SYSTEMIC
Circular solutions for biowaste

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Nitrogen fertilising products based on manure and organic residues
Supporting literature of the SYSTEMIC factsheets

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The EU H2020 project SYSTEMIC has taken up the challenge to recover nutrients from animal manure and biowaste. Biowaste, like animal manure, sewage sludge and food and feed waste, forms the most abundant waste stream in Europe and hence the most prominent potential resource for the production of biogas and the recovery and reuse of mineral nutrients like phosphorus (P), nitrogen (N) and potassium (K). The application of nutrient recovery from waste is hindered by regulatory requirements amongst others the Nitrates Directive 91/676/EEG. This report gives an overview of the agronomic and environmental performance of nitrogen fertilising products made from manure. These products are ammonium sulphate and ammonium nitrate from air scrubbers and ammonia strippers, mineral concentrates produced by reverse osmosis, condensated ammonia water from capturing ammonia and liquid digestate produced by separation of digestate. For each fertilising product the state of the art of information on the technology, characteristics, composition, agronomic effectivity and risk assessment on contaminants, pathogens and other components is given. The information is condensed to a factsheet. These factsheets are also found at the website of the SYSTEMIC product (https://systemicproject.eu/downloads/).

Keywords: Nitrogen, recovery, animal manure, digestate, ammonium sulphate, ammonium nitrate, mineral concentrate, separation techniques, stripping, reverse osmosis, liquid fraction, solid fraction

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Contents

Preface

The research was undertaken as part of the project called 'SYSTEMIC: Systemic large scale eco-innovation to advance circular economy and mineral recovery from organic waste in Europe (https://systemicproject.eu/). In this project innovative nutrient recovery techniques at large scale digestion plants in order to produce biobased fertilisers which can be used as new type of fertilisers on agricultural land.

The European Commission has recognised that new products coming from nutrient recovery plants may have the potential to be as agronomically effective and have the same environmental performance as chemical/synthetic/mineral fertilisers and therefore could, potentially, therefore be exempted from the 170 kg N per ha per year limitation (without derogation) of the Nitrates Directive. In order to propose this update of the implementation of the Nitrates Directive, EC DG Environment have mandated EC Joint Research Centre (JRC) with a two year study (Safemanure) to look into the product quality, agronomic efficiency and environmental performance of fertilising products derived from manure.

In order to facilitate the Safemanure study a SYSTEMIC and AGROCYCLE policy-science workshop was held on the 30th May 2018 in Brussels entitled 'Fertilising products based on animal manure under the Nitrates Directive and the Circular Economy'. During this workshop preliminary factsheets on nitrogen-rich mineral products derived from animal manure were discussed with respect to agronomic, environmental and legislation aspects. It was concluded to update the factsheets and to write also a report on the agronomic and environmental aspects.

This report documents of the agronomic and environmental performance of nitrogen fertilising products made from manure: ammonium sulphate and ammonium nitrate from air scrubbers and ammonia strippers, mineral concentrates produced by reverse osmosis, condensated ammonia water from capturing ammonia and liquid digestate produced by separation of digestate from manure. The final factsheets can be found at the SYSTEMIC website (https://systemicproject.eu/downloads/).

Summary

The EU H2020 project SYSTEMIC has taken up the challenge to recover nutrients from animal manure and biowaste. Biowaste, like animal manure, sewage sludge and food and feed waste, form the most abundant waste stream in Europe and hence, the most prominent potential resource for the production of biogas and the recovery and reuse of mineral nutrients like phosphorus (P), nitrogen (N) and potassium (K). Nowadays, these nutrients are often not being recovered, posing severe challenges in terms of inefficient resource use, disposal and environmental pollution mainly because the composition of those biowaste resources does not meet the crop requirements (https://systemicproject.eu/).

SYSTEMIC with its large scale demonstration of targeted technologies is a milestone towards widespread implementation of more sustainable management of animal manure and other biomass like (digested) animal manure, sludge and other types of bio-waste focussed on the recovery of the nutrients. These large-scale demonstrations can give a boost to the Circular Economy and support the targets of the European Commission. The SYSTEMIC project explicitly focus on an increase of the nutrient use efficiency of nutrients from the organic biomass and derived (mineral) products therefrom to reduce the use of scarce natural and/or non-renewable resources. For this evaluation, the agronomic, environmental and socio-economic aspects are taken into account, together with the applicable legislation (European directives and national legislations). Nutrient recovery from animal manure and bio-waste across Europe is only viable if there is an effective market for the final products and these final products are not hindered by regulatory European requirements.
The applicable legislation has given an impetus to this report. A major barrier to the advancement of a viable market for nutrients recovered from manure are the limitations of the Nitrates Directive.

This report documents of the agronomic and environmental performance of nitrogen fertilising products made from manure. These products are ammonium sulphate and ammonium nitrate from air scrubbers and ammonia strippers, mineral concentrates produced by reverse osmosis, condensated ammonia water from capturing ammonia and liquid digestate produced by separation of digestate from manure. For each fertilising product the state of the art of information on the technology, characteristics, composition, agronomic effectivity and risk assessment on contaminants, pathogens and other components is given. The information is condensed to a factsheet. These factsheets are also found at the website of the SYSTEMIC product (https://systemicproject.eu/downloads/).

1 Introduction

Phillip Ehlert, WENR

Waste and resource use are minimized in a circular economy. The European Commission stimulates circular economy and encourages sustainability and competitiveness in the long term. EU Research and Innovation programme H2020 is an EU instrument implementing the Innovation Union, a Europe 2020 flagship initiative aimed at securing Europe's global competitiveness. One of the research projects is SYSTEMIC.

The EU H2020 project SYSTEMIC has taken up the challenge to recover nutrients from animal manure and biowaste. Animal manure, sewage sludge and food and feed waste, form the most abundant waste streams in Europe and hence, the most prominent potential resources for the production of biogas and the recovery and reuse of mineral nutrients like phosphorus (P), nitrogen (N) and potassium (K). Nowadays, these nutrients are often not being used in an efficient manner, posing severe challenges in terms of inefficient resource use, disposal and environmental pollution, mainly because the composition of those biowaste resources does not meet the crop requirements (https://systemicproject.eu/).

SYSTEMIC with its large-scale demonstration of targeted technologies focusses on implementation of more sustainable management of animal manure and biowaste and is focussed on the recovery of the nutrients. These large-scale demonstrations can give a boost to the Circular Economy and support the targets of the European Commission. The SYSTEMIC project explicitly focuses on an increase of the nutrient use efficiency of organic biowaste and (mineral) products derived thereof, in order to reduce the use of scarce and non-renewable resources (phosphorus) or resources produced via energy demanding process (nitrogen). For this evaluation, the agronomic, environmental and socio-economic aspects are taken into account, together with the applicable legislation (*i.e.* European directives and national legislations). Nutrient recovery from animal manure and biowaste across Europe is only viable if there is an effective market for the final products and when these final products are not hindered by regulatory European requirements.

The applicable legislation has given an impetus to this report. A major barrier to the advancement of a viable market for nutrients recovered from manure are the limitations of the Nitrates Directive. Currently 170 kg N per ha per year of nitrogen (N) from livestock manure can be applied in Nitrate Vulnerable Zones, including processed manure and nutrients recovered from manure (article 2g). On top of that, farmers can apply synthetic N fertiliser to meet crop demands in amounts that are laid down in national fertiliser regulations. The European Commission has recognised that new products coming from nutrient recovery plants may have the potential to be as agronomically effective and have the same environmental performance as chemical/synthetic/mineral fertilisers and therefore could, potentially, therefore be exempted from the 170 kg N per ha per year limitation (without derogation) of the Nitrates Directive. In order to propose this update of the implementation of the Nitrates Directive, EC DG Environment have mandated EC Joint Research Centre (JRC) with a two year study (Safemanure) to look into the product quality, agronomic efficiency and environmental performance of fertilising products derived from manure.

Other applicable legislation comes forth of regulation of free trade of fertilising products within EU28 or EU-27. On June 25th 2019 the new EU regulation on fertilising products has been published in the Official Journal of the European Union (L 170, 25 June 2019), entitled as the Fertilising Products Regulation (FPR). This a major step forward towards a durable use of resources of nutrients. This new regulation is a facultative regulation meaning that a producer of a fertilising product can choose if the European regulation will be followed or still applicable national regulations. New of the FPR is that if a waste material meets the criteria for a CMC an end-of-waste status is reached and the waste can be used as component material for production of fertilising products or as fertilising products. All fertilising products of this report can be placed under FPR although at the time of writing this report

not all aspects of the new FPR are clear yet. The current regulation of mineral fertilisers only (2003/2003) will be withdraw on July 16th, 2022 thus meaning that FPR will come into force on July 17th, 2022. The coming years up to 2022 are needed to address amongst others notifying authorities, notifying bodies and standard for analyses of fertilising products. Also the end-points for animal by-products, one of them being processed animal manures, have to be assessed.

On 30 May 2018, H2020 projects SYSTEMIC and AgroCycle[1] organised a policy-research workshop on 'Fertilising products based on animal manure under the Nitrates Directive and Circular Economy'. This workshop aimed to feed the EC JRC process by reporting and discussing the characteristics of different groups of fertilising products from manure treatment and to identify what further information is needed. Prior to the workshop, SYSTEMIC had provided factsheets of so-called top priority N-products recovered from manure (ammonium sulphate, ammonium nitrate and mineral concentrate). In each factsheet the available information was given on the nutrient recovery technique from manure, quality of the recovered products, and the agronomic and environmental aspects of these fertilising products and finally legal aspects (https://systemicproject/download/). The present report provides additional supporting scientific information to the already available factsheets. Ammonia water and liquid fraction of digestate were also included since they may be of interest as N fertilising product whereas struvite was omitted because struvite is essentially a P fertiliser considering its high PN ratio.

In chapter 2 the method of supporting the factsheets with scientific information is given. For each of the fertilising products a separate chapter is given. Each chapter describes the technology, the characteristics and composition of the fertilising product, its agronomic effectivity and includes a risk assessment. Information on the liquid fraction of digestate, ammonium sulphate, ammonium nitrate, mineral concentrate and condensated ammonia water is given in respectively chapter 3, 4, 5, 6 and 7.

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[1] Agrocycle: A blueprint and eu policy-forming protocol for the recycling and valorisation of agri-food waste, http://www.agrocycle.eu/

2 Data acquisition and methodology

Phillip Ehlert, WENR

Information on the fertilising products was obtained for liquid fraction of digestate, ammonium sulphate, ammonium nitrate, mineral concentrate and condensated ammonium water. Information was collected with the focus on the nitrogen use efficiency of these fertilising products.

Data acquisition was based on information in peer-reviewed journals, scientific reports and other journals. All sources are referenced and are available in the public domain and information was collected by different partners of the SYSTEMIC consortium.

Data were collected and, if needed, adapted by standard statistical analyses to parameters (mean, median, standard deviation, counts) to harmonise information on the different fertilising products of this report. Data on liquid fraction of digestate given in chapter 3 is collected by Tambone, Zilio and Adani of UNIMI. Data on ammonium sulphate and ammonium nitrate is mainly based on Sigurnjak of Genth University. Data on mineral concentrates was collected by Ehlert of Wageningen Environmental Research. Data on condensated ammonia water is collected by Verbeke of Flemish Coordination Centre for Manure Processing.

The agronomic effectivity of nitrogen (N) was assessed as follows. The N fertiliser value (N Replacement Use Efficiency; NRUE and/or N Fertiliser Replacement Value; NFRV) was calculated depending on the presence or the absence of a control (=unfertilised) treatment in an experimental design. NRUE (%) and NFRV (%) were respectively calculated according [1] and [2]:

$$\text{NRUE (\%)} = \frac{(\text{crop N uptake}_{\text{fertilising product}}/\text{total N applied}_{\text{fertilising product}})}{(\text{crop N uptake}_{\text{reference}}/\text{total N applied}_{\text{reference}})} \times 100 \quad (2.1)$$

$$\text{NFRV (\%)} = \frac{((\text{crop N uptake}_{\text{fertilising product}} - \text{crop N uptake}_{\text{control}})/\text{total N applied}_{\text{fertilising product}})}{((\text{crop N uptake}_{\text{reference}} - \text{crop N uptake}_{\text{control}})/\text{total N applied}_{\text{reference}})} \times 100 \quad (2.2)$$

With:

Fertilising product: ammonium sulphate, ammonium nitrate, mineral concentrate, concentrated ammonium water and (liquid fraction of) digestate;

Reference: reference fertiliser (often calcium ammonium nitrate (CAN) and chemical/synthetic mineral nitrogen fertiliser;

N Uptake: N uptake by the (test) crop in pot- or field experiment. This is the total quantity of nitrogen present in the crop at a given harvest determined by yield and nitrogen content (N uptake = yield x N content).

Total N applied: application rate of N. Unit depends on the type of experiment. To calculate the NRUE or NFRV, N applied in the fertilising product and reference must be the same. Then the term total N applied falls out in equation 2.2.

At the start of the project, also struvite ($NH_4MgPO_4 \cdot 6H_2O$) was selected as a nitrogen fertilising product derived from animal manure. The product contains in pure form 5.7% N in the form of NH_4-N . Due to its low NP ratio however, struvite is used as a phosphorus fertiliser. The phosphorus content is 12.6% P (28.9% P_2O_5) and the magnesium contents is 9.9% Mg (16.4% MgO). There is ample information on the efficiency of phosphorus but information on NFRV was not traced.

Condensated ammonia water was added as a new resource for mineral N fertilising products and is seen as a new development although its chemically derived counterpart has been used asas mineral nitrogen fertilising product for more than 50 years.

Liquid fraction of separation of digestate is seen as a new resource for replacing N fertilising products and was added as a new fertilising product.

3 Liquid fraction digestate

Fulvia Tambone, Massimo Zilo and Fabrizio Adani (University Milan, UNIMI)

This section is based on some scientific papers and technical documents selected from the international bibliography and referring to previous articles of the participants to the Systemic project. This section focusses on liquid fraction of digestate of manure and co-digested manure.

3.1 Description of technology

Solid-liquid separation of digestate generates two outputs, the liquid and the solid fraction of digestate. Digestion leads to mineralisation of organic N and hence liquid fraction (LF) of digested manure generally has a higher content of mineral N as compared to non-digested manure. The Liquid Fraction (LF) of digestate is represented by a pumpable liquid fraction richer in nitrogen (Lukehurst et al., 2010; Tambone et al., 2010; Riva et al., 2016). On the other hand, the solid fraction contains usually more fibrous material and has a higher organic matter content as compared to the LF. There are several digestate separation methods such as the belt press, sieve drum, screw press, sieve or decanter centrifuge (Figure 3.1). Furthermore, chemicals (i.e. flocculants and coagulants) can be used to improve separator efficiency (Lukehurst et al., 2010). All these methods show different efficiencies in dry matter, N, P, or K portioning into liquid and solid fraction.
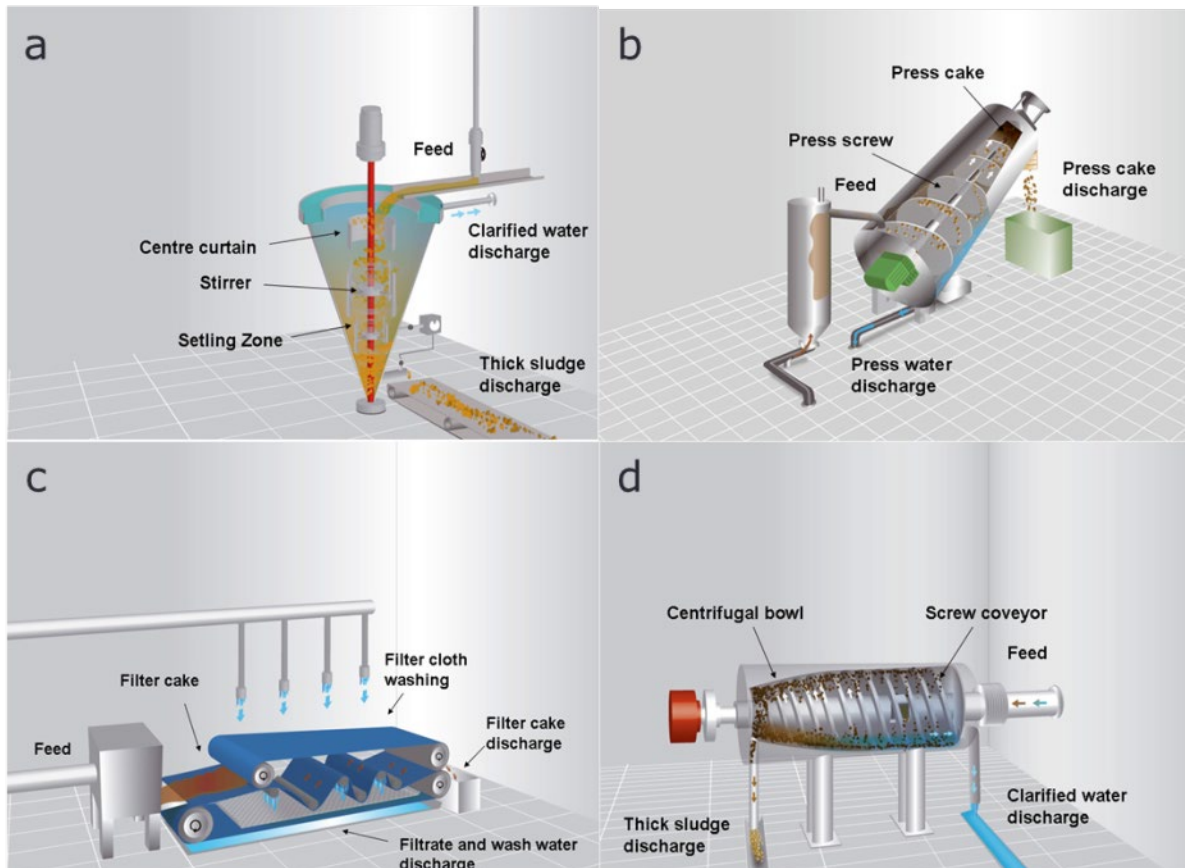
Figure 3.1. Examples of mechanical solid/liquid separators [a. thickener for sedimentation; b. typical screw press; c. typical belt separator with pressure rolls; d. typical decanter centrifuge] (Hjorth et al., 2009).

3.2 Characteristics and composition

Akhiar et al. (2017) reported a high range of variation of chemical, physical and biological characteristics of liquid fraction because of the type of solid-liquid separation along with the type of substrates used to feed the digester. Centrifugation and screw press with coagulant were the most efficient separation techniques, which resulted in the lower total solids concentration in liquid fraction of digestate. On the contrary, screw press only and vibrating screen were the least efficient separation techniques, which resulted in almost the same total solids concentration in liquid fraction of digestate than in the raw digestate. The origin of substrates, especially manure, seems to have major impact on characteristics of liquid fraction of digestates.

Unfortunately, not many data are available in literature for liquid fraction characterization. Anyway a recent study (Tambone et al., 2017) indicated that, by screw-press separation, on a mass balance, the liquid fraction still contains the majority of dry matter (67%) of the total of digestate and that, in absolute terms, the 87% of the total nitrogen and the 71% of the phosphorous flow in the liquid fraction.

Table 3.1 reports the chemical characteristics of liquid fractions obtained from 13 Italian full-scale anaerobic digestion plants (Tambone et al., 2017; Tambone et al., 2019) and 11 French full-scale co-digestion plants (Akhiar et al., 2017) where the infeed biomasses consisted of different mix of pig and cow slurry, energetic crops, agro-industrial residues, organic fraction of municipal solid waste and sludge.

Table 3.1. Chemical characteristics of liquid fraction of digestate samples, maximum (max), minimum (min), median (med) and average (av) s of three publications and the database of EBA).

Parameter	Unit	Tambone et al., 2017, 2019				Akhiar et al., 2017				Database EBA			
		Max	Min	Med	Av	Max	Min	Med	Av	Max	Min	Med	Av
DM	g kg^{-1} FM	62.3	33.8	43.9	44.8	82.7	10.3	38.4	42.9	257	0.23	51	53.9
pH	[-]	ND	ND	ND	ND	8.4	7.6	8.2	8.1	8.70	7.20	7.90	7.91
Conductivity	mS cm^{-1}	ND	ND	ND	ND	38	14	29	26.8	ND	ND	ND	ND
TOC	g kg^{-1} DM	415	324	358	358	ND	ND	ND	ND	525	0.02	395	383
COD	g L^{-1}	ND	ND	ND	ND	83.1	10.3	40.2	40.9	ND	ND	ND	ND
BOD$_5$		ND	ND	ND	ND	9.3	1.2	4.5	4.8	ND	ND	ND	ND
TKN	g kg^{-1} DM	124	73	85.1	97.5	ND	ND	ND	ND	959	17.9	96.7	131
TAN	g kg^{-1} DM	87.6	29.1	51.7	59.9	ND	ND	ND	ND	397	2.74	53.6	80.4
TAN/TKN	%	72.1	39.2	58.4	59.8	73.1	18.7	40.9	38.2	99.8	9.6	58	59.9
P$_2$O$_5$ total	g kg^{-1} DM	57.9	24.7	32.9	38.7	ND	ND	ND	ND	312	0.6	31.9	25.4
C/N	[-]	4.93	2.70	3.35	3.7	ND	ND	ND	ND	ND	ND	ND	ND
Biological stability OD$_{20}$	mg O$_2$ g DM^{-1} 20 h^{-1}	70.2	13.1	37.2	40.1	ND	ND	ND	ND	ND	ND	ND	ND
Alkalinity	g L^{-1}	ND	ND	ND	ND	24.8	7.4	14.1	16.5	ND	ND	ND	ND

DM: dry matter; TOC: total organic carbon; COD: chemical oxygen demand; BOD$_5$: biochemical oxygen demand after 5 days; TKN: Total Kjeldahl Nitrogen; TAN: total ammoniacal nitrogen; ND: not determined

Other data can be extrapolated from the database provided by the European Biogas Association. The data in this case concern a total of 208 products (liquid fraction of digestate) produced by as many plants located in Austria, Germany, Finland, France, Great Britain. The data sets reported in the Table 3.1 indicated a good agreement between them.

Data reported in Table 3.1 show that, despite the different composition of the infeed biomasses, in general liquid fraction of digestate showed similar values for median and average around 5% (despite the range 0.23-257 mg kg^{-1} of DM content) and it has an alkaline pH. The high N content, above all in plant-available form (see values of TNK/TAN) suggests this fraction to be used as substitute of mineral N fertilisers.

TOC content in the liquid fraction is high (on dry matter) indicating the high presence of organic matter (OM) that showed high biological stability, in line with that of compost (OD$_{20}$ value), because of the anaerobic digestion process that degrades the labile fractions of OM (Tambone et al., 2019). This

suggest the liquid fraction acting, also, as organic soil improver (Tambone et al., 2019; Akhiar et al., 2017) though it's nutrient contents are generally too high to supply organic matter in large amounts; the nutrients determine the agronomical use of the liquid fraction.

Due to the fertiliser value of liquid fraction of digestate but, at the same time, the impossibility to meet always the requirement in the surrounding production areas, some authors propose the transformation of LF into solid form (granules) to be easily stored and transported with benefits in economic and environmental terms (Cotabarren et al., 2019). In addition, the possibility of adapting the properties of the solid product to give proper nutrient release profiles would reduce the leaching problem associated with the direct application of liquid fertiliser. Some studies have been performed for the granulation of a liquid digestate in high-shear units, verifying the feasibility of the process and obtaining a product with adequate particle strength, size and nutrient distribution (Mangwandi et al., 2013 a, b). Granulation was performed combining a liquid fraction of digestate with zeolite, dolomite or calcium sulphate (agricultural gypsum) of different size fractions (Cotabarren et al., 2019). Data obtained demonstrated that fluidized-bed granulation is a promising technique to add value to a residue of good agronomic properties. Indeed, it was shown that the products obtained after coating with liquid digestate present nutrients, such as phosphorus and potassium, in concentrations as much as ten times more than in the liquid binder.

3.3 Agronomic effectivity

3.3.1 Yield, product quality

The use of liquid fraction of digestate as fertiliser is recent and so few data on NFRV are available to support, in open field, its effectiveness in substitution of commercial mineral fertiliser. Nevertheless, here are reported the results obtained by two different trials (Riva et al., 2016; Sigurnjak et al., 2019). The first (Riva et al., 2016) is a short-term experiment performed to substitute mineral N fertilisers (urea) with digestate and products derived from it to the crop silage maize. Digestate and the liquid fraction of digestate were used onto soil at pre-sowing and as topdressing fertilisers in comparison with urea, by surface application and subsurface injection. Results obtained indicated that sub-surface injection of digestate and derived products at pre-sowing and topdressing, gave crop yields similar to those obtainable with the use of urea.

The second paper (Sigurnjak et al., 2019) is relative to a 3-year field experiment conducted to evaluate the impact of using the liquid fraction of digestate as a (partial) substitute for synthetic N fertiliser. In this case, the results indicated that the liquid fraction of digestate can substitute synthetic N fertilisers without crop yield losses, according with result of Riva et al., 2016). In this 3-year field trial, the liquid fraction of digestate, exploited as a NK- source in treatments with animal manure or digestate, showed similar effects on biomass yields and soil properties as the classical fertilisation regime, which uses animal manure and synthetic NK- fertilisers. However, from a sustainability point of view, the ecological benefits of using LF of digestate were considerably higher compared to synthetic NK-fertilisers. In all the studies, yields obtained by fertilizing with liquid fraction of digestate showed no significant differences with those obtained with conventional practices (using only synthetic N or synthetic N in combination with animal manure). Finally, economic and ecological benefits were found to be higher when liquid fraction of digestate was used as a synthetic N substitute. Future perspectives indicate that nutrient variability in biobased fertilisers will be one of the greatest challenges to address in the utilization of these products.

3.3.2 Nitrogen use efficiency

The use of the liquid fraction of digestate as a fertiliser in agriculture is a recent practice and so the available data are very limited in the literature. Currently, two papers have reported data on Nitrogen Use Efficiency (NUE) of liquid fraction of digestate used as a fertiliser, but unfortunately both have been carried out in pot experiment. The information extrapolated from the two works is shown in Table 3.2.

Table 3.2. *Nitrogen use efficiency (NUE) of liquid fraction of digestate used as a fertiliser*

Crop	N dosed	NUE (%)	Reference
Barley	300 mg N kg^{-1}	61	Maurer et al. 2019
	500 mg N kg^{-1}	47	
Lettuce	210 kg N ha^{-1}	62	Sigurnjak et al. 2016

The NUE values reported in Table 3.2 show variability depending on crop type used during the experiments (barley and lettuce), and above all to the amount of nitrogen dosed in the form of liquid fraction of digestate. The NUE values reported for the liquid fraction of digestate are lower than those reported for conventional synthetic fertilisers. Sigurnjak and colleagues report a NUE value for calcium ammonium nitrate (CAN), used as a fertiliser, of 71% (Sigurnjak et al. 2016).

3.4 Risk assessment

3.4.1 Contaminants

Because of the origins of the matrices from which digestate and the relative fractions (liquid and solid) are obtained, i.e. animal slurry plus by-products and energy crops, heavy metals content and presence of pathogenic microorganisms must be considered.

3.4.1.1 Heavy metals

Table 3.3 report the results relative to a study (Tambone et al., 2017) on 13 samples of liquid fraction were the principal heavy metals have been determined.

