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Closing the nutrient cycle by using bio-digestion waste derivatives as synthetic fertilizer substitutes: A field experiment

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Abstract

In the transition from a fossil to a bio-based economy, it has become an important challenge to maximally recycle valuable nutrients that currently end up in waste streams. Nutrient resources are rapidly depleting. Significant amounts of fossil energy are required for the production of synthetic fertilizers, whereas costs for energy and fertilizers are increasing. Meanwhile, biogas production through anaerobic digestion produces nutrient-rich digestates, which could potentially be reused as green fertilizers in agriculture, thereby providing a sustainable substitute for synthetic fertilizers. The aim of this study was to evaluate the impact of using bio-digestion waste derivatives instead of synthetic fertilizers and/or animal manure on soil and crop production. In a field trial, nutrient balances were assessed and the physicochemical soil fertility and quality were evaluated. The biogas yield of the harvested energy crops was determined. An economic and ecological evaluation was conducted. Application of bio-digestion waste derivatives induced small, albeit statistically insignificant improvement in crop yield, soil fertility and quality compared to current common practices using animal manure and synthetic fertilizers. Moreover, the use of these products might stimulate nutrient mobilization from the soil, thereby increasing the use efficiency of soil minerals. For all reuse scenarios the calculated economic and ecological benefits were significantly higher than the reference. It is clear that the reuse of bio-based products as nutrient supply in agriculture should be stimulated in European legislation. Further field research is on-going in order to validate the results and evaluate the impact on soil quality in the longer term.

Keywords: anaerobic digestion, digestate processing, cradle-to-cradle nutrient recycling, bio-based fertilizers, sustainable agriculture, environmental management

Abbreviations: LF = Liquid Fraction, NUE = Nitrogen Use Efficiency, SAR = Sodium Adsorption Ratio

1. Introduction

Nutrient recovery from digestate sludge and cradle-to-cradle reuse as sustainable fertilizers in agriculture has become an important challenge in the further development of sustainable agriculture, green chemistry and renewable energy production through anaerobic digestion, both from an economic as an ecological point of view [1]. Waste water resulting from NH_3-removal by an acidic air scrubber could potentially be reused as a formulated N-S-fertilizer, whereas concentrates resulting from membrane filtration of liquid digestate could potentially be reused as N-K-fertilizer [1]. In this way sustainable alternatives for fossil-based mineral fertilizers could be provided, while valuable nutrients are being recycled. Furthermore, in light of phosphorus levels for soil application that become more and more strict in European legislation, reuse of the P-poor liquid fraction (LF) after mechanical separation of raw digestates, or a mixture ($\phi = 0.5$) of raw digestate and LF might be of important interest in the near future.

Despite the potential economic and ecological benefits, closing nutrient cycles in this sector proved to be difficult to realise due to obstacles in (national) legislative systems and lack of insights in the composition and properties of these digestate derivatives, as well as in their impact on crop yield and soil quality. In 2010-2011, Wageningen UR (NL) has conducted a field trial aiming to evaluate the fertilizer value of concentrates produced by reversed osmosis membrane filtration of liquid manure and digestate [2]. However, pot and field trials with bio-digestion waste products are currently lacking.

This study aims to demonstrate the fertilizer potential of digestate sludge and its derivatives by means of a field trial in which eight different cultivation scenarios will be compared. In these scenarios liquid fractions (LF) of digestate, waste water from an acidic air scrubber for ammonia removal, and a mixture ($\phi = 0.5$) of raw digestate and LF-digestate will be applied to soil, either as substitute for synthetic fertilizers or animal manure, for the cultivation of energy maize. It is hypothesized that the use of these products will not cause significant differences in crop yield and nutrient uptake compared to the common practice (animal manure + synthetic fertilizers). In order to evaluate the potential environmental impact using these bio-based products in agriculture, nutrient balances will be assessed and the physicochemical soil quality, including the nitrate residue, leaching, salt content, pH, organic carbon content, sodium adsorption ratio (SAR), as well as phosphorus and heavy metal accumulation will be evaluated. Finally, the biogas yield of the harvested energy maize will be determined. As such, the nutrients coming from the digestate are again recycled to the anaerobic digestion plant and nutrient cycles are maximally closed.

