

# The use of digestates and recovered ammonium sulfate from NH<sub>3</sub>-scrubbing as sustainable substitutes for chemical fertilizers: A field-scale assessment

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## Abstract

Nutrient recovery from bio-waste as renewable fertilizers with high nutrient use efficiency (NUE) has gained increased attention in order to meet both regulatory drivers (increasingly stringent fertilization and discharge levels) and market demands, while producing an internal revenue source, hence turning the waste problem into an economic opportunity. The aim of this study was to validate the agronomic effectiveness of fertilization strategies using bio-digestion waste derivatives as compared to conventional practices using animal manure and chemical fertilizers. In a two-year field trial, NUE's and nutrient balances were assessed for N, P, K, S, Ca, Mg and Na. An economic and ecological evaluation was also conducted. Complete substitution of chemical fertilizer N by wastewater from NH<sub>3</sub>-scrubbing resulted in higher N and P use efficiencies, whereas the use of digestate mixtures resulted in significantly higher K and P use efficiencies. Small increases in crop yield were obtained when the liquid fraction of digestate was used as NK-fertilizer in addition to animal manure. As added benefits to the generation of bio-fertilizers from waste, renewable energy is produced, and the economic and ecological impact of plant production is significantly reduced. Moreover, an additional supply of organic carbon, Ca, Mg and S is delivered.

**Keywords:** ammonium sulfate, bio-based fertilizers, digestate, nutrient recovery, nutrient use efficiency, water resource recovery facility

## Introduction

Anaerobic digestion is an established technology to convert animal manure, wastewater sludge, organic biological waste and/or energy crops into renewable energy and nutrient-rich digestates. The recovery of nutrients from these digestates for reuse as renewable mineral fertilizers in agriculture has become an important challenge in the transition towards a bio-based economy, both from an ecological and an economic perspective (Vaneekhaute et al., 2013a). However, until now this opportunity 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 products, as well as in their impact on crop yield and soil quality.

Because of these constraints, a field trial has been conducted in 2011 aiming to evaluate the impact of using bio-digestion waste derivatives as substitute for fossil reserve-based chemical fertilizers and/or as phosphorus (P) poor equivalent for animal manure on soil and crop production (Vaneekhaute et al., 2013b). The products used in this field trial were recovered ammonium sulfate (AmS, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) wastewater from an acidic air scrubber for ammonia (NH<sub>3</sub>) removal (after NH<sub>3</sub>-stripping), the liquid fraction (LF) of digestate following mechanical separation, and a mixture of raw digestate and LF digestate. Through the first study year it was observed that the

use of digestate derivatives as substitute for chemical fertilizers and/or animal manure in agriculture can be beneficial both from an environmental and an economic perspective. In order to validate the obtained results and to investigate interesting observations in more detail, the field trial was repeated in 2012 at the same site. The current paper aims to evaluate the impact on soil fertility and soil quality of this two-year field experiment by use of high level performance indicators measuring farming's pressure on the environment and how that pressure is changing over time. It is hypothesized that the use of bio-digestion waste products will not significantly diminish crop yield and NUE's as compared to common practices using animal manure additionally supplied with chemical fertilizers. Yet more, a positive impact on the economy and ecology of intensive plant production is expected.

## Material and Methods

### *Site description and fertilization strategies*

The test site was a 0.8 ha large sandy field located in Wingene, Belgium (51° 3' 0" N, 3° 16' 0" E). The field was divided into 4 blocks (representing 4 replicates per treatment: n = 4) and each block was divided into 8 subplots of 9 m by 7.5 m, which were randomly assigned to the 8 treatments (Sc1-8) under study (Table 1). The soil characteristics before the field trial (April 21 2011) can be found in Vaneckhaute et al. (2013b). Based on the soil characteristics, the advice given on fertilizer requirements was formulated at 150 kg effective N ha<sup>-1</sup>, 180 kg K<sub>2</sub>O ha<sup>-1</sup> and 30 kg MgO ha<sup>-1</sup> in 2011, and 135, 250 and 60 kg ha<sup>-1</sup>, respectively, in 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). Furthermore, for P<sub>2</sub>O<sub>5</sub> the maximum allowable dosage of 80 kg ha<sup>-1</sup> for the cultivation of maize was respected in the experimental design (FMD, 2011). It should be remarked that the actual rates of application (based on product characterizations at the moment of fertilizer application) were sometimes different than 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 1** Eight different fertilization scenarios (Sc) expressed as effective nitrogen (kg ha<sup>-1</sup>); Additional application of synthetic K<sub>2</sub>O (kg ha<sup>-1</sup>); Dosage of P<sub>2</sub>O<sub>5</sub> (kg ha<sup>-1</sup>).

