-0.001	-0.184	0.009	0.787	0.009	0.791
S_N_min3_	0.244	137.593	0.350	943.289	-0.014	-1.884	-0.027	-2.403	-0.027	-2.404
S_Na	0.139	79.538	-0.130	-355.207	0.012	1.644	-0.048	-4.328	-0.048	-4.325
S_O_0_	0.001	0.569	8.43E-05	0.227	4.18E-04	0.054	-0.011	-0.953	-0.011	-0.958
S_P	-0.045	-25.190	0.043	115.218	0.011	1.398	0.003	0.273	0.003	0.275
S_Propionate	0.001	0.605	-1.68E-04	-0.454	-0.013	-1.644	-0.012	-1.067	-0.012	-1.061
S_S_6_	-0.058	-32.707	0.054	145.271	0.007	0.915	-0.004	-0.325	-0.004	-0.327
S_S_min2_	3.68E-04	0.209	1.06E-04	0.287	-0.004	-0.462	-0.013	-1.135	-0.013	-1.131
S_Valerate	-0.001	-0.655	2.32E-04	0.628	-0.001	-0.157	0.006	0.499	0.006	0.495
CH_4_g_	-0.002	-0.881	-1.63E-04	-0.444	-0.002	-0.294	0.008	0.745	0.008	0.739
CO_2_g_	-0.001	-0.752	-2.60E-05	-0.070	-0.001	-0.121	-0.009	-0.786	-0.009	-0.784
H_2O_g_	-0.001	-0.754	-4.61E-05	-0.126	0.000	0.065	0.004	0.381	0.004	0.387
H_2S_g_	1.75E-04	0.099	-1.64E-04	-0.443	-0.008	-1.035	-0.005	-0.461	-0.005	-0.468
H_2_g_	-0.002	-1.333	3.44E-04	0.928	0.004	0.569	-0.004	-0.338	-0.004	-0.343
N_2_g_	-0.003	-1.909	2.01E-04	0.548	0.006	0.755	0.003	0.266	0.003	0.264
NH_3_g_	1.14E-04	0.065	-2.11E-04	-0.571	0.005	0.688	0.002	0.186	0.002	0.193
O_2_g_	-1.47E-04	-0.083	0.001	1.801	-0.003	-0.409	-0.008	-0.748	-0.008	-0.748
d_gas	0.001	0.794	-4.03E-04	-1.097	-0.004	-0.568	0.016	1.438	0.016	1.442

(Continuation)	NH_3 removal efficiency		Effluent S_N_min3_		Precipitation CO_3		Air requirement[a]		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
P_gas_in	2.97E-04	0.169	-0.001	-1.517	-0.004	-0.536	0.440	39.480	0.440	39.485
Temp_gas_in	-0.001	-0.634	-1.81E-04	-0.490	0.006	0.845	0.004	0.388	0.004	0.389
pH_liq	4.61E-05	0.026	3.42E-04	0.929	0.009	1.132	-0.002	-0.146	-0.002	-0.157
Temp_liq	0.153	86.924	-0.144	-391.549	0.005	0.671	-0.711	-63.620	-0.711	-63.620
Q_gas_in	-0.001	-0.785	-2.33E-04	-0.630	-0.010	-1.338	0.015	1.326	0.015	1.325
Q_liq_in	0.001	0.832	7.25E-05	0.197	0.963	126.562	0.354	31.789	0.354	31.793
u	-0.001	-0.674	-3.94E-04	-1.066	-0.006	-0.795	-0.025	-2.204	-0.025	-2.203
k_Aragonite	0.001	0.671	-2.67E-04	-0.721	-0.011	-1.490	0.018	1.611	0.018	1.612
k_Artinite	0.001	0.773	7.93E-05	0.216	0.007	0.930	0.009	0.844	0.009	0.846
k_Brucite	0.003	1.443	2.98E-05	0.081	0.001	0.145	0.004	0.340	0.004	0.349
k_$Ca_3(PO_4)_2$_am1	0.002	1.165	-0.001	-2.583	-0.005	-0.627	-0.001	-0.096	-0.001	-0.109
k_$Ca_3(PO_4)_2$_am2	3.03E-04	0.172	-1.96E-04	-0.532	-0.011	-1.460	0.010	0.926	0.010	0.932
k_$Ca_3(PO_4)_2$_beta	-0.001	-0.420	2.37E-04	0.643	-0.002	-0.204	0.016	1.430	0.016	1.430
k_$Ca_4H(PO_4)_3$:$3H_2O$	-0.001	-0.804	0.001	1.617	-0.006	-0.727	0.001	0.081	0.001	0.081
k_$CaHPO_4$:$2H_2O$	-0.001	-0.444	0.001	2.229	-0.005	-0.635	4.08E-04	0.037	3.57E-04	0.032
k_$CaHPO_4$bis	-1.52E-04	-0.086	-4.34E-04	-1.165	-0.006	-0.719	0.010	0.846	0.010	0.852
k_Calcite	0.001	0.304	1.89E-04	0.509	-0.006	-0.728	-0.013	-1.116	-0.013	-1.115
k_Diaspore	0.002	0.861	0.001	2.022	0.008	1.022	-0.021	-1.918	-0.022	-1.921
k_Dolomite	-0.001	-0.599	-4.39E-04	-1.175	-0.016	-2.029	-0.006	-0.489	-0.006	-0.491
k_Dolomite_dis	-0.002	-0.881	-2.77E-04	-0.747	-0.007	-0.924	0.002	0.221	0.002	0.215
k_$Fe(OH)_2$	-0.001	-0.549	-1.75E-04	-0.478	0.008	1.050	-0.009	-0.797	-0.009	-0.792
k_Hercynite	0.001	0.843	6.50E-05	0.176	-0.003	-0.439	-0.018	-1.619	-0.018	-1.622
k_Huntite	0.001	0.491	-4.11E-04	-1.111	0.001	0.081	0.005	0.485	0.005	0.484
k_Hydromagnesite	0.002	1.411	-0.001	-1.650	-0.006	-0.794	0.014	1.237	0.014	1.242
k_Hydroxyapatite	0.003	1.850	3.14E-04	0.851	-0.002	-0.216	-0.016	-1.451	-0.016	-1.444
k_Kstruvite	-0.002	-1.329	-2.77E-04	-0.755	0.007	0.869	-0.009	-0.810	-0.009	-0.814
k_Magnesite	0.001	0.736	-0.001	-1.816	0.001	0.163	-0.004	-0.370	-0.004	-0.371
k_$Mg_3(PO_4)_2$	-0.001	-0.568	2.40E-04	0.645	-0.002	-0.317	0.013	1.181	0.013	1.176
k_$MgHPO_4$:$3H_2O$	0.002	1.285	-0.001	-1.605	0.001	0.158	0.010	0.860	0.010	0.857
k_$Mg(OH)_2$_act	0.001	0.772	-0.001	-1.762	-0.004	-0.526	0.008	0.710	0.008	0.707
k_Periclase	0.002	0.962	-3.37E-04	-0.911	-3.09E-04	-0.040	0.010	0.888	0.010	0.878
k_Portlandite	-7.50E-05	-0.043	2.50E-04	0.679	0.002	0.220	0.012	1.049	0.012	1.048
k_Siderite	-0.001	-0.705	1.22E-04	0.332	0.012	1.538	-0.004	-0.334	-0.004	-0.323
k_Spinel	0.003	1.647	-3.09E-06	-0.008	0.001	0.095	-7.13E-05	-0.006	-1.75E-04	-0.016
k_Struvite	-0.001	-0.658	2.13E-04	0.576	-4.62E-05	-0.006	0.010	0.917	0.010	0.919

