European Sustainable Phosphorus Platform

SCOPE NEWSLETTER

7th June 2023 Brussels & hybrid — White Ammonia Research Meeting

Summary of ESPP's
1st White Ammonia & Nitrogen Recovery Research Meeting (WARM)

This SCOPE Newsletter summarises ESPP's first workshop on nitrogen recovery research, 7th June 2023 Brussels and hybrid. The workshop attracted 70 participants in Brussels and 50 online. A wide range of routes for reusing N in organic waste streams were presented. Different N recovery routes discussed included using waste streams to feed biomass production (algae, duckweed, microbial protein), N-recovery from separately collected urine, manure N stabilisation or local processing to organic fertilisers, recovery of ammonium sulphate solution, or production of ammonia gas for industry use (e.g. by adsorption from waste liquors or offgas followed by desorption as ammonia gas). Discussion suggested that ammonia sulphate solution is mainly adapted for local distribution to farmers (not economic to transport, even if concentrated, unless in specific use chains). Industry participants suggested that further R&D is needed on identified possible new technologies (adsorption/desorption by ionic liquids, geopolymers, recovery logistics for ammonia gas, recovery from NO_x/N_2O stripping) where information on feasibility is lacking or adaptation is needed of processes currently designed for other purposes, whereas researchers proposed more modelling studies.

The WARM workshop took as starting points the first ESPP workshop on nitrogen recovery SCOPE Newsletter n°145 and the summary and analysis of recent R&D into nitrogen recovery in SCOPE Newsletter n°147.

WARM slides and recordings (of plenary and parallel sessions 3 and 4), as well as full list of participants (with contact details) are available online via Swapcard for all registrants. Further information at: www.phosphorusplatform.eu/NRecovery

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Editorial

The first WARM meeting in Brussels brought together the research community and industry to discuss different nitrogen recovery opportunities.

From a personal standpoint I was hoping to see ideas for a process to make a solid nitrogen product, to avoid the thermal footprint required to evaporate an aqueous salt solution to a granule. Transport over significant distances of aqueous solutions is not economic, making impractical sale into industrial fertiliser or chemical markets.

Some possible solutions to this challenge were shown, such as materials capable of trapping ammonia then releasing it as gas (zeolites, geopolymers, ionic liquids, struvite), routes to recover nitrogen as a solid precipitate. However, recovery other than as aqueous solutions is still hypothetical and process design, testing and feasibility assessment are needed.

Another area which seems open for research is moving from NO_x removal in industry and combustion chimneys to nitrogen recovery.

Local N-recovery circles are today effective and proven, but need support for benchmarking and demonstration. These include biological N recovery (algae, biomass), stabilised/upgraded manure (e.g. plasma treatment), organic fertilisers, separative urine products, aqueous N solution use by local farmers. Operational processes can be found in ESPP's Nutrient Recovery Technology Catalogue.

But I see the challenge as still open to find new processes to enable industrial N recovery.

I wish you a good read of this SCOPE newsletter.

Robert Van Spingelen, ESPP President

Context and opportunities

Chris Thornton and **Olivier Bastin, ESPP,** summarised work engaged by ESPP since late 2022 on nitrogen recovery and recycling:

- operator mapping, over 170 papers and reports analysed, identifying over 300 technologies (here)
- first ESPP workshop on nitrogen recovery (150 participants): SCOPE Newsletter n°145
- summary and analysis of 80+ recent R&D publications on nitrogen recovery: SCOPE Newsletter n°147
- establishment of Nitrogen Recovery Working Group
- consensus definition of "White ammonia" (here)
- initial data on N-recovery potential quantities (see below)

This work shows that nitrogen recovery is a highly active R&D field, with many actors, both in research and start-up companies, but with **very few full-scale-recovery installations operating commercially**. There are many full scale nitrogen removal installations (ammonia or NO_x scrubbing) operating, but not with N-recovery. Successful N-recovery operations to date are producing fertilisers for local use (e.g. as organic fertilising products, or ammonium sulphate solution for local use by farmers) or are specific applications (e.g. separate urine processing).

There is however a **considerable potential for development**, because ammonia stripping and NO_x/N_2O scrubbing are expected to increase considerable, with the expansion of anaerobic digestion for renewable methane production and with tightening limits on ammonia and N_2O (greenhouse gas) and ammonia emissions.

Jeanne De Jaegher (European Commission, DG ENV) outlined the EU Integrated Nutrient Management Action Plan (INMAP) process underway.

INMAP, expected to be published by the European Commission in 2023, aims to implement the **Biodiversity Strategy and Farm-to-Fork target to reduce by 2030 excess nutrients lost to the environment by at least 50%** and to bring EU nitrogen and phosphorus management back within planetary boundaries, including addressing nutrient pollution hotspots and promoting nutrient recycling, in synergy with climate change action.