| Group <sup>a</sup> | Sc | Year | Chemical start N | Chemical N | Air scrubber N | Animal manure N | Digestate mixture N | Raw digestate N  | LF digestate N | Chemical K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> <sup>b</sup> |
|--------------------|----|------|------------------|------------|----------------|-----------------|---------------------|------------------|----------------|---------------------------|--|
| 0                  | 1  | 2011 | 25               | 29         |                | 98              |                     |                  |                | 78                        | 80   |
| 0                  |    | 2012 | 30               | 30         |                | 58              |                     |                  |                | 213                       | 45   |
| I                  | 2  | 2011 | 25               |            | 29             | 98              |                     |                  |                | 78                        | 108 <sup>e</sup>                           |
| I                  |    | 2012 | 30               |            | 30             | 58              |                     |                  |                | 213                       | 45   |
| I                  | 3  | 2011 |                  |            | 54             | 98              |                     |                  |                | 78                        | 108 <sup>e</sup>                           |
| I                  |    | 2012 |                  |            | 60             | 58              |                     |                  |                | 213                       | 45   |
| II                 | 4  | 2011 | 25               | 18         |                |                 | 105 <sup>c</sup>    |                  |                | 29                        | 75   |
| II                 |    | 2012 |                  |            |                |                 | 139 <sup>d</sup>    |                  |                | 0                         | 101 <sup>e</sup>                           |
| II                 | 5  | 2011 | 25               |            | 18             |                 | 105 <sup>c</sup>    |                  |                | 29                        | 75   |
| II                 |    | 2012 | 33               |            |                |                 |                     | 141 <sup>e</sup> |                | 46                        | 159 <sup>e</sup>                           |
| II                 | 6  | 2011 |                  |            | 43             |                 | 105 <sup>c</sup>    |                  |                | 29                        | 75   |
| II                 |    | 2012 |                  |            | 33             |                 |                     | 141 <sup>e</sup> |                | 46                        | 159 <sup>e</sup>                           |
| III                | 7  | 2011 | 25               |            |                | 86              |                     |                  | 36             | 33                        | 105 <sup>e</sup>                           |
| III                |    | 2012 | 33               |            |                | 52              |                     |                  | 39             | 121                       | 49   |
| III                | 8  | 2011 |                  |            |                | 80              |                     |                  | 60             | 0                         | 105 <sup>e</sup>                           |
| III                |    | 2012 |                  |            | 33             | 52              |                     |                  | 39             | 121                       | 49   |

<sup>a</sup> Group: 0 = Reference = conventional fertilization, I = Substitution of chemical fertilizer N by air scrubber water, II = Anaerobic digestion of animal manure and field application of digestate with or without the substitution of chemical fertilizer N by air scrubber water, 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 air scrubber water; <sup>b</sup> No chemical P was used; <sup>c</sup> Mixture of 50 vol. % raw digestate and 50 vol. % LF digestate; <sup>d</sup> Mixture of 60 vol. % LF digestate and 40 vol. % raw digestate; <sup>e</sup> Maximum allowable fertilization level was exceeded.

Group 0 (Sc1) represents the reference scenario in which only animal manure and chemical fertilizers (N, K<sub>2</sub>O) 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. Digestate mixtures were spread to the field, with partial, complete or without the simultaneous substitution of chemical N by air scrubber water. While P<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> over effective N is in general lower for digestate compared to animal manure. Based on the product characterizations, the combination of raw digestate and its LF after mechanical separation was optimized to provide a concentrated mixture with high effective N-content, but low P<sub>2</sub>O<sub>5</sub>-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 satisfy the fertilizer N-requirements without exceeding the maximum allowable P<sub>2</sub>O<sub>5</sub>-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.