Table 3.3. *Heavy metals content in liquid fraction of digestate, poultry manure, sewage sludge and compost compared the new EU fertilising products regulation 2019/1009 and requirements according EU Fertiliser products regulation 2019/1009, in mg/kg dry matter except Cd in fertilising products with more than 5% P_2O_5. Here the value is 60 mg Cd/kg P_2O_5.*

Metal	Liquid Fraction 1	Liquid Fraction 2	Poultry Manure 3	Sewage Sludge 4	Compost 5	EU Fertiliser products regulation 2019/10096		
						1 A II liquid organic fertiliser	1 B II liquid organo mineral fertiliser	I C I (b) liquid inorganic macronutrient fertiliser
Ni	9.8 ± 4.8	10.4 ± 5.6	4.4 ± 1.1	354 ± 221	28 ± 14	50	50	100
Zn	245 ± 117	361 ± 320	249 ± 132	2218 ± 905	251 ± 202	800	1500	1500
Cu	55 ± 27	90 ± 89	62 ± 58	888 ± 334	129 ± 99	300	600	600
Pb	1.7 ± 0.8	78 ± 11	1.7 ±1.7	225 ± 109	92 ± 95	120	120	120
Cd	0.3 ± 0.2	0.4 ± 0.2	0.2 ± 0.2	7.7 ± 5.1	2.7 ± 1.2	1.5	3 (P_2O_5 < 5%) 60 (P_2O_5 ≥ 5%)	3 (P_2O_5 < 5%) 60 (P_2O_5 ≥ 5%)
Cr	11.6 ± 6.3	12 ± 11	8.4 ± 8.0	561 ± 529	28 ± 18	*	*	*
CrVI	*	*	*	*	*	2	2	2

[1] Tambone et al., 2017 (average of 13 samples);

[2] European Biogas Association database;

[3] Nicholson et al., 1999; Guerra-Rodriguez et.al., 2001; Amanullah et al., 2007; Hirzel and Walter, 2008; Dorivar et al., 2008; Malik et al., 2013; Delgado Arroyo et al., 2014;

[4] Benerjee et al., 1997; Navas et al., 1998; Debosz et al., 2002; Pavan Fernandes et al., 2005; Tambone et al., 2010 ;

[5] Genevini et al., 1997 (average of 30 compost);

[6] EU fertiliser products regulation 2019/1009,
https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32019R1009

The results reported in Table 3.3 show that heavy metals contents in liquid fractions originated from different infeed biomasses are in line with typical organic fertilisers such as poultry manure or compost and are absolutely below to the values of EU Regulation 2019/1009. Values for sewage sludge in

general exceed criterions of EU regulation 2019/1009. However fertilising products of sewage sludge are not yet regulated by EU regulation 2019/1009[2].

3.4.1.2 Pathogens

The principal factors affecting pathogen decay during anaerobic digestion are the hydraulic retention time (HRT), temperature, volatile fatty acids (VFA) present, batch or continuous digestion, bacterial species and available nutrients (Sahlström et al., 2008). In general, anaerobic digestion reduces pathogen content, above all when thermophile conditions are adopted (Franke-Whittle and Insam, 2013) because of high temperature. A study conducted on ten full-scale biogas plants characterized by different plant designs (e.g. single digesters, parallel or serial digesters), plant powers (ranging from 180 to 999 kWe), hydraulic retention time (HRT) (ranging between 20 to 70 days) and feed mixes monitored pathogens both ingestates and digestates (Orzi et al., 2015). Being liquid fraction directly derived from digestate, we can assume that the data are applicable also to the relative fractions. The results of this research show that pathogens studied (Enterobacteriaceae, fecal Coliform, *Escherichia coli* and *Clostridium perfringens*) were significantly reduced during the process, both because of ammonia production and because of competition for substrate between pathogens and indigenous microflora. Plants showed different abilities to reduce pathogen indicators, depending on the pH value and toxic ammonia content. Similar results, on fecal coliforms, *E. coli*, *Salmonella*, *Campylobacter* spp. and *Y. enterocolitica*, were previously obtained in a psychrophilic anaerobic digestion plant (Massé et al., 2011).

3.4.2 Emission

Odour emissions constitute a problem when they affect public health because of the diffusion of diseases and nuisance to the surrounding population. Land application of manure can be a major source of odour emission in rural communities. Manures emit odours, Volatile Organic Compounds (VOC) and non-VOCs (ammonia, hydrogen sulphide) that represent a concern for inhabitants close to field application sites. In Europe, new legislation on environmental protection will require methods to reduce both ammonia and odour emission due to the spreading on the land of animal slurries. Among different methods proposed to reduce emissions, slurry treatment through anaerobic digestion and the direct injection of digestate into the soil have been proposed as successful practices (Orzi et al., 2018).

3.4.2.1 Ammonia volatilisation

As example of ammonia volatilisation during the utilization of digestate and liquid fraction of digestate is reported in Riva et al. (2016) in a short-term experiment, in which digestate products were used as substitutes for mineral (N) fertiliser in a corn cultivation. In brief, digestate and the liquid fraction of digestate were applied to soil at pre-sowing and as topdressing fertilisers in comparison with urea, both by surface application and subsurface injection. After each fertiliser application, ammonia emissions were measured. Ammonia emission data indicated, as expected, that the correct use of digestate and derived products, injected into the soil, avoided ammonia volatilisation. Subsurface injection allowed the reduction of ammonia emissions to levels that were similar to those obtained by using urea.

3.4.2.2 Odour emission

Odours emissions are related to the anaerobic digestion process. Indeed, the perception of odour is linked to the emission of volatile organic compounds (VOCs), (sulphur compounds, VFA, indoles and phenols) derived from fermentation and/or anaerobic respiration of degradable organic matter during the AD process (Orzi et al., 2010). On this topic, a research (Orzi et al., 2015) has been conducted, with the aim to assess the effect of biological processes during mesophilic anaerobic digestion in reducing potential odour impact. Ten full-scale biogas plants characterized by different plant designs (e.g. single digesters, parallel or serial digesters), plant powers (ranging from180 to 999 kWe), hydraulic retention time (HRT) (ranging between 20 to 70 days) and feed mixes were monitored, and odours were measured in both ingestates and digestates. Results obtained indicated a reduction in the odour (OU) from, on average, OU ingestate = 99106 ± 149173 OU m^{-2} h^{-1} (n = 15) to OU digestate

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[2] In due course phosphate precipitates and ashes of sewage sludge will be regulated.

= 1106 ± 771 OU m^{-2} h^{-1} (n=15). Mesophilic anaerobic digestion reduced the potential odour impact of biomasses because of the degradation of organic matter and the acquirement of a high degree of biological stability. Potential odour impact can be reduced, on average by 98%. Apart the effect of the anaerobic process by itself, some open field experiments (Orzi et al., 2015 and Orzi et al., 2018) compared the use of digestate and liquid fraction of digestate with untreated cow and pig slurries, testing different spreading methods: surface *vs* injection. Odours were measured by using dynamic olfactometry and qualitatively by using an electronic nose. When the digestate and liquid fraction of digestate were dosed on soil, odours emitted were much lower than those from soils on which untreated slurries were used. Furthermore, slurries/digestate injection reduced much more odour emitted, until reaching a value similar to the untreated soil. This approach allowed to establish that anaerobic digestion together with digestate injection strongly reduce odour impact during manure spreading.

3.4.2.3   Nitrate leaching

The leaching of nitrate in the soil following fertilisation is considered one of the major environmental impact problems arising from agriculture. In general, organic fertilisers such as cattle and pig manure, or digestate, are considered more susceptible to the problem of nitrate leaching. This is due to the slow release of nitrogen involved in organic bonds, which may not be readily absorbed by the roots, and then leached.

However, the information reported in the literature regarding the risk of leaching after fertilisation with digestate liquid fraction, although few, are encouraging. Sigurnjak and colleagues (Sigurnjak et al. 2017), in field trials carried out in Belgium on maize crops, measured the nitrate content in the soil at a depth of 90 cm after the harvest period. The nitrate concentration of the parcels fertilized with digestate liquid fraction was always slightly higher than the concentration measured in the control plots, fertilized with chemical fertilisers. However, the values do not exceed the legal limits imposed in Dutch (75 kg NO_3-N ha^{-1}) (VLM, 2015).

Also, in Belgium, Tsachidou and colleagues (Tsachidou et al. 2019) carried out a similar experiment on a grassland soil used for grazing. In this case, the concentration of nitrate at 90 cm depth for the parcels fertilized with digestate liquid fraction was always lower than that found at the same depth for the parcels fertilized with ammonium nitrate. Furthermore, it has been reported that by increasing the amount of nitrogen dosed from 230 kg ha^{-1} to 350 kg ha^{-1}, the concentration of nitrate detected at 90 cm depth in the parcels fertilized with ammonium nitrate has quadrupled, while no differences were found in the parcels fertilized with digestate liquid fraction.

These results strongly confirm our hypothesis that, in the short-term, digestate liquid fraction applied as the sole nitrogen source and at the maximum rate of 350 kg N ha^{-1} yr^{-1} do not increase the potential nitrate leaching risk in contrast to chemical fertilisers.

3.5 Factsheet

The factsheet is given below and can be found on the website of SYSTEMIC (https://systemicproject.eu/).

Technology description

The solid/liquid separation of digestate generates two outputs, the liquid and the solid fraction of digestate. The liquid fraction of digestate is a pumpable liquid fraction, richer in nitrogen than digestate. The solid fraction consists of stackable fibrous material, rich in organic matter. There are several separation methods, such as belt press, sieve drum, screw press, sieve or decanter centrifuge (Figure 1 below). Furthermore, chemical aids (i.e. flocculants and coagulants) can be used to improve separation efficiency. All these methods combined with aids result in differences in separation efficiency of dry matter, N, P, or K portioning into liquid and solid fractions.
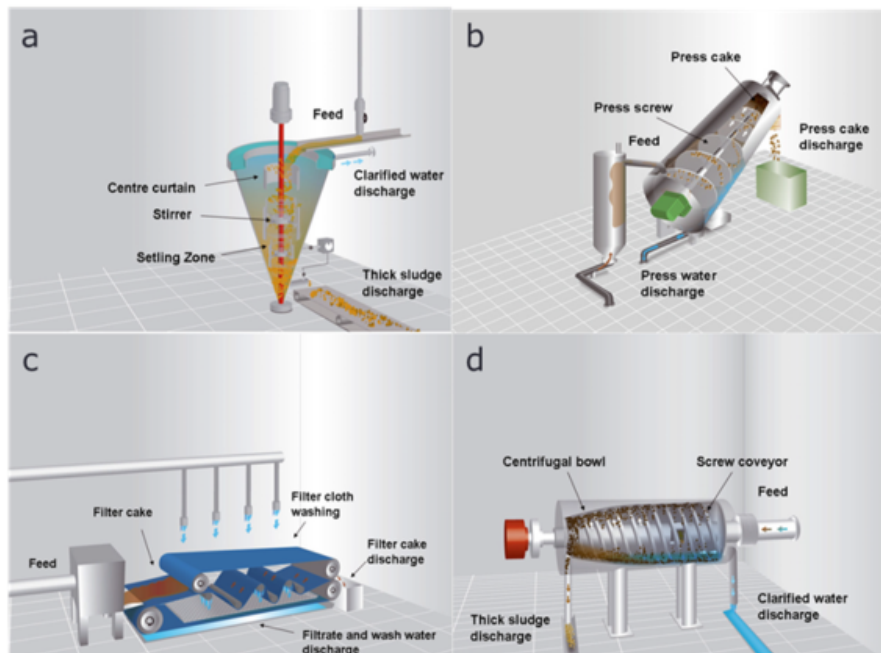
Figure 1: Examples of mechanical solid/liquid separators: a. thickener for sedimentation; b. typical screw press; c. typical belt separator with pressure rolls; d. typical decanter centrifuge (Hjorth et al., 2009).

Product characteristics

The liquid fraction of digestates has a high range of variation of chemical, physical and biological characteristics due to the type of solid-liquid separation, the chemical aids along with the type of substrates used to feed the digester. Centrifugation and screw press with coagulant are the most efficient separation techniques, which result in low total solids concentration in liquid fraction of digestate. Screw press or vibrating screen are the least efficient separation techniques, which lead to similar total solids concentration in liquid fraction of digestate as in ingoing raw digestate. The origin of substrates, especially manure, determines the characteristics of liquid fraction of digestate.

1

Table 1 reports the chemical characteristics obtained from 13 Italian full-scale anaerobic digestion plants (Tambone et al., 2017; 2019), 11 French full-scale co-digestion plants (Akhiar et al., 2017) and data of the EBA database with different feedstocks.

Parameter	Unit	Median	Mean	Minimum	Maximum	Reference
Dry matter (DM)	g kg^{-1} FM	51.0	53.9	0.23	257	EBA
pH	[-]	7.90	7.91	7.20	8.70	EBA
Conductivity	mS cm^{-1}	38	14	29	27	Akhiar et al, 2017
TOC	g kg^{-1} DM	395	383	0.02	525	EBA
COD	g L^{-1}	40.2	40.9	10.3	83.1	Akhiar et al, 2017
BOD$_5$	g L^{-1}	4.5	4.8	1.2	9.3	Akhiar et al, 2017
TKN	g kg^{-1} DM	96.7	131	17.9	959	EBA
TAN	g kg^{-1} DM	53.6	80.4	2.74	397	EBA
TAN/TKN	[-]	55.4	61.4	15.3	41.4	EBA
P$_2$O$_5$ total	g kg^{-1} DM	4.21	4.42	0.06	13.8	EBA
C/N	[-]	3.35	3.70	2.70	4.93	Tambone et al, 2017
Biological stability OD$_{20}$	mg O$_2$ DM^{-1} 20 h.	37.2	40.1	13.1	70.2	Tambone et al, 2017
Alkalinity	g L^{-1}	14.1	16.5	7.4	24.7	Akhiar et al, 2017

Table 1. Chemical characteristics of liquid fraction of digestate samples based on three sources, their maximum (max) minimum (min), median (med) and average (av).

Agronomic aspects

The use of the liquid fraction of digestate as fertiliser is recent and few data are freely available to support its effectiveness in substitution of commercial synthetic fertiliser. Results of two trials were reported. Riva et al. (2016) indicated that sub-surface injection of digestate and derived products at pre-sowing and topdressing, gave crop yields similar to those obtainable with the use of urea. Sigurnjak et al. (2019) found in a three-year field trial that the liquid fraction of digestate used as a NK-fertiliser next to treatments with animal manure or digestate, showed similar effects on biomass yields and soil properties as the traditional fertilisation regime with animal manure and synthetic NK- fertilisers.

In both studies, yields obtained by fertilising with liquid fraction of digestate showed no significant differences with those obtained with conventional practices (using only synthetic N or synthetic N in addition to animal manure). Future perspectives indicate that nutrient variability in bio-based fertilisers will be one of the greatest challenges to address in the utilisation of these products.

2

Nitrogen use efficiency

The use of the liquid fraction of digestate as a fertiliser in agriculture is a recent practice and thus data on nitrogen use efficiency are scarce. Currently, two papers report data on Nitrogen Use Efficiency (NUE) of liquid fraction of digestate (Table 2). Both are based on pot experiments.

Crop	N application rate, mg N/kg soil	NUE, %	Reference
Barley	300	61	Maurer et al, 2019
Barley	500	47	Maurer et al, 2019
Lettuce	210	62	Sigurnjak et al, 2016

Table 2. Nitrogen use efficiency (NUE) of liquid fraction of digestate used as a fertiliser

The NUE values show variability depending on crop (barley and lettuce) and the application rate of nitrogen. NUE values reported for the liquid fraction of digestate are lower than those reported for conventional synthetic fertilisers. Sigurnjak and colleagues report a NUE value for liquid fraction of digestate of 62% which was lower than the NUE for Calcium Ammonium Nitrate (CAN) which amounted to of 71% (Sigurnjak et al. 2016).

Environmental aspects

Because of the origins of the matrices from which digestate and the relative fractions (liquid and solid) are obtained, i.e. animal slurry plus by-products and energy crops, heavy metals content and presence of pathogenic microorganisms must be considered.

Heavy metals

Table 3 reports the results of Tambone et al. (2017) on 13 samples of liquid fraction on principal heavy metals which are in line with the concentrations of poultry manure, sewage sludge and compost.

Metal	Tambone et al, 2017	EBA
Cd	0.3 ± 0.2	0.4 ± 0.2
Cr	11.6 ± 6.3	12 ± 11
Cu	55 ± 27	90 ± 89
Ni	9.8 ± 4.8	10.4 ± 5.6
Pb	1.7 ± 0.8	1.7 ± 0.8
Zn	245 ± 117	361 ± 320

Table 3. Heavy metals content in liquid fraction of digestate in mg/kg dry matter

3

Pathogens

The main factors affecting pathogen decay during anaerobic digestion are the hydraulic retention time (HRT), temperature, volatile fatty acids (VFA) present, batch or continuous digestion, bacterial species and available nutrients (Sahlström et al., 2008). In general, anaerobic digestion reduces pathogen counts, above all when thermophile conditions are adopted (Franke-Whittle and Insam, 2013) because of high temperature.

A study conducted on ten full-scale biogas plants characterised by different plant designs (e.g. single digesters, parallel or serial digesters), plant powers (ranging from 180 to 999 kWe), hydraulic retention time (HRT) (ranging between 20 to 70 days) and feed mixes monitored pathogens both ingestates and digestates (Orzi et al., 2015). Pathogens studied (Enterobacteriaceae, fecal Coliform, *Escherichia coli* and *Clostridium perfringens*) were significantly reduced during the process, both because of ammonia production and because of competition for substrate between pathogens and indigenous microflora. Plants showed different abilities to reduce pathogen indicators, depending on the pH value and toxic ammonia content. Similar results, on fecal coliforms, *E. coli*, *Salmonella*, *Campylobacter* spp. and *Y. enterocolitica*, were previously obtained in a psychrophilic anaerobic digestion plant (Massé et al., 2011).

Emission

In the EU, new legislation on environmental protection will require methods to reduce both ammonia and odour emission due to the spreading on the land of animal slurries. Among different methods proposed to reduce emissions, slurry treatment through anaerobic digestion and the direct injection of digestate into the soil have been proposed as successful practices (Orzi et al., 2018).

Ammonia volatilisation

As example of ammonia volatilisation during the utilisation of digestate and liquid fraction of digestate is reported in Riva et al. (2016) in a short-term experiment, in which digestate products were used as substitutes for mineral (N) fertiliser in a corn cultivation. In brief, digestate and the liquid fraction of digestate were applied to soil at pre-sowing and as topdressing fertilisers in comparison with urea, both by surface application and sub-surface injection. After each fertiliser application, ammonia emissions were measured. Ammonia emission data indicated, as expected, that the correct use of digestate and derived products, injected into the soil, avoided ammonia volatilisation. Sub-surface injection allowed the reduction of ammonia emissions to levels that were similar to those obtained by using urea.

Odour emission

Odour emissions are related to the anaerobic digestion process and are caused by the emission of volatile organic compounds (VOCs), (sulphur compounds, VFA, indoles and phenols) derived from fermentation and/or anaerobic respiration of degradable organic matter during the AD process (Orzi et al., 2010).

Mesophilic anaerobic digestion reduced the potential odour impact at ten full-scale biogas plants with different designs (Orzi et al., 2015). A reduction was found compared with odour from ingestates from 99106 ± 149173 OU m^{-2} h^{-1} (n = 15) to OU digestate = 1106 ± 771 OU m^{-2} h^{-1} (n=15). Apart from the effect of the anaerobic process by itself, some open field experiments (Orzi et al., 2015 and Orzi et al., 2018) compared the use of digestate and liquid fraction of digestate with untreated cow and pig slurries, testing different spreading methods: surface *vs* injection.

When the digestate and liquid fraction of digestate were dosed on soil, odours emitted were much lower than those from soils on which untreated slurries were used. Furthermore, slurries/digestate injection reduced much more odour emitted, until reaching a value similar to the untreated soil (Orzi et al., 2015 and Orzi et al., 2018).

Nitrate leaching

Sigurnjak (Sigurnjak et al. 2017) measured the nitrate content in the soil at a depth of 90 cm after the harvest period of maize crops, in field trials carried out in Belgium. The nitrate concentration of the parcels fertilised with digestate liquid fraction was always slightly higher than the concentration measured in the control plots fertilised with chemical fertilisers. However, the values do not exceed the legal limits imposed in Dutch (75 kg NO$_3$-N ha^{-1}) (VLM, 2015).

4

A similar experiment in Belgium was carried out by Tsachidou (Tsachidou et al. 2019) on a grassland soil used for grazing. In this case, the concentration of nitrate at 90 cm depth for the parcels fertilised with digestate liquid fraction was always lower than that found at the same depth for the parcels fertilised with ammonium nitrate. Furthermore, it was reported that by increasing the amount of nitrogen dosed from 230 kg ha^{-1} to 350 kg ha^{-1}, the concentration of nitrate detected at 90 cm depth in the parcels fertilised with ammonium nitrate has quadrupled, while no differences were found in the parcels fertilised with digestate liquid fraction.

These results strongly suggest, in the short-term, that digestate liquid fraction applied as the sole nitrogen source and at the maximum rate of 350 kg N ha^{-1} yr^{-1} does not increase the potential nitrate leaching risk in comparison to chemical fertilisers.

Current legal view on liquid fraction of digestate

EU member states have national requirements for use of digestate as a fertilising product. These national regulations differ amongst the member states. If the requirements of these national regulations are not met, the digestate has to be treated as waste. The new EU Regulation for fertilising products 2019/1009 set standards for Fresh Crop Digestate (CMC 4) and Digestate Other Than Fresh Crop Digestate (CMC 5). From CMC 4 and CMC 5 fertilising products (organic fertiliser, organo-mineral fertiliser, organic soil improver, growing media) can be produced which can be labelled with a CE marking.

The national regulations will implement the new EU Regulation 2019/1009 and this will have an effect on the designation of feedstock substrates and their criterions. This process will be finalised in July 2022. Then it will be clear which feedstock substrates meet the requirements of the new EU Regulation and which will not and thus need additional national regulations. EU Regulation 2019/1009 is a facultative one and thus a manufacturer of a digestate can choose if the digestate is labelled with a CE marking or not.

Digestates which use manure are designated as manure and thus they have to fulfil the requirements on use of the Nitrates Directive (91/676/EC).

Some relevant references

Akhiar, A., et al., 2017, 'Comprehensive characterization of the liquid fraction of digestates from full-scale anaerobic co-digestion', Waste Management, 59, pp. 118–128: https://bit.ly/36IJfkH

Sigurnjak, I., et al., 2017, 'Fertilizer performance of liquid fraction of digestate as synthetic nitrogen substitute in silage maize cultivation for three consecutive years' Sci. Total Environ., 599–600, 1885–1894: https://bit.ly/2CfwLTq

Tambone, F., et al., 2017, 'Solid and liquid fractionation of digestate: Mass balance, chemical characterization, and agronomic and environmental value' Biores. Technol., 243, pp. 1251–1256: https://bit.ly/2WNB2H0

Tambone, F., et al., 2019, 'Measuring the organic amendment properties of the liquid fraction of digestate' Waste Management, 88, pp. 21–27: https://bit.ly/2JSUEnS

All references are given in: Ehlert, Phillip, Ivona Sigjurnak, Erik Meers, Marieke Verbeke, Fabrizio Adani, Massimo Zilio, Fulvia Tambone and Oscar Schoumans, 2019. Nitrogen fertilising products based on manure and other organic residues. Supporting literature of the SYSTEMIC factsheets. Wageningen, Wageningen Environmental Research, Report

5

4 Ammonium sulphate

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Ammonium sulphate solutions are produced by a variety of production processes and are often allowed for use as a fertilising product. For example in Germany ammonium sulphate solutions of designated origin are allowed to be used as a fertilising product if certain criteria on composition (value giving components and contaminants) are met. Designated origins (DüMV[3]) are:

1. Exhaust air cleaning:
   a. Production and processing of food, food and feed and alcohol production,
   b. Power generation,
   c. Livestock farms
   d. Sewage treatment plants
   e. Treatment of bio-waste
   f. Mechanical-biological waste treatment
2. Emission incinerators
3. Wastewater treatment municipal and industrial wastewater treatment
4. Aerobic or anaerobic treatment of organic substances
5. Biotechnological treatment of designated process
6. Production of hydrocyanic acid
7. Production of food and beverages
   a. Production of sweetener
   b. Processing of sugar beet
8. Treatment of aluminium salt slags
   a. Absorption of ammonia gas
9. Metal processing
   a. Extraction and processing of tungsten
10. Treatment of wood with ammonia gas
    a. Wood smokehouse with ammonia gas
11. Recycling of used ammonium sulphate solutions
1. Regeneration of NH_4-loaded zeolites during the treatment of used ammonium sulphate solutions

In contrast to ammonia sulphate solutions made from animal manure (including co-digested manure) which have to meet requirements of the Nitrates Directive, ammonium sulphate solutions of other origin are not bound to restrictions on use of nitrogen from animal manure. In this chapter information on ammonium sulphate solutions from animal manure is given.

The production of ammonium sulphate solution and its use as a nitrogen fertiliser is a common agricultural practice in some member states. This is caused by the obligatory requirement of ammonia (NH_3) removal through air cleaning of intensive pig and poultry livestock farms (e.g. in the Netherlands, Belgium).

Ammonia stripping as an industrial manure treatment process is only recently introduced in agriculture. In the Netherlands, currently (June 2019) two strippers are operational, a third is currently under construction.

