CHAPTER FOUR

Assessing Nutrient Use Efficiency and Environmental Pressure of Macronutrients in Biobased Mineral Fertilizers: a Review of Recent Advances and Best Practices at Field Scale

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Contents

1.	Intro	oduction	139
2.	Field	d Experiments: Guidelines for Good Practice	142
	2.1	Site Description and Fertilization Strategies	142
	2.2	Sampling, Fertilizer Application and Field Follow-Up	145
	2.3	Physicochemical Analysis	147
		2.3.1 Product Analysis	147
		2.3.2 Soil Analysis	148
		2.3.3 Plant Analysis	149
	2.4	Performance Indicator Calculations	149
		2.4.1 Nutrient Use Efficiency	149
		2.4.2 Nutrient Balances and Apparent Recovery	150
	2.5	Model Simulations	151
	2.6	Statistical Analysis	151
	2.7	Analysis of Biogas Potential	151
3.	Imp	act of Fertilization Strategy on Crop Production and Biogas Potential	152
4.	Imp	act of Fertilization Strategy on Nutrient Dynamics in the Environment	153
	4.1	Nitrogen Dynamics	153
		4.1.1 Nitrogen Use Efficiency, Plant Uptake, and Soil NO ₃ –N Residue	153
		4.1.2 Nitrogen Balances and Apparent Recovery	154

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137

Céline Vaneeckhaute et al.

-		
	4.2 Phosphorus Dynamics	157
	4.2.1 Phosphorus Use Efficiency, Plant Uptake, and Soil Availability	157
	4.2.2 Phosphorus Balances and Apparent Recovery	163
	4.3 Potassium	167
	4.3.1 Potassium Use Efficiency, Plant Uptake, and Soil Availability	167
	4.3.2 Potassium Balances and Apparent Recovery	168
	4.4 Dynamics of Secondary Macronutrients	168
5.	Impact of Fertilization Strategy on General Soil Quality	170
6.	Fertilizer Markets, Legislations, and Recommendations	175
7.	Economic and Ecological Evaluation	176
8.	Conclusions and Further Research	177
Ac	cknowledgments	177
Re	eferences	178

Abstract

138

Anaerobic digestion is an established technology to convert biowaste into renewable energy and nutrient-rich digestates. Nutrient recovery from these digestates as renewable fertilizers with high-nutrient use efficiency or as P-poor alternative fertilizers has gained increased attention in order to meet both regulatory drivers and market demands, while producing an internal revenue source. However, until now, this opportunity has been difficult to realize due to obstacles and inconsistencies in legislative systems, and lack of insights into the composition and properties of these products, as well as in their impact on crop yield and soil quality. The aim of this review is to prove the effectiveness of fertilization strategies using biodigestion waste derivatives as compared to conventional practices using animal manure and chemical fertilizers. As adequate field-scale data are lacking in the literature, a ground-breaking three-year field trial has been performed. The value and impact of these biobased fertilizers are demonstrated by the use of high-level performance indicators measuring farming pressure on the environment and how that pressure is changing over time. Bottlenecks for marketing and legislative constraints are discussed. An economic and ecological evaluation is also assessed. The proof of concept provided in this chapter should help to better classify these biobased products into fertilizer and environmental legislations and serve as a support to stimulate their use in the farming community. Moreover, this review should stimulate and provide guidance for further field research on biobased fertilizers, which is highly essential in the development and implementation of more effective and environmentally friendly farming strategies.

ABBREVIATIONS

AmS Ammonium Sulfate
CaUE Calcium Use Efficiency
DW Dry Weight
EC Electrical Conductivity
FAO Food and Agricultural Organization of the United Nations
FMD Flemish Manure Decree

Biobased Mineral Fertilizers

FW Fresh Weight
KUE Potassium Use Efficiency
LF Liquid Fraction
MgUE Magnesium Use Efficiency
NUE Nitrogen Use Efficiency
OC Organic Carbon
PUE Phosphorus Use Efficiency
SAR Sodium Adsorption Ratio
Sc Scenario
SOC Soil Organic Carbon
SUE Sulfurous Use Efficiency

1. INTRODUCTION

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 efficiency across all sectors simultaneously provide the foundation for a greener economy to produce more food and energy while reducing environmental pollution (Drinkwater and Snapp, 2007; Gourley et al., 2012; Sutton et al., 2013).

Anaerobic (co)digestion is an established, environmentally friendly and efficient technology to convert animal manure, wastewater sludge, organic biological waste, and/or energy crops into renewable energy and digestates rich in bioavailable (macro)nutrients (Fehrenbach et al., 2008). Despite its great potential, the further sustainable development of this technique is currently hindered, because these digestates need to be processed further and cannot or only sparingly be returned to agricultural land in their crude unprocessed form, especially in high-nutrient regions due to legislative constraints (Lemmens et al., 2007). The recovery of nutrients from these digestates for reuse as renewable mineral fertilizers in agriculture has become an important challenge in the transition toward a biobased economy, both from an ecological and an economic perspective (Vaneeckhaute et al., 2013a).

In general, digestate processing starts with the separation into a liquid and thick fraction. Most of the N and K end up in the liquid fraction (LF), while most of the organic matter, P, Ca, and Mg end up in the thick fraction. In light of P levels for soil application that become stricter in environmental legislations, reuse of this P-poor LF might be of important interest in the near future. In addition, an interesting path for N recovery at manure- and

digestate-processing facilities is the absorption of gaseous ammonia (NH₃) in H_2SO_4 using an acidic air scrubber, for example, after air stripping of NH₃ from the LF. Through an economic and ecological study of different biobased and conventional fertilization scenarios, Vaneeckhaute et al. (2013a) concluded that the resulting $(NH_4)_2SO_4$ solution has high potential for reuse as a formulated N-S fertilizer, thereby providing a sustainable alternative for fossil reserve-based mineral fertilizers. However, until now, the opportunity to implement completely biobased fertilization scenarios has been difficult to realize due to obstacles and inconsistencies in (national) legislative systems, and lack of insights into the composition and properties of these recovered products, as well as in their impact on crop yield and soil quality. Field-scale assessments are lacking in the literature, though essential to demonstrate the fertilizer value of (a formulated combination of) these products in terms of plant nutrient availability and their applicability for several cropping systems. In addition, field trials are essential to evaluate the effective environmental impact of recovered biobased products (Johnston, 1997).

Because of these constraints, a field trial has been conducted in 2011-2012 aiming to evaluate the impact of using biodigestion waste derivatives as substitute for fossil reserve-based chemical fertilizers and/or as P-poor equivalent for animal manure on soil and crop production (Vaneeckhaute et al., 2013b). The products used in this field trial were the LF of digestate following mechanical separation, recovered (NH₄)₂SO₄ wastewater from an acidic air scrubber for NH₃ removal, and a mixture of raw digestate and LF digestate. In order to evaluate the potential environmental impact when using these biobased products in agriculture, nutrient balances were assessed and the physicochemical soil quality, including the nitrate residue, leaching, salt content, pH, organic carbon (OC) content, sodium adsorption ratio (SAR), as well as P and heavy metal accumulation, was evaluated. The biogas yield of the harvested energy crops was also determined by means of an anaerobic digestion batch test. As such, the nutrients coming from the digestate are cradle-to-cradle recycled to the anaerobic digestion plant, and nutrient cycles are maximally closed (Figure 4.1). Finally, an economic and ecological evaluation was conducted for the use of these products as compared to the conventional scenario using animal manure additionally supplied with chemical fertilizers (Vaneeckhaute et al., 2013a). Hereby due attention was given to the fertilization cost for the various scenarios as well as to the assessment of their carbon footprint and nutrient losses.

Throughout the first study year, it was observed that the use of biodigestion waste derivatives as substitutes for chemical fertilizers and/or animal manure in agriculture can be beneficial from an environmental point of view, as well as

Biobased Mineral Fertilizers



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

from an economic perspective. In order to validate the obtained results, the field trial was repeated in 2012–2013 and 2013–2014 at the same site.

This chapter reviews current knowledge on the fertilizer potential of biodigestion waste derivatives and their environmental impact, based on the results of this ground-breaking field experiment. Where available, observations from the literature were added. The impact on soil fertility and soil quality of biobased fertilization strategies using digestate (mixtures) and recovered (NH₄)₂SO₄ compared to conventional fertilization using animal manure additionally supplied with chemical fertilizers is demonstrated by the use of high-level performance indicators measuring farming pressure on the environment and how that pressure is changing over time. In addition, nutrient and OC dynamics are modeled in the longer term. Fertilizer markets, legislations, and economics are also discussed. As such, this review should help to better classify these biobased products in fertilizer and environmental legislations and serve as a support to stimulate their use in the farming community. Moreover, the reuse of biodigestion waste can improve the economic viability of anaerobic digestion plants, especially in highnutrient regions, thereby meeting both regulatory drivers and producing an internal revenue source, hence turning the waste and energy problem into an economic opportunity. Finally, this chapter aims to stimulate and provide guidance for further field research on biobased fertilizers, which is highly essential in the development and implementation of more effective and environmentally friendly farming strategies.

Céline Vaneeckhaute et al.

2. FIELD EXPERIMENTS: GUIDELINES FOR GOOD PRACTICE

This section provides guidelines for conducting field trials aiming to prove the effectiveness of biobased fertilizers as compared to traditional fertilization scenarios, using animal manure and chemical fertilizers. To this end the best management practices used in the field tests performed to date using biodigestion waste are presented.

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. The soil characteristics before the field trial (April 21, 2011) can be found in Table 4.1.

