Production and performance of bio-based mineral fertilizers from agricultural waste using ammonia (stripping-)scrubbing technology

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ABSTRACT

Development and optimization of nutrient recovery technologies for agricultural waste is on the rise. The full scale adoption of these technologies is however hindered by complex legal aspects that result from lack of science-based knowledge on characterization and fertilizer performance of recovered end-products. Ammonium sulfate (AS) and ammonium nitrate (AN), end-products of (stripping-)scrubbing technology, are currently listed by the European Commission as high priority products with the potential of replacing synthetic N fertilizers. The legal acceptance of AS and AN will be highly dependent on critical mass of scientific evidence.

This study describes four different (stripping-)scrubbing pathways to recover ammonia with an aim to (i) assess product characteristics of ammonium nitrate (AN) and ammonium sulfate (AS) produced from different installations, (ii) evaluate fertilizer performance of recovered end-products in greenhouse (*Lactuca sativa* L.) and full field (*Zea mays* L.) scale settings and (iii) compare the observed performances with other published studies. Results have indicated that the recovered products might have a different legal status, as either mineral N fertilizer or yet as animal manure, depending on the used (stripping-)scrubbing process pathway. Nevertheless, no significant differences in respect to product characterization and fertilizer performance of AN and AS have been identified in this study as compared to the conventional use of synthetic N fertilizers. This indicates that recovered AS and AN are valuable N sources and therefore might be used as N fertilizers in crop cultivation.
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1. Introduction

1.1. Paradox of synthetic mineral nitrogen requirement in nutrient surplus regions

Intensification of the livestock sector has increased production efficiency and simultaneously induced detrimental effects on the environment. The livestock sector is currently responsible for 14.5% of all human-induced greenhouse gas (GHG) emissions (Sakadevan and Nguyen, 2017). Moreover, it generates large nutrient surpluses of on-farm nitrogen (N) and phosphorus (P) that may lead to a pollution of water bodies. To protect European watercourses, the Nitrates Directive (91/676/EEC) was implemented in 1991 with the aim to limit the application of N from animal manure up to 170 kg N ha^{-1} y^{-1} in Nitrate Vulnerable Zones (NVZs) (European Commission, 1991). These zones are mostly located in European regions known for high livestock density, such as Flanders (Belgium), the Netherlands, Denmark, Brittany (France), Po Valley (Italy), Ireland, Aragon and Catalonia (Spain). In Flanders and the Netherlands, farmers are confronted not only with the limitation on N application from animal manure but also with strict

limitations on P inputs to avoid further build-up of P in soil (Sigurnjak et al., 2017a). All these limitations have led to the current situation where animal manure surplus needs to be processed and/or exported to regions of relative shortage. Ironically, nutrient surplus regions are also amongst the largest consumers of synthetic mineral fertilizers in order to meet crop requirements, in addition to what is allowed to be fertilized in the form of raw animal manure. This basically implies, low (negative) value of nutrients present in raw animal manure and high (positive) economic value for products that could potentially substitute synthetic mineral fertilizers all within the same geographic region.

In nutrient surplus regions animal manure is often separated, directly or after anaerobic digestion, into a P-rich solid fraction and a nitrogen and potassium rich (NK-rich) liquid fraction. The former is usually exported to P-deficient regions, while NK-rich liquid fraction is further treated. One of the most used treatment options for the liquid fraction is a conventional aerobic treatment (Foged et al., 2011; VCM, 2016; Loyon, 2017; Hou et al., 2017) that involves nitrification-denitrification of N into N_2 gas. For example, 81 out of 118 manure processing installations in Flanders used aerobic treatment as a primary technique in 2015, accounting for the loss of around 12.7 million kg N in the form of inert N_2 gas (VCM, 2016). At the same time, however, the intensive crop production systems require a high input of nutrients to optimize yields. Due to the imposed limitations on the application of N and P from animal manure on the arable land, the allowable application of N from animal manure is lower than the crop N demand. To fill the gap synthetic N fertilizers, synthesized via energy intensive Haber-Bosch process, are used by farmers to satisfy the crop N requirements. For example, around 70 million kg of N are applied annually on Flemish soil by using synthetic N fertilizers (Lenders et al., 2013) despite existing N excess from animal manure.

1.2. Pathways for nitrogen recovery using (stripping-)scrubbing technology

In the emerging circular bio-based economy, the loss of N from aerobic treatment should be prevented by recovering N from animal manure and using it as a replacement for synthetic N fertilizers. As such, a more sustainable option would be to subject NK-rich liquid fraction to ammonia (stripping-)scrubbing process and subsequently produce N rich fertilizer, rather than to biologically convert N to N_2 and capture it back via Haber-Bosch process. The operating principle of (stripping-)scrubbing is that ammonia (NH_3) can be stripped by air, steam or vacuum through the N rich waste stream in an ammonia stripping reactor (eg. packed bed tower, mixer and microwave-assisted air reactors), resulting in NH_3 transfer from the aqueous phase to a gas phase (Guštin and Marinšek-Logar, 2011; Kinidi et al., 2018). The released NH_3 is removed in a chemical air scrubber by washing it with a strong acidic solution such as sulfuric or nitric acid. The reaction of NH_3 with sulfuric acid (H_2SO_4) results in ammonium sulfate (AS), whereas reaction with nitric acid (HNO_3) results in ammonium nitrate (AN). Due to the high N concentration, both end-products have a potential to be used as N fertilizers. To obtain optimal removal of NH_3, often the pH of the waste stream and temperature are adjusted. Depending on the used pH and temperature, the NH_3 removal efficiencies have been reported to vary in range of 70–99% (MB31/05/2011; Melse and Ogink, 2005; Zhang et al., 2012; La et al., 2014; Van der Heyden et al., 2015; Limoli et al., 2016). The highest NH_3 removal efficiency of 99% was demonstrated at pH 10 and 70 °C (Lemmens et al., 2007; Melse and Ogink, 2005; Van der Heyden et al., 2015).

In Europe, the following pathways (PW) have been identified to recover NH_3 via (stripping-)scrubbing on a full scale (Fig. 1):

(i) **PW1. Air cleaning pathway** only makes use of scrubbing unit to treat NH_3 rich indoor air from animal stables, drying units and composting installations, especially those mechanically ventilated (Melse and Ogink, 2005). In essence this pathway makes use of capturing volatile NH_3 in its gaseous form by an acid scrubber. A scrubber is a reactor filled with inorganic packing material, with large porosity and large specific area. Water is sprayed with nozzles over the packing material, without leaving any dry area, to prevent the loss of unwashed exhaust air. Part of it is continuously recirculated, the remaining fraction is discharged and replaced by fresh water. Air from animal stables, drying units and composting installations is blown into the system either horizontally (cross-current) or upwards (counter-current). The contact between air and water facilitates the mass transfer between the two phases. In chemical scrubbers, the pH is controlled between 1.5 and 4 by addition of acid substances to the recirculation water, shifting the equilibrium towards ammonium and thus increasing its absorption into the aqueous phase (Van der Heyden et al., 2015). Long term monitoring of acid scrubbers at five farm locations was carried out in the study by Melse and Ogink (2005), reporting average NH_3 removal efficiency 90–99% with a minimum and a maximum peak of respectively 40 and 100%.

(ii) **PW2. Ammonia removal and recirculation pathway** where (stripping-)scrubbing unit is coupled to an anaerobic digester with the aim to reduce potential NH_3 inhibition in the digester. Several variations on this particular pathway can be encountered – e.g. (i) after mechanical separation of the digestate, the liquid fraction is stripped and recirculated to the anaerobic digester, or (ii) the raw digestate is stripped using biogas as a stripping agent after which biogas rich in NH_3 is scrubbed and the stripped digestate is re-circulated to the anaerobic digester. Previously reported laboratory experiments on recirculation have been carried out with column temperatures ranging between 35 °C and 85 °C and with the addition of CaO, Ca(OH)$_2$ and NaOH to adjust the pH to a value around 10 (Serna-Maza et al., 2014, 2015). After stripping, the treated digestate was recycled to the digester and biogas was circulated through traps to remove NH_3. Removal of NH_3 from the gas stream is achieved by means of a condensate trap followed by bubbling through water and then through H_2SO_4 before recirculating biogas to the digester (Zhang et al., 2017).

(iii) **PW3. End-of-pipe pathway** where digestate from anaerobic digestion or raw animal manure is first separated into liquid and solid fraction, and subsequently the liquid fraction is treated in a (stripping-)scrubbing unit instead of being, for example, subjected to biological treatment. This pathway involves the use of additives (eg. lime) to increase the pH of the treated liquid fraction in order to increase the NH_3 emission. In studies by Ledda et al. (2013) and Bolzonella et al. (2018) end-of-pipe pathway has allowed the treatment of 50–100 m^3 day^{-1} digestate from which after separation 17–33% of N found initially in digestate was recovered as ammonium sulfate.