This chapter is mainly based on Sigurnjak et al. (2019).
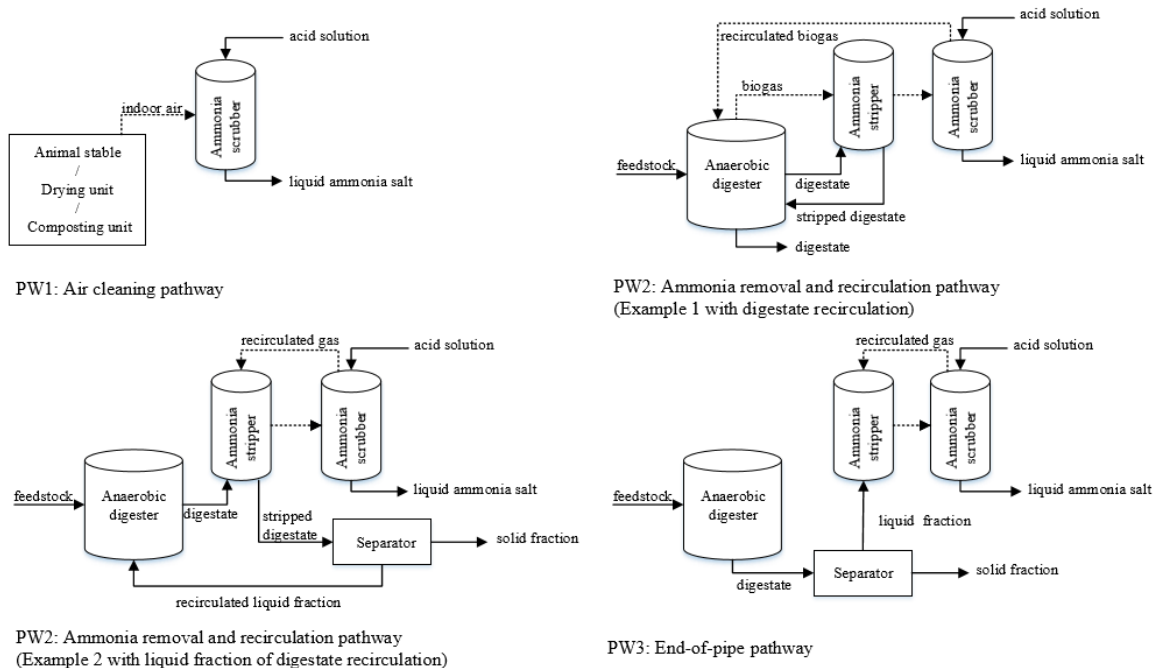
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[3] https://www.gesetze-im-internet.de/d_mv_2012/

4.1 Description of technology

Ammonium sulphate recovery from manure and other nitrogen (N) rich biomass can be obtained by removal (i.e. stripping) and/or capture (i.e. scrubbing) of ammonia (NH_3) contained in these streams. The operating principle of (stripping)-scrubbing technology is that ammonia (NH_3) can be stripped by air, steam or vacuum through the N rich stream in a packed bed tower, resulting in NH_3 transfer from the aqueous phase to a gas phase (Guštin and Marinšek-Logar, 2011). Latest research indicates also the possibility to use electrodialysis to transfer NH_3 (Ippersiel et al., 2012) and an option to scrub CO_2 by adding the third column next to the usual stripping and scrubbing columns (Boehler et al., 2015). In general, scrubbing can be done in a chemical or biological manner, or even combination of both, by using acid or ammonia oxidising bacteria, respectively (Van der Heyden et al., 2015). Due to the higher NH_3 removal efficiency (70-99%; Melse and Ogink, 2005; Van der Heyden et al., 2015) as compared to biological scrubbers (10-99%; Van der Heyden et al., 2015), most installations in practice would use chemical scrubbers. The released NH_3 in a chemical air scrubber is removed by capturing it by absorption with a strong acidic solution such as sulphuric acid. The reaction of NH_3 with sulphuric acid (H_2SO_4) results in ammonium sulphate (AS). To obtain optimal removal of NH_3, often pH of the N rich stream and temperature are adjusted to 10 and 70°C, respectively (Lemmens et al., 2007). Higher temperatures during the stripping phase have a double advantage, in the form of raising the fraction of free NH_3 in the treated stream and of increasing NH_3 volatilisation into the gas phase as a consequence of a higher saturated vapour pressure (Walker et al., 2011). Various systems for ammonia stripping and air scrubbing have been tested to decrease toxic NH_3 in digesters (Ghyselbrecht et al., 2018; Lauterböck et al., 2014; Pedizzi et al., 2017), or to remove excess nitrogen from manure, or produce concentrated nitrogen fertilisers similar to mineral fertilisers (Ghyselbrecht et al., 2018; Starmans and Timmerman 2013a).

In Europe, within Systemic project (Horizon 2020), the following pathways (PW) have been identified to recover NH_3 via (stripping)-scrubbing on a full scale (Figure 4.1):

1. **PW1. Air cleaning pathway** makes use of only 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 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 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. According to Melse and Ogink (2005), the efficiency of acid scrubbers decrease when NH_3 content is above 35 ppm or when retention time of gas is lower than 1 second (Melse and Ogink, 2005).

2. **PW2. Ammonia removal and recirculation pathway** where (stripping)-scrubbing unit is coupled to 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 digestate, liquid fraction is stripped and recirculated to anaerobic digester (Demo plant Systemic – Acqua & Sole), or (ii) 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 anaerobic digester (Demo plant Systemic – Benas). 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).

3. **PW3. End-of-pipe pathway** where digestate from anaerobic digestion or raw animal manure is first separated into liquid and solid fraction, and subsequently liquid fraction is treated in (stripping)-scrubbing unit (Digesmart, 2016b) instead of being, for example, subjected to aerobic treatment.

PW1: Air cleaning pathway

PW2: Ammonia removal and recirculation pathway
(Example 1 with digestate recirculation)

PW2: Ammonia removal and recirculation pathway
(Example 2 with liquid fraction of digestate recirculation)

PW3: End-of-pipe pathway

Figure 4.1. Pathways (PW) for nitrogen recovery using scrubbing and stripping technology. Scrubbing techniques produce ammonia solutions with lower nitrogen concentrations (40-65 kg N tonnes^{-1}; Leirs et al., 2017), whereas (stripping)-scrubbing techniques result in higher nitrogen concentrations (> 80 kg N tonnes^{-1}).

4.2 Characteristics and composition

4.2.1 Characteristics

Ammonium sulphate is recovered as a liquid product by contact between the stripped NH_3 rich air (from manure and biomass) and sulphuric acid (Eq. 4.1) that is added to the washing water.

$$2NH_4OH + H_2SO_4 \leftrightarrow (NH_4)2SO_4 + 2H_2O \hspace{3cm} \text{(Eq. 4.1)}$$

The produced ammonium sulphate is an inorganic salt that will precipitate if the maximum solubility of the salt is exceeded (772 g l^{-1} or 164 g [N] l^{-1} at 20°C), resulting in clogging and higher energy requirement (Weast, 1975; Holmén and Liss, 1984; Van der Heyden et al., 2015). To prevent unwanted precipitation, in Flanders and the Netherlands, the maximum concentration of ammonium sulphate in the washing liquid is 58.8 g N L^{-1} (Van der Heyden et al., 2015). As an inorganic salt, ammonium sulphate has a quite high dry matter (DM). This means in theory that product can also be dried and used in a solid form but the design of such a drying unit is technically a challenging task and no running installations exist yet. At the temperature above 250°C ammonium sulphate will decompose into NH_3, SO_4 and water.

Considering the mentioned circumstances of the process, the product is known for a high sulphur (S) content, electrical conductivity (EC) and a wide range of pH values (from acidic to neutral), depending on the added amount of the sulphuric acid and recirculation frequency of washing water. The low pH value can result in a corrosion of metal equipment and machinery that gets into contact with the product. If needed, the pH can be corrected by adding base such as NaOH (Vaneeckhaute et al., 2013).

Due to the maximum solubility of $(NH_4)_2SO_4$ the concentration in the scrubbers is always below 164 kg N tonnes^{-1} (Van der Heyden et al., 2015). The pH should be lower than 3 or 4 depending on the apparatus, and the conductivity should be lower than 250 mS cm^{-1} (Melse et al., 2018). The N concentration can be increased by drying the suspension.

Composition

Similar as in synthetic N fertilisers, ammonium sulphate contains total N entirely in mineral form, as NH_4-N. Since the product is obtained by means of sulphuric acid, ammonium sulphate is also an important source of sulphur (S). Depending on the amount of added acid not only S concentration will vary, but also pH and EC. Low pH and high EC values could be of concern during product application since it can cause corrosion of machinery (Table 4.1).

Table 4.1. *Composition of ammonium sulphate (from air cleaning pathway = PW1) on fresh weight basis reported in published studies (Vaneeckhaute et al., 2013; Vaneeckhaute et al., 2014; Chen et al., 2014; Sigurnjak et al., 2016) and unpublished data from Systemic project. In Systemic project ammonium sulphate was obtained from ammonia removal and re-circulation (WP2) pathway where digestate (PW2 Example 1) and liquid fraction of digestate (PW2 Example 2) were stripped and recirculated.*

Parameters	PW1	PW2 (Example 1)	PW2 (Example 2)
DM (%)	14 - 33	32	25
OC (%)	0.04	0.04	ND
pH	2.40 – 6.43	6.7	7.6
EC (mS cm^{-1})	152 - 262	ND	182
NH$_4$-N (g kg^{-1})	30 - 86	74	40.4
NO$_3$-N (g kg^{-1})	NA	NA	NA
N$_{total}$ (g kg^{-1})	30 - 86	74	40.4
Effective N (%)	100	100	100
S (g kg^{-1})	30 - 114	98	50
P (g kg^{-1})	<0.06 - 0.11	0.02	ND
K (g kg^{-1})	0.18 - 0.20	0.01	ND
Ca (g kg^{-1})	0.26	0.07	ND
Mg (g kg^{-1})	0.06	<0.01	ND
Na (g kg^{-1})	0.14	0.03	ND
Fe (mg kg^{-1})	ND	<10	ND
Mn (mg kg^{-1})	ND	1.2	ND
Cd (mg kg^{-1})	ND	<0.25	ND
As (mg kg^{-1})	ND	<1	ND
Ni (mg kg^{-1})	ND	<1	ND
Hg (mg kg^{-1})	ND	<0.25	ND
Cu (mg kg^{-1})	0.3	<5	ND
Zn (mg kg^{-1})	2.9	2.9	ND
Pb (mg kg^{-1})	ND	<1	ND
Cr (mg kg^{-1})	ND	<1	ND
Fluorides (mg kg^{-1})	ND	<1	ND
Chlorides (mg kg^{-1})	ND	<1	ND

DM: dry matter; OC: organic carbon; EC: electrical conductivity; Effective N: percentage of total N present in mineral form; ND: not determined; NA: not applicable.

Even though ammonium sulphate chemically consists of only NH_4-N, SO_4 and water (Eq. 4.1.), other macro-and microelements can be found in trace. These concentrations (Table 4.1.) are negligible and seen as a result of dissolved volatile compounds entering the stripping scrubbing system and/or as a consequence of recirculating reused acid through the system. For example, in PW1 by scrubbing ammonia rich gas from animal stables also other particles from pig stables (e.g. dust) can be scrubbed and as such end up in ammonium sulphate. In other PWs the scrubbing of other components can be better controlled as it involves stripping step that takes place in a closed unit.

4.2.1.1 Value giving components

Ammonium sulphate contains water, total N completely present in NH_4-N form and SO_4 (Eq. 4.1.). With these main value giving components, ammonium sulphate can be used in agriculture as a fertiliser or in chemical and fertiliser industry as a secondary raw material.

Depending on its pH, ammonium sulphate with pH 5-7 can be used as a synthetic N fertiliser substitute on slightly acidic to neutral soil or with pH < 5 as a fertiliser on alkaline soil to balance the soil pH. In fertiliser industry ammonium sulphate has a potential to be used as a component of CE market fertilizing products.

Compared to urea or ammonium nitrate, whose N concentration in commercial products reaches more than 20%, the N concentration of ammonium sulphate ranges from 3-9% (Table 4.1). According to Bolzonella et al. (2018), the market value for ammonium sulphate (6% N, 30% ammonium sulphate) is around 30 € m^{-3}. Due to its lower N content, it is desirable for this product to have a high purity in order to make it competitive on the interregional market.

#### 4.2.1.2 Contaminants and pathogens

As ammonium sulphate is generated from gas/air in theory it should not contain contaminants. In the case if contaminants are detected they are measured in trace amount and are considered to be negligible (Table 4.1). As mentioned in Section 4.2.1. the main source of contamination comes from the volatile fatty acids (from manure) and dust (from stables) that can be absorbed in an acid.

4.3 Agronomic effectivity

In essence, with a total N present completely as NH_4-N, an ammonium sulphate rich solution will enjoy the same characteristics as synthetic N fertilisers with regard to nitrogen availability to crops. Considering that sulphate is also a required plant nutrient, this on its own is not a problem. However, ammonium sulphate as a source of nitrogen may need to be examined from a sulphate crop requirement as well in order to avoid adding excessive doses of sulphate beyond the crop's requirement. Up to now, ten individual trials on ammonium sulphate have been identified. Their main focus was to assess the effect of the ammonium sulphate on crop yield (Figure 4.2) and to determine N fertiliser value (Figure 4.3). Ammonium sulphate that was used in seven out of ten trials was obtained via PW1 that stands for air cleaning from animal stables via scrubbing system (section 4.1). In regard to ammonium sulphate obtained from (stripping)-scrubbing system, very little information can be found. For now only two German studies, reporting on three pot experiments, where found with some info on N fertiliser value of ammonium sulphate from (stripping)-scrubbing system (Bosshard et al., 2008; Bosshard et al., 2011). For the following three years Systemic partners, University of Milan and demo plant Acqua & Sole, will perform field trials with ammonium sulphate from (stripping)-scrubbing system, and in that way extend the existing data set on N fertiliser value of this product.

4.3.1 Yield, product quality

Current results indicate that compared with calcium ammonium nitrate (CAN; synthetic N fertiliser used in these studies as a reference) there is no positive nor negative effect on crop fresh weight yield if recovered ammonium sulphate is used as a N fertiliser in the cultivation of lettuce and maize, i.e. a similar effectivity is found. In all seven studies on ammonium sulphate from air cleaning, similar yields were obtained as in the reference treatment (CAN) that represented the conventional practice of using only synthetic N (lettuce experiments) or synthetic N in addition to animal manure (maize experiments).
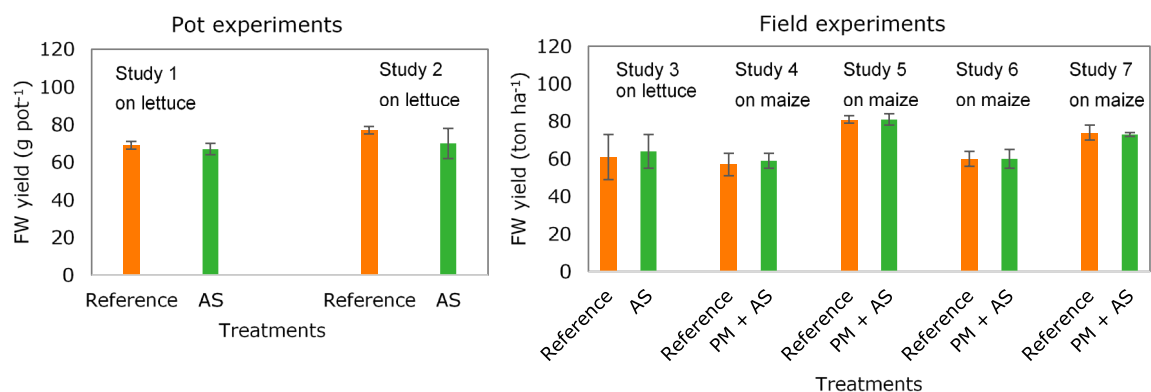
Figure 4.2. *Effect of ammonium sulphate (AS), from air cleaning system (PW1), on fresh weight (FW) yield compared to conventional fertilisation regime in lettuce experiments (Reference = calcium ammonium nitrate (CAN; 27% N) as synthetic N) and maize experiments (Reference = pig manure (PM) + CAN). Study 1, Study 2 and Study 4: Digesmart, 2016a and Sigurnjak et al., 2019; Study 3: Sigurnjak et al., 2016; Study 5: Vaneeckhaute et al., 2013; Study 6: Vaneeckhaute et al., 2014; Study 7: Chen, 2014.*

Although the EC of ammonium sulphate is high and the pH is low, both parameters did not reduce crop yield. The main reason is that due to the high N concentration in ammonium sulphate (30-86 g kg^{-1}), compared to animal manure (c. 3-5 g N kg^{-1}), only low product amounts are applied. Furthermore, the soil also has a buffer capacity to neutralize the potentially low pH of ammonium sulphate. Of course, attention should be taken when applying ammonium sulphate to salt sensitive crops. On the other hand there are crops that can handle high EC values of ammonium sulphate and also benefit from sulphur application (e.g. cabbages, grass 1st and 2nd cuts).

In German studies on ammonium sulphate from (stripping)-scrubbing system (Bosshard et al., 2008; Bosshard et al., 2011) data on crop yield was not reported.
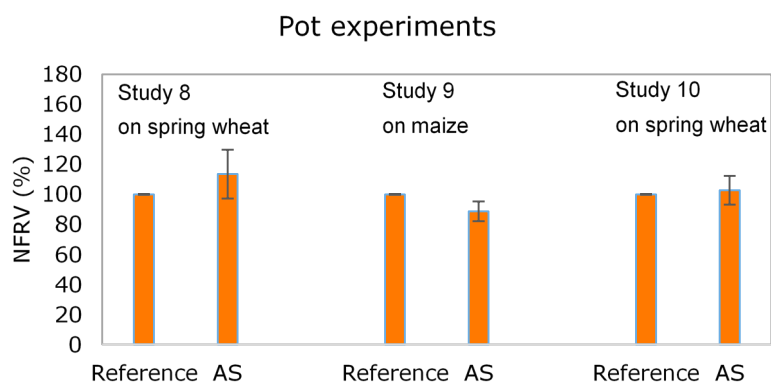
4.3.2 NRUE & NRFV

In six out of seven studies, researchers have reported that NRUE and/or NFRV (Chapter 2; Eq. 2.1 and Eq. 2.2) of ammonium sulphate from air cleaning is similar to the conventional fertilisation regime where synthetic N fertiliser is used as a sole source of N (lettuce cultivation) or on top of pig manure (maize cultivation). Only in study 6 (Figure 4.3) was a significant positive effect reported on NRUE of the manure plus ammonium sulphate treatment (PM+AS) compared to the reference regime, which was a result of higher N uptake by the crop in PM+AS treatment.

In two out of three studies, researchers have reported that NFRV of ammonium sulphate from (stripping)-scrubbing system is similar to the conventional fertilisation regime where synthetic N fertiliser is used as a sole source of N in pot cultivation of spring wheat (Figure 4.4). In pot study with maize, ammonium sulphate from (stripping)-scrubbing system has resulted in lower NFRV than mineral ammonium nitrate that was used as a reference. The studies do not report any information on NRUE.

In general, studies on NRUE and NRFV tend to show a notable variation across different experiments. This variation stems from the effects of variable weather conditions on the performance of both bio-based materials and the used references (Schröder et al., 2013).
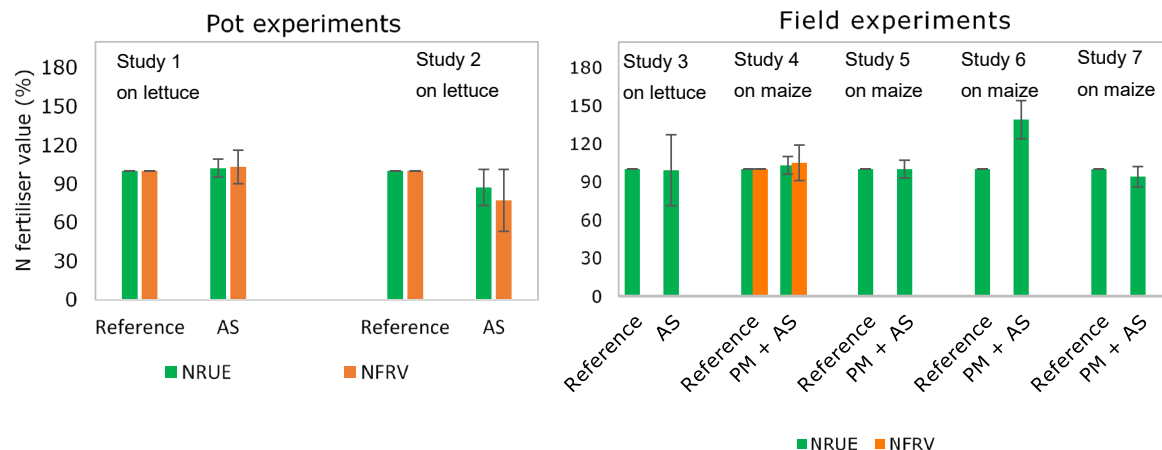
Figure 4.3. *Effect of ammonium sulphate (AS), from air cleaning system (PW1), on nitrogen (N) fertiliser value (%) compared to conventional fertilisation regime in lettuce experiments (Reference = calcium ammonium nitrate (CAN; 27% N) as synthetic N) and maize experiments (Reference = pig manure (PM) + CAN). N replacement use efficiency (NRUE) does not account for the effect of unfertilised treatment, whereas N fertiliser replacement value (NFRV) takes into account the effect of unfertilised treatment. To determine NRUE and NFRV of ammonium sulphate, the reference treatment is considered to be 100% effective. Study 1, Study 2 and Study 4: Digesmart, 2016a and Sigurnjak et al., 2019; Study 3: Sigurnjak et al., 2016; Study 5: Vaneeckhaute et al., 2013; Study 6: Vaneeckhaute et al., 2014; Study 7: Chen, 2014.*

Figure 4.4. *Effect of ammonium sulphate (AS), from (stripping)-scrubbing system, on nitrogen fertiliser replacement value (NFRV; %) compared to conventional fertilisation regime of using commercial ammonium nitrate (reference) in pot experiments with spring wheat and maize. To determine NFRV of ammonium sulphate, the reference treatment is considered to be 100% effective. Study 8 and 9: Bosshard et al., 2008; Study 10: Bosshard et al;, 2011.*

4.4 Risk assessment

4.4.1 Contaminants

Up to now none of the above mentioned ten studies have included the assessment of contaminants, organic micro-pollutants, pathogens, weed seed and other (plastic, glass…) contaminants. The main focus of these studies was to assess the crop production and N fertiliser value.

4.4.1.1   Heavy metals

In above mentioned seven studies on ammonium sulphate from air cleaning, heavy metals were determined in soil and plant at harvest time. In all studies there were no differences observed in soil and plant concentration of heavy metals between the reference and treatments with ammonium sulphate. This is expected since all studies took place for 1 year or maximum 2 years. In order to observe the effect of heavy metal accumulation studies with longer cultivation period are needed.

4.4.1.2   Organic micro-pollutants

See section 4.4.1.

4.4.1.3   Pathogens

See section 4.4.1.

4.4.1.4   Weed seed

See section 4.4.1.

#### 4.4.1.5   Other (plastic, glass...)

See section 4.4.1.

4.4.2   Emission

In above mentioned studies the emission aspect has only been determined in regard to leaching and not in regard to ammonia volatilisation and greenhouse gas emission.

4.4.2.1   Leaching

Environmental aspects have been assessed only in the maize field experiments (with ammonium sulphate from air cleaning) by measuring post-harvest nitrate residue (Figure 4.5). 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).
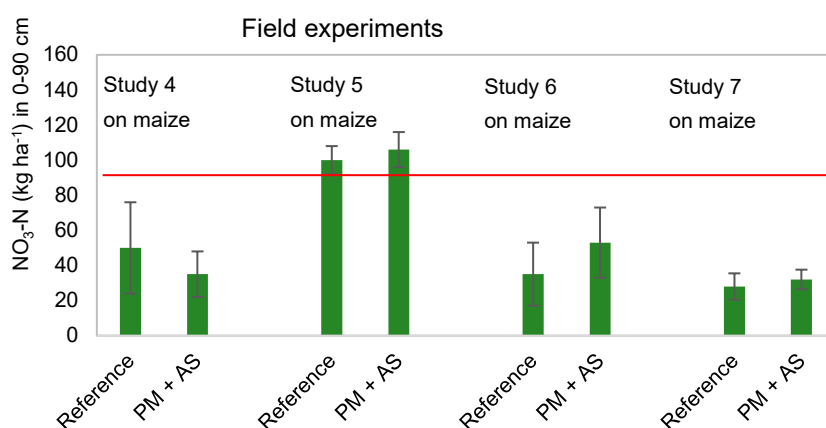
Figure 4.5. Effect of ammonium sulphate from air cleaning (applied in combination with pig manure) and conventional fertilisation (Reference = pig manure (PM) + CAN) on post-harvest nitrate residue (kg ha^{-1}) in 0-90 cm soil layer. The red line indicates the maximum allowable level of nitrate residue in soil (90 kg NO_3-N ha^{-1}) between October 1 and November 15 according to current Flemish environmental standards for maize cultivation in zone where measured NO_3 concentrations in ground water do not exceed 50 mg NO_3 l^{-1}. Study 4: Digesmart, 2016a and Sigurnjak et al., 2019; Study 5: Vaneeckhaute et al., 2013; Study 6: Vaneeckhaute et al., 2014; Study 7: Chen, 2014.

In studies that measured the post-harvest nitrate residue, no significant differences were observed between the reference treatment and the treatment where ammonium sulphate was used as a N source (Figure 4.5). The measured residues were below the maximum allowable level of 90 kg NO_3-N ha^{-1} in 0-90 cm soil layer, with an exception of study 5 where exceedance was observed for the both reference and ammonium sulphate treatment.

Due to the high mobility of nitrate, the measured nitrate residue is highly influenced by weather conditions. Therefore, the observed exceedance in study 5 was attributed to unfavourable weather conditions, warm and dry growing season, which has led to the exceedance of maximum allowable nitrate level in 40% of all taken measurements in West Flanders (Belgium) (Vaneeckhaute et al., 2013). The three studies on ammonium sulphate from (stripping)-scrubbing system do not report on effects in regard to nitrate leaching.

4.4.2.2 Ammonia volatilisation

In general, the risk of ammonia volatilisation will depend on the pH of the product: the lower pH is the lower will be the risk of ammonia volatilisation. In regard to utilisation of ammonium sulphate as a fertiliser there are agricultural practices as incorporation or injection which can reduce significantly potential ammonia volatilisation (Webb et al., 2013). In all above presented pot and field experiments ammonium sulphate was respectively incorporated or injected which would assume a negligible risk for ammonia volatilisation. The actual ammonia volatilisation has not been measured in the currently presented studies.

4.4.2.3 Emission greenhouse gasses (NOx, CO$_2$, CH$_4$)

See section 4.4.2.

4.4.2.4 Safety aspects

Due to the absence of pyrophoric properties, ammonium sulphate is a non-combustible product. There is no presence of chemical groups associated with explosive properties in ammonium sulphate. Storage of ammonium sulphate at temperatures above 235 °C should be avoided, since ammonia emissions may occur. Inhalation of decomposition products may cause pulmonary edema. No flammable gases are generated when put in contact with water (ECHA, 2018a). Accidents on farm may occur as a consequence of mishandling H_2SO_4 which is very corrosive. For example, on a farm in Koekelare (Belgium) a thousand liters of sulphuric acid (98%) spilled from a tank and in Torhout (Belgium) 600 pigs died because sulphuric acid came into contact with manure and the deadly gas hydrogen sulphide was generated in the pig stables (Nieuwsblad, 2013; 2014).

4.5 Factsheet

The factsheet is given below and can be found on the website of SYSTEMIC (https://systemicproject.eu/)

Ammonium sulphate

Technology description

Ammonium (NH_4^+) and ammonia (NH_3) are both the same basic compound, yet the first is water soluble form, whereas the second is the volatile gaseous form. Both these forms are in dynamic equilibrium in which increasing pH and/or temperature will convert more water-soluble ammonium into the gaseous ammonia. In animal housing and manure or digestate-processing facilities, this principle is very important, considering that in stables, ammonia will be emitted from the manure into the ambient air. In environmental performant animal housing, the N-rich air is washed/cleaned via fans: the air is drawn into an air scrubber where the ammonia is captured into water as dissolved ammonium by a low pH 'scrubber' solution. For air washing, a sulphuric acid solution is used (favourable price). In manure or digestate treatment systems, this basic chemical principle can be used to extract ammonium nitrogen from manure via a system that is called 'stripping' (which converts it into volatile ammonia via pH and/or temperature increase) followed by 'scrubbing' to recapture the extracted ammonia back into soluble ammonium through a low pH 'scrubber' solution. Ammonium sulphate can thus be obtained by removing ammonia (NH_3) from nitrogen (N-) rich air or from N-rich biomass streams.