2. Material and Methods

2.1 Site description and experimental set-up

The test site is located in Wingene, Belgium. It concerns a 0.8 ha large sandy-loam field. The field was divided into 32 subplots of 9 m by 0.75 m. The soil characteristics before the field trial (April 21 2011) are given in Table 1. Based on these data the fertilizing advice was formulated at 150 kg ha^{-1} for effective N, 270 kg ha^{-1} for K_2O and 30 kg ha^{-1} for MgO. For phosphate (P_2O_5), the maximum allowable dosage of 80 kg ha^{-1} for the cultivation of maize on non-sandy soils was respected as described in the Flemish Manure Decree [3]. Eight different fertilization scenarios (Sc1-8) were tested in four replicate subplots (n = 4) spread in the field (Figure 1), in order to minimize the potential influence of variable soil conditions on the results. Details of the product, nutrient and carbon doses per scenario are given in Table 2.

On April 12 2011, digestate and LF-digestate were sampled at the site of Sap Eneco Energy, Belgium. This concerns an anaerobic co-digestion plant, with an influent feed of 30 % animal manure, 30 % energy maize and 40 % organic biological waste produced by the food industry. Furthermore, 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. The samples were collected in polyethylene sampling bottles (5 L), stored cool (4 °C) and transported to the laboratory for physicochemical analysis. The data were used to calculate the maximum allowable dosage (Table 2) for the different cultivation scenarios with respect to the Manure Decree [3]. Because the pH of the air scrubber water was very low, it was neutralized by adding NaOH (1 L NaOH per 200 L acidic waste water) before application to the field.

Next, by the end of April 2011, the fertilizers were applied to the soil and again samples were taken for analysis in the same way as described before. LF-digestate was applied manually on April 28 to ensure high precision for the targeted application on the test subplots. The fertilization of the mixture of digestate ($\phi = 0.5$) and its LF ($\phi = 0.5$), as well as pig manure was conducted by use of pc controlled injection (Bocotrance, NL) on April 29. Thereafter the field was ploughed and on April 30 the pH-adjusted air scrubber water and the synthetic fertilizers, ammonium-nitrate (27 % N) and patent-kali (30 % K_2O and 10 % MgO), were applied to the plots by hand-application, again to ensure high precision of the applied dosage. On May 5, energy maize of the species Atletico KWS (FAO Ripeness Index: 280) was sown at a seed density of 102 000 ha^{-1}, while synthetic start fertilizers were applied. The preceding crop was fodder maize. The weather conditions during the field trial are presented in Table 3 [4].

During the growing season, samples of soil and plant were taken on July 5-6, September 5-6 and at the harvest, October 7 (plant samples) and 13 (soil samples) 2011. On October 22, Italian rye-grass was sown as an intercrop and on November 25 again soil samples were taken in order to evaluate the NO_3-residue in the soil. At each sampling moment, one soil sample was taken in the middle of each subplot using a soil core sampler and six plants were harvested manually by use of trimming scissors in a rectangular around the bore hole. The samples were collected in polyethylene sampling bags and transported within 1 h from the test site to the laboratory, carried in cooler boxes filled with ice. In the laboratory, the replicate samples were stored cool (1 °C to 5 °C) for analysis. Also a length measurement was performed on August 17 (n = 320). The harvest was conducted by use of a maize chopper and the crop fresh weight yield was determined at the field.

2.2 Physicochemical analysis

2.2.1 Product analysis

Dry weight (DW) content was determined as residual weight after 72 h drying at 80 °C. Conductivity and pH were determined potentiometrically using a WTW-LF537 (GE) 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 subsequent filtered (MN 640 m, Macherey–Nagel, GE). Total N-content was determined using the Kjeldahl Method and total P was determined using the colorimetric method of Scheel [5]. Ca, Mg and heavy metals were analyzed using ICP-OES (Varian Vista MPX, USA), whereas Na and K were analyzed using a flame photometer (Eppendorf ELEX6361, GE) [5]. Ammonium was determined using a Kjeltec-1002 distilling unit (Gerhardt Vapodest, GE) after addition of MgO to the sample, and subsequent titration [5]. NO_3^-, Cl^- and SO_4^{2-} were analyzed using ionic chromatography (Metrohm-761, CH) after centrifugation and subsequent vacuum filtration (0.45 μm) of the liquid fraction. Cl^- on the solid samples was determined by means of a potentiometric titration using an automatic titrator (Methrohm, CH), provided by a $Hg/(Hg)_2SO_4$ referential electrode [5]. Total S was analyzed as described by Weaver et al. [6]. Plant available amounts of macronutrients were determined in an NH_4OAc-EDTA extract of the samples at pH 4.65 [5].