1.3. Ammonium sulfate and ammonium nitrate as mineral N fertilizers

In 2011, 69 air cleaning installations (as part of manure processing plants) have been identified in the EU at medium and large scale installations, treating 4 million tonnes of livestock manure and other products (Flotats et al., 2013). The current number is unknown, but the interest in this technology is increasing and so are innovations in the field of (stripping-)scrubbing. To date, many
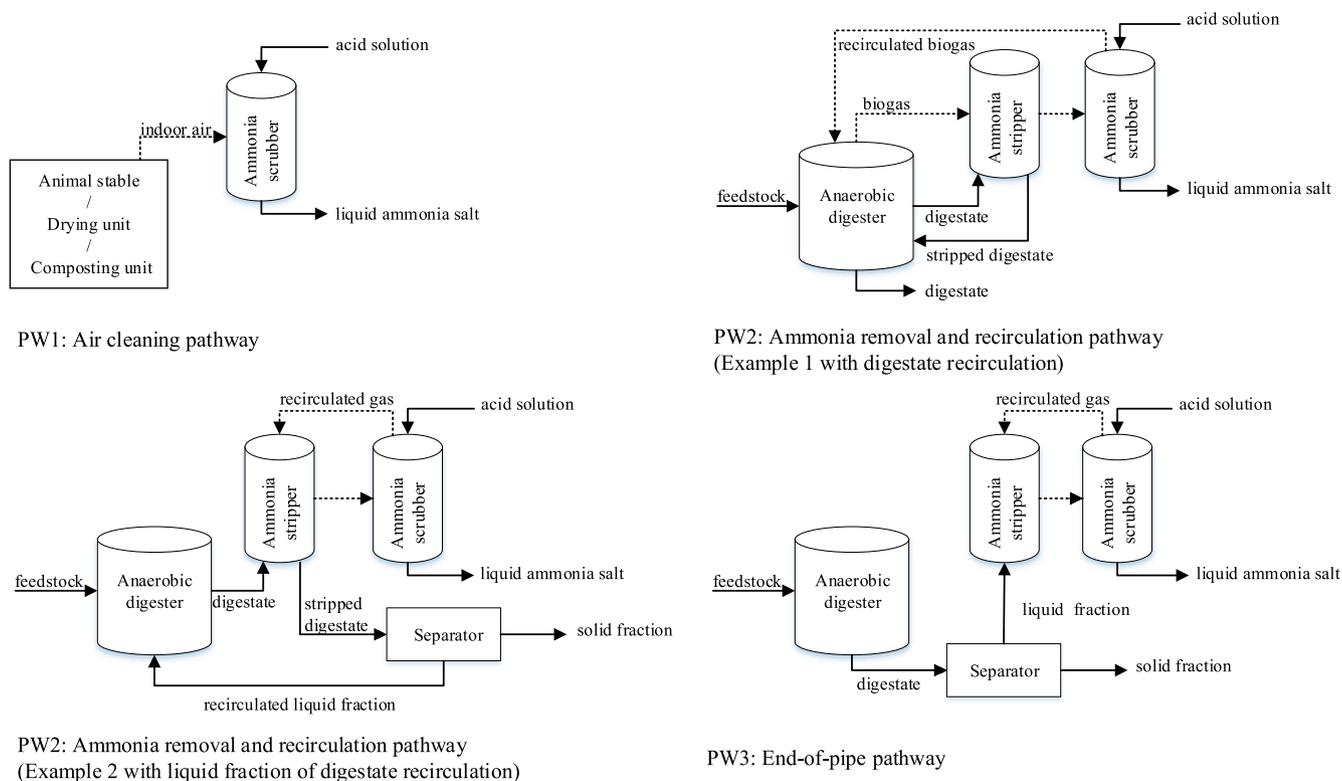
Fig. 1. Pathways (PW) for nitrogen recovery using (stripping-)scrubbing technology.

researchers have focused on technological aspects of (stripping-) scrubbing technology (Melse and Timmerman, 2009; Guštin and Marinšek-Logar, 2011; Serna-Maza et al., 2015; Bousek et al., 2016; Provolo et al., 2017) and little has been reported on the resulting products, AS and AN, and their potential to be used as N fertilizers. To our knowledge, only four studies are currently published on fertilizer performance of AS (Vaneeckhaute et al., 2013, 2014; Chen et al., 2014; Sigurnjak et al., 2016) and none on fertilizer performance of AN. Consequently, European legislation still identifies AS and AN originating from animal manure as an animal manure (European Commission, 1991). The current European legislative framework prohibits application of these end-products on top of 170 kg N ha^{-1} y^{-1}, reduces the market opportunities for the installation owners and hinders the development of circular economy. Therefore, this study describes four full scale installations that use different pathways to recover NH$_3$ via (stripping-)scrubbing with an aim to (i) assess product characteristics of AN and AS produced at these four installations, (ii) evaluate fertilizer performance of recovered end-products in lettuce and maize cultivation and (iii) compare the performance of end-products in this study with results from four other published studies on AS.

2. Materials and methods

2.1. Description of ammonia recovery systems at four full scale installations

2.1.1. Air cleaning pathway (PW1)

AS was collected at a pig farm in Merkem, Belgium. The farm counts in total 7000 pigs out of which 430 are sows and the rest are piglets. Pig manure is collected via a slatted floor and kept in concrete manure storage under the stables (capacity of c. 5000 m^3 with an option of minimum 9 months residence time)

prior to being separated by means of centrifugation and subsequently sent to biological treatment (capacity: 12 000 tonnes y^{-1}). The NH$_3$ is currently recovered only from indoor air of pig stables where air is vented (ventilation capacity: 35 m^3 h^{-1} is needed per pig; Leirs et al., 2017) into a pressure chamber and through lamella (i.e. plastic structures with irregular holes) of the air scrubber (personal communication, VCM). This creates a large contact surface on which the acidified scrubbing water (i.e. water mixed with 96% or 98% H$_2$SO$_4$) is sprayed, capturing NH$_3$ from the air and forming AS. The air scrubber is controlled by the pH of the AS which in this case varies between 1.5 and 5. When the pH is below 5 the AS is recycled and reused again to scrub the air. When the pH is higher than 5, H$_2$SO$_4$ (96% or 98%) is added to reach a pH of 1.5 (personal communication, VCM). On average 1.5 L of H$_2$SO$_4$ is applied to remove 1 kg of NH$_3$ which results in approximately 30 L of AS, depending on the amount of NH$_3$ to be removed and the amount of NH$_3$ that can be in scrubbing water before it is saturated (Leirs et al., 2017). According to the Flemish legislation, NH$_3$ reduction of minimum 70% is achieved by this system (MB31/05/2011).

2.1.2. Ammonia removal and recirculation pathway (PW2)

A first example of AS from ammonia removal and recirculation pathway was provided by the co-digestion plant of Acqua & Sole (Vellezzo Bellini, Italy) within the H2020 Systemic project (unpublished data) and personal communication with operators of the plant. The installation has a capacity of 120 000 tonnes y^{-1} (1.6 MW$_{el}$), treating sewage sludge from a wastewater treatment plant (86%), digested source-segregated food waste (8%) and the liquid fraction of source segregated food waste (6%). The system consists of three digesters placed in series and one storage tank operated at thermophilic temperature (55 °C) with a minimum retention time of 20 days. The first digester is implemented with a side-stream NH$_3$ stripping unit operated at a temperature in range 60–80 °C. NH$_3$ is stripped in a counter flow with biogas as a

medium. Biogas rich in NH_3 is sent into a scrubber where it is neutralized by the addition of H_2SO_4. The generated AS is stored in a steel tank facility, while N-depleted digestate (25% of the digested substrate) and biogas are recirculated back to the first digester (Acqua & Sole, 2011). With this system 22% of NH_4-N contained in the digestate is recovered as AS.