(Continuation)	**NH_3 removal efficiency**		**Effluent S_N_min3_**		**Precipitation CO_3**		**Air requirement[a]**		**Overall**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_Vivianite	0.001	0.467	6.72E-05	0.182	-0.002	-0.227	-0.002	-0.214	-0.002	-0.211
$D\_CH_4\_g\_$	3.03E-04	0.173	-4.38E-04	-1.194	0.008	1.050	0.003	0.283	0.003	0.286
$D\_CO_2\_g\_$	0.003	1.629	-7.42E-05	-0.202	-3.13E-04	-0.041	-0.016	-1.446	-0.016	-1.442
$D\_H_2S\_g\_$	0.004	2.041	-2.24E-04	-0.608	-0.009	-1.239	0.010	0.918	0.010	0.916
$D\_H_2\_g\_$	0.002	1.269	1.09E-04	0.293	0.001	0.125	-0.002	-0.152	-0.002	-0.149
$D\_N_2\_g\_$	-0.001	-0.790	2.68E-04	0.728	-0.021	-2.695	-4.55E-05	-0.004	-2.32E-05	-0.002
$D\_NH_3\_g\_$	9.91E-05	0.056	1.23E-04	0.332	-0.006	-0.740	0.002	0.210	0.002	0.206
$D\_O_2\_g\_$	0.002	0.882	-2.51E-04	-0.687	-0.009	-1.195	-0.001	-0.075	-0.001	-0.073
$theta\_CH_4\_g\_$	-0.001	-0.555	3.69E-04	1.007	-0.015	-2.034	-0.019	-1.701	-0.019	-1.696
$theta\_CO_2\_g\_$	0.002	1.396	-0.001	-1.837	0.009	1.211	0.002	0.174	0.002	0.177
$theta\_H_2S\_g\_$	0.001	0.705	9.69E-06	0.026	-1.88E-04	-0.025	0.013	1.192	0.013	1.188
$theta\_H_2\_g\_$	-1.51E-04	-0.085	-2.39E-04	-0.647	1.06E-04	0.014	0.001	0.098	0.001	0.100
$theta\_N_2\_g\_$	-0.001	-0.647	1.80E-04	0.487	-0.003	-0.342	-0.015	-1.322	-0.015	-1.320
$theta\_NH_3\_g\_$	0.001	0.571	-1.91E-04	-0.518	0.004	0.532	-0.004	-0.388	-0.004	-0.377
$theta\_O_2\_g\_$	3.57E-04	0.202	-1.30E-04	-0.352	0.008	1.013	0.004	0.314	0.003	0.311
$\sum_{j=1}^{p} SRC_j^2$	**1.01**		**0.95**		**0.93**		**0.85**		**0.85**	
R^2	**1.00**		**1.00**		**0.93**		**0.84**		**0.84**	
R^2adj	**1.00**		**1.00**		**0.92**		**0.84**		**0.84**	

[a] Air needed to obtain 90 % NH_3 removal.

Table A10.9 Global sensitivity analyses for the nutrient recovery model of the stripping unit (NRM-Strip): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator for Scenario C (co-digestate; Vlaco, 2012). Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Table 10.6.

	NH_3 removal efficiency		Effluent S_N_min3_		Precipitation CO_3		Air requirement[a]		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
S_Acetate	-0.020	-1.397	0.024	2.014	0.011	0.395	0.004	0.239	-0.010	-0.856
S_Al	0.046	3.196	-0.036	-3.065	-0.060	-2.291	-0.027	-1.853	-0.005	-0.407
S_Butyrate	0.028	1.956	-0.028	-2.367	-0.026	-0.999	-0.013	-0.874	-4.86E-04	-0.042
S_C_4_	0.513	35.886	-0.382	-32.331	0.057	2.168	-0.171	-11.669	0.011	1.015
S_C_min4_	-0.002	-0.171	-0.004	-0.326	-0.032	-1.225	-0.012	-0.818	-0.007	-0.589
S_Ca	-0.025	-1.759	0.026	2.202	0.107	4.077	0.003	0.201	-0.011	-0.924
S_Cl	-0.230	-16.026	0.104	8.811	-0.039	-1.494	0.052	3.52	0.012	1.056
S_DOM	0.042	2.925	-0.041	-3.533	-0.081	-3.137	-0.032	-2.200	-0.005	-0.406
S_Fe	0.041	2.776	-0.029	-2.459	-0.064	-2.424	-0.003	-0.238	0.016	1.385
S_H_0_	0.026	1.826	-0.017	-1.426	0.025	0.938	0.002	0.165	-0.006	-0.522
S_K	-0.010	-0.721	0.007	0.564	0.005	0.188	0.011	0.738	0.004	0.313
S_Mg	0.365	25.498	-0.261	-22.049	0.096	3.670	-0.115	-7.817	0.005	0.480
S_N_0_	0.010	0.723	-0.007	-0.625	0.018	0.678	-0.031	-2.095	0.006	0.496
S_N_5_	-0.005	-0.380	0.003	0.281	0.041	1.571	0.021	1.350	0.003	0.265
S_N_min3_	-0.467	-32.267	0.731	61.026	-0.157	-5.954	0.153	10.355	0.015	1.298
S_Na	-0.036	-2.542	0.025	2.120	0.072	2.777	0.015	1.042	0.005	0.422
S_O_0_	0.008	0.584	-0.001	-0.072	-0.025	-0.971	-0.001	-0.085	-0.003	-0.281
S_P	0.131	9.186	-0.114	-9.607	-0.212	-8.110	-0.082	-5.601	-0.003	-0.274
S_Propionate	-0.014	-0.986	0.012	0.993	-0.012	-0.478	0.023	1.566	0.010	0.895
S_S_6_	0.024	1.672	-0.022	-1.824	-0.011	-0.422	-0.004	-0.300	0.006	0.541
S_S_min2_	0.011	0.759	-0.006	-0.502	-0.007	-0.278	0.004	0.271	0.004	0.331
S_Valerate	0.007	0.512	-0.004	-0.337	0.016	0.592	-0.016	-1.096	-1.67E-04	-0.015
CH_4_g_	0.005	0.350	-0.012	-0.992	-0.006	-0.212	0.011	0.731	0.013	1.163
CO_2_g_	-0.001	-0.075	4.23E-04	0.036	-0.011	-0.416	-0.002	-0.157	0.014	1.236
H_2O_g_	0.006	0.442	-0.009	-0.754	-0.017	-0.636	0.006	0.387	-0.011	-0.949
H_2S_g_	0.003	0.220	-0.007	-0.588	0.021	0.795	0.024	1.661	0.009	0.840
H_2_g_	0.029	2.062	-0.023	-1.956	-0.008	-0.291	-0.021	-1.416	0.003	0.308
N_2_g_	0.003	0.205	0.006	0.536	0.005	0.201	-0.019	-1.277	-0.013	-1.127
NH_3_g_	0.004	0.266	-0.002	-0.181	0.036	1.378	-0.005	-0.334	0.008	0.672
O_2_g_	0.036	2.491	-0.027	-2.278	-0.021	-0.778	-0.015	-1.002	-0.001	-0.062
d_gas	-0.021	-1.493	0.015	1.283	-0.061	-2.313	0.026	1.799	-0.002	-0.145