INMAP is supported by the JRC study "Knowledge for Integrated Nutrient Management Action Plan (INMAP)", published May 2023, see ESPP eNews n°76.

The aim is to establish a **new mindset on nutrients** and an overall political process to reduce nutrient losses, improve stewardship and implement nutrient recycling.

In **discussion**, workshop participants questioned how implementation of nutrient recycling will be supported in practice, suggesting that regulatory obstacles remain to be addressed, complexity of regulation around nutrient recycling needs to be simplified, and that policy tools are needed to address the price difference between virgin and recovered nutrients, for example by nutrient recycling quotas in products.

How much N could recovery supply ?

Theoretical long-term potential for supplying crop needs from secondary N is considerable (source for numbers: EEA, unless indicated otherwise), for EU27:

- *c. 7 - 9 MtN/y in livestock manure (RISE 2016), plus similar order of magnitude N lost to the atmosphere from agriculture (of which around one quarter as climate or pollutant gases: N_2O, NO_x, ammonia) and the remainder as inert N_2 (EEA)*
- *c. 3 MtN/y is lost to water from agriculture (EEA)*
- *NO_x emissions from industry in Europe are around 0.36 MtN/y(estimated from data in CREA 2023)*
- *c. 2 MtN/y in human urine and 2 – 3 MtN/y in sewage sludge (RISE 2016)*

compared to c. 11 MtN/y applied in fertilisers and c. 3 MtN/y in imported animal feed.

***Much of the above secondary N is already today returned to agriculture** (spreading of manure slurry, sewage biosolids). The RISE "Nutrient Recovery and Reuse" report (RISE 2016) concludes (p. 6, pp. 45-48) that 2 – 5 MtN/y are currently not being recovered from manure, sewage sludge and food chain waste, representing 18 – 46 % of EU mineral N fertiliser use.*

This is significantly higher than the recent JRC estimate of 1 – 2 MtN/y recycling potential (INMAP Knowledge Study, see ESPP eNews n°67).

Estimates for potential for N recovery in the USA are:

- *6,2 MtN/y livestock manure*
- *2,6 MtN/y food waste*
- *1,8 MtN/y in agricultural & forestry wastes*
- *0,2 MtN/y in sewage sludge*

Compared to 14 MtN/y in mineral fertilisers
From from Eisa et al., 2022
https://doi.org/10.1021/acssuschemeng.2c03972

*The above **does not include potential from reducing nitrogen GHG/pollutant gas losses**, beyond existing NO_x scrubbing of chimneys (combustion, industry: possible future abatement of NO_x losses from other sources, N_2O from waste water treatment within possible future wastewater treatment climate emission mitigation, ammonia or N_2O/NO_x losses from composting, ammonia stripping from stable air ….*

It also does not cover nitrogen recycled within biomass cycling. Such agricultural cycling is significant (e.g. in nitrogen-fixing cover crops integrated into soil).

N-recovery funding opportunities

Bertrand Vallet, European Commission DG RTD, indicated that Horizon2020 funded a number of projects testing and demonstrating ammonia recovery, and that Horizon Europe may include funding for large scale feasibility trials of nutrient recovery, nutrient circular economy as part of food system resilience and on micropollutants.

Projects testing ammonia recovery from digestates under Horizon 2020 have included this as part of wider trials of nutrient recovery or studies on farmer uptake of sustainable fertilisers: e.g. B-Ferst, Ultimate, SMARTPlant, Newfert, B-WaterSmart, Run4Life, Walnut, P2Green, Novafert, ferplay, NutriBudget, NewHarmonica, NAPSea, NordbaltEcosafe. Nitrogen recovery has generally been approached as ammonia stripping and recovery to ammonia salt solutions. Most of these projects have been analysed from the nutrient management angle in the Horizon Boosters report published September 2023 DOI as DG RTD input for the Integrated Nutrient Management Action Plan.

Other Horizon mechanisms funding R&D into nutrient recovery include the Circular Bio-Based Europe Joint Undertaking, PRIMA (agriculture and water), Water4All partnerships.

Horizon Europe will continue to support nutrient recovery R&D with possible emphasis on optimising resource recovery and recycling rates, with industrial large scale industrial feasibility demonstration.

A call is under assessment on advanced (nano) materials to reduce fertiliser use (first stage submission closed March 2023).

Calls opening in 2023 and closing in 2024 include respecting safe ecological and regional nitrogen and phosphorus boundaries and recovered / recycled fertilising products from secondary raw materials. Links : Horizon Europe work programme and Circular Biobased Economy Joint Undertaking.

Frederico De Filippi, CINEA (European Climate, Infrastructure and Environment Executive Agency), underlines that the EU LIFE programme can flexibly support development and deployment of nutrient circularity technologies and solutions.