A second example of AS from ammonia removal and recirculation pathway was provided by the co-digestion plant of Benas (Ottersberg, Germany) within the H2020 Systemic project (unpublished data) and personal communication with operators of the plant. The farm includes 3500 ha (ha) of arable land, of which 1000 ha nearby the farm and an anaerobic co-digestion installation (103 000 tonnes y^{-1}, 5.24 MW_{el}). The plant consists of six digesters operated at thermophilic temperature with a retention time of about 150 days. The input feed includes corn silage (56%), chicken manure (26%) and agricultural wastes (18%). Digestate is treated in a (stripping-)scrubbing unit (GNS, 2003). The NH_3 stripping unit consists of three stripping columns where NH_3 is transferred from the liquid to gas phase exploiting exhaust heat generated by the combined heat and power (CHP) engines of the plant. The operating temperature is in the range of 50–80 °C and the pH is maintained at a value of 9 without the addition of any chemical. The gas phase, rich in NH_3, enters into a reactor where an aqueous suspension containing gypsum from a flue gas desulfurization plant (FGD-gypsum, $CaSO_4$) is spread to form a suspension containing AS and calcium carbonate ($CaCO_3$). The suspension is further processed by means of a filter press to obtain AS aqueous solution and solid $CaCO_3$. The N-depleted digestate is pumped to a second screw press. The separated liquid fraction (95% of N-depleted digestate) is recirculated back to the digester, whereas the solid fraction is dried in a rotary dryer to produce marketable fibers. With this system 80% of N contained in the digestate is recovered as AS.

2.1.3. End-of-pipe pathway (PW3)

AN was collected from the (stripping-)/scrubbing unit of DETRICON at a pig farm in Gistel, Belgium. The farm has a capacity of 11 000 fattening pigs and the capacity of the manure treatment installation is about 60 000 tonnes y^{-1}. Initially, all NH_3 from the manure was treated via biological treatment with further processing in a constructed wetland. From 2015, anaerobic digestion was installed with a capacity of 12 500 tonnes y^{-1}, treating animal manure (horse manure 9%, solid fraction of pig manure 17% and pig manure 65%) and food waste (9%). The produced digestate is separated by means of centrifugation and the produced liquid fraction of digestate is treated in (stripping-)/scrubbing unit. The liquid fraction of digestate is mixed with CaO or NaOH to induce ammonia volatilization by increasing pH and temperature. The operating temperature and pH are in the range of 42–50 °C and 7.5–9, respectively. The pilot has a capacity of 30 000–40 000 tonnes of liquid fraction of digestate per year, and a ventilation flow of 1000–1800 m^3 h^{-1} with an air speed of 0.2–0.8 m s^{-1}. The stripped NH_3 is sent to a scrubber column where nitric acid is added as a sorbent, resulting in AN. The HNO_3 in the scrubbing step is used instead of other acids due to higher N value of AN in comparison to other ammonium fertilizers such as AS. The (stripping-)scrubbing has a reduction efficiency of 87.5% by reducing NH_3 from average 4 kg NH_4-N tonnes^{-1} to 0.5 kg NH_4-N tonnes^{-1} of the liquid fraction (personal communication, DETRICON).

2.2. Product characterization

Data on product characterization of AS from PW2 has been received from co-digestion plants Acqua and Sole (Italy) and BENAS (Germany). These products were not further tested in this study as the location of pot and field experiments took place in Flanders (Belgium). Hence, onwards, the fertilizer performance of solely AS and AN from PW1 and PW3 will be evaluated, as the removal and re-circulation pathway (PW2) has not been implemented yet in Flanders. Next to the AS from air cleaning (PW1) and AN from end-of-pipe pathway (PW3), pig manure (PM) was also sampled at a pig farm in Ruiselede (120 sows and 750 fattening pigs; manure storage capacity of c. 700 m^3) for the purpose of conducting pot and field experiments. Since the field (May – October 2015) and pot experiment (January – March 2016) were conducted almost a year apart, the used products where collected on two separate occasions. All products were collected in polyethylene sampling bottles (2 L), stored (4 °C) and characterized (Table 1) to determine the required fertilizer dosage. Dry matter (DM) content was determined as the residual weight after 72 h drying at 80 °C. Organic carbon (OC) of pig manure was determined by ashing, whereas OC of AS and AN was determined by using Total organic carbon (TOC) analyzer (Shimadzu, Japan). Electrical conductivity (EC) and pH were determined on fresh sample using a WTW-LF537 (GE) conductivity electrode and an Orion-520A pH-meter (USA), respectively. Total N was determined using Kjeldahl destruction, and NH_4^+-N was determined using a Kjeltec-1002 distilling unit (Gerhardt Vapodest, GE) after addition of MgO to the sample, and subsequent titration (Van Ranst et al., 1999). After ash digestion (5 ml 6 N HNO_3 and 5 ml 3 N HNO_3) of pig manure and wet digestion (2 ml HNO_3 and 1 ml H_2O_2) of AS and AN (Van Ranst et al., 1999), total P, K and S were analyzed using Inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian Vista MPX, USA).

2.3. Product assessment in comparison to synthetic nitrogen fertilizer

2.3.1. Lettuce growth experiment

The pot experiments with lettuce (*Lactuca sativa* L., cv. Cosmopolia) were conducted on loamy-sand (LS) and sandy-loam (SL) soil. The former was collected from 0 to 30 cm soil layer of an experimental field which was used for a maize trial (Section 2.3.2). The soil collection of loamy-sand soil took place two months (December 2015) after the harvest of maize (October 2015). The sandy-loam (USDA texture triangle: 6% clay, 62% sand and 32% loam fraction) soil was collected from 0 to 30 cm soil layer of an arable field in Roeselare (50°54′53″N, 3°6′41″E), Belgium. The characteristics of loamy-sand soil prior to the experiment were pH-KCl = 4.9; electrical conductivity (EC) = 92 µS cm^{-1}; NO_3^--N = 3.5 kg ha^{-1}; NH_4^+-N = 5.6 kg ha^{-1}; S_{total} = 143 mg S kg^{-1}. Similar values were measured for sandy-loam soil amounting to pH-KCl = 5.8; electrical conductivity (EC) = 95 µS cm^{-1}; NO_3^--N = 5.9 kg ha^{-1}; NH_4^+-N = 4.1 kg ha^{-1}; S_{total} = 181 mg S kg^{-1}.

In both pot experiments, AS and AN were compared to the conventional fertilization regime of using solely synthetic N, in the form of calcium ammonium nitrate (CAN; 27% N), as a N source in horticulture. In total, 4 different fertilization treatments in quadruplicate pots were tested (Table 2). The material application rate was calculated according to the nutrient requirements for lettuce (210 N, 125 P_2O_5 and 240 K_2O kg ha^{-1}; personal communication PCG) by taking into consideration the nutrient value of fertilizers (Table 1). In each pot an equal amount of total N was applied amounting to 77 mg N pot^{-1}. In order to achieve an equal application of P and K in all treatments, triple superphosphate (TSP; 46% P_2O_5) and potassium sulfate (PAT; 30% K_2O, 10% MgO and 42.5% SO_3) were added as additional sources of P and K, respectively (Table 2). After fertilization on January 20, 2016, one lettuce plant with a 5 cm soil block was transplanted in each pot. Detailed experimental conditions are described by Sigurnjak et al. (2017b).

Table 1
Characteristics of ammonium sulfate (PW1) and ammonium nitrate (PW3), used in maize and lettuce trials of this study, compared to the mean ranges of ammonium sulfate (PW1) reported in other published studies (Vaneeckhaute et al., 2013, 2014; Chen et al., 2014; Sigurnjak et al., 2016) and unpublished data from Systemic project. No published data on ammonium nitrate has been found.

Parameters	Maize field trial 2015			Lettuce pot trial 2016		Mean ranges from other studies	Systemic (unpublished results)	
	– PS	PW1 AS	PW3 AN	PW1 AS	PW3 AN	PW1 AS	PW2 (Example 1) AS	PW2 (Example 2) AS
DM (%)	7.3	ND	ND	14	48	33	ND	25
OC (%)	2.7	ND	ND	0.04	0.1	ND	0.04	ND
pH	7.70	5.52	7.85	6.43	6.92	2.40 – 2.50	6.7	7.7
EC (mS cm^{-1})	26	152	342	157	332	157–262	ND	ND
NH$_4$-N (g kg^{-1})	3.7	30	76	37	109	30–86	74	53
NO$_3$-N (g kg^{-1})	0	0	56	0	89	0	0	0
N$_{tot}$ (g kg^{-1})	5.9	30	132	37	198	30–86	74	53
Effective N (g kg^{-1})	3.5	30	132	37	198	30–86	74	53
N$_{mineral}$/N$_{tot}$ (%)	63	100	100	100	100	100	100	100
P (g kg^{-1})	1.8	0	0	0	0	0	0	0
K (g kg^{-1})	3.6	0	0	0	0	0	0	0
S (g kg^{-1})	0.94	114	0	30	0	60	98	60

DM: dry matter; OC: organic carbon; EC: electrical conductivity; PS: pig slurry, AN: ammonium nitrate; AS: ammonium sulfate; ND: not determined; PW1: AS from air cleaning pathway; PW2 (Example 1): AS from digestate that has been stripped and re-circulated to anaerobic digester; PW2 (Example 2): AS from liquid fraction of digestate that has been stripped and re-circulated to anaerobic digester; PW3: end-of –pipe pathway.