### ***Sampling, fertilizer application and field follow-up***

Digestate and LF digestate after mechanical separation were sampled at the site of Sap Eneco Energy (BE). It concerns an anaerobic co-digestion 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 (BE) and acidic air scrubber water was collected at the piggery of Ladevo BVBA, Ruiselede (BE) (2011) and Senergho, Hoogdele, (BE) (2012). Two replicate samples of each waste stream were collected in polyethylene sampling bottles (10 L), stored cool ( $\pm 4$  °C) and transported within 1 h to the laboratory for physicochemical analysis. The replicate samples were analyzed separately. Fertilizers were applied to the soil on April 29-30 2011 and May 30 2012 and ploughed one day later. In 2012, the fertilization was conducted late in the season due to the very exceptional wet weather conditions in April of that year (RMI, 2013). On May 5 2011, energy maize of the species *Atletico* (breeder: KWS; FAO Ripeness Index: 280) was sown at a seed density of 102 000 ha<sup>-1</sup>. 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<sup>-1</sup>. Pig manure, digestate and LF digestate were applied to the field by use of PC-controlled injection (Bocotrans, NL), whereas the air scrubber water and the chemical fertilizers, ammonium-nitrate (27 % N) and patent-kali (30 % K<sub>2</sub>O, 10 % MgO), were applied to the plots by hand-application in order to ensure high precision of the applied dosage. 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. Upon sampling, 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 bore holes. The samples were collected in polyethylene sampling bags, stored in cooler boxes filled with ice ( $\pm 4$  °C) and transported within 1 h from the test site to the laboratory. In the laboratory, the replicate samples were stored cool (1-5 °C) for separate analysis. The harvest was conducted by use of a maize chopper and the crop fresh weight (FW) yield was determined at the field.

### ***Physicochemical product, soil and plant analysis***

Dry weight (DW) contents were determined as residual weight after 72 h drying at 80 (product), 50 (soil) or 55 (plant) °C in an oven (EU 170, Jouan s.a., FR). Organic carbon (OC) was determined as loss of ignition (Van Ranst et al., 1999) after incineration of the dry samples during

4 h at 550 °C in a muffle furnace (Nabertherm, GE). Conductivity and pH were determined potentiometrically using a WTW-LF537 (GE) conductivity electrode and an Orion-520A pH-meter (USA), respectively. Total N and NH<sub>4</sub>-contents were determined using the Kjeldahl Method (Van Ranst et al., 1999). Total P was determined using the colorimetric method of Scheel for products and soils, while the Vanadate method was used for plant P-analysis (Van Ranst et al., 1999). Ca, Mg and heavy metals were analyzed using ICP-OES (Varian Vista MPX, USA), while Na and K were analyzed using a flame photometer (Eppendorf ELEX6361, GE) (Van Ranst et al., 1999). NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were analyzed using ion chromatography (Metrohm-761, CH) after product centrifugation and subsequent vacuum filtration (0.45 µm). Soil NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>-contents were determined using an AA3 auto-analyzer (BRAN+LUEBBE, GE) after extraction with KCl. 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. The Sodium Adsorption Ratio (SAR), which refers to the ratio of the monovalent cation Na<sup>+</sup> to the divalent cations Ca<sup>2+</sup> and Mg<sup>2+</sup>, was determined as described by Hillel (2008).

### ***Nutrient use efficiency and nutrient balances***

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

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

It gives an indication of the effectiveness of the fertilizers applied (organic + chemical), without taking in account the amount of soil available nutrients in the field before fertilization (which may mask the actual NUE of the fertilizer itself). NUE's were evaluated through time for the primary macronutrients N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O, 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. Next, 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. The apparent nutrient surplus was calculated using the following equation:

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

in which the 'inputs' refer to the nutrient supply by fertilization and natural deposition (i.e. 30 kg N ha<sup>-1</sup>, 3 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup>, 8 kg K<sub>2</sub>O ha<sup>-1</sup>; 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. Furthermore, the actual environmental pollution was determined by taking in account the measured changes in soil nutrient reserves over time:

$$\begin{aligned} \text{Actual pollution index (kg ha}^{-1}\text{)} = \text{soil nutrient reserves before fertilization (kg ha}^{-1}\text{)} - \\ \text{soil nutrient reserves at harvest (kg ha}^{-1}\text{)} + \text{apparent nutrient surplus (kg ha}^{-1}\text{)} \end{aligned}$$

### ***Model simulations***

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.

### ***Statistical analysis***

Statistical analyses were performed using SPSS Statistics 21. A one-way 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 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 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, a non-parametric Kruskal-Wallis test was applied instead of the one-way ANOVA. Significant parameter correlations were determined using the Pearson correlation coefficient ( $r$ ).