(Continuation)	NH_3 removal efficiency		Effluent S_N_min3_		Precipitation CO_3		Air requirement[a]		Overall	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
P_gas_in	0.004	0.312	-0.007	-0.589	0.018	0.687	0.376	25.603	0.423	37.468
Temp_gas_in	0.021	1.466	-0.017	-1.440	-0.015	-0.566	-0.014	-0.971	-0.014	-1.278
pH_liq	-0.002	-0.107	0.004	0.379	0.008	0.318	0.013	0.881	0.014	1.198
Temp_liq	0.010	0.723	-0.010	-0.825	0.023	0.866	-0.630	-42.902	-0.735	-64.969
Q_gas_in	-0.002	-0.136	0.006	0.477	-0.019	-0.722	0.022	1.480	0.001	0.054
Q_liq_in	-0.024	-1.645	0.014	1.215	-0.059	-2.261	0.312	21.199	0.362	31.941
u	0.004	0.283	0.002	0.169	-0.009	-0.363	0.013	0.904	0.009	0.759
k_Aragonite	0.001	0.036	-0.004	-0.329	-0.002	-0.067	0.001	0.094	-9.41E-05	-0.008
k_Artinite	-0.003	-0.224	0.002	0.182	0.005	0.184	-0.013	-0.871	-0.004	-0.355
k_Brucite	-0.002	-0.116	5.68E-05	0.005	-0.023	-0.896	-0.010	-0.707	0.008	0.674
k_$Ca_3(PO_4)_2$_am1	0.010	0.673	-0.006	-0.486	-0.022	-0.828	0.007	0.475	0.008	0.688
k_$Ca_3(PO_4)_2$_am2	-0.002	-0.119	0.005	0.454	-0.025	-0.971	-0.009	-0.607	-0.011	-0.881
k_$Ca_3(PO_4)_2$_beta	-0.017	-1.203	0.013	1.116	-0.030	-1.172	-0.004	-0.298	-0.008	-0.723
k_$Ca_4H(PO_4)_3{:}3H_2O$	0.010	0.696	-0.003	-0.255	-0.010	-0.391	0.010	0.693	0.005	0.404
k_$CaHPO_4{:}2H_2O$	0.013	0.879	-0.011	-0.974	0.009	0.354	-0.012	-0.840	-0.011	-0.975
k_$CaHPO_4$bis	-0.024	-1.661	0.014	1.181	-0.011	-0.428	0.032	2.207	0.013	1.179
k_Calcite	-0.011	-0.803	0.009	0.771	0.068	2.625	0.004	0.257	0.005	0.417
k_Diaspore	0.009	0.651	-0.008	-0.640	-0.004	-0.148	-0.003	-0.218	0.009	0.834
k_Dolomite	0.034	2.368	-0.028	-2.387	-0.038	-1.442	-0.027	-1.850	-0.018	-1.642
k_Dolomite_dis	-0.008	-0.530	0.015	1.260	0.001	0.043	0.002	0.160	-0.011	-0.959
k_$Fe(OH)_2$	0.002	0.130	-0.001	-0.099	0.012	0.472	-4.43E-05	-0.003	-0.007	-0.656
k_Hercynite	0.020	1.437	-0.021	-1.756	0.009	0.329	-2.70E-05	-0.002	0.011	0.948
k_Huntite	-0.016	-1.121	0.010	0.846	0.023	0.871	-0.004	-0.239	-0.010	-0.892
k_Hydromagnesite	-0.007	-0.498	0.003	0.285	-0.003	-0.108	0.013	0.856	0.004	0.367
k_Hydroxyapatite	0.025	1.767	-0.024	-1.990	-0.001	-0.025	-0.024	-1.640	-0.008	-0.721
k_Kstruvite	-0.021	-1.497	0.018	1.488	-0.012	-0.449	0.018	1.252	0.020	1.800
k_Magnesite	-0.002	-0.125	0.003	0.283	-0.018	-0.670	2.29E-04	0.016	0.009	0.792
k_$Mg_3(PO_4)_2$	0.018	1.248	-0.005	-0.452	-0.020	-0.784	-0.034	-2.348	-0.031	-2.765
k_$MgHPO_4{:}3H_2O$	-0.004	-0.265	-0.007	-0.554	0.012	0.457	0.006	0.385	-0.008	-0.744
k_$Mg(OH)_2$_act	0.028	1.995	-0.020	-1.719	0.020	0.785	-0.016	-1.108	-0.016	-1.458
k_Periclase	0.015	1.082	-0.015	-1.242	-0.007	-0.266	-0.026	-1.802	-0.013	-1.193
k_Portlandite	-0.013	-0.896	0.003	0.237	-0.005	-0.192	0.010	0.685	-0.017	-1.544
k_Siderite	0.003	0.233	-0.003	-0.261	0.025	0.976	-0.005	-0.326	-0.003	-0.251
k_Spinel	0.010	0.694	-0.007	-0.571	0.021	0.803	-0.014	-0.986	-0.008	-0.676
k_Struvite	0.009	0.652	-0.023	-1.949	-0.018	-0.692	-0.006	-0.406	0.010	0.884