Based on the soil characteristics, the advice given on fertilizer requirements was formulated at 150 kg effective N ha⁻¹, 180 kg K₂O ha⁻¹, and 30 kg MgO ha⁻¹ in 2011, and 135, 250, and 60 kg ha⁻¹, respectively, in

Parameter	Soil layer (cm)	Analysis	Target zone	Limit	Evaluation
Texture	0–23	sandy-loam	_	_	_
Density (g kg ⁻¹)	0-30	1.45	-	-	-
	30-90	1.5	-	-	-
pH (KCl)	0–23	7.0	5.5-6	5.3	Favourable
OC ^a (% on DW ^b)	0–23	1.9	1.3-1.6	0.9	Favourable
Ca (mg kg ⁻¹ DW ^b)	0–23	5618	1020	2680	High
K (mg kg ⁻¹ DW ^b)	0–23	121	140-230	-	Rather low
Mg (mg kg ⁻¹ DW ^b)	0–23	214	90-160	-	Favourable
Na (mg kg ⁻¹ DW ^b)	0–23	20	31-67	-	Rather low
P (mg kg ⁻¹ DW ^b)	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	-	-	-

 Table 4.1
 Soil characteristics before fertilization (April 21, 2011)

^aOC = Organic Carbon

^bDW = Dry Weight

2012. The amount of effective N for organic fertilizers was set at 60% of the total N content, as described in the Flemish manure decree (FMD, 2011). Further, for P_2O_5 , the maximum allowable dosage of 80 kg ha⁻¹ for the cultivation of maize was respected (FMD, 2011).

Eight different fertilization scenarios (Sc1–8) were tested in four replicate subplots (n = 4) spread in the field (Vaneeckhaute et al., 2013b), in order to minimize the potential influence of variable soil conditions on the results (Table 4.2).

Group 0 (Sc1) represents the reference scenario in which only animal manure and chemical fertilizers (N, K2O) were used. In Group I, chemical N was partially (Sc2) or completely (Sc3) substituted by wastewater from an acidic air scrubber. In group II (Sc4-6), animal manure was converted into digestate through anaerobic (co)digestion, and digestate mixtures were spread to the field, with partial, complete, or without the simultaneous substitution of chemical N by air scrubber water. While P₂O₅ was the limiting factor for manure application in groups 0 and I, N became the limiting factor in group II, as the ratio of P_2O_5 over effective N is in general lower for digestate compared to animal manure. Based on the product characterizations, an optimal combination was sought between raw digestate and its LF after mechanical separation, in order to provide a concentrated mixture with a high effective N content, but low P_2O_5 content, thereby reducing chemical fertilizer N requirements. In 2011, a mixture of 50 vol.% raw digestate and 50 vol.% LF digestate was used for this purpose. In 2012, the use of a mixture containing 40 vol.% raw digestate and 60 vol.% LF digestate (Sc4) could completely fulfill the fertilizer N requirements, without the addition of chemical N and without exceeding the maximum allowable P2O5 level. Therefore, in Sc5-6, the raw digestate (100 vol.%) was used as such, with partial or complete substitution of chemical N by air scrubber water. Finally, in group III (Sc7-8), 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.

It should be remarked that the actual rates of application (based on product characterizations at the moment of fertilizer application) were sometimes different from the intended doses (based on preliminary product characterizations) 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 Sc5–6 was higher than intended due to technical issues.

Table 4. (kg ha ⁻¹);	2 Eig	ht diffe age of l	erent fertiliza 2 ₂ 0 ₅ (kg ha ⁻¹ Chemical	ation scenari); Values rep Chemical	ios (Sc) expre vresent the in Air	ssed as effect itended dosa Animal	tive nitrogen (ge; Values bet Digestate	kg ha ⁻¹); Additior ween brackets re Raw	al application c present the act LF	of chemical l ual dosage Chemical	<20 20
Group ^a	Š	Year	start N	Z	scrubber N	manure N	mixture N	digestate N	digestate N	K ₂ O	P ₂ O ₅ b
0		2011	25	29		96 (98)				78	80 (1 <i>08)</i> ^e
0		2012	30	30		75 (58)				213	80 (45)
I	0	2011	25		29	96 (98)				78	$80(108)^{e}$
I		2012	30	-	30	75 (58)				213	80 (45)
I	З	2011			54	96 (98)				78	80 (108) ^e
I		2012		_	60	75 (58)				213	80 (45)
II	4	2011	25	18			107^{c} (105)			29	80 (75)
II		2012					134 ^d (139)			0	80 (101) ^e
II	Ŋ	2011	25		18		$107^{c}(105)$			29	80 (75)
II		2012	33					$102 (141)^{e}$		46	$61 (159)^{e}$
II	9	2011		-	43		$107^{c}(105)$			29	80 (75)
II		2012		-	33			$102 \ (141)^e$		46	$61 (159)^{e}$
III		2011	25			84 (86)			35 (36)	33	77 (105) ^e
III		2012	33			67 (52)			35 (39)	121	76 (49)
III	×	2011				78 (80)			59(60)	0	76 (105) ^e
III		2012		-	33	67 (52)			35 (39)	121	76 (49)
I = Substi or withou manure w aGroup: 0 bNo chem cMixture (dMixture e	tution t the G ith or ith or = Re of $50 \cdot 0$ of $50 \cdot 0$ of $60 \cdot 0$ of allow	t of chen substitut without ference ' was use vol. % ra vol. % Ll wable fer	nical fertilizer ion of chemics t the substitution = conventiona d w digestate and F digestate and rillization level	N by air scrul al fertilizer N on of chemica al fertilization d 50 vol. % raw l was exceeded	bber water, II = by air scrubber I fertilizer N by ² digestate v digestate I.	Anaerobic dige water, III = Us 7 air scrubber w	stion of animal 1 e of the liquid fr ater	nanure and field ap action (LF) of diges	plication of digesta tate as P-poor ferti	te with comp lizer in additi	ete, partial on to animal

Advances in Agronomy, First Edition, 2014, 137-180

Céline Vaneeckhaute et al.

Biobased Mineral Fertilizers

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 with respect to FMD (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 4.3).

Digestate and LF digestate after mechanical separation were sampled at the site of Sap Eneco Energy, Aalter, Belgium. It concerns an anaerobic codigestion plant with an influent feed 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, and acidic air scrubber water was collected at the piggery of Ladevo BVBA, Ruiselede, Belgium (2011) and Senergho, Hooglede, Belgium (2012). Two replicate samples of each waste stream were collected each time 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 NaOH (1 L NaOH per 200 L acidic wastewater, based on laboratory experiments), whereas in 2012, it 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.

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 4.4; RMI, 2014).

On May 5, 2011, energy maize of the species *Atletico* (breeder: KWS; Food and Agricultural Organization of the United Nations (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; FAO Ripeness Index: 260) was sown at a seed density of 100,000 ha⁻¹. Pig manure, digestate, and LF digestate were applied to the field by the use of pc controlled injection (Bocotrans, NL), whereas the pH-adjusted air scrubber water and the chemical fertilizers, ammonium-nitrate (27% N), and patent-kali (30% K₂O and 10% MgO) were applied to the plots by hand in order to ensure high precision of the applied dosage.

145

			Anim		Ľ	linet	ote		Daw		lici	id fra	-tion		termotoe	, L
	Year		manu	re a		nixtu	re ^a	diç	gestä	ite	di	iu II a igesta	te	Hd)	astewat I-adjust	ed)
DW (%)	2011	10	+1	0	6.2	+1	0.0	N/A			2.5	+1	0	QN	+1	Ŋ
	2012	4.3	+1	0.0	7.1	+1	0.0	14	+1	0.0	2.5	+1	0.0	QN	+1	QZ
OC (%)	2011	40	+1	0	36	+1	0	N/A			31	+1	0		ą	
	2012	28	+1	0	34	+1	0	32	+1	0	35	+1	0		QZ	
EC (mS cm ^{-1})	2011	35	+1	0	29	+1	0	N/A			34	+1	0	135	+1	0
	2012	31	+1	0	35	+1	0	36	+1	0	34	+1	0	208	+1	0
Hd	2011	7.8	+1	0.0	8.2	+1	0.0	N/A			7.4	+1	0	9.0	+1	0.0
	2012	7.7	+1	0.0	8.0	+1	0.0	8.3	+	0.0	7.8	+1	0.0	6.9	+1	0.0
Total N (g kg ^{-1} FW)	2011	8.1	+1	0.0	4.7	+1	0.0	N/A			3.6	+1	0.0	27	+1	0
)	2012	5.3	+1	0.0	5.6	+1	0.0	7.4	+1	0.0	4.3	+1	0.0	42	+1	0
NH_4 -N (g kg ⁻¹ FW)	2011	5.6	+1	0.0	3.1	+1	0.1	N/A			2.8	+1	0.0	27	+1	0
	2012	3.2	+1	0.1	3.7	+1	0.1	4.5	+1	0.0	3.2	+1	0.1	41	+1	4
P_2O_5 (g kg ⁻¹ FW)	2011	5.4	+1	0.2	2.0	+1	0.3	N/A			5.6	+1	0.3		QZ	
	2012	2.4	+1	0.1	2.3	+1	0.2	5.0	+1	0.4	0.57	+1	0.02		QZ	
K_2O (g kg ⁻¹ FW)	2011	4.4	+1	0.0	2.6	+1	0.5	N/A			3.5	+1	QN		QZ	
	2012	2.9	+1	1.7	4.0	+1	4.0	5.5	+1	3.0	3.0	+1	1.6		QZ	
Ca (g kg ⁻¹ FW)	2011	3.0	+1	0.0	1.3	+1	0.3	N/A			0.11	+1	0.00		QZ	
	2012	1.9	+1	0.0	2.1	+1	0.0	6.5	+1	0.0	0.37	+1	0.00		ŊŊ	
Mg (g kg ⁻¹ FW)	2011	1.3	+1	0.0	0.34	+1	0.04	N/A			0.016	+1	0.000		QZ	
	2012	1.1	+1	0.0	0.86	+1	0.04	2.0	+1	0.1	0.10	+1	0.01		QZ	
Na (g kg ⁻¹ FW)	2011	2.2	+1	0.0	2.0	+1	0.5	N/A			3.1	+1	0.0		QZ	
	2012	2.2	+1	0.0	3.4	+1	0.1	3.8	+1	0.1	3.1	+1	0.0		QZ	
S (g kg ⁻¹ FW)	2011	0.80	+1	0.09	0.39	+1	0.01	N/A			0.11	+1	0.01	31	+1	0
	2012	0.42	+1	0.00	0.84	+1	0.30	1.7	+1	0.1	0.27	+1	0.02	48	+1	0

Céline Vaneeckhaute et al.