In the 2014-2020 LIFE programme, over 40 projects related to resource recovery from water were funded. Examples include LIFE Libernitrate, LIFE Infusion, LIFE Re-Fertilize, LIFE Ulises

The 2021-2027 LIFE programme includes 1.35 bn€ for "Circular Economy and Quality of Life" and can fund any relevant project to develop and demonstrate innovation (close-to-market), promote best practices, to catalyse large-scale deployment and/or support implementation of EU policies.

LIFE "Standard Projects" can be considered bottom-up because any project which fits the overall call objectives, is in principle eligible. However, a slightly higher scoring is provided to projects fulfilling the specific priorities outlined in the call document. Also, project beneficiaries can be private companies, NGOs, public bodies or other organisations. Average EU contribution to Standard Projects is around 1.5 M€ and cofounding must be 60%.

Links: LIFE Call for Proposals 2023 open for submission of Standard Action Projects to 6th September 2023. LIFE EU Info Days 2023 info and recordings. LIFE project database.

Will Brownlie, UK Centre for Ecology and Hydrology (CEH), presented the INMS (International Nitrogen Management System) Database.

This will be an online portal providing summary information on some 170 measures and actions which can reduce nitrogen losses and enable nitrogen recycling. These include actions on e.g. fuel combustion systems, crop systems, livestock, consumer and food system, organic residues management, aquatic systems including aquaculture.

This will feed into a United Nations Environment Guidance Document, under development, on Integrated Sustainable Nitrogen Management.

The nitrogen measures database may also be extended to phosphorus and potassium.

Input on technologies and case studies can be sent to wilown@ceh.ac.uk

Summaries of parallel sessions

Session 1
Membrane & electrodialysis ammonia recovery

Rapporteurs: Céline Vaneeckhaute, University of Laval and Olivier Bastin, ESPP

Speakers:

Membrane-based concept to recover ammonia from industrial liquid side streams – Hannah Kyllonen, VTT

Recovery and concentration of nutrients for hydroponics from centrate with electrodialysis and upstream nitrification in a membrane bioreactor – Anna Hofmann, Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT

Detricon's LIFE INFUSION pilot results – Wouter Naessens, Detricon

Membrane-enhanced stripping for ammonium recovery from pig slurry liquid fraction – Xialei You Chen, Leitat Technological Center

Recovery of ammonia by membrane chemo-sorption from concentrated and dilute streams – Lex van Dijk, Colubris Cleantech BV

Chemical-free ammonium recovery from reject water using bipolar membrane electrodialysis (BPMED) – Gladys Mutahi, TUDelft

***See also** Veera Koskue, Universityy of Melbourne, Session 4.*

Presentations covered different approaches to using membranes in nitrogen recovery systems, including membrane concentration of stripping/scrubbing solutions or of ion-exchange regeneration solutions, membranes used directly in wastewaters and electrodialysis.

Membrane applications for N-recovery are today demonstrated in operational proof-of-concept installations, but further operational experience feed-back is needed.

Combinations of two or three recovery technologies were presented/mentioned, but cost-benefits of these need to be assessed.

Membrane fouling was encountered in some cases, and water transport through membranes (microchannels) leading to transfer of contaminants across the membrane. Micropollutants and other contaminants should be monitored in the recovered nitrogen salt solution.

In all cases, the membrane technologies presented result in a dilute aqueous ammonium salt solution.

Session 2
Ion exchange and adsorbents for ammonia capture

Rapporteur: Willem Schipper, industry consultant.

Speakers:

Ionic liquid-based sorbents for NH_3 capture and recovery – Jose Francisco Palomar Herrero, Universidad Autónoma de Madrid

Ammonia removal and recovery from municipal wastewater – Hacer Sakar, Cranfield University

Geopolymers for ammonium removal and recovery: state of the art and perspectives - Daniela Pinto, Università degli Studi di Bari

Application of nitrogen recovery to produce Smart bio-based fertiliser – Alicia Gonzalez Miguez, Cetaqua - WALNUT Project

Ion exchange for N-removal after a high-loaded municipal waste water treatment plant – Elisabeth Vaudevire, PWNT

Presentations covered removal/recovery of ammonium ions by zeolites, geopolymers, ionic liquids, from wastewater liquors or from ammonia "stripping" (where ammonia is released from waste liquors such as digestates, as a gas mixed with air and water vapour or droplets) or from ammonia offgases (e.g. from stables or manures).

Ammonia removal is the prime objective of most processes developed to date, e.g. from wastewater to improve treatment plant (wwtp) functioning (in some cases avoiding a specific biological nutrient removal step), or to reduce ammonia losses to air. The first driver is thus not nutrient recovery.

Ion exchange processes can remove ammonia 'as ammonium ions' from wwtp liquor streams (such as digestate dewatering liquor) which would otherwise be returned to the sewage works inflow such that ammonium burdens the wwtp denitrification process. However, there are difficulties with resin uptake of competing ions and chemical consumption for regeneration. A dilute ammonia salt solution can be recovered from the ion exchange resin regeneration (e.g. c. 4% N w/w in the Cetaqua Walnut project), where ammonia is mixed with other ions. **A challenge is to find uses for such dilute solutions which have low economic value and high transport costs**, or require significant energy to further concentrate or evaporate to dry crystals.