Table 2
Product and macronutrient dosage in the pot and field experiment for four different fertilization treatments (n = 4).

Treatments	Product application (g pot^{-1})					Total applied (mg pot^{-1})			
	CAN	AN	AS	TSP	PAT	N$_{effective}$	N$_{total}$	P$_2$O$_5$	K$_2$O
Lettuce pot experiment									
Blank	0	0	0	0	0	0	0	0	0
[Ref]CAN + TSP + PAT	0.289	–	–	0.101	0.298	77	77	46	87
AN + TSP + PAT	–	0.394	–	0.101	0.298	77	77	46	87
AS + TSP + PAT	–	–	2.111	0.101	0.298	77	77	46	87

Treatments	Product application (tonnes ha^{-1})					Total applied (kg ha^{-1})			
	PM	AN	AS	CAN	PAT	N$_{effective}$	N$_{total}$	P$_2$O$_5$	K$_2$O
Maize field experiment									
Blank	0	0	0	0	0	0	0	0	0
[Ref]PM + CAN + PAT	18	–	–	0.21	0.58	120	162	75	250
PM + AN + PAT	18	0.43	–	–	0.58	120	162	75	250
PM + AS + PAT	18	–	1.9	–	0.58	120	162	75	250

[Ref] : reference; PM: pig manure; CAN: calcium ammonium nitrate; PAT: potassium sulfate; AN: ammonium nitrate; AS: ammonium sulfate; TSP: triple superphosphate.

2.3.2. Full maize field validation

The field experiment was performed on a 0.8 ha loamy-sand (USDA texture triangle: 4% clay, 75% sand and 21% loam fraction) soil in Beernem (51°09′03″N, 3°18′12″E), Belgium. The soil characteristics of the 0–30 cm soil layer prior to the experiment were pH = 5.2; NO$_3^-$-N = 3.8 kg ha^{-1}; NH$_4^+$-N ≤ 5 kg ha^{-1}; ammonium lactate extractable P (P-AL) = 240 mg kg^{-1} DM; ammonium lactate extractable K (K-AL) = 67 mg kg^{-1}. The NH$_4^-$-N amount in soil prior to the experiment was <4 kg ha^{-1} per each soil layer (i.e. 30–60 and 60–90 cm), whereas for NO$_3^-$-N 2 kg ha^{-1} was measured in 30–60 cm and 3 kg ha^{-1} in 60–90 cm soil layer. As a test crop, maize (*Zea mays* L.) cv. Madras (FAO Ripeness Index: 235) was grown. Silage maize was cultivated during the previous growing season, with a fallow period during winter. The temperate marine climate of the region, with an average annual precipitation of 800 mm and an average annual air temperature of 10 °C (RMI, 2015), is favorable for high crop yields but entails conditions favorable for N leaching.

Experimental treatments were tested in a randomized block design with quadruplicate plots of 6 m × 10 m (n = 4) spread across the field to minimize potential influence of variable soil conditions on the results. Based on the soil characteristics and crop demand, fertilizer application dosage was advised at 120 kg effective N, 75 kg P$_2$O$_5$ and 250 kg K$_2$O ha^{-1}. The effective N is the amount of N from applied bio-based material that is expected to be available for crop uptake in the season of application (Webb et al., 2013). According to Flemish manure regulation the amount of effective N in animal manure is legally accepted to be 60% of the total N content, whereas for AS and AN 100% is accepted (VLM, 2016). This is similar to what is expected from the application of synthetic N fertilizer. As can be seen from Table 2, AS and AN were applied on top of pig manure and compared to the conventional fertilization of using calcium ammonium nitrate as a synthetic N and animal (pig) manure. Entire P$_2$O$_5$ requirements were satisfied via P contribution from pig manure. K$_2$O requirements on the other hand were not sufficient and additional contribution came from applying synthetic K fertilizer in the form of potassium sulfate (PAT; 30% K$_2$O, 10% MgO and 42% SO$_3$). Finally, in order to determine nitrogen fertilizer replacement value (NFRV) blank treatment was introduced where no nutrients were applied to account for the effect of the soil.

Nutrient application rates for three different treatments are summarized in Table 2. PM was applied on May 13, 2015 by use of PC controlled injection (Bocotrans, NL). The synthetic N and K fertilizers were applied together with AS and AN on May 15, 2015. The synthetic fertilizers, AS and AN were applied to the plots by hand-application and subsequently incorporated into the soil. Immediately after incorporation maize was sown at a seed density of 100 000 ha^{-1}.

2.3.3. Plant and soil analysis

Maize was harvested on October 8, 2015. The 7.5 m^2 area in the middle of each plot was measured, and the maize within that surface area was harvested manually by use of trimming scissors. Lettuce was harvested on March 15, 2016, after 54 days of growing period. At harvest, the plants were clipped from the root with a knife and cleaned with demineralized water from soil particles prior to the fresh weight (FW) determination. The dry matter determination of maize and lettuce was done by oven drying at 60 °C for 48 h. The dried samples were ground and sieved to <1 mm using a Culatti DCFH 48 grinder (GE), and subsequently used for determination of total N and S. The total N was analyzed using Kjeldahl method (Van Ranst et al., 1999). For total S content 0.2 g of plant material was mixed with 2.5 ml H_2O_2 and 2.5 ml HNO_3 and allowed to stand for 12 h followed by microwave heating (CEM MARS 5, BE) at 600 W for 10 min at 55 °C, 10 min at 75 °C and 30 min at 100 °C (Van Ranst et al., 1999).

Soil samples were taken during the maize harvest (October 8, 2015) by collecting homogenized soil subsamples per plot at three depths (0–30 cm, 30–60 cm, 60–90 cm) using an auger. The soil samples were collected in polyethylene sampling bags and transported from the test site to the laboratory. Soil from lettuce experiment was taken in a full amount from the pots and homogenized. The moisture content was determined by weight loss after drying the soil sample to constant weight at 105 °C for at least 24 h. Soil potential acidity (pH-KCl) was measured using an Orion-520A (USA) pH-meter after adding 50 ml of 1 M KCl to 10 g of soil and allowing it to equilibrate for 10 min (Van Ranst et al., 1999). Soil EC was measured with a WTW-LF537 (Germany) 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, Germany). After aqua regia digestion (1 g sample + 7.5 ml HCl, 2.5 ml HNO_3 and 2.5 ml demineralized water), total S was analyzed using ICP-OES. The soil nitrate N (NO_3^--N) (ISO 13395:1996) and ammonium N (NH_4^+-N) (ISO 11732:1997) in soil were analyzed from 1 M KCl extract using a continuous flow auto-analyzer (Chemlab System 4, Skalar, the Netherlands).

2.3.4. Calculations and statistical analysis

Statistical analysis was performed using SPSS statistical software (version 22.0; SPSS Inc., Chicago, IL). One-way ANOVA was used to determine the effect of the applied fertilizers on soil properties along with the effect on crop yield and crop N and S uptake, based on the obtained physicochemical data. When significant differences between means were observed, additional post hoc assessment was performed using Tukey's Test (p < 0.05, n = 3). The condition of normality was checked using the Shapiro-Wilk test, whereas the homogeneity was tested with the Levene Test. Additionally, data from other studies published on ammonium sulfate has been processed (Table 1, 3 and 4) to compare those results with this study. Finally, N fertilizer value was determined, depending on the presence or the absence of a control (=unfertilized) treatment in an experimental design, as follows:

N replacement use efficiency (NRUE; %)

$$= \frac{\frac{N\ uptake\ AMM.SOLUTION}{total\ N\ applied\ AMM.SOLUTION}}{\frac{N\ uptake\ REFERENCE}{total\ N\ applied\ REFERENCE}} * 100$$

N fertilizer replacement value (NFRV; %)

$$= \frac{\frac{(N\ uptake\ AMM.SOLUTION - N\ uptake\ CONTROL)}{total\ N\ applied\ AMM.SOLUTION}}{\frac{(N\ uptake\ REFERENCE - N\ uptake\ CONTROL)}{total\ N\ applied\ REFERENCE}} * 100$$

where Amm. solution = treatment with AS or AN, Control = unfertilized treatment and Reference = CAN or animal (pig) manure + CAN.