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Advances in Agronomy, First Edition, 2014, 137-180

146

Biobased Mineral Fertilizers

Table 4.4 Weather conditions in the West of Flanders in 2011 and 2012, and degree of
abnormality by means of the SC based on the reference period 1833–2010 (RMI, 2014)MonthAverage temperature (°C)Total rainfall (mm)

		-	-					
	2011	SC	2012	SC	2011	SC	2012	SC
January	4.0	n	5.1	n	90.5	n	86.4	n
February	5.4	n	3.7	va	44.0	n	30	n
March	7.7	n	8.9	va	22.4	е	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	а
July	16	e	17.3	n	55.6	n	115.7	а
August	17.3	n	19.2	n	189.3	ve	22.5	а
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	а	7.1	n	8.5	ve	44.7	а
December	6.1	e	5.1	n	152.1	а	172.7	ve

SC = statistical characteristic, n = normal, a = abnormal (averages one time in 6 years), va = very abnormal (averages one time in 10 years), e = exceptional (averages one time in 30 years), ve = very exceptional (averages one time in 100 years).

Samples of soils and plants were taken in April, July, September, October (harvest), and November 2011, as well as in April, August, and November (harvest) 2012. 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 the use of trimming scissors in a rectangle (4.5×3.5 m) around the bore holes. 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 °C–5 °C) for separate analysis. The harvest was conducted by the use of a maize chopper and the crop fresh weight (FW) yield was determined at the field.

2.3 Physicochemical Analysis

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., FR). Conductivity and pH were determined potentiometrically using a WTW-LF537 (DE) conductivity electrode and an Orion-520A pH-meter (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 (Macherey–Nagel 640 m, DE). Total N content was determined using a Kjeltec system 1002 distilling unit (Gerhardt Vapodest,

DE) after digestion of the sample in a sulfuric-salicylic acid mixture. The captured ammonia in the distillate was then titrated with $0.01 \text{ mol } L^{-1} \text{ HCl in}$ the presence of a methyl red bromocresol green mixed indicator (van Ranst et al., 1999). Ammonium was determined using a Kjeltec-1002 distilling unit (Gerhardt Vapodest, DE) after the addition of MgO to the sample and subsequent titration (van Ranst et al., 1999). Total P was determined using the colorimetric method of Scheel (1936) after wet digestion of the liquid samples using nitric acid (HNO₃) and hydrogen peroxide (H₂O₂). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, UK). Ca, Mg, and heavy metals were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian Vista MPX, USA) (van Ranst et al., 1999), whereas Na and K were analyzed using a flame photometer (Eppendorf ELEX6361, DE), both after wet digestion of the samples (2.5 g sample +2 mL HNO₃ + 1 mL H₂O₂) (van Ranst et al., 1999). NO_3^- and SO_4^{2-} were analyzed using ionic chromatography (Metrohm-761, CH) after centrifugation and subsequent vacuum filtration (0.45 µm) of the LF. Total S was analyzed as described by Weaver et al. (1994). Plant available amounts of macronutrients were determined after ammonium lactate/acetic acid extraction of the samples (NSI, 2010).

2.3.2 Soil Analysis

Soil samples were dried at 50 °C in a soil oven (EU 170, Jouan s.a., FR) for a minimum of 72 h. The OC was determined after incineration of the dry samples for 4 h at 550 °C in a muffle furnace (Nabertherm, 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). Soil conductivity was measured with a WTW-LF537 (DE) electrode after equilibration for 30 min in deionized water at a 5/1 liquid to dry sample ratio and subsequent filtration (Macherey-Nagel 640 m, DE). To determine the actual soil pH (pH-H₂O), 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} 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 glass electrode (Orion-520A, USA). N in the soil was determined using a Kjeldahl destruction, while P was determined using the method of Scheel (1936), as described in Section 2.3.1. NH₄ and NO₃ were determined using an AA3 autoanalyzer (BRAN + LUEBBE, DE) after extraction with KCl. Na, K, Ca, Mg, and

Biobased Mineral Fertilizers

metals (As, Cd, Cr, Cu, Hg, Pb, Ni, Zn) were analyzed using ICP–OES (Varian Vista MPX, USA) after aqua regia digestion for the determination of total amounts (van Ranst et al., 1999) and after ammonium lactate/acetic acid extraction for the determination of plant available amounts (NSI, 2010). Total S content was determined using the same ICP–OES after microwave destruction. Therefore, 1 g of dry soil was mixed with 2.5 mL HClO₄ and 3.5 mL HNO₃, allowed to rest for 12 h and heated in a microwave (CEM MARS 5, BE) during 40 min at 100 °C and 600 W. The SAR, which refers to the ratio of the monovalent cation Na⁺ to the divalent cations Ca²⁺ and Mg²⁺, was determined as described by Hillel (2008).

2.3.3 Plant Analysis

Plant samples collected in the field were weighed for the determination of the FW biomass yield and oven-dried at 55 °C for determination of the DW content. The dry samples were ground to pass a 1-mm sieve (Retsch SM-2000, DE) and incinerated at 550 °C for 4 h in order to determine the OC content, as described in Section 2.3.2. Total N was determined using the Kjeldahl method (Section 2.3.1) and total P was determined using the method ofVanadate (van Ranst et al., 1999) after incineration of the samples for 4 h at 450 °C and digestion of the residual ash (1 g ash + 5 ml 3 mol HNO₃ L⁻¹ + 5 ml 6 mol HNO₃ L⁻¹). Total amounts of Na, K, Ca, Mg, and metals in the digested samples were determined using ICP–OES (Varian Vista MPX, USA). Total S was determined using the same ICP–OES after microwave destruction of 0.2 g dry and ground plant sample.

2.4 Performance Indicator Calculations

2.4.1 Nutrient Use Efficiency

The nutrient use efficiency (%) was determined using the following equation:

Nutrient use efficiency $(\%) = \frac{Crop \ nutrient \ uptake \ (kg \ ha^{-1})}{Nutrient \ supply \ through \ fertilization \ (kg \ ha^{-1})}$

It gives an indication of the effectiveness of the fertilizers applied (organic + chemical), without taking into account the amount of soil available nutrients in the field 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.

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, which can impact on soil, air, and water quality and on climate change (Defra, 2011; Parn et al., 2012). In this study, nutrient balances were assessed in two different ways. First, the apparent nutrient surplus was calculated using the following equation:

Apparent nutrient surplus $(\text{kg ha}^{-1}) = nutrient inputs (\text{kg ha}^{-1}) - crop nutrient uptake at harvest (\text{kg ha}^{-1})$

in which the "inputs" refer to the nutrient supply by fertilization and natural deposition, that is, 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. Second, the actual environmental pollution was determined by taking in account the measured changes in soil nutrient reserves over time. It was calculated using the following equation:

Actual pollution index (kg ha⁻¹)

= soil nutrient reserves before fertilization (kg ha⁻¹) + nutrient inputs (kg ha⁻¹) - soil nutrient reserves at harvest (kg ha⁻¹) -

crop nutrient uptake at harvest (kg ha⁻¹)

- = soil nutrient reserves before fertilization (kg ha⁻¹)
 - soil nutrient reserves at harvest (kg ha⁻¹) + apparent nutrient surplus (kg ha⁻¹)

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:

Apparent recovery (%) =

 $\frac{\text{crop nutrient uptake at harvest (kg ha^{-1})}}{\text{soil nutrient reserves before fertilization (kg ha^{-1}) + nutrient inputs (kg ha^{-1})}}$

in which the "inputs" refer again to the nutrient supply by fertilization and natural deposition.

Biobased Mineral Fertilizers

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). The physicochemical product, plant, and soil analyses conducted in this study, as well as the particular weather conditions for this site in 2011 and 2012, were used as input to the model. The nutrient balances obtained are thus specific for each scenario. Simulations were conducted over 3 and 30 years. Carbon dynamics in the long term were determined using the "koolstofsimulator" software version 20110706 (LNE, 2006).

2.6 Statistical Analysis

Statistical analyses were performed using SPSS Statistics 21. A one-way analysis of variance (ANOVA) model was used to determine the effect of fertilizer type on plant yield and DW content, plant nutrient uptake, nutrient soil contents, and soil quality parameters. 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 homoscedasticity was found, the significance of effects was tested by the use of an F-test and post hoc pairwise comparisons were conducted using Tukey's honest significant difference test ($\alpha = 0.05$; n = 4). When no homoscedasticity 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 nonparametric Kruskal–Wallis test was applied instead of the one-way ANOVA. Significant parameter correlations were determined using the Pearson correlation coefficient (r).