Adsorbents can (selectively) trap ammonia from wastewater liquors and/or gas streams (zeolites or geopolymers) or from gas streams (ionic liquids) and then **release the ammonia as a gas when heated** (e.g. to 60 – 80°C). Current R&D has captured this ammonia by trapping it in acid, resulting in a dilute ammonia salt solution, facing the same challenges as above. To what extent, the released gas can feasibly be captured (as pure, dry ammonia) by freezing or pressurization remains to be seen.

Ionic liquids (ILs) have been mainly developed as an adsorbent for other uses (e.g. CO_2 capture) but research shows that certain ILs can trap ammonia (and release it as a gas). ILs are tuneable for functionality and for selectivity of adsorption. They need a supporting medium (as liquids, they are too viscous) and microencapsulates seem effective. Offgases are mostly wet and ILs are hygroscopic which will complicate use of ILs.

See also Krajete GmbH in Session 4

For all of these routes, there is a trade-off between speed and effectiveness of ammonia capture/removal against ease of release /recovery. **Economics need to be evaluated**, taking into account chemical costs, maintenance and operation, value and logistics of recovered nitrogen material.

Session 3 (hybridised)
Biological routes for N-recovery

Rapporteurs: Ludwig Herman, Proman and Daniel El Chami, Timac Agro

Speakers:

Microalgae-based ammonium recovery from wastewaters and digestates – Robert Reinhardt, Algen

Microalgae-based bioremediation as an alternative to conventional activated sludge processes – Elena Ficara, Politecnico di Milano

Large scale algal treatment of municipal wastewater – David Fernando, Aqualia

MicroAlgae 4.0: Green microalgae for urban wastewater remediation and nitrogen recovery – Josué Gonzalez-Camejo, Università Politecnica delle Marche

Biological recovery of N from wastewater using duckweed – Reindert Devlamynck, Inagro

Hydroponic cultivation of plants based on N-rich waste streams – Øyvind M. Jakobsen, CIRiS

Results update from SABANA projects – Francisco Gabriel Acien Fernandez, European Algae Biomass Association (EABA)

The session included presentations on using biological materials (micro- and macro-algae, duckweed and hydroponics) for N-recovery from wastewaters.

Algae and plants, as well as taking up nutrients (so potentially contributing to nutrient removal), convert (sun-)light and atmospheric CO_2 into recoverable energy. Drawbacks are high land use, difficulty of separation / extraction of products for valorisation and possible uptake of contaminants from wastewaters.

Presentations addressed three approaches:

- **Algae and microalgae are tried-and-tested** for this purpose. They have been widely used with horizontal and vertical systems for decades. They can produce food-grade and agricultural (animal feed and nutrition) algae. Implementation is medium to high TRL. Some limitations include high land-use requirements (for horizontal systems) and homogeneity of light distribution (for vertical systems).
- **Duckweeds** are another crop that can be used for N-recovery, with potentially interesting agricultural uses for its protein and flavonoid content. This still requires research to adapt systems to operational needs and to improve efficiency.
- **Horticultural production using wastewater** to provide both nutrients and water has been thoroughly studied in the literature. It is agronomically feasible, but has shown limited implementation, probably because of obstacles to social acceptance and operational difficulties (matching wastewater flow to horticultural nutrient and water needs). Active projects include the NTU CIRiS project to produce vegetables in space travel from wastewater and the SUSKULT project in Germany for vertical crop production.

Session 4 (hybridised)
Routes to concentrated recovered N products

Rapporteur: Laia Llenas Argelaguet, BETA Technological Centre

Speakers:

Freeze concentration as potential technology to concentrate diluted ammonium salt solutions – Nagore Guerra Gorostegi, BETA Technological Center

Nitrogen recovery in the LIFE RE-FERTILIZE project (Aqua2N) – Anna Lundbom, EasyMining

Recovering nitrogen from wastewater as a concentrated liquid using (bio)electroconcentration – Veera Koskue, University of Melbourne

Regenerative NOx Removal from Industrial Sources – Status and Outlook – Alexander Krajete, Krajete

Possible routes and challenges for small-scale N-recovery to products adapted to industry or farmer use – Willem Schipper (industry consultant) and Céline Vaneeckhaute (University of Laval)

This session covered different possible approaches to develop industrially feasible nitrogen recovery, building also on Session 2.