2.2.2 Soil analysis

Soil samples were dried at 50 °C in a soil oven (EU 170, FR) for minimum 72 h. Organic carbon was determined after incineration of the samples during 4 h at 550 °C in a muffle furnace [5]. Soil conductivity was measured with a WTW-LF537 (GE) electrode after equilibration for 30 min in deionized water at a 5/1 liquid to dry sample ratio and subsequent filtration (MN 640 m, Macherey–Nagel, GE). To determine the actual soil pH (pH-H_2O), 10 g of air-dried soil was allowed to equilibrate in 50 mL of deionized water for 16 h, and for the determination of 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 [5]. Na, K, Ca, Mg and metals were analyzed using ICP-OES after aqua regia digestion (total amounts) and NH_4OAc-EDTA extraction at pH 4.65 (plant available amounts) of the samples [5]. Total S-content was determined with ICP-OES after microwave destruction. Hereby 1 g of dry soil was mixed with 2.5 mL $HClO_4$ and 3.5 mL HNO_3, 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 was determined as described by Hillel [7].

2.2.3 Plant analysis

Plant samples collected in the field were weighed for determination of the fresh weight biomass yield and oven-dried at 55 °C for determination of the DW. The dry samples were grinded to pass a 1 mm sieve (Retsch SM-2000, GE) and incinerated at 550 °C during 4 h in order to determine the organic carbon content. Total N was determined using the Kjeldahl method and total P was determined using the method of Vanadate [5]. Na, K, Ca, Mg and metals were determined using ICP-OES. Total S was determined using ICP-OES after microwave destruction (Section 2.2.2) of 0.2 g dry and grinded plant sample.

2.3 Analysis of biogas potential

Homogenized subsamples of the harvested plant material were taken for determination of the biogas potential. The four replicate subsamples per treatment were then mixed and again homogenized. The biogas potential of the energy maize was determined in the biogas lab of the university college of West Flanders (Innolab), Kortrijk, Belgium via a 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 dry weight load to the reactor was 4 g L^{-1}. The used inoculum was an exhausted digestate composed of different digestates from stable working biogas reactors. The two controls and the two flasks with inoculum material had the same volume and were incubated at 37 °C. The flasks were connected to gas catch columns, filled with acid water to avoid dissolution of CO_2, and the produced gas was read out on the column.

2.4 Statistical analysis

Statistical analysis was performed with SAS 9.2. A one way ANOVA procedure was used to determine the effect of fertilizer type on plant yield and DW-content, plant nutrient uptake, soil quality parameters and biogas production. Significance of effects was tested by use of a F-test ($\alpha = 0.05$; n = 4) and post hoc pair-wise comparisons were conducted using Tukey's HSD Test ($\alpha = 0.05$; n = 4).

2.5 Nutrient balances

Modeling of N was conducted with the computer model NDICEA *(Nitrogen Dynamics In Crop rotations in Ecological Agriculture)* nitrogen planner 6.0.16 [8]. The physicochemical product, plant and soil analyses conducted in this study were used as input to the model. The nutrient balances obtained are thus specific for each scenario. In addition, nutrient balances for P_2O_5, K_2O, Ca, Mg, Na and S were set up based on the product, plant and soil analyses. Here, the nutrient surplus on the soil balance was calculated by the difference between nutrient supply to the field (synthetic fertilizers, animal manure, digestate derivatives, atmospheric deposition) and crop demand. The obtained nutrient surplus on the soil balance is a measure of potential pollution to soil, air and water by agricultural practices. The lower the surplus, the better for the environment.

2.6 Economic and ecological evaluation

The methodology used for the economic and ecological evaluation of the application of bio-based mineral fertilizers in agriculture can be found in Vaneeckhaute et al. [1]. The economic and ecological benefits were calculated using the following equations:

Economic benefits (€ ha^{-1}) $= SF_{production} + SF_{packing} + SF_{application} + SF_{transport} + DD_{application} + DD_{transport} + AM_{application} + AM_{transport} - AM/DD_{benefits}$ (eq.1)

Energy use (GJ ha^{-1}) = $SF_{production} + SF_{packing} + SF_{transport} + SF_{application} + DD_{transport} + DD_{application} + AM_{transport} + AM_{application}$ (eq. 2)

where "*SF*" are synthetic fertilizers, "*DD*" are digestate derivatives and "*AM*" is animal manure. Furthermore, the greenhouse gas (GHG) emission was calculated for the different scenarios in terms of GHG CO_2 equivalents emission (kg ha^{-1}). It was assumed that diesel is used for the transport and application of fertilizers and that natural gas is used for the production of synthetic fertilizers.

3. Results

3.1 Product characterization

The physicochemical characteristics of pig slurry, the digestate/LF-digestate mixture (ϕ = 0.5) and LF-digestate can be found in Table 4. The N/P/K-ratio was 3.4/1/3.7 for pig slurry, 5.2/1/2.4 for the mixture and 13/1/11 for LF as such, while the C/N-ratio was respectively 5.2, 5.0 and 1.7. The amount of extractable nutrients was mostly higher for digestate derivatives than for animal manure.