2.7 Analysis of Biogas Potential

Homogenized subsamples of the harvested plant material in 2011 were taken for determination of the biogas potential. The four replicate subsamples per treatment were then mixed and again homogenized. The biogas potential of energy maize was determined in the biogas laboratory of the University College of West Flanders (Innolab), Kortrijk, Belgium, via a mesophyllic batch test. A control with inoculum sludge and a flask with an equal amount of sludge to which a known amount of dry grinded biomass was added were prepared in duplicate. The organic DW 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.

3. IMPACT OF FERTILIZATION STRATEGY ON CROP PRODUCTION AND BIOGAS POTENTIAL

Over the whole experimental period, the average biomass yields, on both FW and DW content, were the highest when LF digestate was used as P-poor fertilizer in addition to animal manure (Sc7–8).This effect was significant at the harvest in 2012 (Sc4 < 1/7/8; Sc5 < 8) and in 2011 (Sc2 < 5/7) (Figure 4.2). The average DW content at the harvest was 28 ± 1% in 2011 and 29 ± 0% in 2012 (Figure 4.3). Hence, energy maize was suitable for biogas production (desired: 28–36%; Matjaz et al., 2010). Biogas batch tests in 2011 showed little effect (p = 0.11) of the fertilizers applied on the biogas potential of the harvested crops (mean ± SD = 307 ± 13 m³ CH₄ t⁻¹ DW). However, the energetic potential per hectare was higher for Sc4–7 (=use of digestate) compared to that for Sc1–3 (=use of manure) due to the



Figure 4.2 FW biomass yield (t ha⁻¹) as a function of time for the eight different fertilization scenarios (n = 4); *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons; *significant difference at the 5% level.



Figure 4.3 DW content (%) as a function of time for the eight different fertilization scenarios (n = 4); *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons; *significant difference at the 5% level.

higher average FW biomass yield in these scenarios (Vaneeckhaute et al., 2013b).

4. IMPACT OF FERTILIZATION STRATEGY ON NUTRIENT DYNAMICS IN THE ENVIRONMENT

4.1 Nitrogen Dynamics

4.1.1 Nitrogen Use Efficiency, Plant Uptake, and Soil NO₃-N Residue

The NO₃–N residue in the soil profile (0–90 cm) between October 1 and November 15 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 NO₃–N residues. During this field trial, no significant differences in the NO₃–N residue in the soil were observed between the treatments, except in November 2011 (Figure 4.4: Sc5 > 2/4/6/8).

It should, however, be remarked that at this time all scenarios exceeded the Flemish environmental standard of 90 kg of NO_3 –N ha⁻¹ due to exceptional weather conditions, characterized by an extremely dry spring, wet summer, and hot autumn (Table 4.4; Vaneeckhaute et al., 2013b).

154

Céline Vaneeckhaute et al.



Figure 4.4 Soil NO₃–N residue as a function of time for the eight different fertilization scenarios (n = 4); Red line indicates the Flemish environmental standard of 90 kg NO₃–N ha⁻¹ between October 1 and November 15; *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons; *significant difference at the 5% level. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this book.)

In November 2012, all scenarios showed a NO₃–N residue below the limit of 90 kg ha⁻¹. Also, no significant differences in total soil N content (0–30 cm) were determined during the field trial (Table 4.5). Nevertheless, there was a strong significant effect of the fertilizers applied on the N use efficiency (NUE; Figure 4.5) and the plant N uptake (kg ha⁻¹; Table 4.6) in 2012. The scenarios in which chemical fertilizer N was completely replaced by air scrubber water (Sc3/8) showed the highest NUE and plant N uptake. Further, a strong significant correlation was found between the NUE and the DW biomass yield (r = 0.801; p \approx 0.00).

4.1.2 Nitrogen Balances and Apparent Recovery

At 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 Sc5 and 6 was higher than intended (Table 4.2). Therefore, for 2012, only Sc1, 2, and 3 will be compared with each other, and Sc7 with Sc8.

Biobased Mineral Fertilizers

N (t ha ⁻¹) $\mathbf{p} = 0.97$ $\mathbf{p} = 0.89$ $\mathbf{p} = 0.99$ $\mathbf{p} = 0.845$ $\mathbf{p} = 0.71$ 1 7.2 ± 0.6 7.2 ± 0.6 7.2 ± 0.6 7.4 ± 0.9 7.3 ± 1 2 7.2 ± 0.6 7.2 ± 0.6 7.4 ± 0.7 7.9 ± 0.9 6.4 ± 2 3 7.0 ± 0.2 7.2 ± 0.4 7.3 ± 0.5 8.1 ± 0.8 9.5 ± 0 4 7.2 ± 0.4 7.2 ± 0.6 7.3 ± 0.6 7.9 ± 1.6 9.0 ± 1	114 .8 .6 .8 .9 .0 .1 .2 .9 327
17.2 \pm 0.67.2 \pm 0.67.2 \pm 0.67.2 \pm 0.77.4 \pm 0.97.3 \pm 127.2 \pm 0.67.2 \pm 0.67.4 \pm 0.77.9 \pm 0.96.4 \pm 237.0 \pm 0.27.2 \pm 0.47.3 \pm 0.58.1 \pm 0.89.5 \pm 047.2 \pm 0.47.3 \pm 0.67.3 \pm 0.67.9 \pm 1.69.0 \pm 1	.8 .6 .8 .9 .0 .1 .2 .9
2 7.2 ± 0.6 7.2 ± 0.6 7.4 ± 0.7 7.9 ± 0.9 6.4 ± 2 3 7.0 ± 0.2 7.2 ± 0.4 7.3 ± 0.5 8.1 ± 0.8 9.5 ± 0 4 7.2 ± 0.4 7.2 ± 0.6 7.3 ± 0.6 7.9 ± 1.6 9.0 ± 1	.6 .8 .9 .0 .1 .2 .9
3 7.0 ± 0.2 7.2 ± 0.4 7.3 ± 0.5 8.1 ± 0.8 9.5 ± 0 4 7.2 ± 0.4 7.2 ± 0.6 7.3 ± 0.6 7.9 ± 1.6 9.0 ± 1	.8 .9 .0 .1 .2 .9
4 7.2 \pm 0.4 7.2 \pm 0.6 7.3 \pm 0.6 7.9 \pm 1.6 9.0 \pm 1	.9 .0 .1 .2 .9
	.0 .1 .2 .9
5 7.0 \pm 0.9 7.3 \pm 0.6 7.4 \pm 0.7 8.1 \pm 0.9 8.8 \pm 1	.1 .2 .9 27
6 7.3 \pm 0.7 7.4 \pm 0.2 7.5 \pm 0.4 8.4 \pm 0.1 9.3 \pm 1	.2 .9 27
7 7.1 \pm 0.6 7.5 \pm 0.1 7.4 \pm 0.5 8.4 \pm 0.4 9.7 \pm 0	.9 3 27
8 6.7 \pm 0.5 7.1 \pm 0.5 7.2 \pm 0.3 7.9 \pm 0.3 9.7 \pm 0	\$27
P_2O_5 (t ha ⁻¹) p = 0.78 p = 0.89 p = 0.99 p = 0.566 p = 0.32	
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 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	
8 13 ± 2 12 ± 1 12 ± 1 12 ± 0 11 ± 1	
K_2O (t ha ⁻¹) p = 0.37 p = 0.10 p = 0.56 p = 0.997 p = 0.42	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 $1./\pm 0.1$ $1./\pm 0.4$ 2.1 ± 0.1 1.4 ± 0.3 $1./\pm 0$ S ((1) $^{-1}$) $-$ 0.97 $-$ 0.71 $-$ 0.70 $-$ 0.09($-$ - 0.71	.2
S (t ha ⁻¹) $p = 0.87$ $p = 0.71$ $p = 0.70$ $p = 0.986$ $p = 0.11$	104
$\begin{array}{cccccccccccccccccccccccccccccccccccc$.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$.2
5 1.2 ± 0.0 1.3 ± 0.1 1.3 ± 0.1 1.7 ± 0.5 1.2 ± 0	.0 2
4 1.2 ± 0.1 1.3 ± 0.1 1.2 ± 0.1 1.3 ± 0.4 1.1 ± 0 5 12 ± 0.2 12 ± 0.1 13 ± 0.2 16 ± 0.4 12 ± 0	.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$.∠ 1
7 12 ± 0.1 1.2 ± 0.1 1.3 ± 0.1 1.0 ± 0.5 1.2 ± 0.7 7 12 ± 0.1 12 ± 0.1 13 ± 0.1 15 ± 0.2 12 ± 0.1	0
$\begin{array}{c} 8 \\ 11 \pm 0.1 \\ 12 \pm 0.1 \\ 12 \pm 0.1 \\ 13 \pm 0.1 \\ 13 \pm 0.1 \\ 15 \pm 0.2 \\ 15 \pm 0.2 \\ 14 \pm 0.1 \\ 15 \pm 0.3 \\ 11 \pm 0.1 \\ 10 \pm 0.1$.0
Ca (t ha ⁻¹) $n = 0.72$ $n = 0.98$ $n = 0.96$ $n = 0.629$ $n = 0.72$.± 182
$\begin{array}{c} 1 \\ \mathbf{87+19} \\ \mathbf{85+13} \\ \mathbf{81+13} \\ \mathbf{96+26} \\ \mathbf{86+2} \end{array}$	2
$\begin{array}{c} 2 \\ 8.5 \pm 1.2 \\ 8.1 \pm 1.1 \\ 8.3 \pm 1.2 \\ 9.3 \pm 1.5 \\ 9.1 \pm 1$.7
3 8.6 ± 1.0 8.6 ± 0.7 8.3 ± 0.9 11 ± 1 12 ± 2	