Freeze concentration is a widely used technique in the food industry, with several possible configurations, not all of which present the same performance for aqueous ammonia solutions. Initial lab tests presented potential to extract precipitated ammonia salts from aqueous solutions, both from scrubbing or waste liquors directly. Further work is needed to assess feasibility and lower energy consumption compared to evaporation

Precipitation of struvite (6%N) from waste liquors then ammonia release with recycle of the phosphorus and magnesium back into the process (**EasyMining Aqua2N** process, 4 m^3/h pilot, see SCOPE Newsletter n°145) currently generates an ammonia sulphate solution (2% N) which can be used as a fertiliser. Recovery of a product with higher N content is being investigated.

Industrial pilot trials of **N-recovery from industrial chimney NO_x scrubbing** were presented (**Krajete GmbH**, see also SCOPE Newsletter n°145). Current scrubbing often uses urea to react with NO_x, producing N_2 and water, so consuming virgin nitrogen not recovering. The process uses zeolite adsorbent. NO_x removal is today demonstrated, recovery of nitric acid from regeneration is being pilot tested. Demonstration in real industry chimney operating conditions is now needed, including analysis of contaminants in the recovered nitric acid.

To conclude, **Willem Schipper, industry consultant**, and **Céline Vaneekchaute, University of Laval**, presented an overview of challenges and research needs for **integration of decentralised nitrogen recovery into industry-scale logistics**.

Aqueous ammonia sulphate, as currently often recovered, has low N content and low economic value, so not transportable significant distances (see table in conference Conclusions below). Concentration has high energy and capital/operation costs, but developments may improve this. Local/regional use (to farmers, locally situated industry user) will be appropriate in some cases.

Other possible routes include recovery of ammonia as a gas or a solid, but further research is needed to identify and assess feasibility of such routes.

In all cases, there will be problem of scale leading to cost, as for recycling of many materials. Economies of scale mean that decentralised N-recovery is likely to have capital and operating costs an order of magnitude higher than costs in a large fertiliser plant. Technologies should be kept simple to mitigate this effect.

Session 5
N- recovery form urine, manure , aquaculture

Rapporteurs: Andrea Turolla, Politecnico di Milano and Robert Van Spingelen, ESPP

Speakers:

Nitrogen recovery from urine in research and practice – Kai Udert, Eawag

Life cycle assessment of bio-based fertilizers from fisheries and aquaculture sidestreams – Jan Landert, Research Institute of Organic Agriculture FiBL

Life Cycle Analysis (LCA) of the NPHarvest process, and of struvite precipitation + ammonia stripping – Juho Kaljunen, Aalto University

Optimization of ammonia recovery from urine and digestate using transmembrane chemical absorption – Mathieu Sperandio, Institut national des sciences appliquées de Toulouse

Revolutionizing Agriculture: Urine Recycling as a Green Solution for NPK Fertilizer Production – David de Chambrier, VunaNexus

N recovery as part of the SYNECO solution for recycling manure nutrients in Malta – Henning Lyngsø Foged, Organe Institut

This session showcased nitrogen recovery from different waste streams: separately collected human urine, seafood processing wastes, manure digestate.

Nitrogen recovery from separately collected urine is today operational at the commercial scale, with the company Vunanexus, a spin-off from EAWAG research institute Switzerland, currently producing around 20 m^3/y of 'Aurin' liquid fertiliser (containing c. 1 tN). New projects are underway to install urine separation in new-build for several projects in France and Germany, with populations of 300 – 1000 per project.

Projects for nitrogen recovery from France, Finland, Malta and Norway presented **life cycle analysis** data, suggesting an energy footprint for ammonia salt recovery similar to that of the Haber Bosch process.

Session 6
Different routes for nitrogen recycling

Rapporteurs: Robert Reinhardt, Algen and Elena Ficara, Politecnico di Milano

Speakers:

How can we possibly resolve the planet's nitrogen dilemma? – Wim Moerman, Akwadok

Practical results of N-recovery from municipal wastewater – Gertjan Buffinga, Byosis

SYREN - Acidifying slurry to minimise ammonia emission – Morten Toft, BioCover

Treating and Recovering Nitrogen from digested sludge – two cases from the Netherlands – Herman Evenblij, Royal HaskoningDHV

This session discussed different approaches to reducing ammonia losses and recovering nitrogen.

Ammonia stripping from liquors such as digestate or manure can often be achieved without using chemicals for pH correction by temperatures and CO_2 stripping. Nitrogen is recovered as aqueous solution, often of ammonium sulphate, which generally limits to local use. The technology is known, easy to install.

Ammonia removal can reduce requirements for denitrification in sewage works, **so reducing N_2O emissions**. Gruber et al. 2021 (DOI) estimate that wastewater treatment N_2O may be c. 1% of national greenhouse gas emissions.

Struvite precipitation can be used to remove ammonia, but either phosphorus and magnesium reactants must be input (ammonia molar concentrations are much higher than P or Mg), or the struvite must be broken down and these reused, or remaining ammonia must be removed by other methods.

If gaseous ammonia is recovered, an option could be **NH_3 cracking to H_2**. Possibly this could be more feasible than purification and compression of NH_3, but it would imply further onsite technology and significant energy loss.