The physicochemical characterization of acidic air scrubber water is given in Table 5, before and after pH-adjustment. The N-content was approximately 3.0 g kg^{-1} FW before pH-adjustment and 2.7 g kg^{-1} FW thereafter, whereas the S-content amounted to 3.4 and 3.1 g kg^{-1} FW, before and after pH-adjustment respectively. The N-use efficiency (NUE) reached the maximum of 100 %. It should be noted that the pH after adjustment in practice in the field was a bit higher than predicted under laboratory conditions, 8 instead of 7. Also the salt content of this product was very high compared to traditional fertilizers.

3.2 Biomass yield and dry weight content

There was a statistically strong effect (p = 0.0075) of the variable treatment on the fresh weight biomass yield at the harvest, where Sc7 and Sc5 showed higher values than Sc2 (Figure 2). During the growing season no significant differences between the eight treatments were observed at the 5 % level ($p_{July} = 0.59$; $p_{Sept} = 0.10$). The DW-content of Sc4 and Sc8 was significantly (p = 0.03) higher compared to Sc3 in July (Figure 3), but no statistically significant differences were observed in DW-content in September (p = 0.47) and at the harvest (p = 0.94). Also, no significant differences were noticed in the DW biomass yield among the eight treatments during the growing season (July: 4.3±0.2 t ha^{-1}, p = 0.56; Sept: 17±1 t ha^{-1}, p = 0.50), nor at the harvest (23±2 t ha^{-1}, p = 0.68). Finally, the length measurement in August showed not much effect of the variable treatment throughout the field

(3.61±0.03 m, p = 0.19), nor did the cob percentage on DW-content (31±3 %). Nevertheless, Tukey HSD tests indicated that through the different measurements Sc7 always had the highest mean DW-yield and length.

3.3 Crop nutrient uptake

The crop nitrogen, phosphorus, potassium, calcium, magnesium, sodium and sulfur uptake (kg ha^{-1}) are represented in Table 6. First, for N no statistically significant differences ($p = 0.68$) in crop uptake were observed at the harvest, and also during the growing season there was not much effect ($p_{July} = 0.11$; $p_{Sept} = 0.33$) of the variable treatment on the crop N-uptake. Next, for P_2O_5 also no statistically significant effect was observed at the 5 % level of the variable treatment on the crop uptake in July ($p = 0.10$), nor in September ($p = 0.40$) and at the harvest ($p = 0.67$). Nevertheless, it was observed that the mean P_2O_5-uptake at the harvest was slightly higher for Sc4-8 compared to Sc1-3. Furthermore, during the growing season no significant differences ($p_{July} = 0.18$; $p_{Sept} = 0.94$) in crop K_2O-uptake were observed. However, there is strong statistical evidence ($p = 0.0038$) that at the harvest the K_2O-uptake was significantly higher for Sc4-5 compared to the reference (Sc1), as well as for Sc5 compared to Sc2. Scenario 6 also showed a higher mean K_2O-uptake, but due to the rather high standard deviation on the result, the Tukey HSD test did not indicate a statistically significant difference with the reference at the 5 % level for this scenario. Interestingly, in Sc1-3 the K_2O-uptake did not increase much more after September 6, while that of Sc4-6 kept on rising.

For Ca, there was no statistically significant difference ($p = 0.53$) in crop uptake among the different treatments at the harvest, and also during the growing season only a very weak effect of the variable treatment was observed on the crop uptake ($p_{July} = 0.17$; $p_{Sept} = 0.089$). The mean Ca-uptake at the harvest was the highest for Sc5 and the lowest for Sc6. Subsequently for Mg, no statistically significant difference ($p = 0.56$) in crop uptake was found among the eight treatments at the harvest, and also during the growing season not much effect of the variable treatment was recorded on the crop Mg-uptake (p_{July} = 0.16; p_{Sept} = 0.13). The mean crop uptake at the harvest was the highest for Sc7 and the lowest for Sc6, similar as for Ca.

Large variations in Na-uptake by the crops between the different treatments were observed, but also large standard deviations on the measurements per treatment were obtained. Therefore, at the 5 % level no statistically significant differences could be derived in crop Na-uptake during the growing season (p_{July} = 0.090; p_{Sept} = 0.64), nor at the harvest (p = 0.56). The mean crop Na-uptake at the harvest was the highest for Sc7. Finally, a significant effect (p = 0.036) was observed of the variable treatment on the crop S-uptake in July. Hereby the crop S-uptake was significantly higher for Sc7 compared to Sc8. However, in September (p = 0.095) this effect was only weak and at the harvest (p = 0.45) no more significant differences were observed among the eight treatments at the 5 % level. It can however be seen that in Sc4-8 the mean S-uptake at the harvest was slightly higher compared to Sc1-3.