(Continuation)	**NH_3 removal efficiency**		**Effluent S_N_min3_**		**Precipitation CO_3**		**Air requirement[a]**		**Overall**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
k_Vivianite	0.007	0.493	-0.005	-0.456	-0.007	-0.271	0.012	0.809	0.009	0.763
D_CH_4_g_	-0.004	-0.264	0.001	0.052	0.018	0.697	0.010	0.688	0.013	1.176
D_CO_2_g_	-0.002	-0.148	-4.51E-04	-0.038	-0.007	-0.287	-0.003	-0.228	-2.27E-04	-0.020
D_H_2S_g_	0.012	0.817	-0.003	-0.283	0.015	0.580	-0.014	-0.948	-0.005	-0.474
D_H_2_g_	0.018	1.216	-0.013	-1.101	0.015	0.563	-0.026	-1.729	-0.017	-1.516
D_N_2_g_	0.025	1.73	-0.019	-1.579	-0.019	-0.733	-0.029	-1.961	-0.005	-0.481
D_NH_3_g_	-0.012	-0.833	0.020	1.720	-0.044	-1.656	0.035	2.365	0.020	1.792
D_O_2_g_	0.016	1.118	-0.006	-0.527	-0.005	-0.210	0.011	0.756	3.84E-04	0.034
theta_CH_4_g_	-0.010	-0.703	0.006	0.485	0.019	0.717	-0.013	-0.902	-0.017	-1.515
theta_CO_2_g_	-0.03	-2.104	0.034	2.910	-0.008	-0.313	0.017	1.159	0.005	0.486
theta_H_2S_g_	0.011	0.778	-0.014	-1.225	0.054	2.079	-0.003	-0.204	0.002	0.137
theta_H_2_g_	-0.003	-0.215	0.006	0.518	-0.014	-0.522	-0.028	-1.922	-0.018	-1.571
theta_N_2_g_	-0.009	-0.611	0.005	0.449	-0.036	-1.376	0.012	0.803	0.008	0.677
theta_NH_3_g_	-0.025	-1.759	0.014	1.147	-0.022	-0.842	0.017	1.116	0.004	0.344
theta_O_2_g_	0.001	0.050	-0.006	-0.496	0.062	2.384	-0.005	-0.320	-0.006	-0.544
$\sum_{j=1}^{p} SRC_j^2$	**0.71**		**0.79**		**0.16**		**0.73**		**0.86**	
R^2	**0.75**		**0.83**		**0.15**		**0.73**		**0.84**	
R^2adj	**0.73**		**0.82**		**0.10**		**0.72**		**0.83**	

[a] Air needed to obtain 90 % NH_3 removal.

Table A10.10 Global sensitivity analyses for the nutrient recovery model of the scrubbing unit (NRM-Scrub): standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator. Dark grey = cut-off threshold 1 (CFT1); grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4).For description of factor symbols: see Chapter 10: Table 10.7.

	NH_3 recovery efficiency		**Fertilizer S_N_min3_**		**Fertilizer pH**		**Acid requirement**		**Overall**	
Factor	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**	**SRC**	**tSRC**
CH_4_g_	-0.043	-2.028	0.059	6.521	0.033	2.532	0.019	0.902	-0.001	-0.058
CO_2_g_	0.390	18.580	-0.012	-1.355	-0.310	-24.051	0.398	18.767	-0.299	-24.551
H_2O_g_	-0.012	-0.563	0.007	0.740	0.007	0.537	0.006	0.276	0.016	1.312
H_2S_g_	0.008	0.365	0.014	1.547	-0.005	-0.365	0.020	0.955	-0.001	-0.110
H_2_g_	-0.073	-3.481	0.072	7.907	0.056	4.325	-0.064	-3.004	0.069	5.658
N_2_g_	-0.007	-0.357	0.001	0.078	-0.004	-0.346	-0.022	-1.045	0.014	1.111
NH_3_g_	-0.590	-27.813	0.900	97.918	0.814	62.469	-0.623	-29.296	0.860	70.638
O_2_g_	0.278	13.332	-0.309	-34.269	-0.231	-18.063	0.248	11.731	-0.271	-22.381
S_S_6_	0.240	11.482	-0.154	-16.959	-0.175	-13.643	0.255	12.036	-0.170	-14.012
pH_liq	-0.010	-0.457	-0.001	-0.163	0.002	0.189	0.032	1.486	0.006	0.474
Temp_liq	-0.074	-3.520	-0.015	-1.663	-0.025	-1.934	-0.019	-0.914	-0.021	-1.772
d_gas	-0.008	-0.361	0.002	0.235	-0.014	-1.056	-0.025	-1.173	0.013	1.089
P_gas_in	0.007	0.358	0.021	2.356	-0.005	-0.397	0.018	0.864	-0.033	-2.735
Temp_gas_in	0.019	0.903	-0.046	-5.146	-0.011	-0.836	0.025	1.181	-0.027	-2.265
u	-0.029	-1.367	0.003	0.301	-0.011	-0.857	0.011	0.517	0.001	0.066
Q_liq_in	-0.009	-0.451	0.001	0.117	0.005	0.405	-0.015	-0.702	-0.017	-1.432
D_CH_4_g_	-0.025	-1.192	-0.020	-2.186	0.010	0.802	-0.017	-0.790	-0.001	-0.068
D_CO_2_g_	-0.011	-0.531	0.003	0.314	-0.015	-1.181	0.025	1.175	-0.014	-1.161
D_H_2S_g_	-0.014	-0.649	2.15E-04	0.024	1.63E-04	0.013	0.012	0.586	-0.013	-1.069
D_H_2_g_	0.014	0.650	-0.008	-0.882	0.013	1.043	-0.018	-0.849	-0.002	-0.127
D_N_2_g_	0.006	0.306	-0.009	-1.015	0.018	1.364	0.024	1.122	-0.004	-0.349
D_NH_3_g_	0.015	0.715	-0.005	-0.510	3.66E-04	0.028	0.012	0.565	-0.014	-1.177
D_O_2_g_	-0.025	-1.207	0.009	0.996	-0.006	-0.449	0.012	0.577	0.005	0.397
k_$(NH_4)_2SO_4$	0.006	0.282	0.001	0.073	-0.013	-1.020	0.016	0.757	0.001	0.075
theta_CH_4_g_	-0.013	-0.644	0.004	0.463	0.002	0.183	-0.023	-1.113	-0.001	-0.045
theta_CO_2_g_	-0.005	-0.241	0.003	0.359	-0.009	-0.681	-0.024	-1.137	-0.007	-0.603
theta_H_2S_g_	-0.015	-0.725	0.009	0.987	-0.001	-0.081	-0.016	-0.741	0.004	0.311
theta_H_2_g_	0.002	0.085	0.016	1.745	0.003	0.201	-0.035	-1.663	0.003	0.267
theta_N_2_g_	-0.001	-0.060	-0.005	-0.573	0.005	0.396	-0.029	-1.379	0.013	1.090
theta_NH_3_g_	-0.007	-0.346	0.002	0.180	-0.014	-1.076	0.006	0.267	-0.005	-0.439
theta_O_2_g_	0.011	0.516	-0.011	-1.237	0.011	0.882	0.018	0.858	-0.004	-0.328
$\sum_{j=1}^{p} SRC_j^2$	**0.65**		**0.94**		**0.85**		**0.69**		**0.94**	
R^2	**0.68**		**0.94**		**0.88**		**0.67**		**0.89**	
R^2adj	**0.66**		**0.94**		**0.87**		**0.65**		**0.89**	

Table A10.11 Global sensitivity analysis for the pig manure treatment train: standardized regression coefficient (SRC) and its t-statistic (tSRC) per performance indicator. Grey = cut-off threshold 2 (CFT2); light grey = cut-off threshold 3 (CFT3); salmon = cut-off threshold 4 (CFT4). For description of factor symbols: see Chapter 10: Tables 10.4-10.7.