Photo 1: air scrubber (left) and ammonia stripping / scrubbing installation (right) (© VCM)

Product characteristics

Similarly to synthetically produced mineral N fertilisers, ammonium sulphate contains total N entirely in mineral form, as NH_4-N. Since the product is obtained by means of sulphuric acid, ammonium sulphate is also an important source of sulphur (S). Depending on the amount of added acid, it is not only S concentration that will vary, but also the pH and EC. Low pH and high EC values should be taken into account during the product application process since it can cause the corrosion of machinery.

Table 1. Product characteristics of ammonium sulphate (air washing) in ranges based on average values reported in scientific studies

Parameter	Ammonium sulphate
Dry matter (%)	14 - 33
pH	2.40 - 6.43
EC* (mS cm^{-1})	157 - 262
N total (g kg^{-1})	30 - 86
NH_4-N (g kg^{-1})	30 - 86
N mineral/N total (%)	100
S (g kg^{-1})	30 - 114

*EC: electrical conductivity

Ammonium sulphate

Agronomic aspects

Plants (and by extension, crops) require nitrogen in mineral form to take it up. For example, a common synthetic nitrogen fertiliser of which full plant availability is assumed is CAN (Calcium Ammonium Nitrate). In essence, an ammonium sulphate-rich solution will enjoy the same characteristics as CAN with regard to nitrogen availability to crops. Ammonium sulphate solutions will differ from ammonium nitrate solutions (see corresponding factsheet) by its lower overall nitrogen concentration and additionally by the fact that sulphate will be present in the ammonium sulphate solution. Considering that sulphate is also a required plant nutrient, this on its own is not a problem. However, ammonium sulphate as a source of nitrogen may need to be examined from a sulphate crop requirement as well in order to avoid adding excessive doses of sulphate beyond the requirement of the crop.

So far, seven individual agronomic trials of ammonium sulphate have been identified. Their main focus was to assess the effect of the ammonium sulphate on crop yields and to determine N fertiliser value (Figure 1 below).
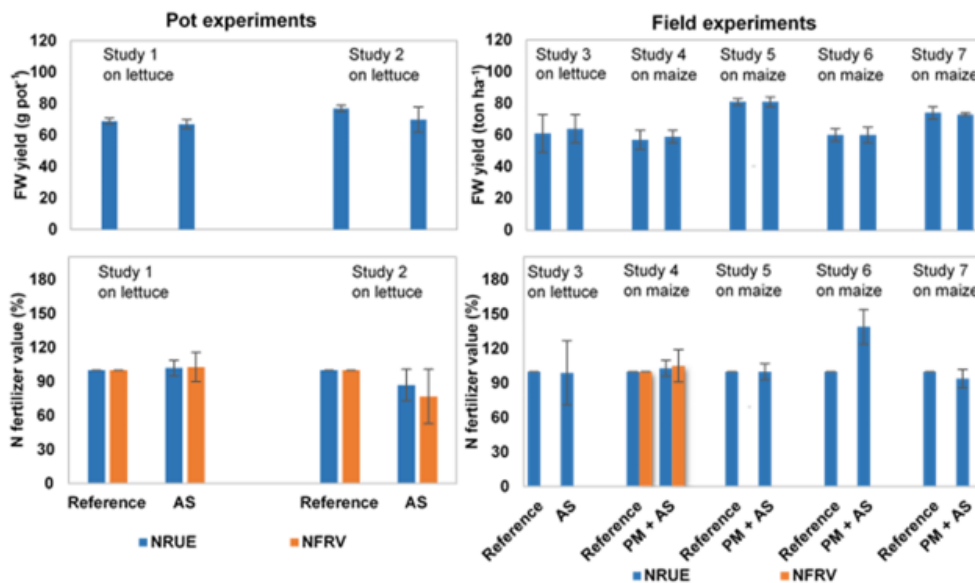

Figure 1. Effect of ammonium sulphate (AS) on fresh weight (FW) yield and its nitrogen (N) fertiliser value compared to conventional fertilisation regime in lettuce (Reference = Calcium Ammonium Nitrate (CAN; 27% N) as synthetic N) and maize (Reference = pig manure (PM) + CAN). N replacement use efficiency (NRUE) does not account for the effect of unfertilised treatment, whereas N fertiliser replacement value (NFRV) takes into account the effect of unfertilised treatment. To determine NRUE and NFRV of ammonium sulphate, the reference treatment is considered to be 100% effective.

Determination of the N fertiliser values (N Replacement Use Efficiency; NRUE and N Fertiliser Replacement Value; NFRV) depends on the presence or the absence of a control (=unfertilised) treatment in an experimental design, and hence can be determined as follows:

$$NRUE (\%) = \frac{(\text{crop N uptake AMM. SULPHATE} / \text{total N applied AMM. SULPHATE})}{(\text{crop N uptake REFERENCE} / \text{total N applied REFERENCE})} *100$$

$$NFRV (\%) = \frac{((\text{crop N uptake AMM. SULPHATE} - \text{crop N uptake CONTROL}) / \text{total N applied AMM. SULPHATE})}{((\text{crop N uptake REFERENCE} - \text{crop N uptake CONTROL}) / \text{total N applied REFERENCE})} * 100$$
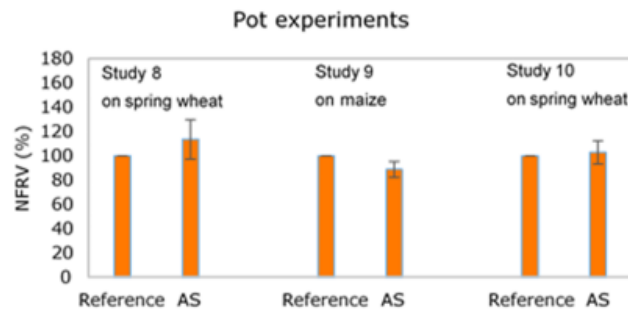
Figure 2. Effect of ammonium sulphate (AS), from (stripping)-scrubbing system, on nitrogen fertiliser replacement value (NFRV; %) compared to conventional fertilisation regime of using commercial ammonium nitrate (reference) in pot experiments with spring wheat and maize. To determine NFRV of ammonium sulphate, the reference treatment is considered to be 100% effective.

Current results indicate that compared to chemical synthetic nitrogen fertiliser (CAN), there is no positive nor negative effect on crop fresh weight yield if recovered ammonium sulphate (from air cleaning) is used as an N fertiliser in the cultivation of lettuce and maize, i.e. a similar effectivity is found. In all seven studies, similar yields were obtained as in the reference treatment that represented the conventional practice of using only synthetic N or synthetic N in addition to animal manure.

Although the EC of ammonium sulphate is high and the pH is low, both parameters did not reduce crop yield. The main reason is that due to the high N concentration in ammonium sulphate ($27 - 86$ g kg^{-1}), compared to animal manure (c. 3-5 g N kg^{-1}), only low amounts are applied. Furthermore, the soil also has a buffer capacity to neutralise the potentially low pH of ammonium sulphate. Of course, attention should be paid when applying ammonium sulphate to salt-sensitive crops. On the other hand, there are crops that can handle high EC values of ammonium sulphate and also benefit from sulphur application (e.g. cabbages).

In six out of the seven studies, researchers reported that NRUE and/or NFRV of ammonium sulphate is similar to the conventional fertilisation regime where synthetic N fertiliser is used as a sole source of N (lettuce cultivation) or on top of pig manure (maize cultivation). Only in study 6 (Figure 1) was a significant positive effect reported on NRUE of the manure plus ammonium sulphate treatment (PM+AS) compared to the reference regime, which was a result of higher N uptake by the crop in PM+AS treatment. In two out of three studies, researchers reported that NFRV of ammonium sulphate from (stripping)-scrubbing system is similar to the conventional fertilisation regime where synthetic N fertiliser (ammonium nitrate) is used as a sole source of N in pot cultivation of spring wheat (Figure 2). In pot study with maize, ammonium sulphate from (stripping)-scrubbing system resulted in lower NFRV than mineral ammonium sulphate from (stripping)-scrubbing system resulted in lower NFRV than mineral ammonium nitrate that was used as a reference. The studies do not report any information on NRUE.

In general, studies on NRUE and NRFV tend to show a notable variation across different experiments. This variation stems from the effects of variable weather conditions on the performance of both bio-based materials and the used references.

Environmental aspects

Environmental aspects have been assessed in the field experiments on ammonium sulphate from air cleaning by measuring post-harvest nitrate residue. The measured nitrate residue gives an estimation of the nitrate amount that can potentially leach to ground and surface water. This procedure has been used in Flanders (Belgium) since 2004 and in Bretagne (France) since 2014. In studies that measured the post-harvest nitrate residue, no significant differences were observed between the reference treatment and the treatment where ammonium sulphate was used as an N source (Figure 3 below). The measured residues were below the maximum allowable level of 90 kg NO_3-N ha^{-1} in 0-90 cm soil layer, with an exception of study 5 where exceedance was observed for both the reference and ammonium sulphate treatment.
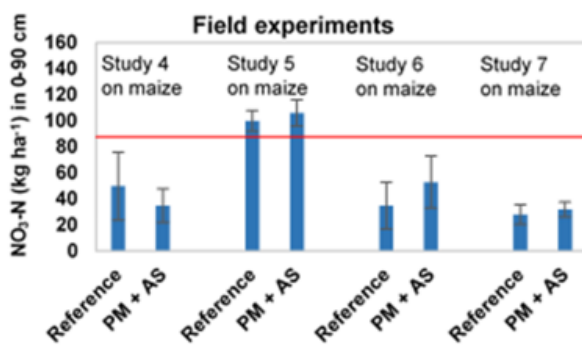
Figure 3. Effect of ammonium sulphate from air cleaning (applied in combination with pig manure) and conventional fertilisation (Reference = pig manure (PM) + CAN) on post-harvest nitrate residue (kg ha^{-1}) in 0-90 cm soil layer. The red line indicates the maximum allowable level of nitrate residue in soil (90 kg NO_3-N ha^{-1}) between October 1 and November 15, according to current Flemish environmental standards for maize cultivation in zone where measured NO_3 concentrations in ground water do not exceed 50 mg NO_3 l^{-1}.

Due to the high mobility of nitrate, the measured nitrate residue is highly influenced by weather conditions. Therefore, the observed exceedance in study 5 was attributed to unfavorable weather conditions – a warm and dry growing season, which has led to the exceedance of maximum allowable nitrate level in 40% of all taken measurements in West Flanders (Belgium).

Current legal view on ammonium sulphate

In livestock farming, air washing was developed to reduce the ammonia from the N-rich air of the stable. In some EU regions, air washing is used frequently, yet the end product (ammonia sulphate) is a recognised fertiliser and can be used locally under the same conditions as a chemical fertiliser. By (stripping-)scrubbing ammonia directly from manure, the ammonia sulphate has a relative high N-concentration (3-9%; Table 1). To date, NH_3-stripping/scrubbing from manure is not used frequently in practice, but more initiatives are arising. According to the current fertiliser Regulation EU2003/2003, ammonium sulphate is a nitrogen fertiliser solution and recognised 'EC fertiliser' (category C1 n°1) as long as the N-concentration is at least 15%. This threshold is higher than the N-concentrations obtained from the current N-stripping/scrubbing installations using sulphuric acid. In the new EU Regulation for fertilising products (EC2019/1009), lower criteria (1.5 or 3%) are set for 'inorganic liquid compound macronutrient fertiliser, which can be met with state-of-the-art NH_3 (stripping)-scrubbing installations. However, it is not clear if an inclusion of ammonium sulphate from manure in CMC 10 (designated animal by-products for fertiliser production) in the new EU fertiliser Regulation is required. Finally, the Nitrates Directive defines this product as animal manure and not as mineral N fertiliser. Therefore, the product has to fulfil requirements of animal manure and therefore has to compete with animal manure (which has no financial value).

Some relevant references

Digesmart, 2016, 'Report on the analysis, regulations and field performance of the mineral fertilisers produced: https://bit.ly/2CebQQP

Sigurnjak, I., et al., 2019, 'Production and performance of bio-based mineral fertilisers from agricultural waste using ammonia (stripping-)scrubbing technology' Waste Management 89, 265-274: https://bit.ly/2pl7IWs

Sigurnjak, I., Michels, et al. 2016, 'Utilization of derivatives from nutrient recovery processes as alternatives for fossil-based mineral fertilizers in commercial greenhouse production of Lactuca sativa', L. Scientia Horticulturae 198, 267-276: https://bit.ly/2CbhZx5

Vaneeckhaute, C., et al. 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://bit.ly/2Cat2GT

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, Belgium, pp. 74.

5 Ammonium nitrate

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This chapter follows and is analogous to Chapter 2 and is also based on Sigurnjak et al. (2019).

5.1 Description of technology

Ammonium nitrate recovery from manure and other nitrogen (N) rich biomass can be obtained in a similar manner as ammonium sulphate (section 4.1). The only difference is that instead of using sulphuric acid, in this case, nitric acid should be used as a scrubbing agent to capture ammonia (NH_3) from gas phase. The reaction of NH_3 with nitric acid (HNO_3) results in ammonium nitrate. Hereinafter, all presented results on ammonium nitrate are obtained by using ammonium nitrate that was produced via PW3 end-of-pipe pathway. The end-of-pipe pathway involves separation of digestate into liquid and solid fraction and subsequent treatment of liquid fraction in a (stripping)-scrubbing unit. Currently, to our knowledge, this is the only pathway where the use of nitric acid has been recorded in the literature (Digesmart, 2016b; Sigurnjak et al., 2019).

5.2 Characteristics and compostion

5.2.1 Characteristics

Ammonium nitrate is recovered via (stripping)-scrubbing as a liquid product by contact between the stripped NH_3 rich air (from manure and biomass) and nitric acid (Eq. 5.1) that is added to the washing water.

$$NH_4OH + HNO_3 \leftrightarrow NH_4NO_3 + H_2O \qquad \text{(Eq. 5.1)}$$

As an inorganic salt, the produced liquid ammonium nitrate has a dry matter (DM) of almost 50% (Table 5.1). This means that product can also be dried and used in solid form. At the temperature above 200°C ammonium nitrate will decompose.

5.2.2 Composition

Similar as synthetic N fertilisers, ammonium nitrate contains total N entirely in mineral form, as NH_4-N and NO_3-N. Usually higher N concentrations (2x) are measured in ammonium nitrate as compared to ammonium sulphate. Depending on the amount of added acid the pH and electric conductivity (EC) can vary (Table 5.1).

Table 5.1. *Composition of ammonium nitrate (from end-of-pipe pathway = PW3) on fresh weight basis reported in Digesmart (2016a) project and Sigurnjak et al. (2019).*

Parameters	Ammonium nitrate
DM (%)	48
OC (%)	ND
pH	6.92 – 7.85
EC (mS cm-1)	332 - 342
NH4-N (g kg-1)	76 - 109
NO3-N (g kg-1)	56 - 89
Ntotal (g kg-1)	132 - 198

DM: dry matter; OC: organic carbon; EC: electrical conductivity; Effective N: percentage of total N present in mineral form; ND: not determined.

Higher pH values can often be observed when compared to ammonium sulphate, which reduces the risk of machinery corrosion, but also results in higher risk of ammonia volatilisation.

5.2.2.1 Value giving components

Ammonium nitrate contains water and total N completely present in NH_4-N and NO_3-N form (Eq. 5.1). With these main value giving components, ammonium nitrate can be used in agriculture as a fertiliser or in chemical and fertiliser industry as a secondary raw material. The second major use of this product is as an industrial explosive.

N concentration in ammonium nitrate ranges between 13-20% (Table 5.1), which is less than what is found in urea and higher what can be measured in liquid ammonium sulphate. These differences in N concentration play an important factor on the market as they can determine transportation advantage or disadvantage as compared to other marketed products.

5.2.2.2 Contaminants and pathogens

Up to now contaminants and pathogens have not been determined in current studies dealing with ammonium nitrate. In theory, ammonium nitrate should not contain any carbon or contaminants as it is generated from gas/air phase. If some carbon and other contaminants are detected, these concentrations are usually considered to be negligible. Nevertheless as mixing of organic compounds and HNO_3 can cause an explosion, Yara set a quality and safety TOC limit in ammonium nitrate of 100 ppm (Evans, 2007).

5.3 Agronomic effectivity

Up to now, three individual trials on liquid ammonium nitrate from PW3 have been identified. They were conducted within the Digesmart project (2016a) and reported in Sigurnjak et al. (2019) with the main focus to assess the effect of the ammonium nitrate on crop yield (Figure 5.1) and to determine N fertiliser value (Figure 5.2).

5.3.1 Yield, product quality

Current studies reported slightly higher crop yield when ammonium nitrate was applied as a N source in lettuce cultivation (Figure 5.1). In maize cultivation, no significant differences were observed on crop fresh weight yield when ammonium nitrate was used as a N fertiliser compared to the conventional fertilisation regime (=reference) of using synthetic N on top of animal manure.
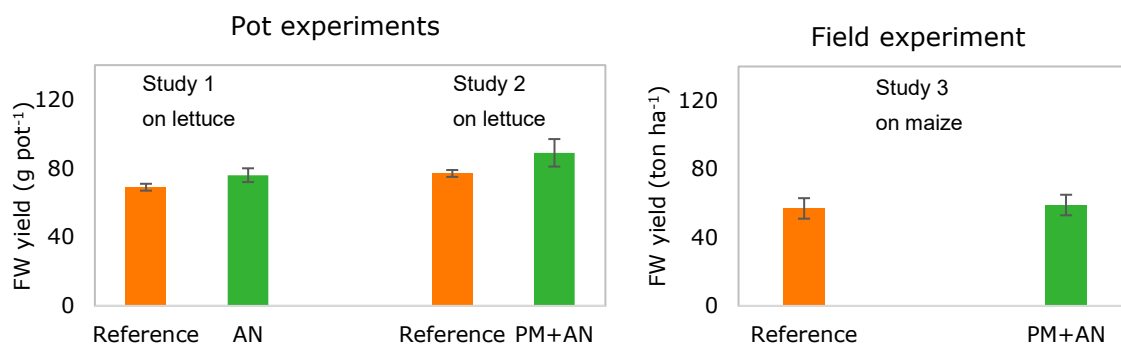
Figure 5.1. *Effect of ammonium nitrate (AN) from end-of-pipe pathway (section 4.1) on fresh weight (FW) yield compared to conventional fertilisation regime in lettuce (Reference = calcium ammonium nitrate (CAN; 27% N) as synthetic N) and maize (Reference = pig manure (PM) + CAN). Study 1, Study 2 and Study 3: Digesmart, 2016a and Sigurnjak et al., 2019.*

5.3.2 NRUE & NRFV

As a consequence of higher lettuce yield in pot experiments, treatments with ammonium nitrate also resulted in higher NRUE/NFRV values (Chapter 2; Eq. 2.1 and Eq. 2.2) as compared to conventional fertilisation regime where synthetic N fertiliser is used as a sole source of N. In maize cultivation, no differences were observed in regard to NRUE/NFRV when ammonium nitrate was used as a N fertiliser compared to the conventional fertilisation regime of using synthetic N on top of animal manure. This means that ammonium nitrate exhibits similar effect on crop yield as synthetic N fertiliser, and as such can be used as a valuable N source.
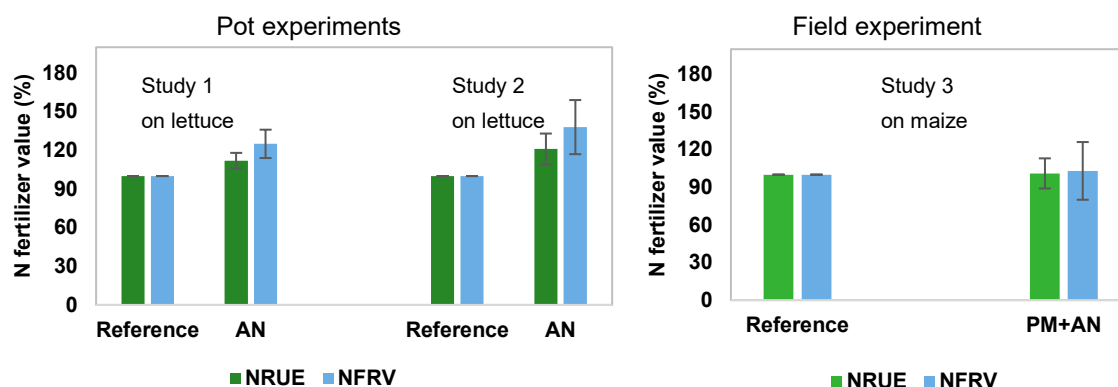
Figure 5.2. *Effect of ammonium nitrate (AN) from end-of-pipe pathway (section 4.1) on nitrogen (N) fertiliser value compared to conventional fertilisation regime in lettuce (Reference = calcium ammonium nitrate (CAN; 27%N) as synthetic N) and maize (Reference = pig manure (PM) + CAN). N replacement use efficiency (NRUE) does not account for the effect of unfertilised treatment, whereas N fertiliser replacement value (NFRV) takes into account the effect of unfertilised treatment. To determine NRUE and NFRV of ammonium nitrate, the reference treatment is considered to be 100% effective. Study 1, Study 2 and Study 3: Digesmart, 2016a and Sigurnjak et al., 2019.*

5.4 Risk assessment

5.4.1 Contaminants

As mentioned in section 5.2.2.2, an ammonium nitrate is generated from gas/air and as such in theory should not contain any carbon or contaminants. Up to now none of the above mentioned studies have included the assessment of contaminants, organic micro-pollutants, pathogens, weed seed and other (plastic, glass…) contaminants. The main focus of these studies was to assess the crop production and N fertiliser value.

5.4.1.1   Heavy metals
In above mentioned studies, heavy metals were determined in soil and plant at harvest time. In all studies there were no differences observed in soil and plant concentration of heavy metals between the reference and treatments with ammonium nitrate. This is expected since all studies took place for 1 year or even less than 3 months (e.g. pot experiments). In order to observe the effect of heavy metal accumulation studies with longer cultivation period are needed.

5.4.1.2   Organic micro-pollutants
See section 5.4.1.

5.4.1.3   Pathogens
See section 5.4.1.

5.4.1.4   Weed seed
See section 5.4.1.

5.4.1.5   Other (plastic, glass…)
See section 5.4.1.

5.4.2 Emission

In above mentioned studies the emission aspect has only been determined in a field trial and in regard to leaching, and not in regard to ammonia volatilisation and greenhouse gas emission. Leaching and other potential pathways of emissions were not determined in pot experiments.

5.4.2.1   Leaching
Environmental aspects have been assessed in the maize field experiment by measuring post-harvest nitrate residue. 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.

Since the nitrate residue is measured on field scale, only results from field experiment with ammonium nitrate are reported (Figure 5.3). In maize trial, no significant differences were observed between the reference treatment and the treatment where ammonium nitrate was used as a N source (Figure 5.3).

Both the reference treatment and PM+AN treatment were below the maximum allowable level of 90 kg NO_3-N ha^{-1} in 0-90 cm soil layer.
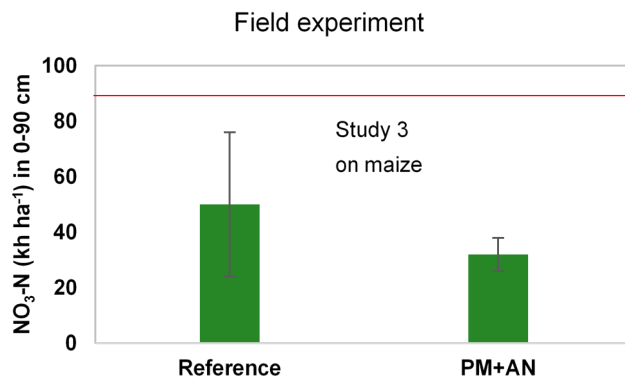
Figure 5.3. *Effect of ammonium nitrate (AN) (applied in combination with pig manure) and conventional fertilisation (Reference = pig manure (PM) + synthetic N) on post-harvest nitrate residue (kg ha^{-1}) in 0-90 cm soil layer. The red line indicates the maximum allowable level of nitrate residue in soil (90 kg NO_3-N ha^{-1}) between October 1 and November 15 according to current Flemish environmental standards for maize cultivation in zone where measured NO_3 concentrations in ground water do not exceed 50 mg NO_3 l^{-1}. Study 3: Digesmart, 2016a and Sigurnjak et al., 2019.*

5.4.2.2 Ammonia volatilisation

The high pH of ammonium nitrate indicates a potential risk of ammonia volatilisation, which in practice is also influenced by weather conditions, method of fertiliser application and pH of soil. In regard to utilisation of ammonium nitrate as a fertiliser there are agricultural practices as incorporation or injection which can reduce significantly potential ammonia volatilisation. In above presented pot and field experiment ammonium nitrate was respectively incorporated or injected which would assume a negligible risk for ammonia volatilisation. The actual ammonia volatilisation has not been measured in the currently presented studies.

5.4.2.3 Emission greenhouse gasses (NOx, CO_2, CH_4)

See section 5.4.2.

5.4.2.4 Safety aspects

Ammonium nitrate is classified as an oxidizing product (ECHA, 2018b) and its use can lead to several risks:

- Promoting the ignition of flammable substances
- Explosion if mixed with combustible substances
- Harmful by ingestion, eye contact and inhalation

As reported by the Belgian Seveso inspection services (2009), at a temperature around 170 °C, ammonium nitrate decomposes, forming HNO_3 and NH_3. At higher temperatures (185 °C) N_2O and NO_x are formed. The production of the latter may be particularly important especially above 280 °C, as they could lead to deflagration and detonation events.

Decomposition of ammonium nitrate can be accelerated by several parameters:

- High temperatures
- Nitrogen concentration
- Presence of catalysts that enhance decomposition reactions. These catalysts include chlorides, zinc, copper, acids, cobalt, manganese, chromium, metal powders, organic materials.
- Other factors influencing ammonium nitrate decomposition are porosity, grain size, pH, contaminants.

Inhalation of toxic flue gases, containing oxides of nitrogen and ammonia, can cause irritation and corrosive effects on the respiratory system (ECHA, 2018b). Accidents can occur due to the mishandle of HNO_3. In 2017, a leak of HNO_3 from a tank occurred at Flemish manure processing company located in Gistel (Belgium). The cause of the accident was the use of an inappropriate tank material for storing HNO_3 which led to the situation where HNO_3 dissolved the tank material and led to a HNO_3 leakage. The accident did not lead to any human or animal injuries. Nonetheless the emergency plan included the evacuation of more than 500 houses nearby (Nieuwsblad, 2017).

5.5 Factsheet

The factsheet is given below and can be found on the website of SYSTEMIC (https://systemicproject.eu/)

Ammonium nitrate solution

Technology description

Ammonium (NH_4^+) and ammonia (NH_3) are both the same basic compound, yet the first constitutes the water soluble form, whereas the second is the volatile gaseous form. Both these forms are in dynamic equilibrium; increasing pH and/or temperature will convert more water soluble ammonium into the gaseous ammonia and visa versa. In manure or digestate treatment systems, this basic chemical principle can be used to extract ammonium nitrogen from manure via a system that is called 'stripping' (which converts it into volatile ammonia via pH and/or temperature increase) followed by 'scrubbing' to re-capture the extracted ammonia back into soluble ammonium through a low pH 'scrubber' solution. If a nitric acid solution is used, ammonium nitrate will be formed. Ammonium nitrate is currently not obtained for NH_3 recovery from animal housing via air washing with nitric acid because this is more expensive than the most commonly used sulphuric acid which produces ammonium sulphate.