3.4 Nutrient balances

Nutrient balances for nitrogen, phosphorus, potassium, calcium, magnesium, sodium and sulfur are presented in Table 7. In all scenarios the crop demand was higher than the manure supply of N, P_2O_5, K_2O, Ca and Mg, resulting in a net nutrient deficit on the soil balance. The additional supply was provided by the decomposition of organic matter and/or extraction of difficult available nutrients from the soil matrix. For Na, the supply by manure application was always higher than the crop demand, resulting in a net surplus on the soil balance. In the scenarios where air scrubber water was used (2, 3, 5 and 6) the S-supply was higher than the crop demand, yet in the other scenarios there was a S-deficit.

3.5 Soil quality

First, a statistically strong effect ($p = 0.0031$) of the variable treatment on the NO_3-residue in the soil (0-90 cm) was observed on November 25 (Figure 4). All scenarios, except Sc5, exhibited lower NO_3-residues than the conventional fertilization (Sc1). The NO_3-residue was significantly higher for Sc5 compared to 2, 4, 6 and 8, which on their turn showed significantly lower NO_3-residues compared to the reference (Sc1). All the other treatments showed no significant difference with the reference at the 5 % level. It should be remarked that only for treatment 4, 6 and 8 the average NO_3-residue (0-90 cm) on November 25 was lower than the limit of 90 kg NO_3-N ha^{-1} as described by the Flemish Manure Decree [3]. In addition, modeling of N-dynamics with NDICEA indicated that average NO_3-leaching was lower for all scenarios, except Sc7, compared to the reference (Table 7).

Next, there is strong statistical evidence ($p < 0.0001$) that the pH-H_2O was significantly lower for Sc5 compared to the other treatments in the beginning of July (Table 8). However, in September and October no more significant differences ($p_{Sept} = 0.49$; $p_{Oct} = 0.54$) were observed in the pH-H_2O between the different scenarios. The pH-KCl (Table 8) did not significantly differ among the eight treatments during the growing season ($p_{July} = 0.51$; $p_{Sept} = 0.98$), nor at the harvest ($p_{Oct} = 0.99$). The EC (Table 8) was quite variable between the different treatments, but also large standard deviations on the measurements per treatment were observed. A weak effect of the variable treatment on the soil EC was recorded in July ($p = 0.07$), yet in September ($p = 0.23$) and in October ($p = 0.94$) no significant differences in the EC could be derived at the 5 % level. The soil organic carbon content (% on DW) was at each sampling moment rather high for a sandy-loam soil (July: 3.4±0.3 %; Sept: 3.3±0.1 %; Oct: 3.0±0.0 %), but no statistic significant differences in organic carbon were observed between the different treatments ($p_{July} = 0.66$; $p_{Sept} = 0.94$; $p_{Oct} = 0.99$).

The SAR in the soil solution was measured in July and October and was each time very low (< 1) for all scenarios. The LSD test indicated a significant difference ($p = 0.020$) in SAR between the different scenarios in July, but due to the large standard deviations per measurement, no significant differences were found with the Tukey HSD test. However, it can be derived from the boxplots presented in Figure 5 that the mean SAR was slightly higher for Sc5-8, compared to Sc1-4. This is in line with the total amount of Na, which is also significantly higher in July ($p = 0.030$) and weakly higher in September ($p = 0.11$) for these scenarios. Nevertheless, in October not much effect was observed of the variable treatment on the SAR ($p = 0.16$) and total soil Na ($p = 0.23$).

Further, no significant differences ($p_{July} = 0.78$; $p_{Sept} = 0.91$; $p_{Oct} = 0.71$) were observed in P-accumulation between the eight different treatments during the field trial (Table 7). The amount of available P_2O_5 in the soil at the harvest was the lowest for Sc8. Finally, for heavy metals, it was observed that the Cu-concentration in the soil was approximately the double of the Flemish environmental quality standard of 17 mg kg^{-1} dry soil [9] in all scenarios, including the reference, at each sampling moment (July: 34±1 mg kg^{-1}; Sept: 33±1 mg kg^{-1}; Oct: 33±1 mg kg^{-1}). The amount of As, Cd, Cr, Hg, Pb, Ni and Zn was always lower than the environmental quality standard of 19, 0.8, 37, 0.55, 41, 9 and 62 mg kg^{-1} DW respectively [9].