3. Results and discussion

3.1. Product quality of end-products from (stripping-)scrubbing technology

Similar as synthetic mineral N fertilizers, produced via Haber-Bosch process, recovered AS and AN contain total N entirely in mineral form (Table 1). The total N in AS is present 100% in the form of NH_4-N, whereas total N in AN can be found in the form of NH_4-N and NO_3-N. The percentage of NH_4-N and NO_3-N in AN measured in this study was 55 and 45%, respectively (Table 1). The use of nitric acid not only contributes to the presence of NO_3-N, but also increases the N concentration in the recovered product. In this study, over the two sampling moments (2015 and 2016), 4.9 times higher N concentration was measured on average in AN than in AS (Table 1). By comparing average N concentration of AN from this study with an average N concentration of AS reported in other published studies and produced within the Systemic project, 2.7 times more N was found in AN than in AS. This also indicates high N variability between AS (30–86 g N kg^{-1}) and AN (132–198 g N kg^{-1}) recovered at different (stripping-) scrubbing installations.

The concentration of N in AS is lower due to the use of sulfuric acid, which makes AS also a rich source of S. Depending on the amount of added H_2SO_4 not only S concentration will vary, but also pH (2.40–7.70) and EC (152–262 mS cm^{-1}) values (Table 1). Low pH values could be of concern during product application since it can cause corrosion of machinery, leaf burning and soil acidification after long-term application (Vaneeckhaute et al., 2013). In previous published studies this was mitigated by addition of NaOH and tap water to increase the pH of ammonium sulfate prior to fertilization (Vaneeckhaute et al., 2013, 2014; Sigurnjak et al., 2016). Another option is to reduce the consumption of acid, which has been adopted by installations in this study. In general, higher pH values were measured in AN, compared to AS, which reduces the risk of machinery corrosion, but might result in higher risk of NH_3 volatilization during the fertilization. The high EC values could be of concern while utilizing this type of products in cultivation of salt sensitive crops (Manurecomine, 2016; Sigurnjak et al., 2016). Another important aspect of these products is non-presence of P that allows them to satisfy crop N requirements without exceeding strict P application rates. Moreover, high N concentration reduces the transport costs of these products as compared to animal manure, and other end-products from animal manure processing, whose N concentration is ≤ 1% (Sigurnjak et al., 2017a). Finally, as both AS and AN are generated from NH_3 rich air, they should not contain carbon (Table 1) or contaminants.

A recent survey among farmers from 7 European countries (Belgium, Denmark, France, the Netherlands, Germany, Croatia and Hungary) investigated the features that a bio-based fertilizer should have in order to be accepted as replacement for synthetic fertilizers (Tur-Cardona et al., 2018). The authors identified the certainty of nutrient content as one of the most decisive traits for the purpose of determining the farmer's choice between different bio-based fertilizers. The researchers reported that, compared to animal manure, AS is positively welcomed by farmers for its reduced uncertainty on the nutrient content and hygienization.

3.2. Effect of end-products from (stripping-)scrubbing on crop yield and nitrogen fertilizer replacement value

In previous published studies, (Vaneeckhaute et al., 2013, 2014; Chen et al., 2014; Sigurnjak et al., 2016) AN and AS were tested in the cultivation of lettuce and maize, and without the unfertilized treatment as control. These two crops were also selected as test

Table 3

Mean ± standard deviation of crop fresh weight (FW) yield, dry weight (DW) yield, N uptake, S uptake, N use efficiency (NUE), N replacement use efficiency (NRUE), apparent N recovery (ANR) and N fertilizer replacement value (NFRV) in tested treatments and other published studies dealing with ammonium nitrate and ammonium sulfate as N fertilizers.

Test crop	Experimental scale	Treatment	FW yield	DW yield	N uptake	S uptake	NUE	NRUE	ANR	NFRV	Reference
			g pot^{-1}	g pot^{-1}	mg crop^{-1}	mg crop^{-1}	–	%	–	%	
Lettuce	Pot experiment on loamy sand (LS) soil	Blank	37 ± 1	2.9 ± 0.3	57 ± 6	5.2 ± 0.7	–	–	–	–	*This study*
		[Ref]CAN + TSP + PAT	69 ± 2a	5.4 ± 0.3	111 ± 6a	14 ± 1	1.44 ± 0.07a	100a	0.71 ± 0.07a	100a	
		AN + TSP + PAT	76 ± 4b	5.4 ± 0.5	125 ± 6b	14 ± 1	1.62 ± 0.08b	112 ± 6b	0.89 ± 0.08b	125 ± 11b	
		AS + TSP + PAT	67 ± 3a	4.8 ± 0.2	113 ± 7ab	15 ± 1	1.47 ± 0.10ab	102 ± 7ab	0.73 ± 0.10ab	103 ± 13ab	
Lettuce	Pot experiment on sandy loam (SL) soil	Blank	39 ± 3	2.9 ± 0.3	47 ± 2	4.8 ± 0.5	–	–	–	–	*This study*
		[Ref]CAN + TSP + PAT	77 ± 2a	5.1 ± 0.3	106 ± 10ab	13 ± 1	1.38 ± 0.13ab	100a	0.78 ± 0.13ab	100a	
		AN + TSP + PAT	89 ± 8b	5.8 ± 1.0	129 ± 13b	16 ± 3	1.68 ± 0.17b	121 ± 12b	1.07 ± 0.17b	138 ± 21b	
		AS + TSP + PAT	70 ± 8a	4.9 ± 0.6	93 ± 15a	13 ± 2	1.20 ± 0.19a	87 ± 14a	0.60 ± 0.19a	77 ± 24a	
			ton ha^{-1}	ton ha^{-1}	kg ha^{-1}	kg ha^{-1}	–	%	–	%	
Lettuce	Greenhouse experiment (2 greenhouses)	[Ref]CAN + TSP + PAT	61 ± 12	3.4 ± 1.3	151 ± 57	11 ± 5	0.72 ± 0.27	100	NA	NA	Sigurnjak et al. (2016)
		AS + TSP + PAT	64 ± 9	3.4 ± 1.0	147 ± 41	12 ± 4	0.70 ± 0.20	99 ± 28	NA	NA	
		[Ref]CAN + TSP + PAT	55 ± 5	2.9 ± 0.5	130 ± 23	9.3 ± 2.2	0.61 ± 0.11	100	NA	NA	
		AS + STR + CW	59 ± 3	2.8 ± 0.2	116 ± 11	9.5 ± 0.6	0.56 ± 0.06	92 ± 9	NA	NA	
		AS + STR + PAT	56 ± 1	2.9 ± 0.1	128 ± 16	9.4 ± 0.8	0.64 ± 0.08	103 ± 13	NA	NA	
Maize	Field experiment	Blank	35 ± 5	10 ± 2	80 ± 10	8.7 ± 1.2	–	–	–	–	*This study*
		[Ref]PM + CAN + PAT	57 ± 6	16 ± 2	164 ± 31	15 ± 3	1.01 ± 0.19	100	0.52 ± 0.19	100	
		PM + AN + PAT	59 ± 6	17 ± 2	167 ± 20	16 ± 1	1.03 ± 0.12	101 ± 12	0.54 ± 0.12	103 ± 23	
		PM + AS + PAT	59 ± 4	17 ± 1	169 ± 12	16 ± 1	1.04 ± 0.07	103 ± 7	0.55 ± 0.07	105 ± 14	
Maize	Field experiment Year 1	[Ref]PM + CAN + PAT	81 ± 2	23 ± 0	306 ± 42	23 ± 3	1.41 ± 0.19	100	NA	NA	Vaneeckhaute et al. (2014, 2013)
		PM + CAN + AS + PAT	80 ± 3	22 ± 1	300 ± 21	23 ± 1	1.38 ± 0.10	98 ± 7	NA	NA	
		PM + AS	81 ± 3	23 ± 1	308 ± 20	24 ± 2	1.42 ± 0.09	100 ± 7	NA	NA	
Maize	Field experiment Year 2	[Ref]PM + CAN + PAT	60 ± 4	19 ± 3	140 ± 23a	14 ± 1	0.89 ± 0.14a	100a	NA	NA	
		PM + CAN + AS + PAT	62 ± 5	18 ± 1	157 ± 40ab	15 ± 1	1.00 ± 0.25ab	112 ± 28ab	NA	NA	
		PM + AS	60 ± 5	18 ± 1	195 ± 21b	17 ± 2	1.24 ± 0.13b	139 ± 15b	NA	NA	
Maize	Field experiment	[Ref]PM + CAN + PAT	74 ± 4	23 ± 2	299 ± 25	18 ± 1	1.55 ± 0.13b	100b	NA	NA	Chen (2014)
		PM + CAN + AS + PAT	75 ± 2	23 ± 0	325 ± 27	19 ± 1	1.46 ± 0.12b	94 ± 8b	NA	NA	
		PM + AS	73 ± 1	21 ± 1	294 ± 24	19 ± 2	1.13 ± 0.09a	73 ± 6a	NA	NA	

Lower case letters a and b in a single column indicate significant different means (Tukey's Test p < 0.05) between treatments within one study (blank excluded); CAN: calcium ammonium nitrate; TSP: triple superphosphate; PAT: potassium sulfate; AN: ammonium nitrate; AS: ammonium sulfate; STR: struvite; CW: effluent from constructed wetlands; PM: pig manure; NA: not applicable.

plants in this study, along with control (i.e. unfertilized treatment) to assess the potential soil effect and determine NFRV.