Manure acidification is a recognised technology (see ESPP Nutrient Recycling Technology Catalogue). Manure/slurry pH sensors, an indicator of plant N availability, can enable intelligent spreading. These techniques allow significant reductions in nitrogen losses. The main challenge to uptake is farmers' demand for simple application systems. Legislation enforcement would significantly contribute to the EU Green Deal nutrient loss reduction targets.

Sewage treatment N_2O emissions

Long-term monitoring study suggests that waste water treatment N_2O emissions represent 0.3 – 1.4 % of total greenhouse emissions.

One year or longer monitoring at seven Swiss sewage works suggest that N_2O emissions vary widely with treatment works configuration, seasons and operating conditions. Continuous N_2O concentration measurement in offgas from aeration tanks was multiplied by pumped air flow volumes. Literature suggests that N_2O emissions are mainly from biological denitrification – nitrification, but also from side stream treatment of sludge liquors and from surface waters after discharge, but fewer than ten continuous monitoring studies are reported. This study showed also high N_2O emissions from one plant operating carbon removal without nitrification-denitrification, depending on operating conditions. Average N_2O emissions for the seven sewage works studied were 1.6% of works total nitrogen inflow, but with a very wide range (0.1% - 8%). This is comparable to literature values (1.1 – 2.9 % of inflow N) and to the IPCC 2019 Guidance for National Greenhouse Gas Inventories.

The study results suggest that N_2O emissions from all wastewater treatment works in Switzerland represent around 1% of the country's total greenhouse gas emissions.

A strong relation is shown between N_2O emissions and the ratio of effluent nitrite (NO_2^-) / influent total N, with emissions peaks corresponding to nitrite accumulation in the treatment process. The study suggests that operational measure have potential to significantly reduce N_2O emissions: ensuring denitrification all year, avoiding nitrite accumulation, control of sludge age in carbon removal.

"Estimation of countrywide N2O emissions from wastewater treatment in Switzerland using long-term monitoring data", W. Gruber, L. von Känel et al., Water Research X 13 (2021) 100122, DOI.

Conference discussions

Willem Schipper, industry consultant, showed estimated economic transport distance for ammonium sulphate solutions, depending on concentration (based on typical current prices).

% Ammonium Sulphate (% AS in water)	% Nitrogen (% N / wet weight)	Value to industry user (after costs of water evaporation)	Economic transport distance
16%	3,4%	0 €/t	0 km
20%	4,2%	30 €/t	14 km
25%	5,3%	55 €/t	50 km
30%	6,3%	72 €/t	163 km
35%	7,4%	84 €/t	266 km
40%	8,4%	93 €/t	336 km
Note: saturated ammonium sulphate solution = 43%.AS			
100% (dry solid)	21,0%	130 €/t	508 km

Because ammonium sulphate has a low nitrogen content and is a low-value commodity chemical, and because industry users generally will need to expend energy evaporating water (energy is not recovered in fertiliser granulation), **recovery of ammonium salt solutions will not be compatible with transport and industry use, except in specific circumstances** (niche value product, proximity to a fertiliser factory). Ammonium salt solutions can be appropriate for local/regional use by direct distribution to farmers, but even then concentration is important to reduce transport costs, storage costs and tractor traffic for application.

Laura Pirro, Yara, suggested that more research on **new business models** is needed to see how to recycle recovered nitrogen in decentralised logistics in a profitable way: technological research alone might not suffice and more creativity in the approach to market is required.

Conference participants called for policy to drive nitrogen recycling. Market value of recovered nitrogen materials will not drive recycling. Regulatory targets and tools are needed to integrate nitrogen recovery into Green Deal environmental policies to reduce nitrogen losses (water policy, air quality, greenhouse gas emissions), to provide financial initiatives for N-recovery.

Giulia Sagnotti, ACEA ELABORI SPA Italy, for the water treatment industry, underlined the benefits of use of treated sewage sludge (biosolids) in agriculture: recycling of phosphorus, nitrogen and organic carbon. More research is needed to ensure safe management of micropollutants in sludges and into interactions between new sewage works configurations, stability of biosolids and greenhouse gas emissions.

Industry participants noted that N-recovery as ammonia salt solutions is generally incompatible with current fertiliser industry operation (centralised production and logistics).