3.6 Biogas potential

There was statistically not much effect ($p = 0.11$) of the variable treatment on the biogas potential (m^3 ha^{-1}) of the energy maize at the harvest (Table 9). However, a higher energetic potential per hectare was found for Sc4-7 compared to Sc1-3. Furthermore, there was a very strong linear correlation ($Y = 6.053X – 32.771$; $R^2 = 1$) between the biogas potential (m^3 t^{-1} FW; Y) and the DW-content of the biomass (%; X), where higher DW-contents resulted in a higher biogas potential.

3.7 Economic and ecological evaluation

The economic benefits, the energy use and GHG-emission for the eight different scenarios are presented in Figure 6-7. For all reuse scenarios the calculated economic benefits were significantly higher than the reference (Sc1), whereas the GHG-emission and energy use were significantly lower. Both the economic benefits and the energy and GHG-reduction were the highest for Sc8.

4. Discussion

4.1 Fertilizer impact on crop production and biogas potential

The DW-content of the biomass and DW-yield at the harvest are key parameters for determination of the biogas yield [10], [11], [12], and [13]. Before energy maize is digested, the maize first has to be ensilaged in order to reach a maximum yield [11]. Therefore a minimum DW-content in the total plant of 28 % is required in order to prevent sap losses in the silage. The DW-content may also not exceed 35 %, because then the fermentation potential diminishes due to the higher lignin content of more ripened maize [12]. The energy maize species under study was Atletico (KWS), which is a late cultivar with a FAO ripeness index of 280. These species bloom later in the season, so that they have a longer vegetative period in which they can grow more biomass [11], [13]. The DW biomass yield in this study was at the harvest approximately the same in all scenarios, 23±1 t ha^{-1}, which is regular for the cultivation of this species in Flanders and higher than that of silo maize, 15 t ha^{-1} [12]. The average DW-content at the harvest was 28±1 %, so the energy maize was suitable for biogas production (desired 28-36 %).

Nevertheless, in this study the average biogas production potential of the energy maize expressed as methane production (307±13 m^3 t^{-1} DW) was slightly lower than in the study of Calus et al. [10], where 345 m^3 t^{-1} DW in average was reported. Otherwise, when taking in account the biomass yield, the methane production potential of the energy maize (7 135±364

m^3 ha^{-1}) was higher for each treatment in this study compared to the range of 4 856-6 621 m^3 ha^{-1} obtained in Calus et al. [10] and to the average energetic potential of 220 GJ ha^{-1} obtained in Veldeman et al. [14]. Interestingly, it was found that although there was not much effect of the fertilizers used on the biogas potential, the energetic potential per hectare was higher for Sc4-7 compared to Sc1-3, due to the higher fresh weight biomass yield in these scenarios.

4.2 Fertilizer impact on soil fertility and soil quality

The crop demand was in each scenario covered by the availability of N from manure and soil supply, so it is likely that the amount of NH_3-evaporation was not specifically higher in the scenarios where the pH-adjusted waste water was used. Also, there were no significant differences in N-uptake by the plant, demonstrating that the air scrubber water can be a valuable substitute for synthetic fertilizer N. Furthermore, nitrogen balances are roughly similar for each scenario and in equilibrium, indicating that the amount of NO_3-leaching was not much influenced by the fertilizer type. However, modeling of N-dynamics with NDICEA showed that average NO_3-leaching was slightly lower, except for Sc7, compared to the reference. Although Italian rye-grass was sown on the field as an intercrop in October, the NO_3-residue was only in treatment 4, 6 and 8 lower than the maximum allowable NO_3-N level of 90 kg ha^{-1} [3]. As there is no connection between the NO_3-residue and the fertilizer type applied, other factors must have caused this undesired effect.

At first, the exceptional dry spring and wet summer, as well as the autumn characterized by exceptional high temperatures, can explain the higher NO_3-residue values for maize. The Flemish Land Agency [15] has reported that in 2011 approximately 40 % of the NO_3-residue measurements in West Flanders exceeded the allowable level. Further, it might also be possible that the dose of 150 kg ha^{-1} effective N, which is the advice for the cultivation of maize on non-sandy soils [3], was too high for the field under study, since during the experiment it was observed that the 0-90 cm soil layer was rather sandy than sandy-loam. In all respects, these high NO_3-residues may increase the risk for NO_3-leaching to ground and surface waters. Therefore, next year guided measures will be implemented at the field [15].

Concerning the intercrop, it is likely that the density of the Italian rye-grass was too low and that the grass was sown too late, so that it could not yet take up its maximum amount of N at the sampling moment. The N-uptake is dependent of the date of sowing and is normally for this species between 40 and 60 kg ha^{-1}, and up to 80 kg ha^{-1} under good conditions. In order to reach a maximum N-uptake, it is advised to sow the rye-grass as soon as possible after the harvest and not later than October 15 [15]. Therefore, in the next experimental year the intercrop will be sown immediately after the harvest to optimally enjoy the maximal benefits.