 Table 4.5
 Total soil nutrient amounts in time for the eight different fertilization
 scenarios (mean \pm standard deviation; n = 4); p-values and small letters refer to

Continued

statistical analys	is using one-wa	av ANOVA and	post hoc pair	wise compari	sons—cont'd
Scenario	Jul/11	Sep/11	Oct/11	Aug/12	Nov/12
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 (t ha^{-1})	p = 0.54	p = 0.38	p = 0.63	P = 0.152	p = 0.103
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})	$p = 0.03^{a}$	p = 0.11	p = 0.38	p = 0.993	p = 0.291
1	$263 \pm 72 \text{ ab}$	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	$320 \pm 76 ab$	225 ± 21	264 ± 10	209 ± 48	257 ± 52
8	266 ± 36ab	238 ± 42	317 ± 46	204 ± 38	237 ± 74

Table 4.5 Total soil nutrient amounts in time for the eight different fertilization scenarios (mean + standard deviation: n = 4): *n*-values and small letters refer to

^aSignificant difference at the 5% level.

Model simulations with NDICEA over 3 years (Table 4.7; Figure 4.6) show that the amount of N leaching to ground and surface waters decreased significantly as more chemical N was replaced by air scrubber water (Sc3 < 1-2; Sc8 < 7), while the amount of N volatilization only slightly increased. Model simulations over 30 years predict that this effect on N leaching will even be more expressed in the longer term, while the amount of N volatilization will remain quasi equal. The latter can be remedied by use of low-emission techniques for fertilizer application.

Further, for all scenarios, the 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 4.8).

The amount of N extracted from the soil, as well as the apparent N recovery, 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



Figure 4.5 NUE (%) as a function of time for the eight different fertilization scenarios (n = 4); *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons; *significant difference at the 5% level.

scrubber water in agriculture might be the breakdown of soil organic matter, similar to that found by Minamikawa et al. (2005) for the use of chemical ammonium sulfate fertilizer. This can also explain the negative value for soil organic matter build-up obtained with model simulations (Table 4.7). However, when simulating over 30 years, it can be observed that the average organic matter breakdown was equal to that of the reference. Indeed, 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 longer term. When comparing Sc7 with Sc8, these findings can be confirmed (unpublished data).

4.2 Phosphorus Dynamics

4.2.1 Phosphorus Use Efficiency, Plant Uptake, and Soil Availability

The P use efficiency (PUE; Figure 4.7) was at each sampling moment significantly affected by the treatment. In 2011, the application of digestate with or without the substitution of chemical fertilizer N by air

Scenario	Jul/11	Sep/11	Oct/11	Aug/12	Nov/12
N (kg ha^{-1})	p = 0.11	p = 0.33	p = 0.68	$\mathbf{p} = 0^{\mathbf{a}}$	$p = 0.032^{a}$
1	119 ± 13	235 ± 26	306 ± 42	68 ± 14c	$140 \pm 23ab$
2	119 ± 12	232 ± 24	300 ± 21	69 ± 16c	157 ± 40ab
3	122 ± 13	227 ± 35	308 ± 20	$104 \pm 20a$	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	$106 \pm 40b$
8	103 ± 6	214 ± 22	305 ± 53	$100 \pm 26a$	173 ± 30ab
$\mathbf{P}_2\mathbf{O}_5$	p = 0.10	p = 0.40	p = 0.67	$p = 0.001^{a}$	$p = 0.01^{a}$
$(kg ha^{-1})$					
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	p = 0.18	p = 0.94	$p = 0.0038^{a}$	$p = 0.014^{a}$	p = 0.838
ha ⁻¹)					
1	164 ± 10	292 ± 29	$333 \pm 28c$	$189 \pm 28ab$	272 ± 92
2	143 ± 9	338 ± 58	346 ± 32b	$164 \pm 21b$	244 ± 52
3	154 ± 9	289 ± 57	352 ± 37 abc	204 ± 34 ab	199 ± 55
4	161 ± 32	304 ± 92	$420 \pm 13ab$	195 ± 20 ab	285 ± 112
5	162 ± 30	321 ± 49	$431 \pm 39a$	$196 \pm 35ab$	224 ± 61
6	176 ± 20	326 ± 44	$406 \pm 62abc$	$211 \pm 57a$	276 ± 38
7	168 ± 7	309 ± 43	$366 \pm 17abc$	$182 \pm 42ab$	254 ± 88
8	153 ± 30	314 ± 85	366 ± 17 abc	$218 \pm 33a$	246 ± 37
S (kg ha ^{-1})	$p = 0.036^{a}$	p = 0.095	p = 0.45	$p = 0.008^{a}$	$p = 0.035^{a}$
1	$6.2 \pm 0.6ab$	18 ± 2	23 ± 3	6.2 ± 0.7 ab	$14 \pm 1ab$
2	$6.3 \pm 0.4ab$	17 ± 3	23 ± 1	5.7 ± 1.7b	$15 \pm 1ab$
3	$6.4 \pm 0.5ab$	$1/\pm 3$	24 ± 2	$8.2 \pm 2.7a$	$1/\pm 2a$
4	$6.1 \pm 0.8ab$	16 ± 3	25 ± 3	7.0 ± 1.1 ab	$13 \pm 2ab$
5	$6.7 \pm 0.4ab$	13 ± 3	26 ± 3	$7.7 \pm 1.5ab$	$14 \pm 1ab$
6	$6.3 \pm 0.8ab$	14 ± 2	24 ± 1	$7.4 \pm 3.2ab$	$16 \pm 2ab$
/	$7.0 \pm 0.3a$	15 ± 4	26 ± 2	$6.1 \pm 0.8ab$	$12 \pm 2b$
8	5.4 ± 0.46	13 ± 3	26 ± 4	8.0 ± 2.0 ab	$15 \pm 2ab$
La	p = 0.17	$\mathbf{p}=0.089$	p = 0.53	$p = 0.000^{a}$	p = 0.643
(kg na ⁻)	10 ± 2	35 ± 2	48 ± 6	$17 \pm 2b$	21 ± 0
1 2	$17 \perp 2$ 16 ± 1	33 ± 2 37 ± ⊑	40 ± 0	$1/ \pm 20$ $1/ \pm 21$	21 ± 7 25 ± 2
4	10 ± 1	31 ± 3	40 <u>1</u> /	14 <u>1</u> 2D	23 ± 3

Table 4.6 Plant nutrient uptake in time for the eight different fertilization scenarios (mean \pm standard deviation; n = 4); *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons

Biobased Mineral Fertilizers

using one-way	y ANOVA and p	oost hoc pairv	wise compariso	ns—cont'd	
Scenario	Jul/11	Sep/11	Oct/11	Aug/12	Nov/12
3	12 ± 8	34 ± 5	47 ± 7	$24 \pm 5a$	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	p = 0.16	p = 0.13	p = 0.56	p = 0.184	p = 0.218
$(kg ha^{-1})$					
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	p = 0.090	p = 0.64	p = 0.56	$p = 0.038^{a}$	$p = 0.019^{a}$
(kg ha ⁻¹)					
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

 Table 4.6
 Plant nutrient uptake in time for the eight different fertilization scenarios
 (mean ± standard deviation; n = 4); p-values and small letters refer to statistical analysis

^aSignificant difference at the 5% level.

scrubber water (Group II) resulted in significantly higher PUEs, while the P dosage was the lowest (Table 4.2). However, in 2012, the PUEs were the lowest for this group, while the P dosage was the highest (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 P content seems preferable, at least in P saturated regions. As the ratio of P2O5 to effective N is in general lower for digestate derivatives than for animal manure (Table 4.3), anaerobic (co)digestion can serve as an interesting step in

maize; N-3: simulation over		Scen	ario 1			Sce	nario 2			Scei	nario 3	
	N-3	N-30	P_2O_5	K ₂ 0	N-3	N-30	P ₂ O ₅	K ₂ 0	N-3	N-30	P ₂ O ₅	K ₂ O
Manure application	186	186	76	216	186	186	76	216	186	186	76	216
Nitrogen binding	0	0			0	0			0	0		
Deposition	30	30	3	8	30	30	3	8	30	30	З	8
Total application	216	216	79	224	216	216	79	224	216	216	79	224
Removal with products	228	228	77	301	240	240	76	292	251	251	82	271
Calculated surplus	-12	-12	1	-77	-24	-24	0	-69	-36	-36	-4	-48
Volatilization	15	15			16	16			17	17		
Denitrification	9	с			IJ.	3			9	3		
Leaching	45	24			41	18			31	0		
Organic matter build-up	-50	-20			-66	-21			-82	-20		



Figure 4.6 Model simulations for scenarios 1 and 3 using NDICEA over 3 years (A) and 30 years (B). 1: Evolution of mineral N in topsoil and subsoil; 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).

the treatment of manure, in order to produce sustainable fertilizers, meanwhile providing renewable energy.