	Net costs	
Factor	SRC	tSRC
NRM_Heat.T_target_AD	-0.011	-0.404
NRM_AD.D_H_2	-0.010	-0.359
NRM_AD.S_Ca	-0.043	-1.562
NRM _AD.S_C_4_	-0.042	-1.550
NRM _AD.Q_liq_in	-0.036	-1.317
NRM _AD.k_La_H_2	0.033	1.209
NRM _AD.k_Al_2O_3	-0.023	-0.837
NRM AD.k_$AlPO_4$	0.030	1.104
NRM AD.k_Anhydrite	0.013	0.457
NRM _AD.k_Aragonite	0.005	0.187
NRM _AD.k_Boehmite	0.006	0.215
NRM _AD.k_$Ca_4H(PO_4)_3$:$3H_2O$	-0.014	-0.512
NRM _AD.k_$CaHPO_4$:$2H_2O$	0.059	2.161
NRM _AD.k_$CaHPO_4$bis	0.003	0.115
NRM _AD.k_Calcite	-0.028	-1.027
NRM _AD.k_Diaspore	0.012	0.455
NRM _AD.k_Dolomite	-0.020	-0.718
NRM _AD.k_FeS_ppt_	0.038	1.375
NRM _AD.k_Gibbsite	0.008	0.295
NRM _AD.k_Hercynite	0.003	0.121
NRM_AD.k_Hydroxyapatite	0.018	0.656
NRM _AD.k_Kstruvite	0.026	0.952
NRM _AD.k_Mackinawite	0.057	2.086
NRM _AD.k_Magnesite	-0.006	-0.207
NRM _AD.k_$Mg_3(PO_4)_2$	0.025	0.900
NRM _AD.k_$MgHPO_4$:$3H_2O$	-0.052	-1.914
NRM_AD.k_Siderite	-0.043	-1.564
NRM _AD.k_Struvite	0.001	0.043
NRM _AD.k_Vivianite	-0.004	-0.141
NRM _AD.kdec_xsrb_ac	0.027	0.987
NRM _AD.kdec_xsrb_bu	0.019	0.703
NRM_AD.kdec_xsrb_h	0.030	1.070
NRM _AD.kdec_xsrb_pro	0.039	1.428
NRM _AD.km_srb_ac	-0.034	-1.243
NRM _AD.km_srb_bu	-0.009	-0.327
NRM AD.km_srb_h	0.005	0.180
NRM _AD.km_srb_pro	-0.004	-0.134
NRM _Chem.Mg_OH_$_2$_Dose	0.015	0.543
NRM _Prec.Q_prec_target	0.004	0.142
NRM_Prec.k_$AlPO_4$	0.019	0.695
NRM _Prec.k_Aragonite	0.062	2.284
NRM _Prec.k_Artinite	0.018	0.663
NRM _Prec.k_Boehmite	-0.013	-0.465
NRM _Prec.k_Brucite	-0.010	-0.377
NRM _Prec.k_$Ca_3(PO_4)_2$:am1	0.002	0.079
NRM _Prec.k_$Ca_3(PO_4)_2$:am2	0.018	0.653
NRM _Prec.k_$Ca_3(PO_4)_2$:beta	0.038	1.384
NRM _Prec.k_$Ca_4H(PO_4)_3$:$3H_2O$	0.005	0.176
NRM _Prec.k_$CaHPO_4$:$2H_2O$	0.038	1.390
NRM _Prec.k_$CaHPO_4$bis	0.009	0.320
NRM _Prec.k_Calcite	-0.041	-1.490
NRM _Prec.k_Diaspore	0.012	0.423
NRM _Prec.k_Dolomite	0.039	1.443
NRM _Prec.k_Dolomite_dis	-0.015	-0.540
	Net costs (continuation)	
Factor	**SRC**	**tSRC**
NRM _Prec.k_Hydroxyapatite	0.029	1.073
NRM _Prec.k_Kstruvite	-0.027	-0.990
NRM _Prec.k_Magnesite	0.004	0.151
NRM _Prec.k_$Mg_3(PO_4)_2$	0.019	0.694
NRM _Prec.k_$MgHPO_4$:$3H_2O$	0.018	0.667
NRM_Prec.k_$Mg(OH)_2$_act	-0.022	-0.819
NRM _Prec.k_Siderite	-0.004	-0.133
NRM _Prec.k_Struvite	0.026	0.945
NRM _Prec.k_Vaterite	-0.040	-1.484
NRM _Prec.k_Vivianite	0.057	2.088
NRM _Strip.D_CH_4_g_	-0.021	-0.766
NRM _Strip.D_CO_2_g_	-0.068	-2.507
NRM _Strip.D_H_2S_g_	-0.025	-0.913
NRM _Strip.D_H_2_g_	0.027	0.981
NRM _Strip.D_N_2_g_	-0.066	-2.428
NRM _Strip.D_NH_3_g_	-0.046	-1.676
NRM _Strip.D_O_2_g_	0.008	0.302
NRM _Strip.Q_gas_in	0.017	0.636
NRM _Strip.k_Aragonite	0.000	-0.016
NRM _Strip.k_Artinite	0.025	0.898
NRM _Strip.k_Brucite	-0.027	-0.971
NRM _Strip.k_$Ca_3(PO_4)_2$_am1	0.016	0.578
NRM _Strip.k_$Ca_3(PO_4)_2$_am2	-0.016	-0.568
NRM _Strip.k_$Ca_3(PO_4)_2$_beta	-0.014	-0.524
NRM _Strip.k_$Ca_4H(PO_4)_3$:$3H_2O$	0.025	0.927
NRM _Strip.k_$CaHPO_4$:$2H_2O$	-0.055	-2.020
NRM _Strip.k_$CaHPO_4$bis	0.010	0.355
NRM _Strip.k_Calcite	0.071	2.618
NRM _Strip.k_Diaspore	-0.019	-0.696
NRM _Strip.k_Dolomite	-0.039	-1.421
NRM _Strip.k_Dolomite_dis	-0.027	-1.002
NRM _Strip.k_$Fe(OH)_2$	-0.070	-2.578
NRM _Strip.k_Hercynite	-0.021	-0.781
NRM _Strip.k_Huntite	-0.024	-0.879
NRM _Strip.k_Hydromagnesite	-0.010	-0.364
NRM _Strip.k_Hydroxyapatite	0.080	2.914
NRM _Strip.k_Kstruvite	0.024	0.877
NRM _Strip.k_Magnesite	-0.056	-2.049
NRM _Strip.k_$Mg_3(PO_4)_2$	0.075	2.750
NRM _Strip.k_$MgHPO_4$:$3H_2O$	-0.019	-0.691
NRM _Strip.k_$Mg(OH)_2$_act	0.002	0.082
NRM _Strip.k_Periclase	-0.025	-0.914
NRM _Strip.k_Portlandite	0.010	0.349
NRM _Strip.k_Siderite	-0.015	-0.546
NRM _Strip.k_Spinel	-0.009	-0.325
NRM _Strip.k_Struvite	0.005	0.198
NRM _Strip.k_Vivianite	0.006	0.229
NRM_Heat.T_target_Strip	-0.037	-1.368
NRM_Scrub.Q_liq_in (acid)	0.064	2.350
NRM_Scrub.k_$(NH_4)_2SO_4$	0.006	0.229
NRM_Scrub.D_CH_4_gas	0.029	1.060
NRM_Scrub.D_CO_2_gas	0.015	0.540
NRM_Scrub.D_H_2S_gas	0.009	0.327
NRM_Scrub.D_H_2_gas	-0.010	-0.358