Product characteristics

Similarly to synthetic produced mineral N fertilisers, ammonium nitrate contains total N entirely in mineral form, as NH_4-N and NO_3-N. Usually, higher N concentrations (2x) are measured in ammonium nitrate as compared to ammonium sulphate. Depending on the amount of added acid, the pH and electric conductivity (EC) can vary. Higher pH values can often be observed when compared to ammonium sulphate, which reduces the risk of machinery corrosion, but also results in higher risk of ammonia volatilisation.

Photo 1. Ammonium nitrate solution (© VCM)

Parameter	Ammonium nitrate
Dry matter (%)	48
pH	6.92 - 7.85
EC* (mS cm⁻¹)	332 - 342
N total (g kg⁻¹)	132 - 198
NH_4-N (g kg⁻¹)	76 - 109
NO_3-N (g kg⁻¹)	56 – 89
N mineral/N total (%)	100

*EC: electrical conductivity

Table 1. Product characteristics of ammonium nitrate after N–stripping/scrubbing of liquid fraction of digestate from animal origin in ranges based on average values reported in Digesmart (2016a) and Sigurnjak et al, (2019).

Agronomic aspects

Plants (and by extension crops) take up nitrogen in a mineral form. For example, a common synthetic nitrogen fertiliser of which full plant availability is assumed is CAN (Calcium Ammonium Nitrate). In essence, an ammonium nitrate-rich solution will present the same crop availability as CAN. Up to now, results from three individually published agronomical trials with ammonium nitrate have been identified. Their main focus was to assess the effect of the ammonium nitrate on crop yield and to determine its N fertiliser value (Figure 1 below).

Determination of the N fertiliser values (N Replacement Use Efficiency; NRUE and N Fertiliser Replacement Value; NFRV) depends on the presence or the absence of a control (=unfertilised) treatment in an experimental design, and hence can be determined as follows:

$$NRUE\ (\%) = \frac{(crop\ N\ uptake\ AMM.\ NITRATE\ /\ total\ N\ applied\ AMM.\ NITRATE)}{(crop\ N\ uptake\ REFERENCE\ /\ total\ N\ applied\ REFERENCE)} *100$$

$$NFRV\ (\%) = \frac{((crop\ N\ uptake\ AMM.\ NITRATE - crop\ N\ uptake\ CONTROL)\ /\ total\ N\ applied\ AMM.\ NITRATE)}{((crop\ N\ uptake\ REFERENCE - crop\ N\ uptake\ CONTROL)\ /\ total\ N\ applied\ REFERENCE)} * 100$$

The identified studies reported slightly higher crop yields when ammonium nitrate was applied as an N source in lettuce cultivation. In maize cultivation, no significant differences were observed on crop fresh weight yield when ammonium nitrate was used as a N fertiliser compared to the conventional fertilisation regime (=reference).

As a consequence of higher lettuce yield in pot experiments, treatments with ammonium nitrate also resulted in higher NRUE/NFRV values as compared to conventional fertilisation regime where synthetic N fertiliser is used as a sole source of N. In maize cultivation, no differences were observed in regard to NRUE or NFRV when ammonium nitrate was used as a N fertiliser compared to the conventional fertilisation regime of using synthetic N on top of animal manure. This means that ammonium nitrate exhibits a similar effect on crop yield as synthetic N fertiliser, and as such can be used as a valuable N source and used as a replacement for synthetic fertilisers.
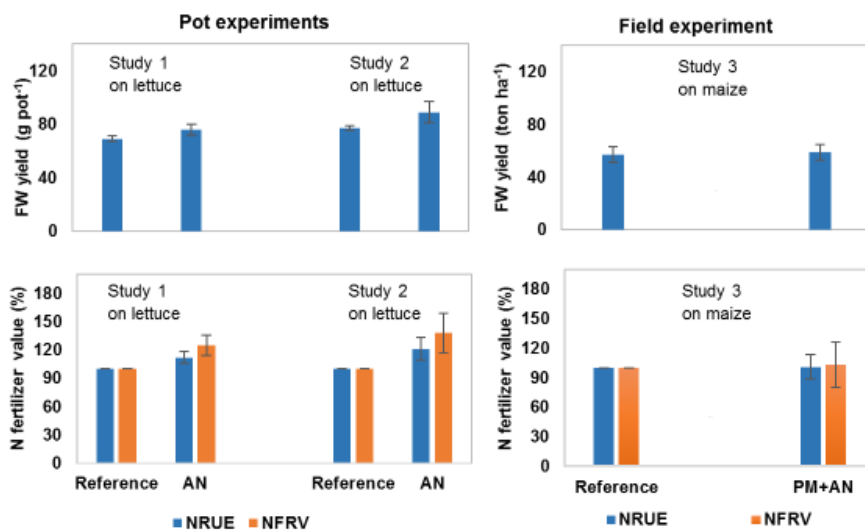
Figure 1. Effect of ammonium nitrate (AN) on fresh weight (FW) yield and its nitrogen (N) fertiliser value compared to conventional fertilisation regime in lettuce (Reference = calcium ammonium nitrate (CAN; 27%N) as synthetic N) and maize (Reference = pig manure (PM) + CAN). N replacement use efficiency (NRUE) does not account for the effect of unfertilised treatment, whereas N fertiliser replacement value (NFRV) takes into account the effect of unfertilised treatment. To determine NRUE and NFRV of ammonium nitrate, the reference treatment is considered to be 100% effective.

Ammonium nitrate

Environmental aspects

Environmental aspects have been assessed in field experiments by measuring post-harvest nitrate residue in soil/water. The measured nitrate residue gives an estimate 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.

Since the nitrate residue is measured on field scale, only results found from field experiment with ammonium nitrate are reported (Figure 2). In maize trials, no significant differences were observed between the reference treatment and the treatment where ammonium nitrate was used as an N source (Figure 2). Both the reference treatment and PM+AN treatment were below the maximum allowable level of 90 kg NO_3-N ha^{-1} in 0-90cm soil.
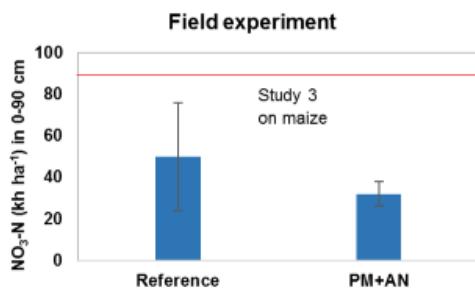
Figure 2. Effect of ammonium nitrate (applied in combination with pig manure) and conventional fertilisation (Reference = pig manure (PM) + synthetic N) on post-harvest nitrate residue (kg ha^{-1}) in 0-90 cm soil layer. The red line indicates the maximum allowable level of nitrate residue in soil (90 kg NO_3-N ha^{-1}) between October 1 and November 15 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}.

Current legal view on ammonium nitrate

By stripping/scrubbing ammonia directly from manure with nitric acid, an end product (ammonium nitrate) is obtained that has a higher N-concentration (13-20%) than the ammonium sulphate produced when using sulphuric acid, since nitric acid also contains nitrogen. According to the current fertiliser Regulation EU2003/2003 ammonium nitrate is recognised as an 'EC fertiliser' (category C1 n°1) if the N-concentration is at least 15%. A concentration of 15% is within the means of current strippers and certainly will fulfil the criteria of the new European regulation on fertilising products (EC 2019/1009) for 'inorganic liquid straight macronutrient fertiliser' (5%). However, it is not clear if an inclusion of ammonium nitrate from manure in CMC 10 (designated animal by-products for fertiliser production) in the new European fertiliser Regulation is required. Finally, the Nitrates Directive defines this product as animal manure and not as mineral N fertiliser. Therefore the product has to fulfil requirements of animal manure and gets into competition with animal manure (which has no financial value).

Main references

Digesmart, 2016, 'Report on the analysis, regulations and field performance of the mineral fertilisers produced: https://bit.ly/2CebQQP

Sigurnjak, I., et al., 2019, 'Production and performance of bio-based mineral fertilisers from agricultural waste using ammonia (stripping-)scrubbing technology' Waste Management 89, 265-274: https://bit.ly/2pl7IWs

6 Mineral concentrates

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Manure can be processed into manure concentrates though a combination of technologies. Foged (2011) distinguishes amongst others microfiltration, ultrafiltration, reverse osmosis, concentration by vacuum evaporation, electro-oxidation, ozoning, ammonium stripping and absorption, struvite (magnesium ammonium phosphate) precipitation and calcium phosphate precipitation as techniques for the production of manure concentrates. This chapter focuses on mineral concentrates derived by means of reverse osmosis from animal manure and co-digested manure.

Mineral concentrates are produced in those regions in Europe with a manure surplus, *i.e.* a higher production of manure than legally can be used on regional agricultural land. Driving forces for the production of mineral concentrates differ. A main driver is to prevent transport of manure with low dry matter contents. To prevent this, liquid manure is separated into a solid and a liquid fraction. Solid fraction is transported to regions with a need for the nutrients and organic matter. The remaining liquid fraction is concentrated by means of different techniques and locally used as a fertilising product. A second driver is to tailor the ratios of nutrients of nitrogen, potassium and sulphur of the fertilising product to the requirements of the crop. Mineral concentrates are usually low in phosphorus but can serve as a nitrogen, potassium and/or sulphur fertilising product. Nitrogen is usually for more than 90% present in mineral form and MC are therefore more attractive as N fertiliser as compared the raw manure.

Application standards for the use of nitrogen and phosphorus in Flanders, Denmark, France, Germany and the Netherlands are a driving force to separate manure into fractions of manure with high (liquid fraction) or low ratios (solid fraction) between nitrogen and phosphorus. Manure processing is obligatory in the Netherlands in the situation of a surplus of manure

This chapter on mineral concentrates of reverse osmosis describes the technology, the characteristics and composition, agronomic performance and deals with risk assessment. Their description documents the factsheet. The majority of the information on mineral concentrates from animal manure is based on studies in the Netherlands in the period 2009-2015. Syntheses of these studies have been published by Velthof (2012, 2012 and 2015). Information on mineral concentrates is mainly based on these synthesis reports and underlying reports.

6.1 Description of technology

6.1.1 General concept

The production of a mineral concentrate starts by separation of liquid manure or digestate into a solid fraction and a liquid fraction. Often, coagulants and/or flocculants are added to improve the separation efficiency (Hoeksma and Buisonjé, 2015). The separation process of the first step of the production process is conducted by use of decanter centrifuge, belt press or auger (Hoeksma and Buisonjé, 2011; Velthof, 2015).

The liquid fraction contains suspended solids which are removed by air flotation (dissolved air unit). The resulting permeate is filtered to remove remaining suspended solids (Figure 6.1). This can be done by micro- or ultrafiltration and prevents membrane fouling in the subsequent reverse osmosis (RO) unit.

The resulting filtrate is concentrated by reverse osmosis (RO), a process that results in a mineral concentrate and an effluent (permeate).

Reverse osmosis is based on the principle that membranes with specific properties selectively let water pass and retain dissolved salts. During this process pressure is building up. The conductivity of the liquid determines the required pressure. As during the concentration step the conductivity increases an increasing pressure is needed (Masse et al., 2010; Hoeksma and Buisonjé, 2015). The pressure[2] (10 – 100 bar) determines both the quality of the mineral concentrate in terms of concentrations of nutrients as well as the quality of the permeate (Hoeksma and Buisonjé, 2015).

For the production of MC, specific semi-permeable membranes are used. During processing these membranes become polluted with precipitated salts which require cleaning. Also, remaining particles in the liquid fraction can cause fouling of the membranes of the RO unit which require also cleaning. Cleaning of these membranes is thus performed on a regular basis (Camilleri-Rumbau et al., 2016). Frequency of cleaning depends of the type of membranes of the RO unit, the efficiency of removing suspended particles, fouling with salts and operational conditions (pressure, temperature, EC etc.). Cleaning results in rinsing liquid which need to be cleaned by use of ion exchangers resulting in a salt solution and clean water. Ion exchangers require regeneration by use of acid and base. Salt solutions from these cleaning processes are recycled in the RO process.
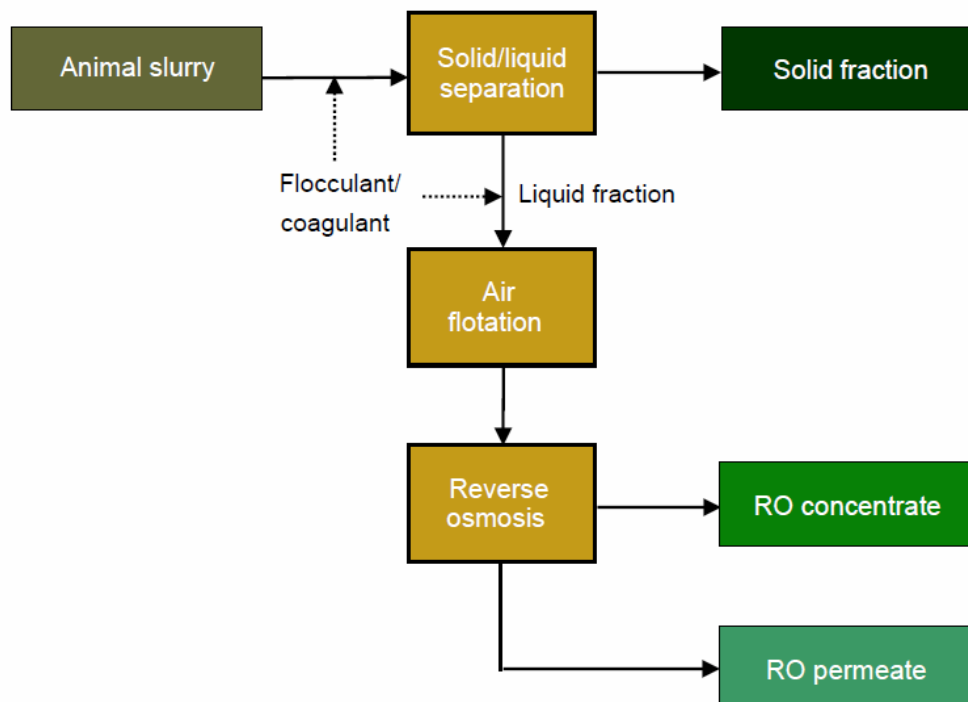
Figure 6.1. *Conceptual presentation of the production process of reverse osmosis (Hoeksma and Buisonjé, 2015).*

Microfiltration, ultrafiltration and nano-filtration are all membrane filtration techniques which require pressure but differ with respect to their cut-off size for particulate matter[4]. Choice for filtration technique, or combination of techniques, leads to differences in performances of the RO unit and compositing of the resulting mineral concentrate. Also process conditions exert an effect. High pressure may shorten the durability (lifespan) of the membranes. Not uncommon is to use modest pressures to increase the lifespan whilst accepting a lower concentration factor.

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[4] Microfiltration: 0.1 -   3 bar, 0.1 - 20 µm;
Ultrafiltration: 2   -   10 bar, 2 nm - 0.1 µm;
Nanofiltration: 5   -   30 bar, 1 nm;
Reverse osmose: 10   - 100 bar, 0.1-1 nm.

Reverse osmosis leads to an increase of nitrogen and potassium concentrations (often a factor 1.5 to 3 compared to the ingoing concentrations of the liquid fraction of manure or digestate. Efforts are under taken to increase these nutrient concentrations. Parallel placed RO-units are used to increase the concentration of nitrogen. Next, other techniques can be used to increase nutrient contents.

Photo 6.1. *An example of the production of mineral concentrate by means of separation with a belt press (upper right) at Van Amstel Loonbedrijf in Lith (NL). Liquid manure (upper left) is mixed with coagulants and flocculants. Flocculated solid fraction is sieved out (upper right and lower left) and stored in a storage bunker (lower right).*

Photo 6.2. *The liquid fraction is stripped from suspended particles by dissolved air flotation (left); stripped liquid undergoes a second cleaning by passing through a paper-filter (right).*

Photo 6.3. *From suspended particles cleaned liquid passes the RO unit (left) which leads to mineral concentrate (middle) and clean water which can be discharged on surface water (right).*

6.2 Characteristics and composition

6.2.1 Characteristics

Mineral concentrates are liquid fertilising products with a brownish – yellowish appearance (photo 6.4). The appearance resemble those of the liquid fraction of the ingoing animal slurry but the differences are found in the composition. Mineral concentrates have a much higher fraction of N being present as mineral N of 90% or more due to removal or organic N in the pre-filtration steps. Total concentrations of N and K are higher due to the RO process. The increase in concentration varies with the conditions of the RO process. In general the increase of the concentration varies between a factor 1.5 and 3 as compared to the ingoing liquid fraction (Velthof, 2015). Higher concentration factors are possible by using other types of membranes and/or higher pressure and/or a combination with other manure processing techniques (forward osmosis, concentration by vacuum evaporation or even eutectic freeze crystallisation (only in test phase)). Being a more concentrated liquid fraction of animal manure, nitrogen, potassium, sulphur and phosphorus as well as a range of secondary and trace elements and organic substances are present which are originating from the liquid fraction. Also bicarbonate can be present.

Photo 6.4. *Mineral concentrates from different plants processing liquid animal manure.*

6.2.2 Composition

6.2.2.1 Value giving components

Value giving components (organic matter and plant nutrients) are given in Table 6.1.

Table 6.1. *Average composition and standard deviation of mineral concentrate from pig slurry in the period 2009 – 2014 of the monitoring program of the pilot mineral concentrate in the Netherlands. Data on bulk parameters and primary nutrient are based on Velthof (2015) citing Hoeksma et al., 2011, Hoeksma and De Buisonjé (2012, 2015), data on secondary and micro nutrients are from Ehlert and Hoeksma (2011).*

Type	Parameter	Unit	Average	Standard deviation	Counts
Bulk parameter	Dry matter	g/kg	33.4	8.11	161
	Organic matter	g.kg	13.3	5.43	162
	pH	[-]	7.94	0.28	162
	EC	mS/cm	56.6	9.23	162
Primary nutrients	Total N	g/kg	7.12	1.67	162
	NH_4-N	g/kg	6.40	1.56	162
	P	g/kg	0.17	0.14	162
	K	g/kg	7.19	1.42	162
	$Ntot/P_2O_5$	[-]	68.8	124	162
	NH_4-N/N-total	[-]	0.90	0.06	162
Secondary nutrients	Mg	g/kg	0.09	0.015	95
	Ca	g/kg	0.23	0.020	95
	S	g/kg	1.07	0.200	95
	SO_4^{2-}	g/kg	2.91	0.694	69
	Na	g/kg	1.77	0.047	97
Micro nutrients	B	mg/kg	2.95	1.51	39
	Co	mg/kg	0.09	0.019	39
	Cu	mg/kg	1.34	2.13	92
	Fe	mg/kg	27.4	72.52	86
	Mn	mg/kg	2.21	0.387	40
	Mo	mg/kg	0.03	0.042	40
	Zn	mg/kg	6.97	45.6	90

The agronomic and economic value of a mineral concentrate is based on its nitrogen content which is mainly ammonical nitrogen (~90% of total nitrogen) and potassium. Next sulphur can be present in quantities which steer the agronomic function of a mineral concentrate as a fertilising product.

6.3 Agronomic effectivity

## 6.3.1 Yield, product quality

Data on crop responses on yield-response curves based on the application mineral concentrates and comparison with reference mineral fertilisers have been published both for pot experiments and field experiments.
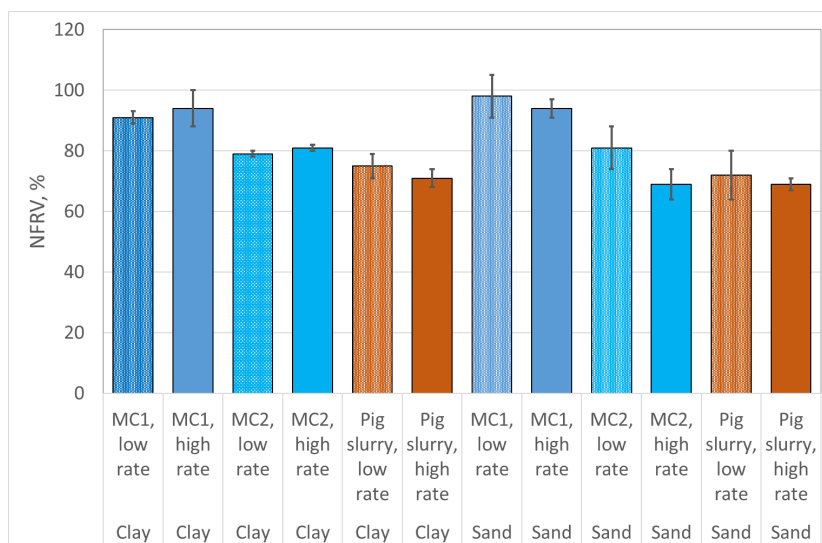
6.3.1.1 Pot experiments

Pot experiments have been carried out by Ehlert et al. (2012), Klop et al. (2012), and Rietra and Velthof (2014).

Klop et al. (2012) reported NFRV for mineral concentrates (MC) based on 26-day greenhouse experiment with rye grass (*Lolium perenne L.*) which were applied by blanket dressing (surface application) or were injected (Figure 6.2). With surface application, NFRV for MCs (62% for MC1 and 37% for MC2) was significantly lower than for reference fertiliser calcium ammonium nitrate (CAN; 100%) and comparable with pig slurry (41%). Klop et al. (2012) attributed this to higher ammonia emissions. After injection, the NFRV of MC was comparable with that of CAN. After injection, MC behaved similarly to inorganic fertilisers (Klop et al., 2012).
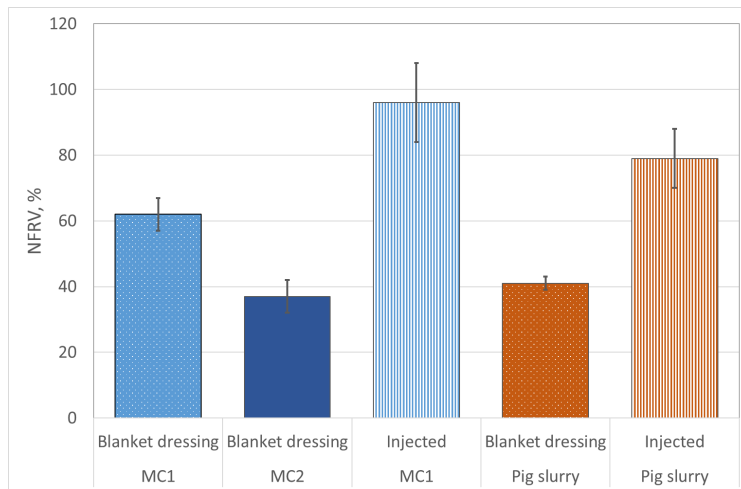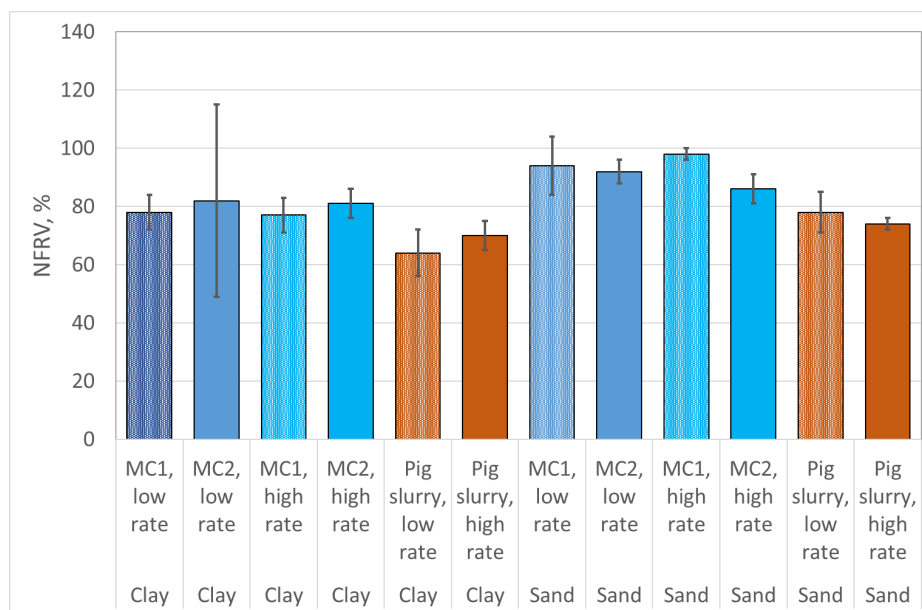
Figure 6.2. *Treatment means and standard errors (n=4) for NFRV for two MC's and pig slurry for two application techniques: blanket dressing (surface application) and injection based on a 26-day pot experiment with rye grass (Lolium perenne L.) with sandy soil (Klop et al., 2012)*

Ehlert et al. (2012) conducted pot experiments with Rye grass (*Lolium perenne L.*) and Swiss Chard (*Beta vulgaris L., var. Groene snijbiet*) with sandy soil and clay soil. A MC from fresh pig slurry with a relatively high content of volatile fatty acids (MC1, 2.3 g volatile fatty acids/kg) was compared with a MC from stored pig slurry with no fatty acids (MC2) and pig slurry at a low application rate (60 kg N/ha) and a high application rate (120 kg N/ha). Four cuts of grass were harvested in a 170-day experiment. Two cuts of Swiss Chard were harvested in a 93-day experiment. Figures 6.3 and 6.4 give NFRV based on total uptake of nitrogen over all cuts. CAN was used as a reference fertiliser.

Figure 6.3. *Treatment means and standard errors (n=4) for NFRV for two MC's and pig slurry for two application rates (low, high) based on a 170-day pot experiment with rye grass (Lolium perenne L.) with clay and sandy soil. Fertilising products were applied with a technique that simulated injection in the field. The low application rate was 60 kg N/ha, the high application rate was 120 kg N/ha. MC1 is produced from fresh pig slurry and contains volatile fatty acids, MC2 is produced from stored and aged pig slurry and contained no fatty acids.*

Figure 6.4. *Treatment means and standard errors (n=4) for NFRV for two MC's and pig slurry for two application rates (low, high) based on a 170-day pot experiment with Swiss Chard (Beta vulgaris L., var. Groene snijbiet) with clay and sandy soil. Fertilising products were applied with a technique that simulated injection in the field. The low application rate was 60 kg N/ha, the high application rate was 120 kg N/ha. MC1 is produced from fresh pig slurry and contains volatile fatty acids, MC2 is produced from stored and aged pig slurry and contained no fatty acids.*

Rye grass differed from Swiss chard in nitrogen uptake. The nitrogen uptake was lower and less efficient than of Rye grass. The soil type exerted an effect. The total uptake of nitrogen on sandy soil is higher than on clay soil (Ehlert et al., 2012). NFRV values were derived by comparing with calcium ammonium nitrate (CAN). NFRV values for MC's were higher than for pig slurries but lower than 100%. MC1 was not significantly different from CAN but MC2 was. MC from fresh pig slurry had in general higher NFRV values than MC of stored (aged) pig slurry. NFRV for Rye grass are similar for both soils, those for Swiss chard are higher for sandy soil when compared to the results for the clay soil. The application rates (60 or 120 kg N/ha) do not exert a major effect. Grass has used nitrogen more efficiently then Swiss chard.