## **Results and Discussion**

### ***Impact of fertilization strategy on crop production***

Over the whole experimental period, the average biomass yields 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 2011 (Sc2 < 5/7) and in 2012 (Sc4 < 1/7/8; Sc5 < 8). The average DW content at the harvest was  $28 \pm 1$  % in 2011 and  $29 \pm 0$  % in 2012. Hence, the energy maize was suitable for biogas production (desired: 28-36 %; Matjaz et al., 2010, Vaneckhaute et al., 2013b).

### ***Impact of fertilization strategy on nutrient dynamics in the environment***

The  $\text{NO}_3\text{-N}$ -residue in the soil profile (0-90 cm) between the 1<sup>st</sup> of October and the 15<sup>th</sup> 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  $\text{NO}_3\text{-N}$ -residues. During this field trial, no significant differences in  $\text{NO}_3\text{-N}$ -residue in the soil were observed between the treatments, except in November 2011 (Sc5 > 2/4/6/8) due to exceptional weather conditions (Vaneckhaute et al., 2013b). The scenarios in which chemical fertilizer N was completely replaced by air scrubber water (Sc3/8) showed a significantly higher nitrogen use efficiency ( $\text{NUE}_N$ ) and plant N-uptake in 2012. Also a strong significant correlation was found between the  $\text{NUE}_N$  and the DW biomass yield ( $r = 0.801$ ). Moreover, model simulations with NDICEA over 3 years (Table 2) showed 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 be even more pronounced in the longer term, while the amount of N-volatilization will remain almost equal. A point of attention when using air scrubber water in agriculture may be the breakdown of soil organic matter (Sc2-3 > 1; Table 2). However, when simulating over 30 years, the mean organic matter breakdown is equal to that of the reference, due to an increased N-provision by the breakdown of crop residues (higher crop N-uptake).

**Table 2** Nutrient balances (N,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ;  $\text{kg ha}^{-1} \text{ year}^{-1}$ ) for scenario 1, 2 and 3 simulated with the NDICEA model (crop type = energy maize). N-3: simulation over 3 years; N-30: simulation over 30 years.

|                         | Scenario 1 |      |                        |                      | Scenario 2 |      |                        |                      | Scenario 3 |      |                        |                      |
|-------------------------|------------|------|------------------------|----------------------|------------|------|------------------------|----------------------|------------|------|------------------------|----------------------|
|                         | N-3        | N-30 | $\text{P}_2\text{O}_5$ | $\text{K}_2\text{O}$ | N-3        | N-30 | $\text{P}_2\text{O}_5$ | $\text{K}_2\text{O}$ | N-3        | N-30 | $\text{P}_2\text{O}_5$ | $\text{K}_2\text{O}$ |
| 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   | 3                      | 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  | 2                      | -69                  | -36        | -36  | -4                     | -48                  |
| 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  |                        |                      |

Next, the plant P-uptake was found to be significantly higher when chemical fertilizers were completely substituted by air scrubber wastewater as compared to the reference ( $Sc_{3/6/8} > Sc_1$ ). 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 (Diwani et al., 2007). Hence, the P-uptake was also highly correlated to the  $NUE_N$  ( $r = 0.932$ ) and the plant N-uptake ( $r = 0.844$ ). Moreover, the more chemical N was replaced by air scrubber wastewater, the higher average extraction of  $P_2O_5$  from the soil was observed (negative apparent surplus). This effect was the highest when simultaneously replacing animal manure with digestate (Sc 4-6) or LF digestate (Sc 7-8). With respect to the depleting 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.

The potassium use efficiency ( $NUE_K$ ) was significantly higher when using digestates or LF digestates (Sc4-8) as compared to conventional scenarios using animal manure additionally supplied with chemical  $K_2O$  (Sc1-3), 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. Because  $K_2O$  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 (Vaneckhaute et al., 2013a).

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 has become a problem in more than 75 countries. Supply of this nutrient could be efficiently achieved 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, and that the ratio of S to effective N increased through anaerobic (co-)digestion. Besides, an S-deficit was detected when no air scrubber water or no digestates were used (Sc1/7). The latter may cause significant S-shortages in the long term, which depending on the S-demand of the agricultural crop might adversely impact yield. Furthermore, a remarkable observation was that free Ca and Mg disappeared in the environment in all scenarios, although Ca and Mg are not considered to be leachable nutrients. That the calcium use efficiency ( $NUE_{Ca}$ ) and especially the magnesium use efficiency ( $NUE_{Mg}$ ) were correlated with the phosphorus use efficiency ( $NUE_P$ ) (2011:  $r_{Mg/P} = 0.990$ ,  $r_{Ca/P} = 0.653$ ; 2012:  $r_{Mg/P} = 0.887$ ,  $r_{Ca/P} = 0.613$ ) might support the hypothesis that these cations combined with P into low soluble P-compounds. As digestate generally contains more Ca and Mg than animal manure, 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. Yet, further research in the long term should study the potential adverse effect of retrogradation (further transformation into immobilized P-complexes), which may render the P in the soil unusable for modern agriculture.