Research needs

Discussions identified the following research needs:

- **New business models for nitrogen recovery**:
  - **local/regional** processing-to-product and commercialisation to market
  - **process integration** with recovery of other nutrients, energy, greenhouse emissions reductions
  - **interactions** with developments such as Green Ammonia, new Haber Bosch processes, grass for green protein

- **Economic and operational evaluation of already well researched technologies** (membranes, electrodialysis, algae and biomass systems …).
  - operational and maintenance **costs**, energy consumption, chemicals consumption, by-products.
  - adaptation and implementation for N-recovery (ammonia salt solutions) of industrially established low-energy approaches for **concentrating** and for crystallisation, e.g. freeze drying, mechanical vapour recompression …
  - technology development and roll-out of **decentralised processes to stabilise reactive nitrogen into organic fertilisers products** (organic carbon containing), such as plasma nitrification, manure acidification, reactive nitrogen reaction with CO_2 …
  - full-scale demonstration of **biomass nutrient recovery systems**, to develop data on costs and performance
  - **optimisation of technologies at small-scale** for N-recovery at sewage treatment plants or on farms, adapted to onsite operator capacities

- **Contaminants and pathogen safety**
  - transfer of pathogens to nitrogen products: ammonia stripping gases, recovered scrubbing solutions, adsorbents …
  - contaminants in recovered nitrogen products, including from sewage, manure, digestates and from industrial/combustion offgases
  - contaminants and pathogen safety of biomass grown on waste streams

- **Technology research needs** - explorative investigation of possible new technologies for N-recovery (blue-sky approaches, technologies with little research to date):
  - **Ionic Liquids** (ILs): design of ILs for ammonia removal/recovery from stripping and other gases, testing in real waste streams (competing ions, water vapour), including chemical safety aspects, support structure, repeated regeneration cycles, scale-up if lab studies successful.

  - **Other adsorbents** (e.g. zeolites, geopolymers) for recovery of ammonia from gas or liquid phase: scale-up in real wastewaters, repeated regeneration cycles, demonstration of feasibility for commercial N-recovery.
  - possible **recovery of ammonia gas** from regeneration of ILs, geopolymers, zeolites, struvite, etc. Feasibility of small scale gas recovery, drying, purification, compression, logistics, regulation and permitting.
  - experimental investigation to look for **new routes to recover ammonia to solid products** rather than aqueous solutions: identify and assess possible insoluble ammonium compounds, feasibility of capture by acidic solid phosphates, …

- **From flue gas N-scrubbing to N-recovery**: current N_2O/NO_x mitigation from flue gases (combustion, industrial processes) transfers reactive nitrogen to either N_2 (consuming urea to do so) or to waste acid scrubbing solution
  - development and demonstration testing onsite (real flue gas treatment: temperature, corrosion, contaminants …) of **technologies to remove N_2O/NO_x and convert to commercial recovered nitrogen products** .

Recent research publications

Ammonium carbonates: a route for nitrogen recovery ?

Ammonium carbonates can fix nitrogen and CO_2 from waste streams such as digestates, but are unstable, releasing ammonia and carbon at room temperature. So are they a desirable route for N-recovery ?

Jonas Baltrusaitis, Lehigh University, suggests that ammonium carbonates offer a possible route for nitrogen recovery, for example from digestates, if they can be formulated into stable fertiliser products. Ammonium bicarbonate was widely used as a fertiliser in China until a few decades ago. However, it is unstable, decomposing back to ammonia and carbon dioxide at room temperature. If methods can be developed to formulate ammonium carbonates into solid materials, which do not release ammonia (toxicity, atmospheric emissions) and supply nitrogen effectively to plants, then it could be a beneficial nitrogen recovery route.

A detailed review paper (**Brondi et al. 2023**) summarises knowledge of ammonium carbonate chemistry, possible N-recovery routes, approaches to increase stability, agronomic value, potential for carbon fixation (rather than release) in soils.

Recovered "ammonium carbonate" is in reality generally a complex system of ammonium sesquicarbonate monohydrate [$(NH_4)4(H_2(CO_3)3H_2O$], ammonium bicarbonate [$(NH_4)2HCO_3$], ammonium carbonate monohydrate [$(NH_4)_2CO_3 \cdot H_2O$] and ammonium carbamate [$NH_4CO_2NH_2$].

The review summarises three studies using commercial NH_3 to trap industrial CO_2 emissions to ammonium carbonate and six studies recovering NH_3 and CO_2 from organic waste streams, with recovery of ammonium carbonate as aqueous solution or precipitate. Precipitation of solid ammonium carbonate was variously achieved by reducing the temperature below 36°C or 20°C, freeze drying or crystallisation.

Methods to stabilise ammonium carbonate are discussed, aiming to enable crop application without ammonia loss, including chemical agents (biochar / humic acids, silica gel), use of denitrification inhibitors, granulation, coatings (polymers, cellulose). Trials of other techniques to improve agronomic use of ammonium carbonate are summarised, including deep soil placement.

One reported study shows that surface broadcasting of ammonium bicarbonate on rice led to 60% loss of total N, whereas placement at 5 cm depth reduced losses somewhat, but with still 45% N loss. Other studies on rice show that ammonium carbonate can be an effective nitrogen fertiliser (compared to zero-N control), but with nitrogen uptake of only 20 – 40 % by crops (even with placement 10 cm depth in soil).