Velthof and Rietra (2019) found an effect of the moisture content of soil on NFRV in a pot experiment with Rye grass (*Lolium perenne L., Barnhem*) if MC were used under conditions that prevented ammonia volatilisation. Blanket dressing of MC was compared with injected MC in a pot experiment with a loamy sand. Also an with sulphuric acidified MC (at pH 5.08) was tested and applied by blanket dressing (Figure 6.5). NFRV was determined by comparison with CAN (WHC 80%).
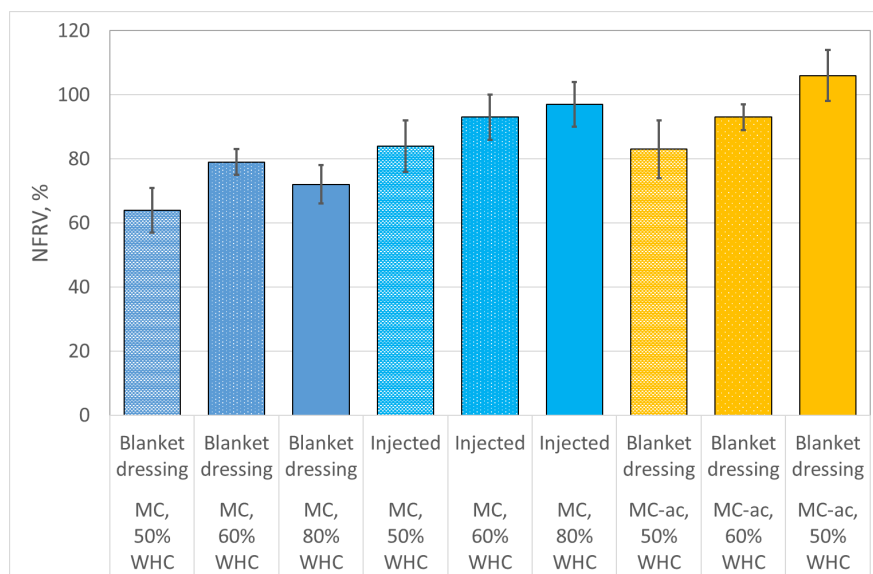
Figure 6.5. *Treatment means and standard errors (n=4) for NFRV for two MC's and an acidified MC (pH 5.08 for three water holding capacities (WHC) based on the total nitrogen uptake of two cuts Rye grass (Lolium perenne L. Barnhem) for a loamy sandy soil.*

Injection of MC or acidification of MC led to an increase in NFRV as compared to non-acidified and surface-applied MC. Surface application of MC led to higher NH_3 emissions as compared to incorporated MC. Acidification of MC followed by surface spreading was also found to increase NFRV values as compared to surface spreading of non-acidified MC due to reduction in NH_3 emissions. Velthof and Rietra (2019) concluded that MC has a similar N fertiliser value as mineral N fertilisers if NH_3 emissions are reduced by either incorporation or acidification (see also § 6.4.2.3).

6.3.1.2 Field experiments
Field experiment were conducted on grassland and arable land.

6.3.1.3 Grassland
Middelkoop and Holshof (2017) conducted seven grassland experiments on sandy and clay soils during a period of 4 years to estimate the nitrogen (N) fertiliser replacement value (NFRV) of MC of pig slurry. Grassland yields fertilised with MC were compared with grassland fertilised with two mineral fertilisers: granulated calcium ammonium nitrate (CAN) and liquid ammonium nitrate (LAN). Treatment application rates included zero N and three nitrogen application rates. Liquid fertilising products were shallow injected (0–5 cm). The NFRV of MCs amounted to 75% on sandy and 58% on clay soil with CAN as reference, and 89% on sandy and 92% on clay soil with LAN as reference (Figures 6.6. and 6.7.). The lower NRFV values found in field trials as compared to pot experiments may be due to higher ammonia volatilisation in field trials.
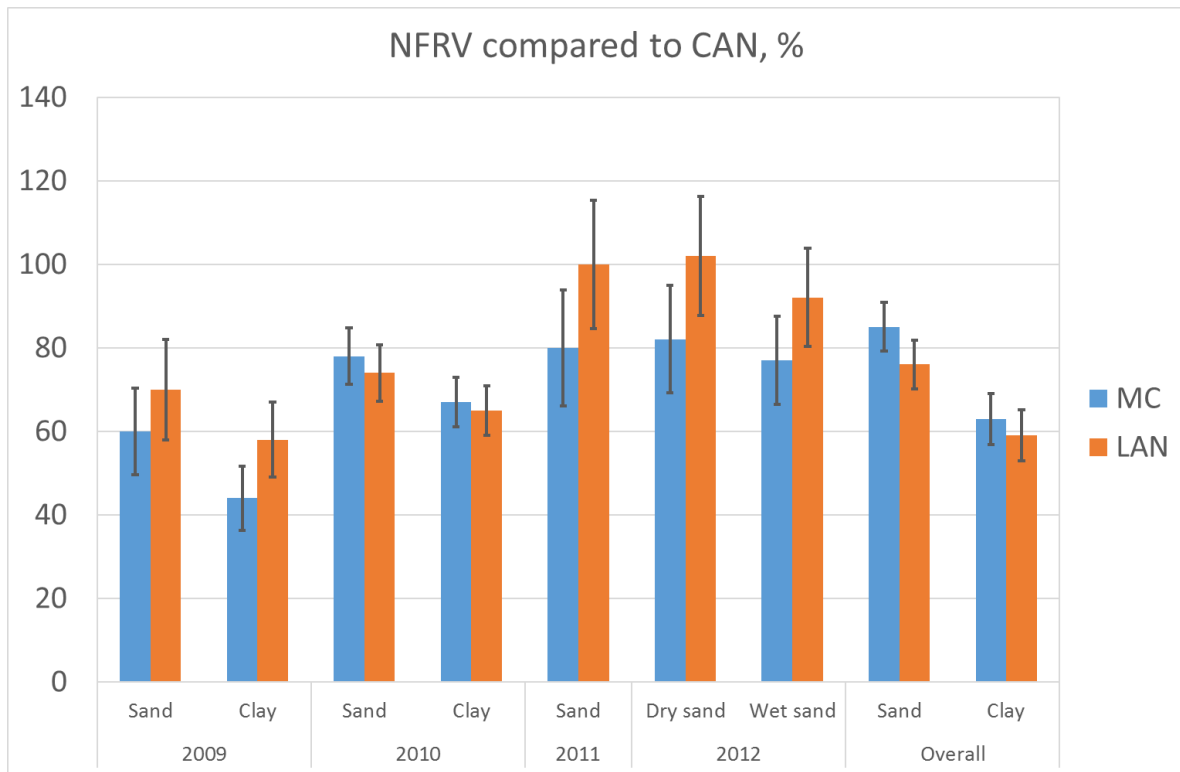
Figure 6.6. *Nitrogen replacement value (NFRV) for mineral concentrate (MC) and liquid ammonium nitrate (LAN) on sandy and clay soil for field trials conducted in the period 2009 to 2012 compared to calcium ammonium nitrate as reference fertiliser (Middelkoop and Holshof, 2017).*
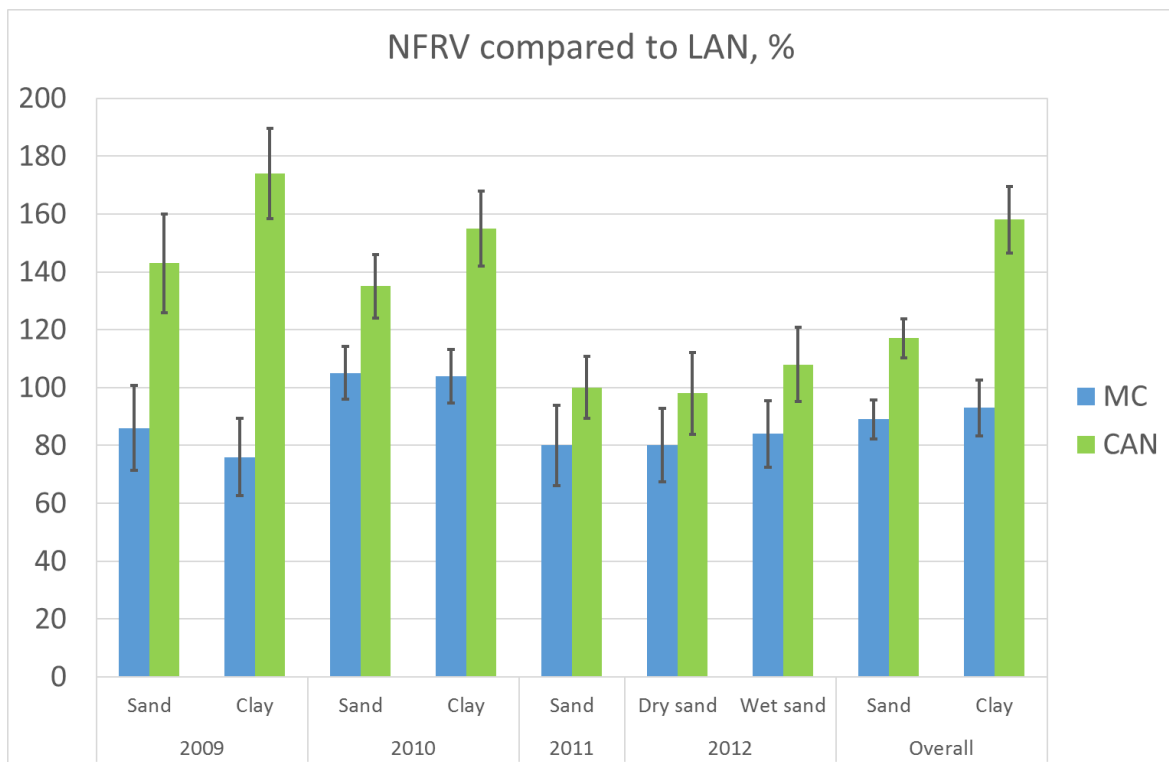
Figure 6.7. *Nitrogen replacement value (NFRV) for mineral concentrate (MC) and calcium ammonium nitrate (CAN) on sandy and clay soil for field trials conducted in the period 2009 to 2012 compared to liquid ammonium nitrate (LAN) as reference fertiliser (Middelkoop and Holshof, 2017).*

6.3.1.4 Arable land

The ability of MCs to substitute calcium ammonium nitrate (CAN) was tested by Schröder et al. (2013a) in two trials on a silty loam soil (ware potatoes, 2009 and 2010) and four trials on sandy soils (starch potatoes, 2009 and 2010; silage maize; 2010 and 2011). The N fertiliser replacement value (NFRV) of spring-injected MCs ranged from 72 to 84% (Table 6.2). This was slightly less than their share of ammonium nitrogen (90-100%, data not given). Schröder et al. (2013a) found NFRVs of MC tended to be negatively related to the ammonium share of MC suggesting that applied ammonium in the form of MC has not been fully available to crops and which was attributed to a possible loss of ammonia due to the high pH of a MC. Schröder et al. (2013a) argued while referring to Chambers and Dampney (2009) that the choice of another synthetic nitrogen fertiliser such as urea, the performance of MCs is as much a function of the arbitrarily chosen mineral fertiliser N reference, as of the characteristics of the MC itself. Chambers and Dampney (2009) reported that around 20 kg ammonia N may be lost per 100 kg total N applied. Schröder et al. (2013a) concluded that injected MCs are an effective substitute for conventional fertilisers in arable crops.

Table 6.2. *Nitrogen replacement value (NFRV) for mineral concentrate (MC) with calcium ammonium nitrate (CAN) as reference nitrogen fertiliser on sandy NFRV for potato and silage maize as related to nitrogen application rate (Schröder et al., 2013a,b). MCs were injected at 5-10 cm depth.*

Crop	Year	Soil	Nitrogen application rate, kg N/ha			Average	Standard deviation
			50	100	150		
Potato	2009	Calcareous silty loam	80	67	81	76	8
Potato	2010	Calcareous silty loam	73	73	78	75	3
Starch potato	2009	Sand	-	89	79	84	7
Starch potato	2010	Sand	75	80	88	81	7
Silage maize	2010	Sand	62	71	82	72	10
Silage maize	2011	Sand	65	109	79	84	22

In an experiment with potato on clay, Van Geel *et al.* (2012a) used a liquid ammonium nitrate fertiliser as reference fertiliser. This fertiliser was injected with the same equipment as the mineral concentrate. The NFRV of mineral concentrate was 117% compared to liquid ammonium nitrate (LAN). The NFRV compared to CAN was 76% in the same experiment. CAN was more efficient than LAN. This shows that the NFRV of mineral concentrate was similar to that of a liquid mineral fertiliser in this experiment (Velthof, 2015).

Velthof (2012) refers to Van Geel who published data on NFVR based on less detailed set-up of field experiments than van Geel *et al.* (2011a). The results of these experiments showed a wide range in NFRV (0 -130%). In 20 experiments the NFRV of mineral concentrate was similar to CAN, in 10 experiments it was lower than CAN and 1 experiment it was higher (Van Geel et al., 2011b, cited by Velthof, 2012).

6.4 Risk assessment

6.4.1 Contaminants

6.4.1.1 Heavy metals

Products from manure processing have been investigated for the heavy metals Cd, Cr, Cu, Ni, Pb, Zn and As (Ehlert and Hoeksma, 2011). Hg was not investigated. In general, it is not anticipated that a mineral concentrate made from manure contains levels of Hg which give cause for concern as the quality of animal feed steers the quality of animal manure (Ehlert and Hoeksma, 2011). The levels of Pb and As for all manure processing products are at or below the detection limit of 0.01 mg/kg. Occasionally a level of 0.03 mg Cd / kg was measured in a pig manure, but generally Cd contents were generally equal to or below the detection limit of 0.01 mg Cd/kg. Levels of Cr, Cu, Ni and Zn were above detection limits. These levels were tested to environmental standards for fertilising products in the Netherlands as set by

the Fertiliser Decree of the Fertiliser Act of the Netherlands. This risk assessment was conducted per RO plant in the Netherlands and per sample of mineral concentrate and solid fractions. In general, the mineral concentrate passes the environmental test. The heavy metals Cd, Cr, Ni, Pb and As do not constitute an environmental risk when used as a fertilising product made from animal manure. Incidentally samples did not pass the environmental test for fertilising products caused by Zn (3 samples of in total 94 samples). A new facultative EU regulation on fertilising products will replace the current EU fertiliser regulation 2003/2003. This new regulation will introduce criterions for heavy metals . Mineral concentrates were tested against these new criterion and will all meet these new criterions except the three samples with higher Zn levels. The new regulation set standards for CrVI. Data on CrVI contents in mineral concentrates are not know. Given the origin of the raw materials and aids, it is however not very likely that mineral concentrates will give a risk due to CrVI.

6.4.1.2 Organic contaminants

A survey was conducted on the presence of organic contaminants in mineral concentrates at four plants (A, B, C and D) (Hoeksma et al., 2011). Per plant two samples of mineral concentrate were analysed on levels of organic micro-pollutants prescribed by the Decree of the Fertilisers Act. Hydrocarbons are calculated as diesel (C10-C24) and a mineral oil (C25- C56). The results of the analyses show that the levels of dioxins, non-ortho PCBs, mono-ortho PCBs, indicator PCBs, PAHs, organochlorine pesticides and mineral oil in mineral concentrates are at or below the detection limit. None of the organic micro-pollutants exceeds the regulatory requirements of the Fertiliser Act of the Netherlands (Velthof, 2012). The survey shows that organic micro-pollutants in mineral concentrates do not poses an environmental risk when applied within the application standards of nitrogen, phosphorus, and manure used in agriculture in the Netherlands (Velthof, 2012).

Currently a monitoring program is being conducted in the Netherlands on new emerging contaminants in mineral concentrates. The report of this monitoring program is foreseen in 2020. This program includes analyses of primary characteristics (dry matter, organic matter, organic carbon, primary nutrients), secondary characteristics (secondary nutrients, NO_3-N, NO_2-N), heavy metals, residues of veterinary medicinal products and bacteria and viruses. In near future polymers in fertilising products which use the CE marking (EU regulation 2019/1009) will have to be fully biodegradable. The biodegradability of these polymers is currently assessed.

6.4.1.3 Pathogens

Hoeksma et al. (2015) conducted a survey on the occurrence of pathogenic microorganisms and a number of possible indicators for pathogens. The survey was based on a limited number of samples which were analysed on the presence of the following bacteria and viruses: Escherichia coli, enterococci, Salmonella, Clostridium difficile, MRSA, ESBL-E. coli, somatic coliphages and Hepatitis E virus. Their survey showed that after mechanical separation the microorganisms are highly concentrated in the solid fraction and that mineral concentrates from reverse osmosis contain slightly lower concentrations of micro-organisms than the liquid manure from which it is produced. Their results indicated that the concentration of microorganisms decreases by anaerobic fermentation. Sanitation by means of composting and by heating results in virtually sterile products. It should be noted that both techniques were only investigated by Hoeksma et al. (2015) in two samples from one installation each. The permeate (effluent) from reverse osmosis is microbiologically almost clean; discharging this product into surface water probably presents no health risks (Hoeksma et al., 2015). Their results show that manure processing by means of reversed osmosis does not reduce the occurrence of indicator micro-organisms. The results of Hoeksma et al. (2015) points that mineral concentrates cannot meet new legal requirement of the new facultative European regulation on fertilising products. This regulation has for indicator micro-organisms the criterion that Salmonella should be absence in 25 g or 25 ml sample and E. coli should not exceed 1 000 numbers of bacteria in 1 g or 1 ml sample. Mineral concentrate cannot meet both criterions without undergoing a sanitation step.

6.4.1.4 Weed and other propagules

Information and/or data on weed seed has not been traced in literature is scientific literature nor in the public domain of the internet. The required thorough cleaning of the liquid by DAF, ultrafiltration,

sometimes followed by an additional cleaning step by means of a filter paper will reduces any risk on the presence of noxious weeds and propagules.

6.4.1.5 Other (plastic, glass…)

Information and/or data on plastic, glass or other materials that needs to be avoided, has not been traced in literature is scientific literature nor in the public domain of the internet. The required thorough cleaning of the liquid by DAF, ultrafiltration, sometimes followed by an additional cleaning step by means of a filter paper will reduces risks on the presence of particles of plastic and glass. In general these particles are not to be expected in fresh animal manure. In digestate plastic or glass cannot be completely ruled out as these material may be present in co-substrates (often wastes) used to enhance biogas-production (so called co-digestion of manure and co-substrates/co-materials).

6.4.2 Emission

6.4.2.1 Leaching

Schils et al. (2014) and Schröder et al. (2013) reported total nitrogen concentrations in upper ground-water on arable land. Schröder et al. (2013) and Middelkoop and Holshof (2017) reported both the quantity of mineral nitrogen present in the soil profile as well as the total nitrogen concentration in the upper groundwater 20 cm below the groundwater level on grassland.

Other experiments on arable land where leaching from MCs has been measured, have not been traced in peer reviewed journals. However an indicator on the risk of nitrate leaching is the quantity of mineral nitrogen present in the soil profile after harvest in autumn (Haberle et al., 2018, Ten Berge et al., 2002, Velthof 2015). Information on this indicator is given in peer reviewed journals and scientific reports. Middelkoop and Holshof (2017), Schröder et al. (2013; 2014), Van Geel et al. (2011a, 2011b) and Schils et al. (2014).

Grassland

Middelkoop and Holshof (2017) measured mineral nitrogen in the soil layers up to 90 cm (0-30, 30-60 and 60-90 cm) below the grass sod in field experiments on sandy and clay soil conducted in the period 2009-2011 within 14 days of the last harvest (Figure 6.8). In 2012 on two locations on sandy soil, one location with a low groundwater table (low GT) and one location with a high groundwater table (high GT) field experiments on grassland with MCs were conducted. Sampling of groundwater took place before the start of the next growing season of 2013 at 20 cm below groundwater surface.

After the growing season, the values of mineral N in de soil layer 0 – 90 cm below surface showed no consistent or systematic effect from the fertiliser type (CAN, LAN or MCs) or the level of the N application rate (Middelkoop & Holshof, 2017). Averaged over all experiments in 2009-2012, the mineral N content (0-90 cm soil layer) at the end of the growing season in soils to which mineral concentrates had been applied was (somewhat) lower than that in soils to which CAN and liquid ammonium nitrate had been applied though this difference was not statistically significant (Holshof and Middelkoop, 2017; Figure 6.8).
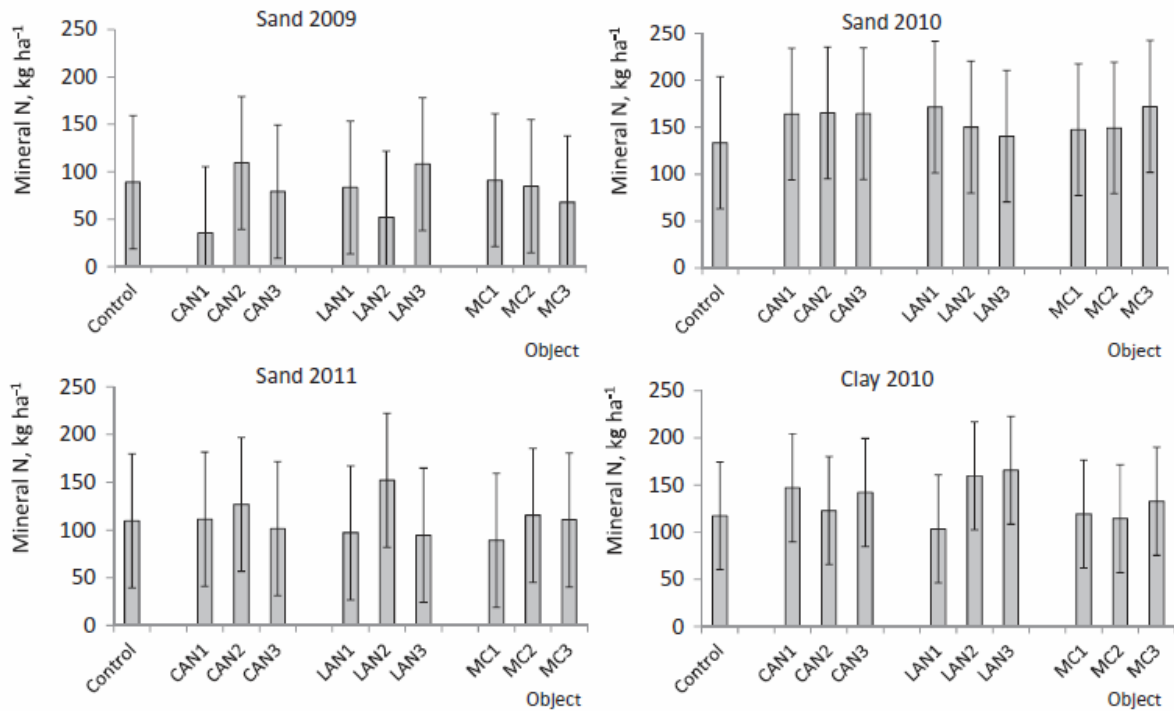
Figure 6.8. *Soil mineral N in the soil layer 0-90 cm of sandy soils in 2009-2011 and clay soil in 2010 on grassland at the end of growing season; No N fertilisation (Control), fertilisation with calcium ammonium nitrate (CAN), liquid ammonium nitrate (LAN) and mineral concentrates (MC) with three levels of N fertilisation (1 to 3). Error bars: least significant difference (P < 0.05). Source: Middelkoop and Holshof (2017).*

Total N in the upper 20 cm groundwater in the experimental fields sampled in spring 2013 showed no effect from N application levels of 2012 or type of fertilising product (Figure 6.9).
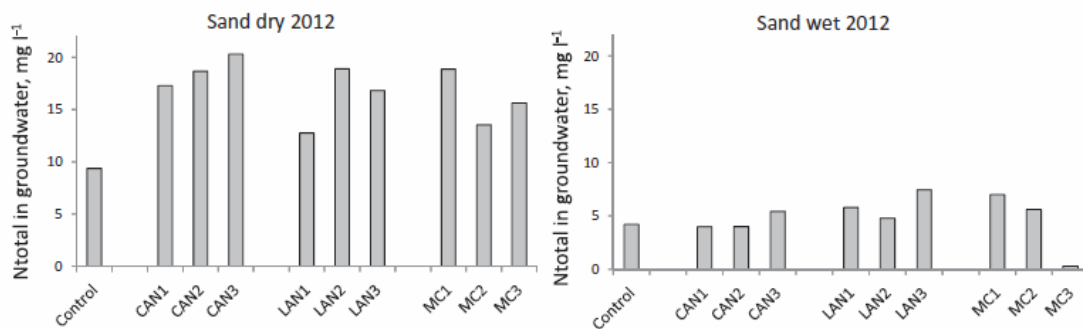
Figure 6.9. *Total nitrogen (N) in upper groundwater 20 cm below groundwater level in dry and wet sandy soil in spring 2013 after experiment in 2012. Dry: average groundwater table 135 cm, wet average groundwater table 79 cm, below surface spring 2013: No N fertilisation (Control), fertilisation with calcium ammonium nitrate (CAN), liquid ammonium nitrate (LAN) and mineral concentrates (MC); and three levels of N fertilisation (1 to 3); MC3 on wet sand: below detection limit. Source: Middelkoop and Holshof, 2017.*

These results indicate that the use of mineral concentrate did not increase the risk of NO$_3$ leaching compared to CAN on grassland.

Schils et al. (2014) measured nitrate concentration in upper groundwater approximately 20 cm below groundwater level in 10 silage maize and 20 grassland fields on farms in field trials which served

comparison of two treatments. In one part of the field mineral fertiliser and cattle slurry were applied and in another part of the field, mineral fertiliser was replaced with mineral concentrate.
The variation in nitrate concentration between the farms was large. The nitrate concentrations were higher in maize land than in grassland (Table 6.3) but were not statistically significant different between treatments on both grassland and silage maize. Replacement of mineral fertiliser with mineral concentrate did not increase nitrate leaching.

Table 6.3. *Average nitrate concentrations (mg/L) in grassland and maize land on sandy soils for plots to which mineral fertiliser (CAN) and slurry were applied and plots to which mineral concentrate and slurry were applied (Schils et al., 2014).*

Culture (crop)	Mineral fertiliser and cattle slurry	Mineral concentrate and cattle slurry	Average
Grassland	48a	45a	46a
Silage maize	142b	169b	155b
Average	95a	107a	101

a,b: difference in letters show statistical significant difference (5%) using REML analysis

Arable land

Schröder et al. (2013) measured both mineral nitrogen after harvest in the soil layer 0-60 cm and nitrate concentrations in upper groundwater (~ 0-20 cm) after the winter period (Table 6.4) after the harvest of silage maize in field experiments with different fertilising products (N source), application rates of nitrogen (N rate) with and without (preceding) winter cover crops (rye, fallow). On average, application of nitrogen increased in 2010 and 2011 the amounts of postharvest residual soil mineral nitrogen (>75% of it consisting of NO_3-N) by respectively 17 and 8 kg N/ha for each 100 kg mineral fertiliser equivalents per ha applied. For CAS and MC this increase, at the highest application rate, was significant in 2010 but not in 2011 (Table 6.4). Nitrate-N concentrations in the upper groundwater responded positively and significantly to the N applied in 2010 regardless of the N source but not for CAS or MC in 2011 (Table 6.4). Schröder et al. (2013) found that regardless of the presence of a cover crop, nitrate concentration responded positively to the applied rate of effective N (total N x NFRV) but less to post-harvest residual soil mineral N. Rye cover crop establishment after the harvest of silage maize reduced nitrate concentration of the upper groundwater by on average, 7.5 mg nitrate-N/L in the first year and 10.9 mg/L in de second year relative to a bare soil. They did not found an effect that the use of effective nitrogen from MC increases the risk on leaching compared to CAS.