In 2012, the plant P uptake was, especially at the harvest, significantly higher when chemical fertilizers were completely substituted by air scrubber wastewater as compared to the reference (Sc3/6/8 > Sc1;Table 4.6). The higher P uptake in these scenarios may be attributed to the higher dosage of NH₄–N by the air scrubber water. Indeed, the uptake of NH⁴₄ by the roots, as well as the nitrification of NH⁴₄ into NO⁻₃ are acidifying processes, which can increase soil P mobilization and uptake in the rhizosphere (Diwani et al., 2007). Hence, the P uptake was also highly correlated to the NUE (r = 0.932; $p \approx 0.00$) and the plant N uptake (r = 0.844, p ≈ 0.00). No significant differences in total soil P₂O₅ and available soil P₂O₅ over time were observed up to now (Tables 4.5 and 4.9). Yet, there was a significant decrease in the time

Tab	le 4.8 Calcul	ated nitrogen	balance (k	g ha ⁻¹), apparen	it recovery (%), and NUE (%) in 2011	and 2012 for	the eight diff	erent fertiliza	tion
scer	arios (Sc). Av	/erage values	are marked	in bold	F		Z				
	:	Available	Manure	:	lotal	Available	Plant	Apparent	Actual	Apparent	
ы	Year	Apr	supply	Deposition	available	Nov	uptake	surplus	pollution	recovery	NUE
-	2011	29	166^{b}	30	225	70	306	-110	151	136	184
	2012	16	132	30	178	24	140	22	-15	78	106
	Average	23	149	30	202	47	223	-44	68	107	145
0	2011	29	173 ^b	30	232	80	300	-97	148	129	174
	2012	16	131	30	177	27	157	4.4	6.3	88	120
	Average	23	152	30	205	53	228	-46	77	109	147
З	2011	29	179 ^b	30	238	66	308	-09	136	130	172
	2012	11	130	30	171	25	195	-35	48	114	150
	Average	20	154	30	204	45	251	-67	92	122	161
4	2011	29	159^{b}	30	218	100	329	-140	211	151	207
	2012	11	157ª	30	198	35	146	41	-17	74	93
	Average	20	158	30	208	67	238	-50	97	113	150
5	2011	29	163 ^b	30	222	57	318	-125	152	143	195
	2012	12	175ª	30	217	29	155	50	-33	72	89
	Average	20	169	30	219	43	236	-37	60	107	142
9	2011	29	169 ^b	30	228	71	310	-112	154	136	184
	2012	11	175ª	30	216	24	165	40	-27	76	94
	Average	20	172	30	222	48	237	-36	64	106	139
	2011	29	168 ^b	30	227	71	345	-147	189	152	205
	2012	12	146 ^a	30	188	24	106	70	-58	56	73
	Average	21	157	30	208	48	226	-38	65	104	139
8	2011	29	167 ^b	30	226	56	305	-108	135	135	183
	2012	10	145 ^a	30	185	24	173	2.3	12	93	119
	Average	20	156	30	206	40	239	-53	73	114	151

Advances in Agronomy, First Edition, 2014, 137-180

Céline Vaneeckhaute et al.

Average

^aDoses exceeded the fertilization level of 135 kg of effective N ha⁻¹ in 2012. ^bDoses exceeded the fertilization level of 150 kg of effective N ha⁻¹ in 2011.



Figure 4.7 PUE, % as a function of time for the eight different fertilization scenarios (n = 4); *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons; *significant difference at the 5% level.

of total soil P₂O₅ for all scenarios (r = -0.415, p ≈ 0.00), while the amount of available P₂O₅ in the soil increased simultaneously (r = 0.420, p ≈ 0.00).

4.2.2 Phosphorus Balances and Apparent Recovery

At first, it should be remarked that in Sc5 and Sc6 the P_2O_5 doses exceeded by far the maximum allowable fertilization level of 80 kg ha⁻¹ in 2012 due to technical issues (cf. 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_5 was extracted from the soil than was supplied (Table 4.10). 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. Moreover, the more the chemical N was replaced by air scrubber wastewater, the higher the average extraction of P_2O_5 from the soil observed. The actual amount of

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Table 4.9 Available soil nutrient amounts through ammonium lactate extraction in time for the eight different fertilization scenarios (mean + standard deviation: n = 4): novalues and small letters refer to statistical analysis using one-way ANOVA and nost hor naivvise

(mean ± standard deviation; n = 4); <i>p</i> -values an	d small letters refe	r to statistical analy	/sis using one	-way ANOVA and po	ist hoc pairwise
Scenario	Apr/11	Jul/11	Oct/11	Apr/12	Aug/12	Nov/12
Extractable P_2O_5 (t ha ⁻¹)		p = 0.78	p = 0.71		p = 0.841	p = 0.312
1	2.8	2.8 ± 0.2	1.9 ± 0.4	3.3	5.6 ± 1.0	3.2 ± 2.1
2	2.8	2.6 ± 0.2	2.0 ± 0.3	3.3	5.6 ± 0.5	3.0 ± 1.9
3	2.8	2.7 ± 0.1	1.8 ± 0.1	3.3	6.1 ± 0.4	4.6 ± 0.6
4	2.8	2.8 ± 0.4	1.8 ± 0.4	3.3	5.2 ± 0.7	4.2 ± 0.8
5	2.8	2.6 ± 0.2	1.8 ± 0.4	3.3	5.9 ± 0.6	4.9 ± 0.6
6	2.8	2.8 ± 0.1	1.9 ± 0.2	3.3	5.7 ± 0.8	4.7 ± 0.4
7	2.8	2.7 ± 0.2	2.0 ± 0.1	3.3	5.7 ± 0.6	4.7 ± 0.2
8	2.8	2.5 ± 0.1	1.7 ± 0.1	3.3	5.4 ± 0.4	4.3 ± 0.2
Extractable K_2O (kg ha ⁻¹)		p = 0.18	p = 0.35		p = 0.129	p = 0.605
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
Extractable Ca (t ha ⁻¹)		p = 0.22	p = 0.40		p = 0.763	p = 0.735
1	19	11 ± 2	5.4 ± 0.9	7.3	7.7 ± 1.6	8.1 ± 1.7
2	19	11 ± 2	5.7 ± 0.4	7.3	8.0 ± 1.2	8.4 ± 1.3
3	19	10 ± 3	5.3 ± 0.4	7.3	8.7 ± 0.4	9.2 ± 0.5
4	19	10 ± 2	5.2 ± 0.8	7.3	7.4 ± 2.1	7.8 ± 2.1

Biobased Mineral Fertilizers

л.	19	12 ± 1	5.5 ± 1.0	7.3	8.9 ± 1.2	9.4 ± 1.2
6	19	11 ± 1	5.4 ± 0.3	7.3	8.3 ± 0.9	8.9 ± 1.1
7	19	10 ± 1	5.5 ± 0.5	7.3	8.2 ± 0.2	8.7 ± 0.1
8	19	10 ± 1	5.1 ± 0.3	7.3	7.7 ± 0.5	8.2 ± 0.5
Extractable Mg (kg ha^{-1})		p = 0.45	p = 0.67		p = 0.152	p = 0.445
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
л Л	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
Extractable Na (kg ha ⁻¹)		$p = 0.01^{a}$	p = 0.07		$p = 0.012^{a}$	$p = 0.015^{a}$
1	68	$173 \pm 10b$	74 ± 16	<68	$120 \pm 28b$	$126 \pm 29b$
2	68	$164 \pm 66ab$	119 ± 53	<68	$123 \pm 1b$	$130 \pm 5ab$
3	68	$165 \pm 49ab$	84 ± 10	<68	$141 \pm 9ab$	$149 \pm 7ab$
4	68	$152 \pm 4ab$	104 ± 19	<68	$169 \pm 40ab$	$177 \pm 40ab$
С	68	$329 \pm 88a$	102 ± 22	<68	$204 \pm 45a$	$215 \pm 51a$
6	68	$251 \pm 49ab$	112 ± 29	<68	$156 \pm 14ab$	$167 \pm 20ab$
7	68	$267 \pm 106ab$	128 ± 27	<68	$147 \pm 13ab$	$155 \pm 13ab$
00	68	$242 \pm 40ab$	122 ± 30	<68	$178 \pm 13ab$	$188 \pm 15ab$
^a Significant difference at the 5% level.						

Advances in Agronomy, First Edition, 2014, 137-180

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Table 4.10 Phosphorus balance (kg P₂O₅ ha⁻¹), apparent recovery (%), and PUE (%) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Average values are marked in bold

		Available	Manure		Total	Available	Plant	Apparent	Actual	Apparent	
Sc	Year	Apr	supply	Deposition	available	Nov	uptake	surplus	pollution	recovery	PUE
-	2011	6391	108ª	3	6502	1890	134	-23	-4477	2.1	121
	2012	7503	44	3	7550	3159	96	-49	-4295	1.3	203
	Average	6947	76	3	7026	2525	115	-36	-4386	1.7	162
0	2011	6391	108^{a}	3	6502	1965	128	-17	-4409	2.0	115
	2012	7503	44	3	7550	3027	116	-69	-4407	1.5	246
	Average	6947	76	3	7026	2496	122	-43	-4408	1.8	181
3	2011	6391	108ª	3	6502	1842	135	-23	-4526	2.1	121
	2012	7503	44	3	7550	4607	155	-108	-2788	2.1	330
	Average	6947	76	3	7026	3224	145	-66	-3657	2.1	225
4	2011	6391	74	3	6468	1751	141	-63	-4576	2.2	182
	2012	7503	98 <mark>a</mark>	3	7604	4246	106	-5.2	-3251	1.4	105
	Average	6947	86 ^a	3	7036	2999	123	-34	-3914	1.8	144
ŝ	2011	6391	74	3	6468	1824	146	-69	-4498	2.3	189
	2012	7503	159ª	3	7665	4936	124	38	-2604	1.6	77
	Average	6947	117 ^a	3	7067	3380	135	-15	-3551	1.9	133
9	2011	6391	74	3	6468	1882	139	-62	-4446	2.2	181
	2012	7503	159ª	3	7665	4667	153	9.3	-2845	2.0	94
	Average	6947	117ª	3	7067	3275	146	-27	-3646	2.1	137
~	2011	6391	105^{a}	3	6499	1965	152	-44	-4381	2.3	141
	2012	7503	48	3	7554	4685	118	-67	-2751	1.6	230
	Average	6947	76	3	7026	3325	135	-55	-3566	2.0	186
ø	2011	6391	105^{a}	3	6499	1707	141	-33	-4651	2.2	131
	2012	7503	48	3	7554	4304	153	-102	-3097	2.0	301
	Average	6947	76	3	7026	3005	147	-68	-3874	2.1	216

Céline Vaneeckhaute et al.