For the carbon in ammonium carbonate, two studies on wheat using radio-dated carbon, show 75% retention of carbon in soil in alkaline soils, but only 40% retention in acid soils (c. 10% uptake by crop and >50% loss of CO_2 back to the atmosphere) – most soils in Europe are naturally acidic (pH < 5.5), see http://eusoils.jrc.ec.europa.eu/library/data/ph/

"Review. Recovering, Stabilizing, and Reusing Nitrogen and Carbon from Nutrient-Containing LiquidWaste as Ammonium Carbonate Fertilizer", M. Brondi et al., Agriculture 2023, 13, 909. https://doi.org/10.3390/agriculture13040909

A web blog from 2019 presents a pilot plant (photo of pilot here) for ammonia recovery from digestate as ammonium bicarbonate (**ABCR Ammonia Bicarbonate Recovery**) using a rotating photo bioreactor where cyanobacteria consume bicarbonate in digestate, so increasing pH and causing stripping ammonia gas. The ammonia is trapped in water, and this solution is used to strip carbon dioxide (and hydrogen sulphide) from digester biogas, producing a solid ammonium bicarbonate precipitate.

As above the use of ammonium bicarbonate as a fertiliser poses questions (CO_2 loss, ammonia loss). The website of the company which developed the pilot plant (Makingenergy) is no longer online.

Centorcelli et al. 2021 do no experimental work but theoretically model solid ammonium bicarbonate recovery from digestate using solar energy to heat a digestate distillation column which is assumed to result in ammonium bicarbonate solution, from which they suggest solid ammonium could be precipitated.

Gypsum for ammonia recovery

Gypsum ($CaSO_4 \cdot 2H_2O$) is a widely available secondary material, with millions tonnes generated from flue gas desulphurisation. It can be used to trap ammonia gas, producing aqueous ammonia sulphate solution.

Brienza et al. 2021 tested full-scale (c. 220 t/day wet weight influent) use of flue gas desulphurisation gypsum (supplied as a solid, around 25% water, 75% DM) to trap ammonia stripped from raw digestate (a side-stream taken from and returned to the digesters). Ammonia stripping was by increasing temperature to 90°C (using residual energy from CHP engines) and increasing pressure to 0.4 – 0.8 bar), so driving off water, ammonia and carbon dioxide (the latter leading to pH increase). The on-farm digesters were treating a mixture of poultry manure and agricultural by-products.

Around 2/3 of the ammonia in the stripper influent was trapped in the gypsum. Because water comes off with ammonia during the stripping, the gypsum can be considered to be in aqueous suspension. This was then treated in a filter press, separating a liming substrate (30% water content, mainly calcium carbonate) and a solution containing around 22% ammonium sulphate (i.e. c. 5 %N/wet weight).

Kim et al. 2023, at lab-scale (1 litre bottles, 8 hour runs), tested saturated gypsum solution (2g/l) for trapping of ammonia gas stripped from dairy manure digestate. The ammonia was stripped by bubbling nitrogen and carbon dioxide through the digestate heated to 70°C.

The gypsum solution trapped around 95% of the throughflow ammonia when the stripping gas contained 10% CO_2, rising to 100% when the stripping gas contained 30% CO_2.

ESPP comments: if flue gas desulphurisation gypsum are used to produce a fertilising product, verification of contaminants would be necessary. Also, in these two studies, the resulting product was an aqueous ammonia sulphate solution, posing the challenges discussed above.

"Techno-economic assessment at full scale of a biogas refinery plant receiving nitrogen rich feedstock and producing renewable energy and biobased fertilisers", C. Brienza et al. J. Cleaner Production 308 (2021) 127408 https://doi.org/10.1016/j.jclepro.2021.127408

"Novel Ammonia Recovery from Anaerobic Digestion by Integrating Biogas Stripping and Gypsum Absorption ", D-G. Kim et al, under review.

Jamaludin et al. 2018 tested citric and acetic acids, gypsum (calcium sulphate, suspension in water), epsom (magnesium sulphate, solution) and water for ammonia trapping (lab. beaker tests). Citric acid (50% w/w to water) was as effective as sulphuric acid, but required twice the dosage because of dissociation. Acetic acid was effective below 20°C but not at temperatures representative of many ammonia offgasing processes because of volatilisation (70% of effectiveness of sulphuric acid at 35°C, 30% at 70°). Water, gypsum (suspension in water) and epsom (aqueous solution) were largely ineffective for ammonia trapping. The authors refer to previous studies showing that gypsum addition to compost or to soil N-fertiliser application reduce ammonia emissions, and hypothesising that this is because gypsum reacts with ammonia and CO_2 to produce ammonium carbonate (Tubail 2008, Zia 2006)

"Evaluation of sustainable scrubbing agents for ammonia recovery from anaerobic digestate", Z. Jamaludin et al., Bioresource Technology 270 (2018) 596–602 https://doi.org/10.1016/j.biortech.2018.09.007

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