Table 6.4. *Residual soil mineral N after harvest (60 cm soil layer, kg N/ha) and nitrate concentration (mg NO_3-N/L) of the upper groundwater as related to the , N source, N rate and (preceding) winter cover crop as related to the year (Schröder et al., 2013).*

Parameter	Date	Product	Winter cover crop and N-rate, kg N/ha								LSD (p<0.05)
			Rye				Fallow				
			0	50	100	150	0	50	100	150	
Residual soil mineral N	22 September 2010	CAN	*	*	*	*	10	18	40	75	14
		MC	*	*	*	*	12	12	13	31	
	21 September 2011	CAN	67	60	63	59	*	*	*	*	37
		MC	54	62	70	49	38	*	*	49	
Nitrate concentration	28 March-13 April 2010	CAN	8.1	7.3	11.5	22.6	13.2	*	*	35.2	4.2
		MC	6.5	6.1	6.2	13.6	14.9	*	*	17.6	
	12 March-3 April 2011	CAN	4.1	4.0	4.4	4.6	14.8	*	*	16.4	3.7
		MC	5.4	3.0	2.1	2.4	13.8	*	*	11.4	

Schröder et al. (2014) and Van Geel et al. (2011a, 2011b reported residual soil mineral N after the harvest of ware potato grown on calcareous silty loam and starch potato on sand. The amounts of residual soil mineral nitrogen at harvest differed strongly across the years. Based on observed rates soil mineral N associated to MCs were not different from the values observed in the treatments with CAN

except for the trials on calcareous silty loam in 2009 were higher quantities were found but not in 2010 or for the experiments with starch potato on sand (2009 and 2010).

Schils et al. (2014) reported nitrate concentrations at the harvest of silage maize (Table 5.3) and found no differences between treatments with CAS and MC's.

These results indicate that the risk on nitrate leaching for MCs is similar to the risk introduced by the use of the mineral nitrogen fertilising product CAS.

6.4.2.2 Ammonia volatilisation

The mineral nitrogen of a MC is ammonium nitrogen (NH_4-N); nitrate nitrogen has not been found. The ration of NH_4/N to total N is 6.40/7.12 = 90% (Table 6.1). MCs have a relatively high pH of 7.94 (Table 6.1). The combination of a high ammonium content and an alkaline pH increases risk of NH_3 emissions (Velthof 2011, 2012 and 2015). The risk of NH_3 emission can be decreased by injection or incorporation into the soil as shown by Velthof and Hummelink (2011).

Velthof and Hummelink (2011) conducted a series of incubation studies where NH_3 emissions from untreated pig slurry, mineral concentrate, mineral fertilisers and the solid fraction from separated slurry have been quantified. Also N_2O emission was measured (see 6.4.2.3). The fertilising products were surface applied (blanket dressing) or injected. These laboratory studies give an impression of the differences in gaseous emissions from fertilisers, but provide no quantitative estimate of emissions that occur under field conditions (Velthof and Hummelink, 2011; Velthof, 2015).

Surface application of mineral concentrate, pig slurry, and urea resulted in high NH_3 emission (Figure 6.10). Incorporation into the soil strongly reduced NH_3 emission. Averaged over the three incubation tests the NH_3 emission from incorporated mineral concentrate was significantly ($P<0.05$) lower than that of incorporated pig slurry (Velthof and Hummelink, 2011). Velthof and Hummelink (2011) contribute this to the lower dry matter contents of mineral concentrates compared to pig slurry, by which mineral concentrate rapidly filtrates in the soil. The NH_3 emission from mineral concentrate incorporated in the soil was low and similar to that of surface applied CAN.
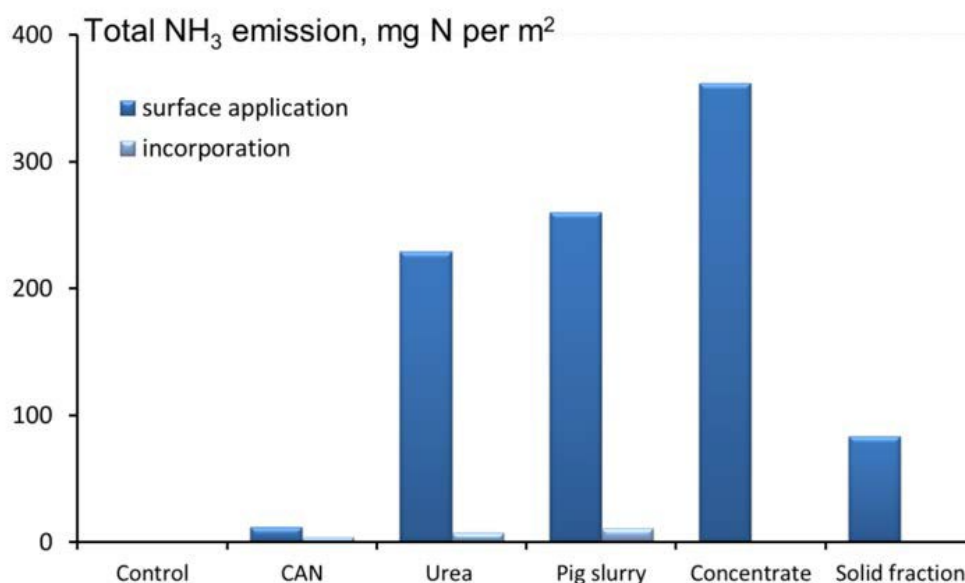
Figure 6.10. *Average NH_3 emission in a laboratory study with arable soil. Calcium ammonium nitrate (CAN), urea, pig slurry, mineral concentrate, and solid fraction of pig slurry were surface-applied or incorporated at the same total N application rate (170 kg N/ha). Fluxes of NH_3 were determined during incubation of 1 month, using a photo-acoustic gas monitor (Velthof and Hummelink, 2011; Velthof 2015).*

NH_3 emission takes place in the first hours after application in the field (Huijsmans and Hol (2011). Field experiments of Huijsmans and Hol (2011) in 2010 showed that the NH_3 emission after sod injection of concentrate to cereals was 3% of the applied NH_4-N in the mineral concentrate and 12% when applied via a trailing hose dosing machine. The NH_3 emission from mineral concentrate applied with sod injection to grassland averaged 8% of the applied NH_4-N. The emission of a MC was lowered by 65% compared to cattle slurry (Huijsmans and Hol, 2011).

With a proper application technique NH_3 emission from mineral concentrate can be reduced strongly (Huijsmans and Hol, 2011; Velthof 2011, 2012 and 2015).

### 6.4.2.3 Emission greenhouse gasses (NO_x, CO_2, CH_4)

Mineral concentrates are not fully inorganic fertilising products. Mineral concentrates contain organic matter (Table 6.1). Part of the organic matter can consist of volatile fatty acids (Hoeksma and De Buisonjé, 2012; Ehlert et al., 2012). Volatile fatty acids are organic compound which are easily biodegraded by micro-organisms. When such biodegradable C is applied to a soil that contains nitrate and soil conditions are wet, denitrifying bacteria (denitrifiers) may use the C as energy source and the nitrate (NO_3-N) can be transformed into gaseous N_2O and N_2 (Velthof, 2015).

Paul and Beauchcamp (1989) showed that volatile fatty acids are effective energy sources for denitrifiers.

Ehlert et al. (2012) determined the potential denitrification rate of an untreated soil and a soil amended with glucose, CAN and three mineral concentrates. The potential denitrification was measured under anoxic conditions, at a temperature of 20° C and in the presence of excess of nitrate. All mineral concentrates increased potential denitrification, showing that the C in mineral concentrate is available for denitrifying bacteria.

The presence of C in mineral concentrate and its effect on denitrification may also affect N_2O emission. Moreover, application of mineral concentrate may result in a high NH_3 concentration in the soil. This may result in NH_3 toxification of nitrifier bacteria which in turn may increase N_2O emission. These effects are likely to be similar as those found in urine patches (Oenema et al., 1997, cited by Velthof, 2015).

In incubation tests of Velthof and Hummelink (2011), N_2O emission was measured after application of mineral concentrate and other fertilising products (manures and inorganic nitrogen fertilisers). The incorporation of mineral concentrate and pig slurry resulted in higher N_2O emissions than surface application (Figure 6.11). The average N_2O emission of incorporated mineral concentrate was higher than the N_2O emission from a similar N rate of surface-applied CAN (Velthof and Hummelink, 2011; Velthof, 2015). The N_2O emission from mineral concentrate was approximately 1.5-fold higher than from untreated pig slurry, averaged over all tests and application techniques (Velthof and Hummelink, 2011; Velthof, 2015). Velthof (2015) cannot give a clear explanation can be given for the relatively high N_2O emission after application of mineral concentrate. Differences in N_2O emission are contributed by Velthof (2015) to the form (species) and content of nitrogen, pH, presence of organic matter and other factors that influence the microbial processes of nitrification and denitrification.
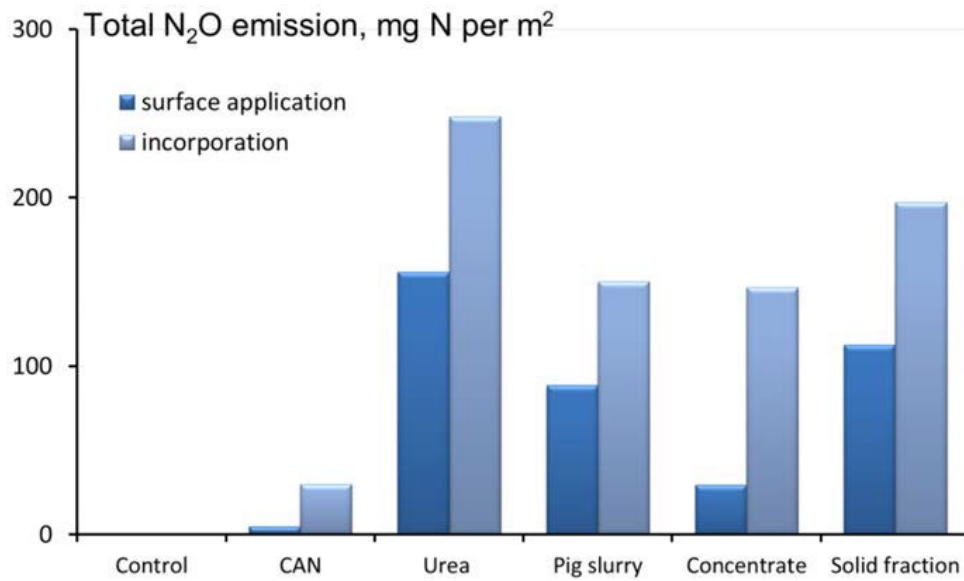
Figure 6.11. *Average N$_2$O emission in a laboratory study with arable soil. Calcium ammonium nitrate (CAN), urea, pig slurry, mineral concentrate, and solid fraction of pig slurry were surface-applied or incorporated at the same total N application rate (170 kg N/ha). Fluxes of N$_2$O were determined during incubation of 1 month, using a photo-acoustic gas monitor (Velthof and Hummelink, 2011; Velthof 2015).*

6.5 Factsheet

The factsheet is given below and can be found on the website of SYSTEMIC (https://systemicproject.eu/).

Mineral concentrate

Technology description

Mineral concentrates come from the processing of manure or digestate (Figure 1). The first step of the process is a solid-liquid separation by means of a decanter centrifuge, auger press or belt press. This leads to a solid fraction and a liquid fraction. The liquid fraction is processed further to remove particles. DAF (Dissolved Air Flotation units), ultr-filtration, nano-filtrations and paper filters are technologies used to remove particles. Coagulation and flocculation processes can be stimulated by use of flocculants. The cleaned effluent enters a Reverse Osmose (RO) unit (Photo 1). Water is pushed under pressure through semi-permeable membranes, leading to a concentrate of minerals and a permeate (cleaned water). Fouling of the membranes by salts and micro-organisms requires regular cleaning and maintenance. The permeate can require an additional treatment by means of an ion exchange resin before discharging to surface water or the soil becomes possible. Initially, mineral concentrates were obtained by a single Reversed Osmosis treatment step. In recent years, multiple (repeated) concentration steps are more often used.

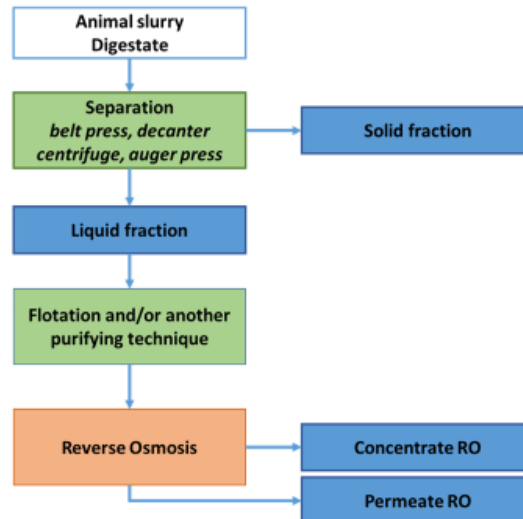*Photo 1. A Reverse Osmosis (RO) installation.*

Figure 1. Example of a scheme for treatment of animal slurry or digestate using Reverse Osmosis.

Product characteristics

Mineral concentrates (Photo 2) predominantly consist of ammonium-nitrogen and potassium. Surveillance across ten pilot plants in the Netherlands showed that on average 90% of the total nitrogen of the mineral concentrates is NH_4-N.

Photo 2. Mineral concentrates from different reverse osmosis installations.

Mineral concentrate

These values corresponded with a single RO concentration step (Table 1 below). The ingoing liquid fraction contains some organic matter which is present in mineral concentrates (1.3% organic matter or 0.6% C_{org}). Compared to pig slurry the ratio between NH_4-N to Total N increased from 66% to 90%. Currently, studies are undertaken to increase the concentration by repeated cycles of RO.

Parameter	Mineral concentrate	Pig slurry	Liquid fraction pig slurry	Solid fraction pig slurry
Dry matter, g/kg	33.4	72.1	17.1	269.3
Organic matter, g/kg	13.3	51.1	7.8	203.5
Total N, g/kg	7.1	6.3	3.6	11.8
NH_4-N, g/kg	6.4	4.1	3.0	5.2
NH_4-N/Total N	0.9	0.7	0.8	0.4
P, g/kg	0.2	1.6	0.1	6.8
K, g/kg	7.2	4.1	3.4	3.6
Ca	0.2	1.9	0.2	8.7
Mg	0.1	1.0	0.1	5.0
S	1.1	0.7	0.6	2.9
Na	0.2	0.9	0.8	0.7
pH	7.9	7.7	8.0	8.2

Table 1. Average chemical composition of mineral concentrates, fattening pig slurry, liquid and solid fraction of fattening pig slurry (Velthof, 2015, Ehlert & Hoeksma, 2011)

Agronomic aspects

Agronomic effectivity of mineral concentrates has been tested under controlled conditions in pot experiments and in field experiments on arable land and grassland. Potassium is equally effective as mineral potassium fertilisers. The nitrogen fertiliser replacement values (NFRV) are given in Table 2 below.

Experiment	Range
Pot experiment grass	86 - 96[a]
Pot experiment Swiss chard	87[a]
Field experiment arable land, potato	75 - 84[a]
Field experiment arable land, silage maize	72 - 84[a]
Field experiment grassland	54 - 81[a]
	79 -102[b]

Table 2. Nitrogen fertiliser replacement values[1] of placed or injected mineral concentrates (MC) compared with chemical reference fertilisers calcium ammonium nitrate (a) or liquid ammonium nitrate (b) in percent (%) compiled from several publications.

[1] Nitrogen Fertiliser Replacement Value (NFRV, %):

$$NFRV = \frac{((\text{crop N uptake}_{mc} - \text{crop N uptake}_{control})/\text{total N applied}_{MC}) *100}{((\text{crop N uptake}_{reference} - \text{crop N uptake}_{control})/\text{total N applied}_{reference}}$$

The fertiliser value of the reference chemical fertiliser is set at 100% although this does not mean that chemical fertilisers are 100% effective. To prevent ammonia volatilisation, mineral concentrates require shallow placement or need to be injected into the soil.

The lower values of NFRV, shown in Table 2, coincide with the earliest experiences with mineral concentrates. The higher values are based on more recent data. This points on a learning process of the production method and successful efforts to increase mineral nitrogen contents. NRFV depends on the used chemical fertiliser as reference. Under controlled conditions (pot experiments) mineral concentrates are only slightly lower compared to calcium ammonium nitrate (NFRV is approaching a full replacement value of 100%). In the field trials however, NFRV values were more variable presumably due to atmospheric losses. More research is needed on the effect of the application techniques on N uptake efficiency.

Environmental aspects

The environmental performance of mineral concentrates was tested by looking at their effect on nitrate accumulation in soil, nitrate accumulation in groundwater, ammonia volatilisation and emission of greenhouse gasses.

There is no evidence that mineral concentrates increase nitrate concentration in groundwater. In fact, relatively low nitrate values are measured in groundwater under fields fertilised with mineral concentrates compared with fields receiving Calcium Ammonium Nitrate (CAN) or manure (Figure 2). Similar results were found in another four-year field trial where no significant differences in nitrate concentrations in soil of fields treated width mineral concentrates, manure or CAN were found (Figure 3).
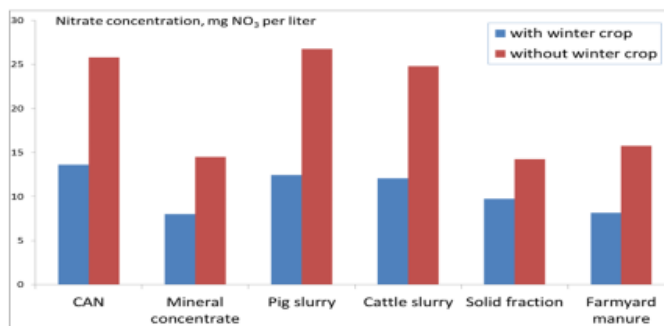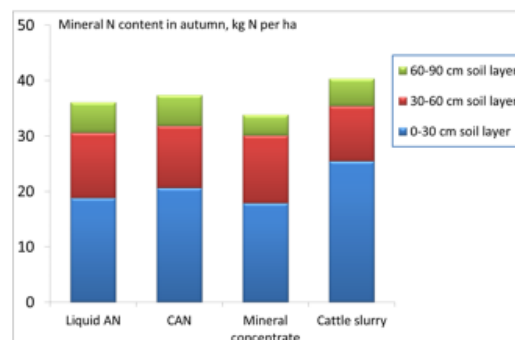

Figure 2. Average nitrate concentration (mg NO_3-N/L) in upper groundwater in a field experiment with silage maize for different fertilising products with and without a winter crop (Schröder et al, 2012)

Figure 3. Average mineral N contents (0-90 cm soil layer) at the end of the season, grassland field experiments in the period 2009 (Holshof and Middelkoop, 2017).

3

Incorporation into the soil prevents ammonia volatilisation but enhances emission of the greenhouse gas N_2O due to de-nitrification (Figure 4). The level of N_2O emissions are between the levels of CAN (low) and urea (high).
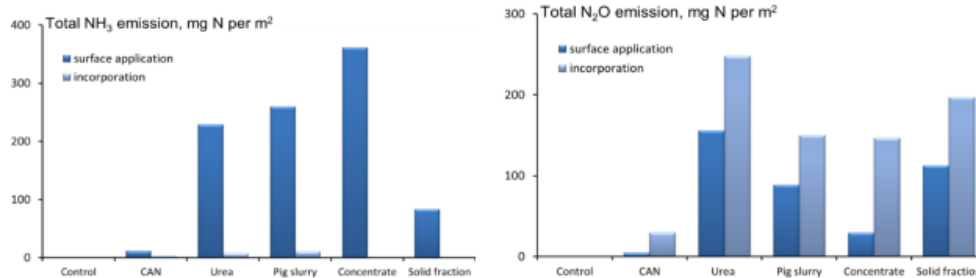

Figure 4. Average NH_3 (left) and N_2O (right) emission in a laboratory study with arable soil from calcium ammonium nitrate (CAN), urea, pig slurry, mineral concentrate (concentrate) and solid fraction. Fertilising products were surface applied or incorporated into the soil. Fluxes of NH_3 and N_2O were determined during incubation of one month, using a photo-acoustic gas monitor (Velthof and Hummelink, 2011).

Current legal view on ammonium sulfate

Mineral concentrates showed under controlled conditions (e.g. pot experiment) a nearly similar agronomic effectivity as CAN but its effectivity is somewhat lower under field conditions. There is no evidence that mineral concentrates lead to a higher risk of accumulation of nitrate in soil or groundwater. Nonetheless, under field conditions attention has to be paid to the method of application. To prevent ammonia volatilisation, mineral concentrates need to be incorporated into the soil. N2O emission caused by mineral concentrates are higher compared to CAN but lower when compared with the chemical fertiliser urea.

Overall agronomic and environmental performances of mineral concentrates is in line with chemical nitrogen fertilisers. Overall, N use efficiency of MC is only slightly lower than of CAN and similar to that of LAN under the condition that MC has been injected or acidified to reduce ammonia volatilisation. The technique of placement of a mineral concentrate requires fine tuning.

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7 Condensated Ammonia Water

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7.1 Description of technology

Evaporation is a technique that is used frequently in food industry and is used on liquid streams. Yet, it is also possible to evaporate (liquid fraction of) digestate. Evaporation (or ammonia stripping) is based on water and ammonia vapour pressures. By bringing the liquid fraction of digestate to its boiling point, a large part of the water will evaporate and volatile components (like ammonia) transfer to the gas phase.

Generally, it is suggested that the pH is raised to about 11 and the feed temperature is 70 ° C in order to reach maximum ammonia removal efficiency. In practice, it has been found that elevating the pH of the input stream, leads to considerable operating costs, which reduces the interest in system deployment despite its potential efficiency. However, for most biogas plants, residual heat is usually available from the CHP and is often present in excess. Also the biogas process already has a pH-increasing effect itself. From the viewpoint of operating costs, it is therefore more reasonable to raise the temperature instead of pH, i.e. raise the temperature to at least 80° C and strip without adjusting the pH. In theory, the recovery rate of ammoniacal N could be 60 to 75% at this temperature.

Figure 7.1: *Falling film evaporator (© France Evaporation)*

To heat up the input stream for evaporation, steam is usually used (cfr. Heat exchanger).
The steam is produced with water and heat preferably recovered from the CHP or the condensed steam.
The amount of heat supplied is proportional to the concentration factor of the digestate (Mykkänen and Paavola 2016).

When cooling down, the water vapour condensates dissolving the volatile components (f.e. NH_3) in it, creating a condensate.

Meanwhile, solids, non-volatile components, salts, fats, etc. do not evaporate and are concentrated in the 'concentrate' (Gruwez 2012). Ammonia on the other, will volatize and is concentrated in the condensate. The result is condensated ammonia water (VCM 2018). Evaporation thus results in an ammonia depleted concentrate and ammonia rich condensated water.

Another options is to keep the ammonia in the concentrate by adding acid to the digestate. This way the NH_3 does not volatize and stays soluble as ammonium in the liquid that gets concentrated. This approach will cause only the water (and some volatile components) to evaporate and create a more concentrated digestate which still includes the ammonia.

Different configurations of the evaporator determine the amount of heat that can be re-used from the evaporation (Gruwez 2012).There are different types of evaporators possible, but for evaporation of (liquid fraction of) digestate mostly long vertical tube evaporators with falling film or forced circulation evaporators with external heat exchangers are used because they have proven to be more suitable for viscous and heat-sensitive liquids (Vondra, Máša, and Bobák 2017).

7.2 Characteristics and composition

7.2.1 Legal framework

Aqua ammonia (condensed ammonia water) is in principle a regular fertiliser. Biobased fertilising products based on capturing ammonia in water (or in an acid) however might not meet regulatory requirements for these regulatory liquid fertilisers. In EU a minimum 15% N (C.1.1. Annex 1 of 2003/2003) for liquid N fertilisers is required, otherwise national legal requirements are in force. For example, in Flanders (BE) 80%N (or with an exemption from VITO)(FOD and FAVV 2013). In Flanders only liquid NH_3 is regulated or ammonium sulphate solution (2%N). Thus, EU regulation rules aqua ammonia in Flanders. In the Netherlands the national legislation requires 5%N in dry matter. It is not clear yet if condensated ammonia water made from ammonia of animal manure is designated within the scope of the Nitrates Directive as animal manure.

If fatty acids are present, than the % of organic carbon (from fatty acids) should be determined to conclude if the ammonia solution falls under the criteria of an inorganic fertiliser (European Commission 2018).

In the KiertoTyp project (RAKI program, Finland, 2016), ammonia water was recovered by evaporation and condensation of the liquid fraction of digestate from waste water treatment sludge. At the end of the project, the Finnish Food Safety Authority Evira went through the analysis results of the ammonium water produced by the experimental plant, stating that it is possible to market ammonium water as a product of the type-name list of national fertiliser products as type 1A1. According to Evira's statement, the product could be used as an inorganic, general bio-derived fertiliser. The minimum amount of nitrogen required for this was 3%. The product of type designation 1A1 is also obtained by raising the nitrogen content to the required level by mixing a small amount of other nitrogen nutrient, for example urea, into ammonium water, if necessary. Ammonium water as an inorganic fertiliser product type 1A1 has no restrictions on the use anymore, in contrast to sewage sludge, which does (Mykkänen and Paavola 2016).

7.2.2 Characteristics

Ammonia water($NH_3 \cdot H_2O$) is a water-like liquid that can be classified as "Aqua ammonia", which is anhydrous ammonia dissolved in water. It is a low-pressure solution in which the ammonium ion in solution exists in equilibrium with unionized (free) ammonia, which can volatize.

NH_3 (gas)=NH_3 (aq) + H_2O = NH_4+(aq) + OH^-(aq)   (eq. 7.1)
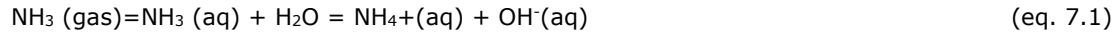
This equilibrium depends on pH and temperature[5].