^aValues exceed the maximum allowable dosage of $80~{\rm kg}~{\rm P}_2{\rm O}_5~{\rm ha}^{-1}.$

Advances in Agronomy, First Edition, 2014, 137-180

166

 P_2O_5 leaching also seems to lower when more air scrubber water was used, while the apparent P recovery was higher. Interestingly, when comparing Sc1 with Sc7, 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 P_2O_5 recovery.

4.3 Potassium

4.3.1 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 Sc4–8 (Table 4.2) as the ratio of K_2O to effective N was higher for digestate and its LF as compared to animal manure (Table 4.3). Nevertheless, when using digestates or LF digestates (Sc4–8), the potassium use efficiency (KUE; Figure 4.8) was significantly higher than in conventional scenarios using animal manure additionally supplied with chemical K_2O (Sc1–3), both in 2011 and 2012. This



Error bars: +/- 1 SD

Figure 4.8 KUE, % as a function of time for the eight different fertilization scenarios (n = 4); *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons; *significant difference at the 5% level.

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 substitution may result in significant ecological and economic benefits for the farmer (Vaneeckhaute et al., 2013a). Further, the plant K_2O uptake was significantly higher for Sc5 compared to Sc3 and for Sc3 compared to Sc2 at the harvest in 2011 (Table 4.6). In 2012, a significant effect was found in August, when Sc6 and Sc8, in which chemical N was completely replaced by air scrubber water, Showed a higher plant K_2O uptake than Sc2. Nevertheless, no significant differences were observed in the total and available soil K_2O content during the field trial (Tables 4.5 and 4.9).

4.3.2 Potassium Balances and Apparent Recovery

Nutrient balances show that the K₂O uptake by the plant (average over time) was for all scenarios higher than the available amount through manure application and deposition, resulting in a K₂O deficit on the soil balance (Table 4.7) and a positive actual pollution index (Table 4.11). The amount of K₂O extracted from the soil and the apparent recovery were much higher when digestate and/or LF digestates (Sc4-8) were used as compared to animal manure additionally supplied with high amounts of chemical K₂O (Sc1-3). On the one hand, this natural mining effect of K₂O 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 K2O fertilization will be required. The use of LF digestate that contains high amounts of soluble K₂O (Section 4.3.1), but low amounts of P_2O_5 , seems to be very useful for this purpose. Further, a valuable and easily transportable N-K fertilizer might exist in concentrates resulting from membrane filtration of LF digestate (Vaneeckhaute et al., 2012). Hence, the use of these products should be further validated at field scale.

4.4 Dynamics of Secondary Macronutrients

Next to the three principal macronutrients (N, P_2O_5 , and 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 >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

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		Available	Manure		Total	Available	Plant	Apparent	Actual	Apparent	
U	Year	Apr	supply	Deposition	available	Nov	uptake	surplus	pollution	recovery	KUE
	2011	496	181	8	686	332	333	-144	-21	49	176
	2012	304	266	8	578	597	268	5.7	288	46	98
	Average	400	224	8	632	465	301	-69	134	48	137
	2011	496	181	8	686	326	346	-157	-14	50	183
	2012	304	266	8	578	626	243	31	292	42	89
	Average	400	224	8	632	476	294	-63	139	46	136
	2011	496	181	8	686	286	352	-163	-47	51	186
	2012	304	266	8	578	690	198	76	310	34	72
	Average	400	224	8	632	488	275	-43	131	43	129
	2011	496	145	8	649	354	420	-268	125	65	275
	2012	304	168	8	480	579	279	-103	379	58	159
	Average	400	156	8	564	467	350	-186	252	62	217
	2011	496	145	8	649	263	431	-279	45	99	283
	2012	304	222	8	534	661	222	8.2	349	42	96
	Average	400	183	8	591	462	327	-135	197	54	190
	2011	496	145	8	649	488	406	-254	246	63	266
	2012	304	222	8	534	706	277	-47	450	52	121
	Average	400	183	8	591	597	342	-151	348	57	193
	2011	496	173	8	677	469	366	-185	158	54	202
	2012	304	214	8	526	677	255	-33	406	48	115
	Average	400	193	8	601	573	310	-109	282	51	159
	2011	496	166	8	670	395	366	-192	06	55	210
	2012	304	214	8	526	660	248	-26	382	47	112
	Average	400	190	8	598	527	307	-109	236	51	161

(Table 4.6), and that the ratio of S to effective N increased through anaerobic (co)digestion (Table 4.3). Besides, a S deficit was detected (Table 4.12) when no air scrubber water or no digestates were used (Sc1/7). 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.

Further, a remarkable observation was that free Ca and Mg disappeared in the environment in all scenarios (Tables 4.13 and 4.14), although Ca and Mg are not considered to be leachable nutrients.

As the calcium use efficiency (CaUE) and especially the magnesium use efficiency (MgUE) were positively correlated with the PUE (2011: $r_{Mg/P} = 0.990$ (p = 0.000), $r_{Ca/P} = 0.653$ (p = 0.079); 2012: $r_{Mg/P} = 0.887$ (p = 0.003), $r_{Ca/P} = 0.613$ (p = 0.106)), it is likely that these free cations created nearly insoluble compounds with P, thereby making P more slowly available. As the digestate generally contains more Ca and Mg than animal manure does (Table 4.3), 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. Finally, until present, no effects of the treatment on the total and available soil Ca, Mg, and S contents were observed over time (Tables 4.5 and 4.9).



5. 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 the 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 latest decennia, 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 to CH₄ and CO₂, while complex organic matter, such as lignin, remains in the digestate, thereby increasing its amount of effective OC, that 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). Significantly more OC was applied to the field in the

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Table 4.12 Sulfur balance (kg S ha⁻¹), apparent recovery (%), and sulfur use efficiency (SUE, %) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Average values are marked in bold

	ולמרוטוו ארבוומווטי	s (oc). Avelaye Available	Manure	arkeu III Dold Total	Available	Plant	Apparent	Actual	Apparent	
Sc	Year	Apr	supply	available	Nov	uptake	surplus	pollution	recovery	SUE
-	2011	ND	16	N/A	129	23	-7.2	N/A	N/A	145
	2012	75	8.0	83	94	14	-5.8	25	17	173
	Average	75	12	83	111	18	-6.5	25	17	159
7	2011	ND	57	N/A	128	23	34	N/A	N/A	40
	2012	75	42	117	06	15	27	-12	13	37
	Average	75	50	117	109	19	30	-12	13	39
3	2011	ND	93	N/A	126	24	69	N/A	N/A	26
	2012	75	77	152	123	17	60	-13	11	22
	Average	75	85	152	124	20	65	-13	11	24
4	2011	ND	40	N/A	124	25	15	N/A	N/A	64
	2012	75	35	110	109	13	22	12	12	37
	Average	75	38	110	116	19	18	12	12	50
ŝ	2011	ND	145	N/A	135	26	119	N/A	N/A	18
	2012	75	54	129	118	14	40	2.9	11	25
	Average	75	66	129	126	20	79	2.9	11	22
9	2011	ND	76	N/A	134	24	52	N/A	N/A	32
	2012	75	92	167	120	16	76	-31	10	17
	Average	75	84	167	127	20	64	-31	10	25
4	2011	ND	16	N/A	133	26	-10	N/A	N/A	166
	2012	75	11	86	117	12	-0.77	43	14	107
	Average	75	13	86	125	19	-5.6	43	14	137
ø	2011	ND	16	N/A	129	26	-10	N/A	N/A	161
	2012	75	49	124	113	15	34	3.5	12	30
	Average	75	33	124	121	20	12	3.5	12	95

Advances in Agronomy, First Edition, 2014, 137-180

N/A = Not Applicable; ND = Not Determined.