In lettuce pot experiments application of AN on two different soil types has resulted in a slight, but still significant, increase of lettuce fresh yield as compared to AS and CAN (Table 3). On average, AN application has led to 9% and 12% higher lettuce yield as compared to CAN and AS on loamy sand soil and to 13 and 21%

higher lettuce yield on sandy loam soil, respectively. This was a result of the higher lettuce N uptake observed in AN treatments, whose distribution of N forms in the applied product (55% NH$_4$-N and 45% NO$_3$-N) was similar to CAN (50:50). Currently, reasons for higher crop yield and N uptake in AN treatments are not clear, and N release patterns should be further examined via laboratory incubation experiments. Next, no significant differences in lettuce

Table 4
Mean ± standard deviation of soil pH-KCl, electrical conductivity (EC), S concentration (in 0–30 cm soil layer) and NO_3-N residue (in 0–90 cm soil layer) in tested treatments and other published studies dealing with ammonium nitrate and ammonium sulfate as N fertilizers.

Test crop	Experimental scale	Treatment	pH - KCl –	EC μS cm^{-1}	S mg kg^{-1} DW (0–30 cm)	NO_3-N residue kg ha^{-1} (0–90 cm)	Reference
Lettuce	Pot experiment on loamy sand (LS) soil	Blank	4.81 ± 0.02	43 ± 6	143 ± 3	NA	*This study*
		[Ref]CAN + TSP + PAT	4.71 ± 0.04	87 ± 3a	159 ± 9a	NA	
		AN + TSP + PAT	4.73 ± 0.06	83 ± 2a	161 ± 11a	NA	
		AS + TSP + PAT	4.58 ± 0.09	131 ± 17b	208 ± 7b	NA	
Lettuce	Pot experiment on sandy loam (SL) soil	Blank	5.79 ± 0.05	52 ± 3	161 ± 5	NA	*This study*
		[Ref]CAN + TSP + PAT	5.52 ± 0.09	91 ± 8a	186 ± 8a	NA	
		AN + TSP + PAT	5.54 ± 0.02	108 ± 9a	184 ± 7a	NA	
		AS + TSP + PAT	5.46 ± 0.11	151 ± 10b	210 ± 14b	NA	
Lettuce	Greenhouse experiment (2 greenhouses)	[Ref]CAN + TSP + PAT	6.07 ± 0.08	598 ± 151	329 ± 26a	NA	Sigurnjak et al. (2016)
		AS + TSP + PAT	6.06 ± 0.07	839 ± 211	403 ± 38b	NA	
		[Ref]CAN + TSP + PAT	6.23 ± 0.06	670 ± 157	318 ± 48	NA	
		AS + STR + CW	6.27 ± 0.11	1021 ± 238	317 ± 28	NA	
		AS + STR + PAT	6.22 ± 0.09	850 ± 245	365 ± 76	NA	
Maize	Field experiment	Blank	5.01 ± 0.15	79 ± 5	324 ± 28	18 ± 3	*This study*
		[Ref]PM + CAN + PAT	5.07 ± 0.07	143 ± 24	354 ± 22	50 ± 26	
		PM + AN + PAT	5.07 ± 0.06	124 ± 25	342 ± 11	32 ± 6	
		PM + AS + PAT	5.00 ± 0.12	134 ± 11	353 ± 22	35 ± 13	
Maize	Field experiment Year 1	[Ref]PM + CAN + PAT	5.30 ± 0.22	103 ± 10	379 ± 39	100 ± 8	Vaneeckhaute et al. (2014, 2013)
		PM + CAN + AS + PAT	5.37 ± 0.08	102 ± 15	376 ± 36	85 ± 19	
		PM + AS	5.33 ± 0.15	102 ± 12	370 ± 31	106 ± 10	
Maize	Field experiment Year 2	[Ref]PM + CAN + PAT	5.66 ± 0.65	75 ± 6.8a	276 ± 61a	35 ± 18	
		PM + CAN + AS + PAT	5.98 ± 0.24	83 ± 8.1a	263 ± 64a	48 ± 30	
		PM + AS	5.86 ± 0.44	104 ± 12b	360 ± 11b	53 ± 20	
Maize	Field experiment	[Ref]PM + CAN + PAT	5.97 ± 0.21	59 ± 16a	165 ± 23	28 ± 8	Chen (2014)
		PM + CAN + AS + PAT	5.95 ± 0.24	81 ± 25ab	177 ± 30	28 ± 4	
		PM + AS	5.84 ± 0.35	121 ± 42b	206 ± 45	32 ± 6	

Lower case letters a and b in a single column indicate significant different means (Tukey's Test $p < 0.05$) between treatments within one study (blank excluded); CAN: calcium ammonium nitrate; TSP: triple superphosphate; PAT: potassium sulfate; AN: ammonium nitrate; AS: ammonium sulfate; STR: struvite; CW: effluent from constructed wetlands; PM: pig manure; NA: not applicable.

fresh yield were observed between AS and CAN. The similar observations were reported by Sigurnjak et al. (2016) where AS was tested in lettuce cultivation on a full-scale plot setting. As the same N dosage was added to all fertilized treatments in pot experiments, the observed variation in lettuce fresh yield and lettuce N uptake was reflected also in NRUE and NFRV. In both pot experiments the highest NRUE and NFRV was calculated for the AN, followed by CAN and AS that had a similar performance. In regard to S, the application of AS did not lead to the increase of the crop S uptake as compare to CAN and AN. In general, the measured lettuce S concentrations in fertilized treatments were within the range of 2–3 g S kg^{-1} DW, which is considered an appropriate range for lettuce grown in a greenhouse setting (Hill Laboratories, 2002).

In order to provide scientific evidence to farmers as well as policy makers, full field validation is a requirement for novel products such as AS and AN generated from nutrient recycling facilities. In the current study, this was done with a maize field trial that was conducted in uncontrolled weather conditions. No significant differences were observed between treatments in regard to maize FW yield, DW yield, N and S uptake, when comparing CAN, AS and AN applied on top of pig manure (Table 3). A similar observation was made in other studies where CAN and AS were compared to synthetic mineral fertilizer (Vaneeckhaute et al., 2013, 2014; Chen et al., 2014; Sigurnjak et al., 2016). In regard to N fertilizer value, both AN and AS have exhibited similar or higher NRUE and NFRV values compared to CAN. This indicates that both products in short-term (<1 year) can replace the synthetic N fertilizer without having a detrimental effect on the crop marketable yield. Finally, there was no difference between calculated NRUE and NFRV values in this study, which indicates that in short-term experiments the presence of unfertilized control treatment is not

crucial to determine the N fertilizer value of tested products. In long-term experiments the approach of using a control treatment is required (Brentrup and Palliere, 2010), and currently long-term experiments (>1 year) on AN and AS utilization are still lacking.

3.3. Effect of end-products from (stripping-)scrubbing on soil properties and nitrate leaching

The utilization of AN and AS in this study did not lead to significant changes of soil pH-KCl as compared to application of CAN. On the other hand, application of AS in lettuce trials has led to significantly higher soil EC values as compared to CAN and AN (Table 4). Interestingly, treatments with AS have exhibited on average 35% higher soil EC values as compared to AN whose EC value (342 and 332 mS cm^{-1}) was double the EC value measured in AS (152 and 157 mS cm^{-1}; Table 1). This can be explained by high N concentration measured in AN that lead to 4 times lower product application than in the case of AS (Table 2), consequently resulting in lower application of salts. Next to the high soil EC values, treatments with AS have also led to high soil S concentrations as a consequence of H_2SO_4 that was used in N recovery. Nevertheless, observed high soil EC and soil S concentrations did not cause negative effect on lettuce yield in this study. In general, soil salinity is known to represses plant growth in the form of osmotic stress (Gupta and Huang, 2014). Researchers in Manurecomine (2016) project have reported that in their pot experiment on viola, application of AS has led to the death of plants. They attributed this to high EC value of the applied product which caused osmotic stress that consequently led to the decrease of the water uptake and probably caused the chemical burning of the roots. Even though viola and lettuce are considered as salt sensitive crops (Grieve

et al., 2012), AS did not exhibit negative effect on the later. Therefore, while using AS as a N source in the cultivation of salt sensitive crops the optimal product application rate should be determined by not exceeding advisable levels of soil EC. In maize field scale experiments, as compare to pot experiments, these issues were not visible at harvest time since crop was cultivated in uncontrolled weather conditions where heavy rainfall can remove salts and some nutrients from the root zone, and subsequently reduce the effect of EC and S concentrations.