### ***Impact of fertilization strategy on general soil quality***

In the two years of the field trial, no significant effect of the fertilization strategy on the soil pH- $H_2O$  ( $6.1 \pm 0.2$ ) and pH-KCl ( $5.2 \pm 0.7$ ) was observed. In August 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 ( $107 \pm 26 \mu S cm^{-1}$ ). Another issue would be an excess of Na over divalent cations (= SAR), leading to a poor soil structure. In 2012, an F-test showed a significant effect of the fertilization strategy on the soil SAR, but using subsequent post-hoc pair-wise comparison tests no statistical significant differences could be detected. In any case, 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 & Bino, 2010). Furthermore, in all scenarios the Flemish environmental soil standard for Cu-accumulation ( $17 \text{ mg kg}^{-1}$  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. A final interesting point is that significantly more organic carbon (OC) was applied to the field in the scenarios in which digestate derivatives were used ( $217 \pm 0$  (Sc1-3) vs.  $1294 \pm 240$  (Sc4-6) and  $329 \pm 0$  (Sc7-8)  $\text{kg OC ha}^{-1}$  in 2012). Recycling of these products could therefore also contribute to counteract OC-depletion in many soils world-wide.

### ***Fertilizer markets and legislation***

Results clearly indicate that wastewater from an acidic air scrubber for  $\text{NH}_3$ -removal can be used as a valuable NS-rich mineral fertilizer. However, to date the product is not often applied due to legislative constraints and farmers' distrust. On the other hand, the world-wide supply of AmS has recently increased, in part due to the production of AmS by direct reaction crystallization from (spent) sulfuric acid and  $\text{NH}_3$ . 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 fulfil the market requirements. However, and obviously, this gap in the supply-demand relationship has led to a rise in AmS-prices. This study proves that AmS from acidic air scrubbers can be beneficially used to fill this gap. Hence, the use of this product should be stimulated in fertilizer legislations and in the farming community.

An important legislative bottleneck for the beneficial use of digestate in many regions, including Flanders (BE), is that the product is currently classified as waste and hence subject to waste regulations if any biodegradable waste material is used in its production. Moreover, all derivatives produced from animal manure, including digestates, are still categorized as animal manure in environmental legislation and can therefore not or only sparingly be returned to agricultural land. The need exists for a 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. 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 N, P and K-content of their end-products. In this respect, the development and use of mathematical models for nutrient and energy recovery can be very valuable for continuous optimization of both process performance and fertilizer quality.

### ***Economic and ecological evaluation***

The use of bio-based fertilizers in agriculture can result in significant economic benefits for the farmer, as well as in ecological benefits through the reduction of energy use and greenhouse gas emissions during production and application (Vaneekhaute et al., 2013a, 2013b). 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. The economic and ecological benefits are highest when both chemical N and  $\text{K}_2\text{O}$  are completely eliminated (2011: Sc8, 2012: Sc4), respectively 3.5 and 4.4 times higher than the reference.

### **Conclusions**

The use of wastewater from an acidic air scrubber for  $\text{NH}_3$ -removal in agriculture as sustainable substitute for chemical fertilizer N resulted in higher N use efficiencies and less N-leaching, while the amount of N-volatilization remained quasi equal. In addition, it was found that the more chemical N was replaced by air scrubber water, the higher the observed crop P-uptake.

Furthermore, the P and K use efficiency 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 NK-fertilizer in addition to animal manure. In any case, equal to higher yields when using bio-based fertilizers in substitution of their fossil-based counterparts, is considered as a positive outcome. As added benefits to the generation of bio-fertilizers 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 bio-based fertilizers also resulted in added supply of organic carbon, Ca, Mg and S, which are absent in chemical mineral NK-fertilizers. We therefore conclude that the use of bio-based fertilizers has a positive impact on the economy, agronomy and ecology of intensive plant production. A better legislative classification of these products could foster the development of more sustainable, effective and environmentally friendly farming practices.

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