Next, an important remark is that the amount of P_2O_5 applied to the soil in Sc1-3 and Sc7-8 exceeded the maximum level of 80 kg ha^{-1} as described by the Flemish Manure regulation [3]. This is caused by the variability in the composition of animal manure between the first and the second sampling moment. The P_2O_5-content in digestates and derivatives seems to be more stable in time, which is an interesting observation in terms of fertilizer application. Although significantly less P_2O_5 was applied to the soil in Sc4-6, a higher crop P_2O_5-uptake was observed in these scenarios. This could be attributed to the higher relative amount of mineral P_2O_5 to total P_2O_5 in the digestate/LF-digestate mixture ($\phi = 0.5$) than in animal manure (Table 4). However, because the P_2O_5-supply could not cover the crop demand in all scenarios, the plants must also have extracted P_2O_5 from the soil pools, especially in Sc4-6. Up to now no significant differences in soil P-content were observed ($p > 0.05$), but in frame of P becoming rapidly depleted [16], this opportunity to mobilize P_2O_5 in the soil can be an interesting way to recover and recycle P_2O_5 in the longer term. An evaluation of the bio-availability of P in the soil and the partitioning among the different P-pools by application of these new fertilizers is required and will be aspect of further research.

A similar effect as for P_2O_5 was found for K_2O. The crop K_2O-uptake was significantly higher for Sc4-6 compared to the reference. Interestingly, in these scenarios approximately three times less synthetic K_2O was used (Table 2). This could turn out in serious economic and ecological benefits, especially in Sc5-6, where synthetic N was simultaneously replaced by air scrubber water. As for P_2O_5, also the relative amount of mineral K_2O to total K_2O was higher in the digestate/LF-digestate mixture ($\phi = 0.5$) than in animal manure (Table 4), and since the crop demand was higher than the K_2O-supply, the crops must also have extracted K_2O from the soil, especially in Sc4-6. As synthetic K_2O is currently extracted through mining, this reduction in synthetic K_2O-use simultaneously with the extra liberalization of K_2O from the soil, might be an interesting path to recycle this valuable macronutrient in a sustainable way.

Next to N, P_2O_5 and K_2O, also S is an essential macronutrient for plants. However, too high doses of sulfate could also lead to salt accumulation in soils [7]. In scenarios 2, 3, 5 and 6, where air scrubber waste water was used, the S-supply was higher than the crop demand, resulting in a potential S-surplus on the soil balance. Reversely, in the scenarios where no air scrubber water was used the crop demand was higher than the S-supply by manure application, resulting in a net S-extraction from the soil. Up to now no significant differences in soil S-content and soil pH were observed during the growing season and at the harvest ($p > 0.05$), but these are parameters that require follow-up in the longer term. An interesting observation is that, while there was no effect of the use of air scrubber waste water on the crop S-uptake, in the scenarios where digestate and/or LF was used as base fertilizer (Sc4-8) the crop S-uptake was slightly higher than in the scenarios where only animal manure was used (Sc1-3). This is likely due to the higher relative amount of mineral S compared to total S in the digestate derivatives (Table 4).

Calcium and magnesium both play an essential role in the development of plants and the flocculation of colloidal clay, hence influencing soil structure. Although in all scenarios the crop demand for Ca and Mg was higher than the supply by manure application, no adverse effects (chlorosis) were observed and the content of Ca and Mg in the plants were in the range of Hillel [7], 0.4-2.5 % Ca and 0.1-0.4 % Mg on DW-content. The plants have thus extracted Ca and Mg from the soil, especially in Sc4-6, where the Ca- and Mg-supply by fertilizer application was the smallest, while the plant uptake was slightly higher compared to the other scenarios. Nevertheless, up to now no significant differences in soil Ca- and Mg-concentration were observed throughout the field. However, in the long term this Ca- and Mg-deficit could have a negative influence on the soil structure, if no additional liming is provided. On the other hand significantly more organic carbon was applied to the soil in the scenarios where digestate derivatives were used as base fertilizers (Sc4-8) compared to the scenarios where only animal manure was used (Sc1-3) (Table 2). This additional carbon supply could significantly improve soil structure, thereby counterbalancing the above mentioned deficit.

Sodium has a minor role as trace element in plant nutrition. Too high doses can cause increased soil salt contents and SAR's, leading to soil degradation in the long term. More Na was applied to the soil in Sc4-8 compared to Sc1-3, while the crop Na-uptake was not significantly different among the treatments. This results in a higher Na-surplus on the soil balance for Sc4-8, where digestate derivatives were used as base fertilizer. Up to now, no significant impact on the soil salt content and the SAR could be observed. These are, however, important parameters that will be followed up in the long term.