Another important aspect in utilization of these products as N fertilizers is their potential effect on nitrate leaching. As nitrate leaching is not of practical importance in pot experiments, only in maize field experiments residual nitrate left in 0–90 cm soil layer, between October 1 and November 15, was determined. The measured nitrate residue gives an estimation of the nitrate amount that can potentially leach to ground and surface water. This instrument is used in Flanders (Belgium) since 2004, and in Bretagne (France) since 2014 (Buysse, 2015). In this study, there were no significant differences in nitrate residue between the tested treatments and the reference (Table 4). This indicates that application of AS and AN does not increase the risk for nitrate leaching as compared to the conventional fertilization regime. Moreover, in all tested treatments, the nitrate residue was below the maximum allowable level of 90 kg NO_3-N ha^{-1} according to current Flemish environmental standards for maize cultivation in zones where measured NO_3 concentrations in ground water do not exceed 50 mg NO_3 l^{-1} (VLM, 2016). Similar observations were reported in other studies on AS (Vaneeckhaute et al., 2013, 2014; Chen et al., 2014), and if there was an exceedance of 90 kg NO_3-N ha^{-1} it was recorded for all treatments since the nitrate residue is highly dependent on weather conditions (Vaneeckhaute et al., 2013).

3.4. Current legal status of ammonium nitrate and ammonium sulfate as mineral N fertilizers

According to the current Fertilizer regulation EU2003/2003 AS and AN are nitrogen fertilizer solutions and can be recognized as 'EC fertilizer' (category C1 n°1) if the N-concentration is at least 15% (European Commission, 2003). This threshold can be reached by AN since the use of HNO_3 increases the N-concentration (13–20%; Table 1) of the end-product. For AS this threshold is higher than the N-concentrations (3–9%; Table 1) obtained from the existing (stripping-)scrubbing installations that use H_2SO_4. The current draft of the new European fertilizer regulation for 'inorganic liquid compound macronutrient fertilizer' proposes lower N-concentration criteria (1.5 or 3%; European Commission, 2016) which could be met by both AS and AN. However, if AN and AS are obtained from animal manure, their utilization is officially limited by the Article 2.g. of the Nitrates Directive where the following is stated: 'livestock manure': means waste products excreted by livestock or a mixture of litter and waste products excreted by livestock, even in processed form (European Commission, 1991). This means that AS and AN from animal manure origin are identified as animal manure and fall under the limitation of 170 kg N ha^{-1}. As a result, these products have to fulfil requirements of animal manure, and therefore have to compete with animal manure. In some EU regions air cleaning pathway is used frequently and therefore a derogation from the Nitrates Directive is currently the subject of a study on safe criteria for processed manure carried out by JRC in the period of 2018–2020 (European Commission, 2017).

4. Conclusion

The study shows that via (stripping-)scrubbing technology the nitrogen from animal manure (<1% N) can be up-concentrated to 3–9% of N in the form of AS and 13–20% of N in the form of AN, depending on the type of acid used. The observed variability in N concentrations of these products is seen as the biggest challenge for their recognition as N fertilizers. Nevertheless, with high N concentration, no presence of P and lack of organics, AN and AS show similar traits as synthetic N fertilizers. This was further demonstrated in pot and field experiments, where utilization of AN and AS has led to a similar effect on crop yield and risk for nitrate leaching as compared to conventional synthetic N fertilizer. Future studies should further investigate the agronomic and environmental fertilizer performance of AN and AS under varying conditions and over multi-year crop rotations.

Acknowledgment

References

Acqua & Sole, 2011. EP2977440A1 Process for the recycling of the nutrient elements used by crops. Available from: <https://patents.google.com/patent/EP2578558A1/en?inventor=Giuseppe+Natta>.

Bolzonella, D., Fatone, F., Gottardo, M., Frison, N., 2018. Nutrients recovery from anaerobic digestate of agro-waste: techno-economic assessment of full scale applications. J. Environ. Manage. 216, 111–119. https://doi.org/10.1016/j.jenvman.2017.08.026.

Bousek, J., Scroccaro, D., Sima, J., Weissenbacher, N., Fuchs, W., 2016. Influence of the gas composition on the efficiency of ammonia stripping of biogas digestate. Bioresour. Technol. 203, 259–266. https://doi.org/10.1016/j.biortech.2015.12.046.

Brentrup, F., Palliere, C., 2010. Nitrogen Use Efficiency as an Agro-Environmental Indicator OECD Workshop on Agri-Environmental Indicators, At Leysin, Switzerland, pp. 1–9.

Buysse, J., 2015. Policy options to improve nutrient recycling. Joint scientific workshop: innovative strategies to improve the recycling of energy, nutrients and organic matter from waste materials, Erfurt, Germany, pp. 1–17.

Chen, A., 2014. Optimizing Nutrient Use Efficiency in Agriculture by Utilizing Manure and Digestate Derivatives as Bio-based Fertilizer Master thesis. Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium, p. 74.

European Commission, 1991. Directive of the Council of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EC). Off. J. Eur. Commun. L375, 1–8.

European Commission, 2003. Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers. Off. J. Eur. Commun. L304, 1–194.

European Commission, 2016. Circular economy packages. Annexes to the Proposal for a regulation of the European Parliament and of the Council laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009.

European Commission, 2017. Developing criteria for the use of processed manure in the context of the Nitrates Directive. Nitrates Expert Group, Brussels, Belgium. Available from: <http://ec.europa.eu/transparency/regexpert/index.cfm?do=groupDetail.groupDetailDoc&id=33119&no=3>.

Flotats, X., Bonmatí, A., Palatsi, J., Foged, H.L., 2013. Trends on manure processing in Europe. In: Book of Proceedings, 2nd International Conference of WASTES: solutions, treatments and opportunities. Braga (Portugal), 11–13 September. Edition: CVR, Centro para a Valorizaçao de Residuos. ISSN: 2183-0568, pp. 587–592.

Foged, H.L., Flotats, X., Bonmati, A., Palatsi, J., Magri, A., Schelde, K.M., 2011. Inventory of manure processing activities in Europe. Technical Report No. I concerning "Manure Processing Activities in Europe" to the European Commission, Directorate-General Environment. p. 138.

GNS, 2003. DE10354063A1 Production of nitrogen fertilizer from organic waste products, comprising heating waste product under reduced pressure to produce gas containing carbon dioxide and ammonia, and absorbing ammonia from gas. GNS – Gesellschaft fuer nachhaltige stoffnutzung MBH, N.S.M.G., Germany. Available from: <https://patents.google.com/patent/DE102005017077A1/en?assignee=Gesellschaft+f%C3%BCr+nachhaltige+Stoffnutzung+mbH&oq=Gesellschaft+f%C3%BCr+nachhaltige+Stoffnutzung+mbH>.

Grieve, C.M., Grattan, S.R., Maas, E.V., 2012. Plant salt tolerance. In: Wallender, W. W.a.T., K.K. (Ed.), ASCE Manual and Reports on Engineering Practice No. 71

Agricultural Salinity Assessment and Management, second ed. ASCE, Reston, VA, pp. 405–459 (Chapter 13).

Gupta, B., Huang, B., 2014. Mechanism of salinity tolerance in plants: physiological, biochemical, and molecular characterization. Int. J. Genom. 2014,. https://doi.org/10.1155/2014/701596 701596.

Guštin, S., Marinšek-Logar, R., 2011. Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. Process Saf. Environ. Prot. 89, 61–66. https://doi.org/10.1016/j.psep.2010.11.001.

Hill Laboratories, 2002. Crop guide: lettuce. R J Hill Laboratories, Hamilton, New Zealand. Website: <http://www.hill-laboratories.com>, last visited September 2013.

Hou, Y., Velthof, G.L., Lesschen, J.P., Staritsky, I.G., Oenema, O., 2017. Nutrient recovery and emissions of ammonia, nitrous oxide, and methane from animal manure in Europe: effects of manure treatemne technologies. Environ. Sci. Technol. 51, 375–383. https://doi.org/10.1021/acs.est.6b04524.