(Continuation)	Net costs			Net costs (continuation)	
Factor	**SRC**	**tSRC**	**Factor**	**SRC**	**tSRC**
NRM _Prec.k_Fe(OH)$_2$_s	-0.027	-0.972	NRM_Scrub.D_N$_2$_gas	0.015	0.540
NRM_Prec.k_Gibbsite	0.034	1.260	NRM_Scrub.D_NH$_3$_gas	0.002	0.082
NRM _Prec.k_Hercynite	-0.048	-1.772	NRM_Scrub.D_O$_2$_gas	0.020	0.717
$\sum_{j=1}^{p} SRC_j^2$	**0.10**				
R^2	**0.91**				
R^{2}adj	**0.20**				

PUBLICATIONS AND COMMUNICATIONS

JOURNAL ARTICLES – A1

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Vaneeckhaute, C., Meers, E., Michels, E., Christiaens, P., Tack, F.M.G., 2012. Fate of macronutrients in water treatment of digestate using vibrating reversed osmosis. Water Air Soil Pollut. 223(4), 1593-1603.

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Vaneeckhaute, C., Belia, E., Tack, F.M.G., Meers, E., Vanrolleghem, P.A., submitted. Roadmap for setting up nutrient recovery strategies.

Vaneeckhaute, C., Adams, P., Rodhe, L., Thelin, G., Styles, D., Prade, T., D'Hertefeldt, T., submitted. Wide-scale use of recycled nutrients: Bottlenecks or opportunities ?

Vanrolleghem, P.A., **Vaneeckhaute, C.**, submitted. Resource recovery from wastewater and sludge: Modelling and control challenges.

Styles, D., Borjersson, P., D'Hertefeldt, T., Birkhofer, K., Dauber, J., Adams, P., Patil, S., Pagella, T., Petersson, L., Peck, P., **Vaneeckhaute, C.**, submitted. Climate regulation, energy provisioning and water purification: Quantifying ecosystem service delivery of bioenergy willow grown on riparian buffer zones using life cycle assessments.

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Vaneeckhaute, C., Lebuf, V., Accoe, F., van Elsacker, S., Ghekiere, G., Ryckaert, B., Michels, E., Meers, E., 2013. Nutrient recovery from digestate in North West Europe. Research Report, Ghent University, Flemish Coordination Center for Manure Processing, Research and Advice Center for Agri- and Horticulture, Ghent, Belgium.

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ORAL PRESENTATIONS AT INTERNATIONAL CONFERENCES

(Note: * indicates additional published abstract)

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Awarded for best presentation.

Vaneeckhaute, C., Meers, E., Michels, E., Tack, F.M.G., 2011. Recuperation and reuse of nutrients from digestate as green fertilizers. 1st Biodigestion forum Flanders, Biogas-e, College West Flanders, Kortrijk, Belgium, September 14 2011. (invited)

Vaneeckhaute, C., Meers, E., Michels, E., Tack, F.M.G., 2011. Recuperation and reuse of nutrients from digestate as green fertilizers. Recuperation and Valorisation of Nutrients from Manure and Digestate, Flemish Advice Center for Manure Processing, Ranst, Belgium, November 16 2011. (invited)

Meers, E., **Vaneeckhaute, C.**, Michels, E., Ghekiere, G., Accoe, F., Vanhove, P., Bamelis, L., De Wilde, D., Tack, F.M.G., 2011. Recuperation and reuse of nutrients from digestate as green fertilizers. Study-day, Fertilizers & Plant Nutrition: New Generation, Ie-Net, Antwerp, Belgium, December 6 2011.

Meers, E., **Vaneeckhaute, C.**, Michels, E., Bamelis, L., De Wilde, D., Ghekiere, G., Accoe, F., Tack, F.M.G., 2012. Green fertilizers from manure and digestate. Innovations in Manure Processing and Marketing, VCM Mestverwerking, Antwerp, Belgium, March 20 2012. (invited)

Vaneeckhaute, C., Meers, E., Ghekiere, G., Accoe, F., Michels, E., Tack, F.M.G., 2012.* Nutrient recycling from bio-digestion waste as chemical fertilizer substitutes. World Congress on Advances in Civil, Environmental and Materials Research, Seoul, South Korea, August 26-30 2012.

Vaneeckhaute, C., Meers, E., Ghekiere, G., Accoe, F., Tack, F.M.G., 2012.* Nutrient recycling from biodigestion waste as synthetic fertilizer substitutes: A field experiment. 4th International Symposium on Energy from Biomass and Waste, Venice, Italy, November 12-15 2012.

Lebuf, V., Accoe, F., **Vaneeckhaute, C.**, Meers, E., Michels, E., Ghekiere, G., 2012.* Nutrient recovery from digestate: Techniques and end-products. 4th International Symposium on Energy from Biomass and Waste, Venice, Italy, November 12-15 2012.

Vanelsacker, S., Accoe, F., Lebuf, V., **Vaneeckhaute, C.**, Michels, E., Meers, E., 2013.* Digestate management in Flanders: Nutrient removal versus nutrient recovery. International Anaerobic Digestion Symposium at BioGasWorld, IBBK Fachgruppe Biogas, Berlin, Germany, April 23-25 2013.

Sigurnjak, I., **Vaneeckhaute, C.**, Michels, E., Ghekiere, G., Lebuf, V., Accoe, F., Tack, F.M.G., Meers, E., 2013.* Field and lab scale assessment of bio-based mineral fertilizer substitutes. Renewable Resources and Biorefineries 9 (RRB9), Ghent, Belgium, June 4-6 2013.

Vaneeckhaute, C., Meers, E., Tack, F.M.G., Vanrolleghem, P.A., 2013.* Critical comparison of nutrient (N,P,K) recovery techniques from sludge, biosolids and manure. 36e Symposium sur les Eaux Usées, Réseau Environnement, Boucherville, Québec, Canada, October 23-24 2013.