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Table 4.13 Calcium balance (kg ha⁻¹), apparent recovery (%), and CaUE (%) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Average values are marked in bold

	פר אמומרש מור	Available	Manure	Total	Available	Plant	Apparent	Actual	Apparent	
Sc	Year	Apr	supply	available	Nov	uptake	surplus	pollution	recovery	CaUE
1	2011	19	59	78	5.4	48	11	-25	61	81
	2012	7.3	35	42	8.1	21	14	-13	49	59
	Average	13	47	09	6.7	34	13	-19	55	70
7	2011	19	59	78	5.7	48	12	-25	61	80
	2012	7.3	35	42	8.4	25	10	6-	58	70
	Average	13	47	09	7.0	36	11	-17	59	75
3	2011	19	59	78	5.3	47	13	-26	59	79
	2012	7.3	35	42	9.2	25	10	-8	60	73
	Average	13	47	60	7.3	36	11	-17	60	76
4	2011	19	50	69	5.2	48	1.6	-16	70	97
	2012	7.3	120	127	7.8	31	89	-89	24	25
	Average	13	85	98	6.5	39	46	-52	47	61
5 2	2011	19	50	69	5.5	53	-2.5	-11	76	105
	2012	7.3	209	216	9.4	27	182	-179	13	13
	Average	13	130	143	7.4	40	06	-95	44	59
6	2011	19	50	69	5.4	40	10	-23	59	81
	2012	7.3	209	216	8.9	16	193	-191	7.6	7.8
	Average	13	130	143	7.2	28	101	-107	33	44
7	2011	19	54	73	5.5	47	6.9	-21	64	87
	2012	7.3	36	43	8.7	23	13	-11	54	65
	Average	13	45	58	7.1	35	10	-16	59	76
8	2011	19	51	70	5.1	48	3.0	-17	68	94
	2012	7.3	36	43	8.2	23	13	-12	54	64
	Average	13	44	57	6.6	36	8	-15	61	79

Céline Vaneeckhaute et al.

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Table 4.14 Magnesium balance (kg ha⁻¹), apparent recovery (%), and MgUE (%) in 2011 and 2012 for the eight different fertilization scenarios (Sc). Average values are marked in bold

		age values al e Available	Manure	Total	Available	Plant	Annarent	Actual	Annarent	
Sc	Year	Apr	supply	available	Nov	uptake	surplus	pollution	recovery	MgUE
-	2011	732	27	759	422	36	-9.6	-301	4.8	136
	2012	541	20	561	393	17	3.0	-151	3.0	85
	Average	637	23	660	407	27	-3.3	-226	3.9	110
7	2011	732	27	759	410	36	-9.7	-313	4.8	136
	2012	541	20	561	363	14	6.0	-184	2.5	70
	Average	637	23	660	386	25	-1.9	-249	3.7	103
3	2011	732	27	759	397	36	-9.5	-325	4.8	135
	2012	541	20	561	371	16	3.7	-174	2.9	82
	Average	637	23	660	384	26	-2.9	-250	3.8	108
4	2011	732	13	745	362	38	-25	-345	5.0	295
	2012	541	36	577	404	17	19	-156	3.0	48
	Average	637	24	661	383	27	-3.0	-251	4.0	172
ŝ	2011	732	13	745	373	37	-24	-335	5.0	291
	2012	541	65	606	334	15	50	-258	2.5	23
	Average	637	39	676	353	26	13	-296	3.7	157
9	2011	732	13	745	400	34	-21	-311	4.6	269
	2012	541	65	606	398	17	48	-191	2.7	26
	Average	637	39	676	399	25	13	-251	3.7	147
~	2011	732	24	756	440	41	-17	-274	5.4	173
	2012	541	19	560	357	14	4.7	-189	2.5	75
	Average	637	21	658	399	28	-6.3	-232	4.0	124
8	2011	732	22	754	376	38	-16	-340	5.1	173
	2012	541	19	560	474	15	3.6	-71	2.7	81
	Average	637	21	657	425	27	-6.3	-206	3.9	127

scenarios in which digestate or its LF was used to (partially) replace animal manure: 217 ± 0 (Sc1-3) versus 1294 ± 240 (Sc4-6) versus 329 ± 0 (Sc7-8) kg OC ha⁻¹ in 2012, and 800 \pm 0 (Sc1-3) versus 835 \pm 15 (Sc4-8) kg OC ha⁻¹ in 2011. Up to date, the SOC was not significantly affected by the treatments, although a significant increase in the mean SOC over time was found (mean in 2011: 1.95%; mean in 2013: 2.4%). Small changes in the 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 over 30 years estimate that the SOC content will be reduced from 1.95% to 1.62% for Sc1, while it would remain approximately stable when the digestate or its LF is used (Sc4-8). Further, in the two years of the field trial, no significant effect of the fertilization strategy on the soil pH- H_2O (mean \pm SD: 6.1 \pm 0.2) and pH-KCl (mean \pm SD: 5.2 \pm 0.7) was observed (Figure 4.9).

In August 2012, after the second fertilization, the electrical conductivity (EC) was significantly higher as more air scrubber water was used, but this effect disappeared again later in the season (mean \pm SD: 107 \pm 26 μ S cm⁻¹). The total amount of soil Na, which also gives an indication of salt accumulation, was significantly higher for Sc5 compared to that for Sc2 and Sc3 in July 2011, but thereafter, no more significant differences were observed (Table 4.5). Another issue would be an excess of Na over divalent cations (=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;



Figure 4.9 $pH(H_2O)$ (left) and pH(KCI) (right) as a function of time for the eight different fertilization scenarios (n = 4); *p*-values and small letters refer to statistical analysis using one-way ANOVA and post hoc pairwise comparisons; *significant difference at the 5% level.

 $p_{nov} = 0.013$), but no statistical significant differences could be detected using post hoc pairwise comparison tests, and the average SAR (<1) was well below SAR 6, which is the internationally accepted level above which soil permeability and structural stability may be affected (Hamaiedeh and Bino, 2010). Finally, in all scenarios, the Flemish environmental soil standard for Cu accumulation (17 mg kg⁻¹ dry soil) was exceeded (FSD, 2007), 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.

6. FERTILIZER MARKETS, LEGISLATIONS, AND RECOMMENDATIONS

This review clearly indicates that wastewater from an acidic air scrubber for NH3 removal can be used as a valuable N-S rich mineral fertilizer. However, the product is not often applied up to now due to legislative constraints and farmers' distrust. Nevertheless, 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 NH₃. 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. 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 between the price of <1 mm crystals and that of granular (2-3 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, the use of this product should be stimulated in fertilizer legislations and recommended in the farming community.

An important legislative bottleneck for the beneficial use of digestate (and its derivatives) in many regions worldwide is that the product

is currently classified as waste and hence subject to waste regulations if any waste material is used in its production, i.e. added as input stream to the anaerobic digester. Moreover, all derivatives produced from animal manure, including digestates, are often, especially in high-nutrient regions, also still categorized as animal manure in environmental legislation and can therefore not or only sparingly be returned to agricultural land. The need exists for better classification of these products based on the particular fertilizer characteristics, and for greater differentiation between soils, crops, and fertilizer types in the recommendations given on N, P, and K fertilizer requirements. Further, a problem still exists in the variability of manure and digestate composition over time. In order to move toward more sustainable fertilization practices, it is crucial that farmers and operators are able to control and stabilize the N, P, and K content 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 up to date an adequate integrated biologicalphysicochemical modeling approach for resource recovery is lacking (Batstone et al., 2012), the development and use of such prototype models will be aspect of further research.

7. ECONOMIC AND ECOLOGICAL EVALUATION

The use of biobased fertilizers in agriculture can result in significant economic benefits for the agriculturist, as well as in ecological benefits through the reduction of energy use and greenhouse gas emissions during production and application (Vaneeckhaute et al., 2013a,b). The complete substitution of chemical fertilizer N by air scrubber water could almost double the economic benefits, while the energy use and greenhouse gas emissions are 2.5 times reduced. When additionally substituting animal manure by the digestate/LF-mixture, the observed benefits are even higher, because in this case, less chemical N is required due to the higher N/P-ratio of the mixture, while also the need for chemical K_2O is less. The economic and ecological benefits are the highest when both chemical N and K₂O are completely eliminated (2011: Sc8, 2012: Sc4; Table 4.2), respectively, 3.5 and 4.4 times higher than the reference. As such, reuse of biodigestion waste (water) streams can also improve the economic viability of anaerobic digestion plants, especially in high-nutrient regions. This, in turn, can serve as a catalyst to meet renewable energy and waste (water) directives across the world.

8. CONCLUSIONS AND FURTHER RESEARCH

Recent ground-breaking field research shows that the use of wastewater from an acidic air scrubber for NH3 removal in agriculture as a sustainable substitute for chemical fertilizer N can result in higher N use efficiencies and less N leaching. In addition, the more the chemical N was replaced by air scrubber water, the higher the observed PUE and apparent P recovery. Model simulations show that the amount of N volatilization may slightly increase, hence the use of low-emission techniques for fertilizer application is recommended. Further, the PUE and KUE could be improved when using digestates 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 biobased fertilizers in substitution of their fossil reserve-based counterparts, is considered as a positive outcome. As added benefits to the generation of biofertilizers from waste by anaerobic digestion, renewable energy is produced, negative environmental impacts of untreated animal manure are avoided, while the economics are also improved. Moreover, the use of biobased fertilizers also resulted in added supply of organic carbon, Ca, Mg and S, which are absent in chemical mineral N-K fertilizers. We therefore conclude that the use of biobased fertilizers has a positive impact on the economy, agronomy and ecology of intensive plant production. The need exists for better classification of these biodigestion waste derivatives based on the particular fertilizer characteristics, and for greater differentiation between soils, crops, and fertilizer types in the recommendations given on N, P, and K fertilizer requirements. Field trials using the presented best management practices to evaluate and prove the performance of (different) biobased fertilizers in the long term are recommended, and will be aspect of further research. Moreover, the development and use of physicochemical models to predict and control recovered fertilizer quality seem very valuable. All of this should foster the development and implementation of more sustainable, effective, and environmentally friendly farming practices.

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180