Kinidi, L., Tan, I.A.W., Wahab, A., Binti, N., Tamrin, K.F.B., Hipolito, C.N., Salleh, S.F., 2018. Recent development in ammonia stripping process for industrial wastewater treatment. Int. J. Chem. Eng. 20,. https://doi.org/10.1155/2018/3181087 3181087.

La, J., Kim, T., Jang, J.K., Chang, I.S., 2014. Ammonia nitrogen removal and recovery from swine wastewater by microwave radiation. Environ. Eng. Res. 19, 381–385. https://doi.org/10.4491/eer.2014.064.

Ledda, C., Schievano, A., Salati, S., Adani, F., 2013. Nitrogen and water recovery from animal slurries by a new integrated ultrafiltration, reverse osmosis and cold stripping process: a case study. Water Res. 47, 6157–6166. https://doi.org/10.1016/j.watres.2013.07.037.

Leirs, H., Degroote, T., Bossin, S., Canniere, E., 2017. Een luchtwasser, wat nu? Chemische luchtwassers. Vemis, consortium kennisopbouw luchtemissies veehouderij. Belgium, pp. 18.

Lemmens, B., Ceulemans, J., Elslander, H., Vanassche, S., Brauns, E., Vrancken, K., 2007. Beste Beschikbare Technieken voor mestverwerking. Academia Press, Belgium, pp. 1–359.

Lenders, S., D'hooghe, J., Tacquenier, B., 2013. Gebruik van energie, gewasbescherming, water en kunstmest in de Vlaamse landbouw. Resultaten op basis van Landbouwmonitoringsnetwerk 2005–2011. Beleidsdomein Landbouw en Visserij, Afdeling en Studie, pp. 1–41.

Limoli, A., Langone, M., Andreottola, G., 2016. Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process. J. Environ. Manage. 176, 1–10. https://doi.org/10.1016/j.jenvman.2016.03.007.

Loyon, L., 2017. Overview of manure treatment in France. Waste Manage. 61, 516–520. https://doi.org/10.1016/j.wasman.2016.11.040.

Manurecomine, 2016. Deliverable 6.1: Report of fertiliser impact on plant growth and plant performance, including trace contaminants, and effect of soil pH on plant nutrient availability ManureEcoMine: green fertilizer upcycling from manure: Technological, economic and environmental sustainability demonstration (ENV.2013.6.3-2/603744) – Grant agreement no. 603744.

MB31/05/2011. Ministrieel besluit van 31 mei 2011 tot wijziging van bijlage 1 van het ministrieel besluit van 19 maart 2004 houdende vaststelling van de lijst van ammoniakemissiearne stalsystemen in uitvoering van artikel 1.1.2. en artikel 5.9.2.1bis. Brussels, Belgium, 2011.

Melse, R.W., Ogink, N., 2005. Air scrubbing techniques for ammonia and odor reduction at livestock operations: review of on-farm research in the Netherlands. Trans. ASAE 48, 2303–2313.

Melse, R.W., Timmerman, M., 2009. Sustainable intensive livestock production demands manure and exhaust air treatment technologies. Bioresour. Technol. 100, 5506–5511. https://doi.org/10.1016/j.biortech.2009.03.003.

Provolo, G., Perazzolo, F., Mattachini, G., Finzi, A., Naldi, E., Riva, E., 2017. Nitrogen removal from digested slurries using a simplified ammonia stripping technique. Waste Manage. 69, 154–161. https://doi.org/10.1016/j.wasman.2017.07.047.

RMI, 2015. Climatology database. Belgium: Royal Meteorological Institute of Belgium (RMI). Website: <www.meteo.be>, last visited December 2015.

Sakadevan, K., Nguyen, M.L., 2017. Chapter four – livestock production and its impact on nutrient pollution and greenhouse gas emissions. In: Donald, L.S. (Ed.), Advances in Agronomy. Academic Press, Ny, pp. 147–184. https://doi.org/10.1016/bs.agron.2016.10.002.

Serna-Maza, A., Heaven, S., Banks, C.J., 2014. Ammonia removal in food waste anaerobic digestion using a side-stream stripping process. Bioresour. Technol. 152, 307–315. https://doi.org/10.1016/j.biortech.2013.10.093.

Serna-Maza, A., Heaven, S., Banks, C.J., 2015. Biogas stripping of ammonia from fresh digestate from a food waste digester. Bioresour. Technol. 190, 66–75. https://doi.org/10.1016/j.biortech. 2015.04.041.

Sigurnjak, I., De Waele, J., Michels, E., Tack, F.M.G., Meers, E., De Neve, S., 2017a. Nitrogen release and mineralization potential of derivatives from nutrient recovery processes as substitutes for fossil fuel-based nitrogen fertilizers. Soil Use Manag. 33, 437–446. https://doi.org/10.1111/sum.12366.

Sigurnjak, I., Michels, E., Crappé, S., Buysens, S., Biswas, J.K., Tack, F.M.G., De Neve, S., Meers, E., 2017b. Does acidification increase the nitrogen fertilizer replacement value of bio-based fertilizers in Lactuca sativa L. cultivation? J. Plant Nutr. Soil Sci. 180, 800–810. https://doi.org/10.1002/jpln.201700220.

Sigurnjak, I., Michels, E., Crappé, S., Buysens, S., Tack, F.M.G., Meers, E., 2016. Utilization of derivatives from nutrient recovery processes as alternatives for fossil-based mineral fertilizers in commercial greenhouse production of Lactuca sativa L. Sci. Horticult. 198, 267–276. https://doi.org/10.1016/j.scienta.2015.11.038.

Tur-Cardona, J., Bonnichsen, O., Speelman, S., Verspecht, A., Carpentier, L., Debruyne, L., Marchand, F., Jacobsen, B.H., Buysse, J., 2018. Farmers' reasons to accept bio-based fertilizers: a choice experiment in seven different European countries. J. Cleaner Prod. 197, 406–416. https://doi.org/10.1016/j.jclepro.2018.06.172.

Van der Heyden, C., Demeyer, P., Volcke, E.I., 2015. Mitigating emissions from pig and poultry housing facilities through air scrubbers and biofilters: state-of-the-art and perspectives. Biosyst. Eng. 134, 74–93. https://doi.org/10.1016/j.biosystemseng. 2015.04.002.

Van Ranst, E., Verloo, M., Demeyer, A., Pauwels, J.M., 1999. Manual for the soil chemistry and fertility laboratory: analytical methods of soils and plants equipment and management of consumables. University of Ghent, International Training Centre for Post-Graduate Soil Scientists, Ghent, pp. 1–243.

Vaneeckhaute, C., Ghekiere, G., Michels, E., Vanrolleghem, P.A., Tack, F.M.G., Meers, E., 2014. 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. In: Donald, L.S. (Ed.), Advances in Agronomy. Academic Press, pp. 137–180. https://doi.org/10.1016/B978-0-12-802139-2.00004-4.

Vaneeckhaute, C., Meers, E., Michels, E., Ghekiere, G., Accoe, F., Tack, F.M.G., 2013. Closing the nutrient cycle by using bio-digestion waste derivatives as synthetic fertilizer substitutes: a field experiment. Biomass Bioenergy 55, 175–189. https://doi.org/10.1016/j.biombioe.2013.01.032.

VCM, 2016. VCM-enquete operationele stand van zaken mestverwerking in Vlaanderen. Vlaams Coördinatiecentrum Mestverwerking, pp. 1–35.

VLM, 2016. Normen en richtwaarden 2016. Flemish Land Agency, Brussels, Belgium. Available from: <https://www.vlm.be/nl/SiteCollectionDocuments/Publicaties/mestbank/bemestingsnormen_2016.pdf>.

Webb, J., Sorensen, P., Velthof, G.L., Amon, B., Pinto, M., Rodhe, L., Salomon, E., Hutchings, N., Burczyk, J., Reid, J.E., 2013. An assessment of the variation of manure nitrogen efficiency throughout Europe and an appraisal of means to increase manure-N efficiency. Adv. Agron. 119, 371442.

Zhang, W., Heaven, S., Banks, C.J., 2017. Continuous operation of thermophilic food waste digestion with side-stream ammonia stripping. Bioresour. Technol. 244, 611–620. https://doi.org/10.1016/j.biortech.2017.07.180.

Zhang, L., Lee, Y.-W., Jahng, D., 2012. Ammonia stripping for enhanced biomethanization of piggery wastewater. J. Hazard. Mater. 199, 36–42. https://doi.org/10.1016/j.jhazmat.2011.10.049.