Vaneeckhaute, C., Tack, F.M.G., Meers, E., Vanrolleghem, P.A., 2013. Anaerobic digestion of bio-waste and valorization of the resulting digestates. Projet Biométhanisation, Ville de Québec, Québec, Canada, November 18 2013. (invited)

Vaneeckhaute, C., Ryckaert, B., 2013.* Closing the nutrient cycle by using manure derivatives as synthetic fertilizer substitute: A field experiment. ManuReSource 2013, Brugge, Belgium, December 5-6 2013. (invited)

Vaneeckhaute, C., Tack, F.M.G., Meers, E., Vanrolleghem, P.A., 2014. Anaerobic digestion of bio-waste and valorization of the resulting digestates. Bio-energy and Residues Valorization Workshop, Lund University, Lund, Sweden, February 27-28 2014. (invited)

Meers, E., Michels, E., Clymans, L. Declerq, I. Sigurnjak, I., **Vaneeckhaute, C.**, Vanrolleghem, P.A., Tack, F.M.G., Buysse, J., 2014.* Energy and nutrient cycling. International Bioenergy Conference, Manchester, United Kingdom, March 11-13 2014. (invited)

Vaneeckhaute, C., 2014. La biométhanisation: Une solution durable pour la gestion des déchets? Jour de la terre, Ville de Baie Saint Paul, Québec, Canada, April 22 2014. (invited)

Vaneeckhaute, C., 2014. La biométhanisation: Une solution durable pour la gestion des déchets? Omerto, Baie Saint Paul, Québec, Canada, May 22 2014. (invited)

Sigurnjak, I., **Vaneeckhaute, C.**, Michels, E., Ryckaert, B., Vandenbulcke, J., Ghekiere, G., Tack F.M.G., Meers, E., 2014.* Nutrient use efficiency of liquid fraction of digestate: A three-year field trial. Renewable Resources and Biorefineries 10 (RRB10), Valladolid, Spain, June 4-6 2014.

Vaneeckhaute, C., Claeys, F.H., Tack, F.M.G., Meers, E., Belia, E., Vanrolleghem, P.A., 2014.* Development, implementation and use of a generic nutrient recovery model (NRM) library. 29th Eastern Canadian Symposium on Water Quality Research, Canadian Association on Water Quality (CAWQ), Montréal, Québec, Canada, October 17 2014. *Awarded for best presentation.*

Vanrolleghem, P.A., **Vaneeckhaute, C.**, 2014.* Resource recovery from wastewater and sludge: Modelling and control challenges. Global Challenges: Sustainable Wastewater Treatment and Resource Recovery, IWA Specialist conference, International Water Association (IWA), Kathmandu, Nepal, October 26-30 2014.

Vaneeckhaute, C., Ghekiere, G., Michels, E., Vanrolleghem, P.A., Tack, F.M.G., Meers, E., 2014.* Nutrient use efficiency in recovered bio-based mineral fertilizers: A field-scale assessment. Global Challenges: Sustainable Wastewater Treatment and Resource Recovery, IWA Specialist conference, International Water Association (IWA), Kathmandu, Nepal, October 26-30 2014.

Vaneeckhaute, C., 2015.* Towards a zerocost-biorefinery using a new model library and global sensitivity analyses. 11th International Conference on Renewable Resources and Biorefineries (RRB-11), York, United Kingdom, June 3-5 2015. (invited)

Vaneeckhaute, C., Claeys, F., Belia, E., Vanrolleghem, P.A., 2015.* Nutrient recovery treatment train set-up using a new model library and global sensitivity analyses. 9th IWA Symposium on Systems Analysis and Integrated Assessment (Watermatex), International Water Association (IWA), Gold Coast, Queensland, Australia, June 14-17 2015.

Vaneeckhaute, C., Claeys, F., Belia, E., Vanrolleghem, P.A., 2015.* Nutrient recovery treatment train set-up using a new model library and global sensitivity analysis. 1st IWA Resource Recovery Conference: Bridging Towards the Chemical Industry (RR2015), International Water Association (IWA), Ghent, Belgium, August 20-September 2 2015.

Vaneeckhaute, C., Claeys, F., Belia, E., Vanrolleghem, P.A., 2015.* Nutrient recovery treatment train configuration and optimization using a new model library and global sensitivity analyses. Water Environment Federation Technical Exhibition & Conference (WEFTEC), Water Environment Federation (WEF), Chicago, USA, September 26-30 2015.

POSTER PRESENTATIONS AT INTERNATIONAL CONFERENCES

(note: * indicates additional published abstract)

Michels, E., Willems, B., **Vaneeckhaute, C.**, Tack, F.M.G., Meers, E., 2010. From biomass to bioenergy. Open Enterprices day, Innova Manure, West-Vleteren, Belgium, October 3 2010. (invited)

Vaneeckhaute, C., Michels, E., Meers, E., Tack, F.M.G., 2010. Sustainable reuse of water from manure processing using wetlands. ie-awards 2010, Royal Flemish Engineer Association (KVIV), Museum for Art and History, Brussels, Belgium, November 25 2010. (invited)

Vaneeckhaute, C., Michels, E., Meers, E., Accoe, F., Thibaut, E., Tack, F.M.G., 2011. Green fertilizers. Study-day: A new market for manure, Flemish Advice Center for Manure Processing, Ghent, Belgium, March 16 2011. (invited)

Vaneeckhaute, C., Michels, E., Meers, E., Accoe, F., Thibaut, E., Tack, F.M.G., 2011. Green fertilizers. First Biodigestion Forum Flanders, Biogas-e, College West-Flanders, Kortrijk, Belgium, September 14 2011. (invited)

Vaneeckhaute, C., Michels, E., Tack, F.M.G., Meers, E., 2012.* Nutrient recycling from bio-digestion waste as green fertilizers. 17th PhD Symposium on Applied Biological Sciences, Leuven, Belgium, February 10 2012.

Vaneeckhaute, C., Michels, E., Tack, F.M.G., Meers, E., 2012. Nutrient recycling from bio-digestion waste as green fertilizers. Innovations in Manure Processing and Marketing, Flemish Coordination Center for Manure Processing, Antwerp, Belgium, March 20 2012. (invited)

Vaneeckhaute, C., Demolder, L., Meers, E., Accoe, F.M.G., 2012. Digestate in Flanders: Bottleneck or opportunity? Innovations in Manure Processing and Marketing, Flemish Coordination Center for Manure Processing, Antwerp, Belgium, March 20 2012. (invited)

Vaneeckhaute, C., Meers, E., Michels, E., Ghekiere, G., Accoe, F.M.G., Tack, F.M.G., 2012.* Cradle-to-cradle recycling of nutrients from bio-digestion waste. Renewable Resources and Biorefineries 8 (RRB8), Toulouse, France, June 4-6 2012.

Vaneeckhaute, C., Janda, J., Meers, E., Michels, E., Tack, F.M.G., 2012. Nutrient use efficiency and plant availability of biobased phosphorus fertilizers. Workshop on Closing the Phosphorus Cycle, Leeds University, Leeds, UK, November 1 2012. (invited)

Vaneeckhaute, C., Meers, E., Michels, E., Ghekiere, G., Accoe, F., Lebuf, V., 2013. Nutrient use efficiency and plant availability of bio-based phosphorus fertilizers. 1st European Sustainable Phosphorus Conference, Brussels, Belgium, March 6-7 2013. (invited)

Vaneeckhaute, C., Meers, E., Michels, E., Ghekiere, G., Accoe, F., Lebuf, V., 2013. Closing the nutrient cycle by using bio-digestion waste derivatives as synthetic fertilizer substitutes. 1st European Sustainable Phosphorus Conference, Brussels, Belgium, March 6-7 2013. (invited)

Sigurnjak, I., **Vaneeckhaute, C.**, Meers, E., Michels, E., Ghekiere, G., Accoe, F., Lebuf, V., Tack, F.M.G., 2013. Nutrient and energy recuperation from digestate. 1st European Sustainable Phosphorus Conference, Brussels, Belgium, March 6-7 2013. (invited)

Vaneeckhaute, C., Ghekiere, G., Michels, E., Vanrolleghem, P.A., Meers, E., Tack, F.M.G., 2013.* Nutrient recovery from biodigestion waste(water) streams and reuse as renewable fertilizers: A two-year field experiment. Nutrient Removal and Recovery Conference 2013: Trends in Resource Recovery and Use, International Water Association & Water Environmental Federation, Vancouver, Canada, July 26-29 2013.