Ammonia solutions decrease in density as the concentration of dissolved ammonia decreases. This happens when air temperatures increase and it is therefore best stored in closed low-pressure tanks that are kept cool (University of Nebraska Cooperative Extension 1999). Aqua ammonia is corrosive to copper, copper alloys, aluminium alloys and galvanized surfaces and is also an excellent acid neutralizer (Tanner Industries Inc. 1998)
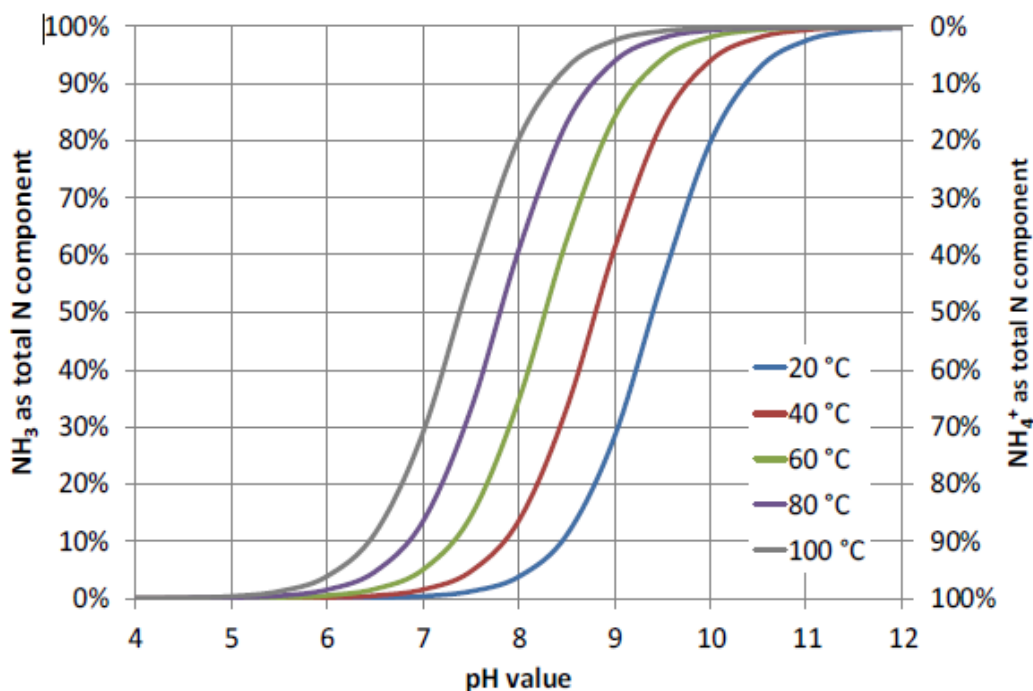
Figure 7.2: *Equilibrium of NH_3 and NH_4^+ in water at different pH and different temperatures*

7.2.3 Composition

7.2.3.1 Value giving components

Ammonia water from evaporation of digestate contains water, dissolved ammonium and - depending on the efficiency of the anaerobic digestion- could contain some traces of other dissolved volatile components like fatty acids, bicarbonate and H_2S (e.g. less volatile fatty acids with stable digestion process; Gerardi 2003).

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[5]The base ionization constant is Kb = $1.8 \times 10-5$ and within the temperature range of 0°C-50°C and a pH range of 6.0 to 10.0, the relation with temperature is pKa = 0.0901821 + 2729.92/Tk
where Tk is temperature in degrees Kelvin, Tk = °C + 273.2.

Condensated ammonia water from the steam stripping process can be used directly as a fertiliser or as secondary raw product for fertiliser production or for the reduction of NOx of flue gas to molecular nitrogen in the Denox process (SNCR)(Mykkänen and Paavola 2016; Tanner Industries Inc. 1998).

Condensed ammonia water from evaporation of digestate usually contains 10-15% ammonia which can be concentrated up to 20% by an extra distillation step. Table 7.1 shows some indicative values of analyses done on ammonia water with and without acidification.

Table 7.1. Analyses on the ammonia water from evaporation of (liquid fraction of) digestate

Parameter	Ammonia water after evaporation[1]	Ammonia water after evaporation and RO[2]	Ammonia water after evaporation[4]	Ammonia water after evaporation and acidification[5]	Ammonia water after evaporation[6]	Ammonia water after evaporation[7]
pH		10.3	9.88	6.8	10	9.5
EC (μS/cm)		120000	11090	92		
Density (kg/L)	1	1				
Dry matter (%)	0.08	0.03				
Organic matter (%)		0.25				
BOD5 (mg/L)				<9		
COD (mg/L)			447	32		
TKN (g N/L)	80	84.5	4750			
Ammonium (g NH_4-N/L)		69		12	120000	28000
Ammonium nitrogen (% of total nitrogen)	90	82				
Nitrite (mg NO_2/L)				0.02		
Nitrate (mg NO_3/L)		2.3		<1		
Phosphorus (mg P_2O_5/L)	<5	<5		<0.04		
S (mg/L)		112		14		
AOX (mg/L)				<0.05		
Mineral oil ΣC10-C20 (mg/L)		130.0[3]				
Mineral oil ΣC20-C40 (mg/L)		<20.0[3]				
Mineral oil ΣC10-C40 (mg/L)		130.0[3]				
Petrogenic concentration C20-C40 (mg/kg DS)		<5[3]				

1 Average from 15 samples of Biogas Plant 1, one of the biogas plants involved in the SYSTEMIC project, evaporation liquid fraction of digestate

2 Average from 6 samples Biogas Plant 1 one of the biogas plants involved in the SYSTEMIC project, evaporation liquid fraction of digestate

3 1 sample Biogas Plant 1 one of the biogas plants involved in the SYSTEMIC project, evaporation liquid fraction of digestate

4 Average from 1 sample Biogas Plant 2, one of the biogas plants involved in the SYSTEMIC project, evaporation test with 1500 ml liquid fraction of digestate

5 Average from 1 sample Biogas Plant with evaporation technology with acidification (Wessling), evaporation liquid fraction of digestate

6 Average from 2 samples from pilot test of evaporator on liquid fraction of digestate after a belt press an DAF

7 Mykkänen, E., & Paavola, T. (2016). Jätevesitypen talteenotto ja hyödyntäminen kierrätysravinteena KiertoTyppi -hanke Loppuraportti, (Miestentie 1), 1–11.

7.3 Agronomic effectivity

In the USA, aqua ammonia, is a popular liquid N fertiliser. It can be injected, but this does not need to be as deeply as NH_3-gas, (which can and is still used as fertiliser in the USA). It is also frequently added to irrigation water and used in flooded soil conditions (International Plant Nutrition Institute 2015).

Use of ammonia water in agriculture in the USA enables sharply reducing labour costs compared to other fertilising products due to full mechanization of the process of transportation, storage and application of fertilisers (Eurochem 2018). It has also advantages over anhydrous ammonia: placement need not be as deep, and high-pressure applicators are not required (Vitosh 1996).

7.3.1 Yield, product quality

Results of field trials with artificial fertilisers and digestate supplemented with ammonia water recovered from digestate by evaporation showed no significant difference in maize yield between artificial fertiliser and digestate derivative application (Inagro 2015; Ojong 2015).

7.3.2 Fieldtrials with condensated ammonia water

In field trials performed in 1996-1997 by Goos and Johnson, aqua ammonia was injected into the soil on 30 cm centres at a depth of 10 cm at 84kg N/ha on 3th October 1996. 15 May 1997, the plots were planted to spring wheat with 60kg/ha monoammonium phosphate (starter fertiliser). Based on residual NH_4, nitrification was at least half complete by late October.

Quantification of the leaf colour at the 6-7 leaf stage of the wheat and at maturity, showed that the plants sowed at the aqua ammonia fertilised soils gave greener plants than the control (no N added), and the apparent N uptake efficiency into the grain and straw was increased with 24% (Goos and Johnson 1999).

A 3 year (2004-2006) field experiment was conducted on a clay soil near Québec City, where different Nitrogen fertilisers -Aqueous ammonia, urea ammonium nitrate (UAN), calcium ammonium nitrate (CAN)- were banded 5 cm below the soil surface between corn rows (Zea mays L.;100, 150, and 200 kg N/ha) at the six-leaf stage every year. After application, the furrows were covered immediately with soil and lightly compacted to avoid NH_3 volatilisation.
The measured grain N, was not significantly (P = 0.05) different between the fertiliser sources. Aqua ammonia responded to N application as for the other fertiliser sources although the maximum yield, as estimated by the linear-plus-plateau model, was slightly lower numerically (Gagnon and Ziadi 2010).

7.4 Risk assessment

7.4.1 Contaminants

7.4.1.1 Heavy metals
Analyses on different samples of ammonia water from (liquid fraction of) digestate show that heavy metal levels are low, due to the fact that these components will not evaporator with the water and therefore stay in the concentrate.

Table 7.2. Analyses on heavy metals in samples of the ammonia water from evaporation of (liquid fraction of) digestate.

	Ammonia water after evaporation [1]	Ammonia water after evaporation and RO [2]	Ammonia water after evaporation and acidification [4]
Hg (mg/L)		<0.010[3]	<0.0002
As (mg/L)		<0.10[3]	<0.005
Pb (mg/L)		<0.50[3]	<0.005
Cd (mg/L)		<0.025[3]	<0.0005
Cr (mg/L)		<0.25[3]	<0.005
Cu (mg/L)	<1	<0.3[3]	<0.003
Ni (mg/L)		<0.13[3]	<0.005
Zn (mg/L)	<5	0.0[3]	<0.01
Sn (mg/L)			<0.005

[1] Average from 15 samples of Biogas Plant 1, one of the biogas plants involved in the SYSTEMIC project, evaporation liquid fraction of digestate

[2] Average from 6 samples Biogas Plant 1 one of the biogas plants involved in the SYSTEMIC project, evaporation liquid fraction of digestate

[3] 1 sample Biogas Plant 1 one of the biogas plants involved in the SYSTEMIC project, evaporation liquid fraction of digestate

[4] Average from 1 sample Biogas Plant with evaporation technology with acidification (Wessling), evaporation liquid fraction of digestate

7.4.1.2 Organic micro-pollutants

In the KiertoTyp project (RAKI program, 2016), liquid fraction of digestate from waste water sludge was treated by evaporation to remove a part of the ammonia. An ammonia water condensate with 2,8% (or 28kg/m³) NH_3-N was produced and analysed on a selection of organic pollutants (PAHs, PBDEs, PFOSs / PFASs) and drugs (ibuprofen, ketoprofen, diclofenac, carbamazepine, ciprofloxacin). Based on the analyses, only PAH's were found in the ammonia water. PAHs are, of course, easily evaporated, and are likely to end up in an evaporation condensate. However, the PAH concentrations found in the ammonia water were very low (29 µg /L or 0.029 mg /L) and in relation to the nitrogen content that determines the yield per hectare, clearly lower than the input of the evaporator (ammonia water 0.2 µg / g N vs. liquid fraction digestate 0.6 µg /gN)(Mykkänen and Paavola 2016).

The analyses results of one sample of one of the biogas plants involved in SYSTEMIC (sample date 28-08-2018),confirm similar amounts of PAH's in the ammonia water (Table 7.3[1]).

Table 7.3. *Analysis on micro-pollutants in ammonia water after evaporation of digestate*

Polyaromatic hydrocarbons	Concentration in ammonia water after evaporation and RO [1]	Ammonia water after evaporation [2]
Naphthalene (µg/L)	<10.0	6.5
Benzo(a)pyrene (µg/L)	<10.0	
Phenantrene (µg/L)	<40.0	7.8
Fluoranthene (µg/L)	<40.0	1.5
Benzo(a)anthracene (µg/L)	<10.00	
Chrysene (µg/L)	<10.0	<0.30
Benzo(b)fluoranthene (µg/L)	<40.0	
Benzo(k)fluoranthene (µg/L)	<20.0	<0.30
Benzo(g,h,i)perylene (µg/L)	<20.0	<0.30
Ideno (1,2,3-c,d)pyene (µg/L)	<20.0	<0.30
Acenaphtylene (µg/L)	<40.0	<0.30
Acenaphtalene (µg/L)	<40.0	4.2
Fluorene (µg/L)	<40.0	5.4
Antracene (µg/L)	<20.0	2.2
Pyrene (µg/L)	<10.0	1.4
Dibenz(a,h)antracene (µg/L)	<20.0	<0.30

[1] one sample of the ammonia water from evaporation and reversed osmosis of (liquid fraction of) digestate of Biogas Plant 1, one of the plants involved in the SYSTEMIC project

2 Mykkänen, E., & Paavola, T. (2016). Jätevesitypen talteenotto ja hyödyntäminen kierrätysravinteena KiertoTyppi -hanke Loppuraportti, (Miestentie 1), 1–11.

7.4.1.3 Pathogens
Different studies determined of the amount and different species of pathogens done in digestate after AD (Bagge 2009; Bonetta et al. 2011; Neuhaus, Shehata, and Krüger 2014) And it can be concluded that the AD process itself reduces indicator-organisms and a few pathogens. If hygienisation (1h 70°C) is applied on the input streams, this will cause a further reduction of pathogens and indicators. Spore forming bacteria, like clostridium and bacillus are not reduced by hygienisation and AD.

Yet the risk on introduction of Clostridium botulinum in a digester is estimated to be very low, if only feedstocks are used of the list of allowed substances (Heezen et al. 2015).

Evaporation requires another heating step (80°C) and if subsequent distillation (100°C) is applied to further concentrate the ammonia water, this will (depending on the time) also further reduce indicator-organisms and pathogens.

Analysis of one sample of one of the biogas plants involved in SYSTEMIC (sample date 28-08-2018), confirm this by showing the absence of E. Coli and Salmonella in the ammonia water produced from liquid fraction of digestate (Table 7.4).

Table 7.4. *Analysis on pathogens in one sample of the ammonia water from evaporation and reversed osmosis of (liquid fraction of) digestate of Biogas Plant 1, one of the plants involved in the SYSTEMIC project.*

Pathogens	Amount in ammonia water after evaporation and RO
E.Coli – partial sample 1 (CFU/g)	<1
E.Coli – partial sample 2 (CFU/g)	<1
E.Coli – partial sample 3 (CFU/g)	<1
E.Coli – partial sample 4 (CFU/g)	<1
E.Coli – partial sample 5 (CFU/g)	<1
Salmonella – partial sample 1 (/25g)	absent
Salmonella – partial sample 2 (/25g)	absent
Salmonella – partial sample 3 (/25g)	absent
Salmonella – partial sample 4 (/25g)	absent
Salmonella – partial sample 5 (/25g)	absent

7.4.1.4 Weed seed

7.4.1.5 Other (plastic, glass...)

7.4.2 Emission

As mentioned in 7.2.2, volatilisation and subsequent removal of ammonia from a solution is temperature and pH dependent. In theory, at neutral pH range and typical water temperatures (10-30°C), most ammonia is in ionized form (NH_4^+). Therefore, volatilisation should have a negligible impact on ammonia removal under these conditions.

Ammonia water, made by dissolving anhydrous ammonia in water, has been used as a fertiliser in the past by adding it to irrigation water (Humbert and Ayres 1957).

In the '80s, it became clear that, when this ammonia water (20-24,6%) was used as a nitrogen fertiliser, it must be injected under the soil surface to avoid loss of ammonia (gaseous) nitrogen to the air. It is not suitable for surface application at any time and application should not be made until soil temperatures at the 10 cm depth have dropped to at least 10°C (Mengel 1986).

However, the volatilisation behaviour of ammonia water in the soil is impacted by more parameters than pH, temperature and concentration. Humbert and Ayres mention also the percentage ammonia saturation of the surface soil layers, the permeability of the surface soil.

Laboratory studies of aqua ammonia applied directly to the surface of acid soils showed losses up to 15%. In alkaline soils where application rates exceed the ammonia saturation capacity of the soil, volatilisation losses can exceed 50% even when placed at depths of 4 inches. However, field trials done in the 50's show very low volatilisation losses from injection (Humbert and Ayres 1957).

However, during field trials with ammonia water from digestate in the framework of the MIP Nutricycle project (2015), ammonia smell was noticeable during injection and the lower leaves and growing plants were severely burned from the volatilisation losses. This was a realistic scenario, since the pH (recovered) ammonia water used in these field trials was high (e.g. ± 10), which gives even at normal ambient temperatures (f.e. 15°C) 75% of the total ammonium in the solution to be present as ammonia gas (NH_3).

Since the focus of the field trials was on agronomical value of "green fertilisers" this observation of noticeable volatilisation was not included in reports or publications.

In general, based on the use and experiences of aqueous ammonia as a fertiliser in the past, surface application is not suitable at any time due to potential ammonia volatilisation.

Soil application of ammonia water at low concentrations (1-3%) is best done by injection. To prevent ammonia losses to the air, the pH of the ammonia water can be brought to neutral pH or it can be mixed with manure or compost, which needs to be directly worked into the soil (Mykkänen and Paavola 2016).

7.4.3 Leaching

Ammonium present in ammonia water will, when injected in the soil, attach to clay and organic matter particles, thus preventing it from leaching away. During the growing season, soil microorganisms convert the ammonium to nitrate (nitrification), which is the main form taken up by plants. The soil conditions that promote nitrification include: a soil pH of 7, moisture at 50% of the soil's water-holding capacity, and a soil temperature of 25°C. Under the following conditions, nitrification will not occur, and ammonium is susceptible for leaching: a pH below 5.5,a waterlogged moisture condition, and temperature under 5°C, i.e. during wet autumns and winters (Mengel 1986).

In the 50's, laboratory and field studies show, that at the high concentrations of ammonia obtained by injection, nitrification is retarded. This minimizes loss by leaching and results in effective utilization of the applied nitrogen (Humbert and Ayres 1957).

Field trials in 2015 also showed that the treatment with "green fertilisers" did not influence the residual nitrate levels of 80 kg/ha for sandy-loam and a reduction in nitrates loss to the environment was observed (Inagro 2015).

The 3 year (2004-2006) field experiment by Gagnon and Ziadi mentioned earlier, showed that throughout the season, soil NO_3-N content was often higher with CAN and UAN than with aqueous ammonia. This result can be attributed to the high supply of NO_3 from CAN and UAN and also to reduced nitrification with the aqueous ammonia treatment.

Lower precipitation following N application, especially in 2005, favoured nitrate retention in the applied band (Gagnon and Ziadi 2010).

Banding compared with broadcast applications can slow down the nitrification rate of fertiliser N, thereby reducing the nitrate accumulation in the soil (Power, Wiese, and Flowerday 2000). Furthermore, packing soil above the fertiliser band reduces water flow through the fertiliser band and further reduces NO_3-N movement (Ressler et al. 1997).

This concludes that leaching of NO_3^- can be minimized when the ammonia water is applied by injection and incorporation, especially when a dryer period follows after application of the fertiliser.

7.4.3.1   Emission greenhouse gasses (NO_x, CO_2, CH_4)
Waterhouse et al. performed field trials on corn in 2012 with application of different fertilisers by sidedress injection, among which aqueous ammonia. N_2O emissions were calculated (Waterhouse et al. 2017).

The fertiliser with the highest concentration of NH_4^+ as part of the formulation produced the greatest N_2O emissions, with the aqueous ammonia treatment having 42% higher cumulative N_2O emissions than the UAN treatment and 300% higher emissions than the calcium nitrate-fertilized plots. Several factors may have contributed to this.

Several observations in this study indicated that nitrification pathways contributed to N_2O production in the ammoniacal fertiliser treatments.
- the N_2O emissions decreased significantly with decreasing proportion of ammoniacal N

- When nitrification inhibitor and urease was added with application of the fertiliser, this significantly lowered the N_2O emissions.
- the highest emissions were observed within 3 weeks of the fertiliser application, coinciding with the period in which NH_4^+ was nitrifying to NO_3^-.

Although nitrification-coupled denitrification may have occurred in the ammoniacal fertiliser treatment, this pathway is unlikely to have produced greater N_2O emissions than denitrification (Waterhouse et al. 2017).

The fertiliser formulation may also have affected the location where most of the N_2O was formed and hereby influenced the emission rates. Fe when N_2O is produced deeper in the soil (by deeper penetration of NO_3^-, in case of UAN or CAN), it had a greater opportunity to be converted to N_2 (Wolff et al. 2017).

7.5 Factsheet

The factsheet is given below and can be found on the website of SYSTEMIC (https://systemicproject.eu/)

Condensated ammonium water

Technology description

Evaporation technology can be used to remove water or other liquids from liquid-based mixtures. The process of evaporation is already for quite some time used in the food industry to concentrate fruit juice and sugar and to produce milk, whey powder and condensed milk. Recently, the technique is more frequently used on wastewater and even manure of digestate of anaerobic digestion.

In the concentration process, heat is added at a certain temperature and pressure, which vaporises most of the water from a solution and concentrates the nutrients, salts, solids and other non-volatile components.

Increasing pH and/or temperature pushes the equilibrium from water-soluble ammonium (NH_4^+) towards gaseous ammonia (NH_3) and this will volatise during the evaporation process. The water vapour containing volatile components is recovered through condensation as ammonia solution.

To prevent volatilisation of ammonia in temperature ranges from 20°C to 100°C, the pH of the input stream of the evaporator can be adjusted to <5,5.

To use the heat of the evaporator as efficiently as possible, multiple configurations are possible. Vacuum evaporation makes use of lowering the pressure and hereby lowering the boiling point of water, whereas less heat is required. Multiple effect evaporation re-uses the heat of the first evaporator in the following evaporating steps which each have lower pressures, and therefore require less energy to heat up.

*Photo 1.* Falling film evaporator (France Evaporation ©)

For evaporation of digestate, two types of evaporators are used frequently: falling film evaporation or forced circulation evaporation.

In practice, it has been found that elevating the pH of the digestate, leads to considerable operating costs, which reduces the interest in system deployment, despite its potential efficiency. From this point of view, it will be more reasonable for most biogas plants that have an excess of residual heat from the CHP to raise the temperature to at least 80°C and strip at the existing pH. In theory, the recovery rate of ammoniacal N could be 60 to 75% at this temperature.

Product characteristics

Since ammonium solution is obtained after evaporation and condensation of water and volatile components, it is free of suspended particles, metals and pathogens. Also phosphorus, potassium and other minerals are not volatised.

In theory, it is a solution of anhydrous ammonia dissolved in water. This is a low-pressure solution in which the ammonium ion in solution exists in equilibrium with unionised (free) ammonia, which can volatise.

$$NH_3 \text{ (gas)} = NH_3 \text{ (aq)} + H_2O = NH_4^+(aq) + OH^-(aq) = NH_4OH(aq)$$
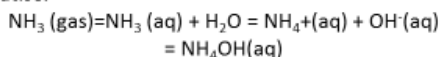
This equilibrium depends on pH and temperature. From digestate, an ammonium solution of 10-15% ammonium can be obtained.

Table 1. Indicative product characteristics of ammonia solution after evaporation of liquid fraction of digestate

Parameter	Ammonium solution
pH	9-10,5
EC (mS/cm)	11-120
Dry matter (%)	0,02-0,1
Ammonium total (NH4+ and NH3) (g N kg^{-1})	28-200
N mineral/N total (%)	82-90
P_2O_5 (g kg^{-1})	<0-0,5
K_2O (g kg^{-1})	<0-0,06
Sulphur (g kg^{-1})	2
Sulphates (g SO_3 kg^{-1})	4,93

*EC: electrical conductivity

Through an additional distillation step, a concentration of 20% ammonium can be reached. By acidifying the ammonium water, the chemical equilibrium is pushed towards ammonium and this stays in solution.

Agronomic aspects

In the USA, aqua ammonia (synthetic), is a popular liquid N fertiliser. It can be injected, but this does not need to be as deeply as NH_3 gas, (which is still used as fertiliser in the USA). It is also frequently added to irrigation water and used in flooded soil conditions.

In field trials performed in England in 1996-1997, injection of aqua ammonia showed that wheat plants gave greener plants than in the control fertilisation, and the apparent N uptake efficiency into the grain and straw was increased with 24%. A study in the USA (2010-2012) confirmed the positive influence on measured N uptake in maize. Additionally, they measured increased biomass with anhydrous ammonia application.

A three-year field experiment (2004-2006) was conducted on a clay soil near Québec City, comparing the fertilising value of Aqueous ammonia, urea ammonium nitrate (UAN) and calcium ammonium nitrate (CAN) on corn (Zea mays L.), no significant difference in grain N content was measured.

Results of field trials in Flanders (Belgium) in 2014 comparing artificial fertilisers and digestate supplemented with ammonia water recovered from digestate showed no significant difference in corn yield.

Environmental aspects

Emissions to the air

In general, based on the widespread use and experiences of aqueous ammonia (pH>10) as a fertiliser in the past and present, surface application is not suitable at any time due to potential ammonia volatilisation at concentrations >10% ammonium at ambient temperatures.
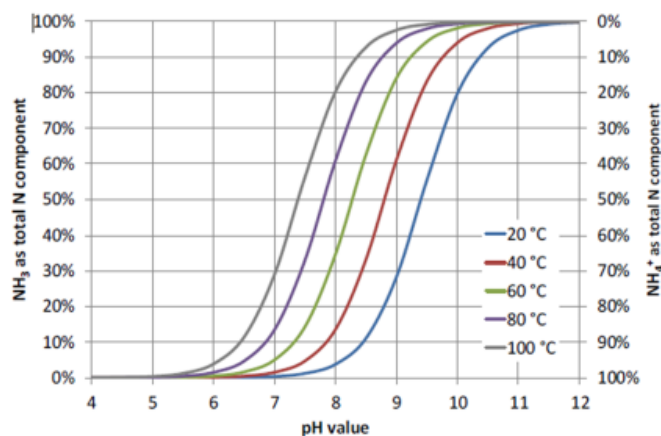

Figure 1. Equilibrium of NH_3 and NH_4^+ in water at different pH and different temperatures

Therefore, reducing the pH to neutral, using solutions with a low ammonium concentration (1-3%) or a mix of ammonium solution with manure or compost can prevent ammonia losses to the air.

However, the volatilisation behaviour of ammonium water in the soil is also influenced by the ammonia saturation and the permeability of the surface soil layers, climate, application and management practices, making it difficult to estimate ammonia emissions, let alone to quantify and monitor them.

When N_2O emissions were calculated, the concentration of NH_4^+ as part of the formulation seemed to produce the greatest N_2O emissions. Several observations in this study indicated that nitrification pathways contributed to the N_2O production, but when N_2O is produced deeper in the soil (by deeper penetration of NO_3^-, or injection in the soil), it had a greater opportunity to be converted to N_2 by de-nitrification before escaping to the surface.

Condensated ammonium water

Leaching

Ammonium present in ammonia water will, when injected in the soil, attach to clay and organic matter particles, thus preventing it from leaching away. During the growing season, soil microorganisms convert the ammonium to nitrate (nitrification), which is the main form taken up by plants. The soil conditions that promote nitrification include: a soil pH of 7, moisture at 50% of the soil's water-holding capacity, and a soil temperature of $25^{\circ}C$. Under the following conditions, nitrification will not occur, and ammonium is susceptible for leaching: a pH below 5.5, a waterlogged moisture condition, and temperature under $5^{\circ}C$, i.e. during wet autumns and winters.

In general, both NH_3 and N_2O emissions and NO_3^- leaching can be minimised when the ammonia water is applied by soil injection and incorporation into the soil after application.

Current legal view on condensated ammonium water

Condensated ammonium water (Aqua ammonia) is in principle a regular fertiliser although its position with the Nitrates Directive has to be clarified. Bio-based fertilising products based on capturing ammonia in water (or in an acid) however, might not meet regulatory requirements for these regulatory liquid fertilisers. In the EU, a minimum 15% N (C.1.1. Annex 1 of EC 2003/2003) for liquid N fertilisers is required, otherwise national legal requirements are in force. If the national regulations do not specifically describe ammonium solution or aqua ammonia, the EU Regulation rules.

If fatty acids are present in the ammonium solution, the % of organic carbon (from fatty acids) should be determined to conclude if it falls under the criteria of an inorganic fertiliser (European Commission 2018).

However, in some EU countries, it is possible to ask a national derogation for application of any bio-derived fertiliser for a specific application area or time period ('pilot status'), taking into account additional criteria or conditions that maybe imposed.

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Systemic large-scale eco-innovation to advance circular economy and mineral recovery from organic waste in Europe

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