Because digestate is the waste product of the co-digestion of animal manure, energy crops and organic biological waste from the food industry, it could also contain an important amount of micronutrients and heavy metals. Moreover, raw animal manure can contain significant amounts of Cu and Zn [17]. On the one hand Fe, Mn, B, Zn, Cu, Mo, Co and Ni are all essential trace elements for plants, but on the other hand there also exist soil environmental quality standards for Cu, Zn and Ni, as well for As, Cd, Cr, Hg and Pb [9]. Results have shown that the standards were only exceeded for Cu in all scenarios, including the reference. It should, however, be remarked that the Cu-enrichment in this region is likely the legacy of the millions of shells that were fired during the First World War [18].

4.3 Technical and legislative implications

It is clear that waste water from an acidic air scrubber for ammonia removal can be a valuable N-S-rich mineral fertilizer. No differences in crop yield, soil fertility and soil quality were observed by use of the air scrubber water as compared to the reference. However, there still remain some technical and legislative implications, hindering its use. First, the pH of the acidic air scrubber water in this study amounted to 2, which is practically very low for use as a fertilizer. The low pH could cause corrosion to application instruments, leaf burning, and soil acidification after long-term application. Moreover it causes a potential hazard for the farmer. It is therefore advised to neutralize the acidic pH. In this study this was conducted by addition of NaOH. However, environmental technical solutions are required to neutralize the pH of this waste stream in a practical, economic and ecological way. Possibilities could be to adjust the pH with waste water of an alkaline air scrubber, or to develop air scrubbers that directly produce air scrubber water with a higher pH.

Another technical implication is the way of spreading the air scrubber water to the field. As the N-content of this product is only 2-3 g kg^{-1} FW, approximately 1 000 L ha^{-1} has to be applied, implying that the farmer must drive much slower than when applying animal manure, which usually only amounts to 300 L ha^{-1}. One potential way to overcome this problem is to evaporate (part of) the water and crystallize the ammonium-sulfate, but then significant amounts of energy have to be used. Modified or new application techniques should be investigated for this new type of fertilizer and/or methods to concentrate the N-content in an economic and ecological way should be discovered. Although waste water from an acidic air scrubber has high potential as mineral fertilizer, it has not often been applied up to now due to legislative constraints and farmers' distrust. Therefore, it is highly important that the results obtained in this study are widely spread and that the European Commission stimulates the use of air scrubber water.

Next, from the results it is clear that the substitution of animal manure by digestate and LF-digestate does not reduce the crop yield, physicochemical soil fertility and soil quality. It is even observed that the substitution can result in a higher P_2O_5- and K_2O-extraction from the soil, thereby increasing the use efficiency of soil minerals. Furthermore, the nutrient availability in these products is mostly higher than in animal manure, indicating that they have better mineral fertilizer properties, next to the organic properties. Therefore, the use of these bio-based products should be stimulated in European legislation. It is reasonable that they may no longer be classified as animal manure and that the introduction of a new legislative framework, in which these products are classified based on their own specific fertilizer properties, is indispensable.

4.4 Economic and ecological evaluation

The application of bio-based fertilizers in agriculture can result in significant economic benefits for the agriculturist, as well as ecological benefits through energy use and GHG-emission reduction [1]. The complete substitution of synthetic fertilizer N by air scrubber water (Sc3) could almost double the economic benefits, while the energy use and GHG-emissions were 2.5 times reduced. When meanwhile substituting animal manure by the digestate/LF-mixture (Sc4-6), the observed benefits were even higher, because here less synthetic N was required due to the higher N/P-ratio of the mixture, while also the need for synthetic K_2O was less. The economic and ecological benefits were the highest for Sc8, respectively 3.5 and 4.4 times higher than the reference, as both synthetic N and K_2O were completely eliminated in this treatment.

5. Conclusion

The use of waste water from an acidic air scrubber for ammonia removal, digestates and liquid fraction of digestates as substitute for animal manure and/or synthetic fertilizers in agriculture causes small, albeit insignificant, improvement in energy maize yield, physicochemical soil fertility and soil quality by one year application. In addition, the energetic potential per hectare of harvested energy maize is slightly higher, and the economic and ecological benefits significantly higher, when digestate derivatives are used, compared to animal manure additionally supplied with synthetic fertilizers. It is clear that the use of these products should be stimulated in European legislation and that the results obtained in this study should be widely spread. This one-year field trial is continued in 2012 in order to validate the results and evaluate the impact on soil quality in the longer term.

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