PRESS AND INTERVIEWS

Vaneeckhaute, C., 2010. News letter TNAV, Flemish Network on Water Technologies, Topic: Winner 'Water technology award 2010', December 16 2010. Available from: http://www.tnav.be/NL/nieuws/actua/3e_tnav_watertechnologieprijs_alle_12_ingediende_eindwerken_over_water_en_slibtechnologie_van_hoog_niveau.html

Vaneeckhaute, C., 2010. Carreer news, NovaForum Business Media: Waterforum, Topic: Winner 'Water Technology Award 2010', December 16 2010. Available from: www.waterforum.net

Vaneeckhaute, C., Galvin, D., 2011. Interview workshop CIBELES project (European Commission), National television, Tajikstan, April 21 2011.

Vaneeckhaute, C., Galvin, D., 2011. Interview workshop CIBELES project (European Commission), National News Paper, Kyrgyzstan, August 8 2011.

Vaneeckhaute, C., 2011. Interview on green fertilizers, Proeftuinnieuws 01-02, Blum., K. (author), Trefdag Proclam: Meer met minder, January 7 2011. (in Dutch)

Vaneeckhaute, C., 2014. Interview on biosolids, national television, Canada, January 14 2014. Available from: http://ici.radio-canada.ca/regions/manitoba/2014/01/14/007-biosolides-utilisation-consultations-publiques-propositions.html

Vaneeckhaute, C., 2014. News letter and Year Report, Canadian Association on Water Quality, Topic: Winner 'Philip H. Jones Award 2014', October 17 2014.

Vaneeckhaute, C., 2014. Speech at Conference INFRA (Infrastructures Municipales), Topic: Winner 'Prix de la Relève en Infrastructures Municipales 2014', Centre d'Expertise et de Recherche en Infrastructures Municipales (CERIU), Montréal, QC, Canada, December 3 2014.

Vaneeckhaute, C., 2015. Video interview at the North American Partnership for Phosphorus Sustainability (NAPPS) stakeholder event, Arizona State University, Washington DC, USA, May 21 2015.

ACTIVE PARTICIPATION AT CONFERENCES AND WORKSHOPS (RESEARCH RELATED)

CEDA Dredging days: Dredging Facing Sustainability. Central Dredging Association, Antwerp, Belgium, October 1-3 2008.

IFEST: Trade Fair for Environmental Technology. Flanders Expo, Ghent, Belgium, October 21-23 2008.

Upgrading of Purified Effluents from Manure into Reusable Water for Agriculture. Provincial Research and Advice Center for Agri- and Horticulture, Rumbeke-Beitem, Belgium, October 1 2009.

Sustainability, Energy & Africa: State of the Art. Africa Matters, Ghent, Belgium, November 13 2009.

Don't Waste your Biowaste. Flemish Public Waste Agency (OVAM), Committee Of The Regions, Brussels, Belgium, September 21, 2010.

Phytomanagement of Metal-Contaminated Soils in the Campine Region. Study day, Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, Ghent University, Belgium, September 22 2010.

Opening night, Platform Sustainability, speech Peter Tom Jones: The Transition to Ecological Sustainability: Beyond the Technological Optimism. Faculty of Bioscience Engineering, Ghent University, Belgium, October 26 2010.

Sustainable Biomass for European Energy. Belgian EU Presidency conference, Committee Of The Regions, Brussels, Belgium, November 29-30 2010.

Climate day, speech Erik Wood: Global Drought - Historical Perspective and Future Projection. Faculty of Bioscience Engineering, Ghent University, Belgium, March 17 2011.

Formation evening, permanent training environmental coordinator (recognized by the Department of Environment, Nature and Energy of the Flemish Government): Towards a Green Cycle. Speech, Stef Denayer: Waste does not exist, Emmanuel Van Houtte: Sustainable water reuse. Faculty of Bioscience Engineering, Ghent University, Belgium, April 27 2011.

Round Table on Sustainable Materials Management, Flanders in Action Pact 2020, Workshop 1: Bio-based economy and closed nutrient cycles, Workgroup: Closing nutrient cycles (water reuse): Problems or opportunities?; Workshop 2: Flanders - A mine of materials?, Workgroup: End processors of yesterday, raw material suppliers for tomorrow? Flemish Public Waste Agency (OVAM), Convention Center Elewijt, Belgium, June 6 2011.

Risk Management and Approach of Metal Contaminated Soils. Workshop, PHL University College, Center for Environmental Sciences, Campus Diepenbeek, Hasselt University, Belgium, June 9 2011.

Manure Refining at Company Level. Environmental Theme Day, Flemish Coordination Center for Manure Processing, Biogas-e, Provincial Research Center for Agriculture and Horticulture, Eddie Ter Braack, Green Energy Technologies, North Sleen, the Netherlands, June 22 2011.

Cleantech Festival. Platform for Environmental Innovation (MIP), Ghent, Belgium, October 20 2011.

Flemish Manure Products on the French Market: What and How? Study day, Flemish Coordination Center for Manure Processing, Kortrijk, Belgium, January 31 2012.

Agriculture Workshop 2012. Can Flanders guide his farming practices? Faculty of Bioscience Engineering, Ghent University, Belgium, February 8 2012.

Strategic Challenges in the EU-Brazil Relationship: Sustainable Development, Climate Change and Energy. Ghent, Belgium, May 11-12 1012.

Lake Winnipeg Basin Workshop for students and young professionals. Canadian Water Network, Manitoba, Canada, August 19-23 2013.

Webcast: Towards a Renewable Future: Assessing Macro Nutrient Recovery as a Viable Treatment Alternative. Water Environment Federation, September 4 2013.

Salon des Technologies Environnementales du Québec (TEQ), Centre des congrès de Québec, Québec, Canada, March 11-12 2014.

Webcast: Wastewater Treatment Modeling 101. Water Environment Federation, May 14 2014.

INFRA, Infrastructures Municipales 2014. Centre d’Expertise et de Recherche en Infrastructures Urbaines. Palais des Congrès de Montréal, Montréal, Québec, December 1-3 2014.

The Climate Show. Marche Action on Climate, Capitole de Québec, Québec, Canada, April 11 2015.

Webcast: Wasted Food to Energy: How Six Water Resource Recovery Facilities are Boosting Biogas Production and the Bottom Line. Water Environment Federation, April 15 2015.

North American Partnership for Phosphorus Sustainability (NAPPS) stakeholder event and Phosphorus Research Coordination Network (P RCN) meeting, Arizona State University, Washington DC, United States, May 18-21 2015.