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Mitigation of ammonia and methane emissions in pre-treatment of fertilizer recovery process

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Abstract

Ammonia is an excellent fertilizer, but when used in excess, it causes waterbodies to become more eutrophic and acidic which endangers the biodiversity of the water. Ammonia pollution is primarily dependent on technology advancements to reduce emission. Cost, recovery efficiency, and end-product are the main factors that are considered in different recovery technologies currently available in the market. This thesis focuses on the ammonia recovery part of the NPHarvest project, an Aalto University initiative that provides a wastewater treatment solution for recycling ammonia as an ammonia salt fertilizer. In the NPHarvest recovery process, production of fertilizer uses significantly less energy with a high recovery efficiency which makes the technology economically and ecologically viable.

This thesis is a follow-up to research conducted in Sweden's Öresund WWTP in 2021 that showed increased eutrophication and acidification impacts due to excessive ammonia emissions. Focus of the study examines the magnitude of emissions caused by the design and materials of the pilot. To properly examine the leading cause of ammonia and methane emissions, smaller version of the pilot was created to test the factors in a supervised laboratory condition. A comprehensive analysis of the process and its influence on the magnitude of emissions is required to decrease high emissions of NPHarvest technology while maintaining ecological viability.

The testing included three factors that contributed to the amount of emissions: pH-level, wastewater type, and open surface area. Although pH and wastewater type affect the quantity of emissions, open surface area was the most emission contributing factor in the NPHarvest pilot process. Experimental results demonstrate that open surface areas of 3.1 cm² (2 cm diameter) and 200 cm² (16 cm diameter) release 0.0049 g-NH₃/m³ of wastewater and 0.6445 g-NH₃/m³ of wastewater, respectively. On a national level, if used to treat all the reject water of Finland, NPHarvest technology would emit 4.1 ton-NH₃ per year and 0.735 g/(PE, year) of NH₃ emissions, and 2.0 ton-CH₄ per year and 0.355 g/(PE, year) of CH₄ emissions. Theoretical calculations yielded similar results for Finland's national emissions, confirming the reliability of the experimental results. Our tests reveal that the ammonia emissions reported in Sweden may have been overestimated. Nonetheless, if it is necessary to extract emitted ammonia, effective ammonia recovery technologies such as acid scrubbers and bio-filtration technology solutions can be applied for further emission mitigation. Although the findings show smaller impact on eutrophication and acidification than in Sweden's research, mitigating procedures are important to consider in full-scale operation of NPHarvest process.

Keywords Ammonia, methane, greenhouse gas, wastewater treatment plant

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Tiivistelmä

Ammoniakki on erinomainen lannoite, mutta liiallisena se aiheuttaa rehevöitymistä ja happamoitumista vesistöissä, mikä vaarantaa vesien luonnon monimuotoisuuden. Ammoniakkipäästöjen vähentäminen on ensisijaisesti riippuvainen teollisen tekniikan kehityksestä. Kustannukset, talteenottotehokkuus ja lopputuote ovat tärkeimmät tekijät, jotka huomioidaan markkinoilla tällä hetkellä saatavilla olevista talteenottoteknologioista. Tämä diplomityö keskittyy Aalto-yliopiston NPHarvest-projektin ammoniakkin talteenotto-prosessiin, joka tarjoaa jätevedenpuhdistusratkaisun ammoniakkin kierrätykseen ammoniakkisuolalannoitteena. NPHarvest-talteenotto-prosessissa lannoitteiden tuotanto käyttää huomattavasti vähemmän energiaa korkealla talteenottotehokkuudella, mikä tekee tekniikasta taloudellisesti ja ekologisesti kannattavan.

Tämä diplomityö on jatkoa Ruotsin Öresundin jätevedenpuhdistamolla vuonna 2021 tehdyille tutkimukselle, joka osoitti liiallisten ammoniakkipäästöjen lisääntyneen rehevöitymisen ja happamoitumisen vaikutuksen. Tutkimuksen painopiste tarkasteli pilotin suunnittelussa päästöjä lisääviä tekijöitä. Ammoniakki- ja metaanipäästöjen johtavan syyn tutkimiseksi luotiin pienempi versio pilotista testaamaan päästötekijöitä valvotussa laboratorio-olosuhteissa. Kattavaa analysointia NPHarvest-prosessista ja sen päästöjen suuruudesta tarvitaan, jotta on mahdollista vähentää päästöjä ja säilyttää ekologisen elinkelpoisuuden tila. Testaukseen sisältyi kolme päästöjen määrään vaikuttavaa tekijää: pH-taso, jätevesityyppi ja avoin pinta-ala. Vaikka jäteveden pH ja jätevesityyppi vaikuttavat päästöjen määrään, avoin pinta-ala NPHarvest-pilottiprosessissa oli vaikuttavin tekijä päästöjen suuruuteen. Koetulokset osoittivat, että avoimet pinta-alat $3,1 \text{ cm}^2$ (2 cm halkaisija) ja 200 cm^2 (16 cm halkaisija) vapauttavat $0,0049 \text{ g-NH}_3/\text{m}^3$ ja $0,6445 \text{ g-NH}_3/\text{m}^3$. Laskennalliset päästöt olivat keskimäärin 4,1 tonnia- NH_3 vuodessa ja $0,735 \text{ g}/(\text{PE}, \text{ vuosi}) \text{ NH}_3$:a, ja 2,0 tonnia- CH_4 vuodessa ja $0,355 \text{ g}/(\text{PE}, \text{ vuosi}) \text{ CH}_4$:a, mikäli kaikki Suomen rejektivedet käsiteltäisiin NPHarvestilla. Teoreettiset laskelmat tuottivat samanlaisia tuloksia Suomen kansallisista päästöistä vahvistaen kokeellisten tulosten luotettavuutta. Laboratoriotutkimukset osoittavat, että Ruotsissa raportoidut ammoniakkipäästöt on saatettu yliarvioida. Jos karannutta ammoniakkia on tarpeen ottaa talteen ilmasta, voidaan päästöjen vähentämiseksi käyttää tehokkaita ammoniakkin talteenottotekniikoita, kuten happopesureita ja biosuodatusteknologiaratkaisuja. Vaikka löydökset osoittivat pienempiä vaikutuksia rehevöitymiseen ja happamoitumiseen kuin Ruotsin tuloksissa, lieventäviä toimenpiteitä on tärkeää ottaa huomioon NPHarvest-prosessin täysimittaisessa toiminnassa.

Avainsanat Ammoniakki, metaani, kasvihuonekaasu, jätevedenpuhdistamo

Preface

This thesis is a part of the current NPHarvest project at Aalto University, which focuses on nitrogen and phosphorus nutrient recovery. This study was motivated by the previous pilot results which had a large eutrophication and acidification impact on the environment. The focus of the research was the factors contributing most significantly to the magnitude of emissions due to several factors impacting the emissions.

I want to extend my sincere appreciation for the entire NPHarvest team, helping me accomplish the project. At first, I would like to give a special thanks to my thesis adviser Juho Uzkuurt Kaljunen for his guidance and constructive criticism throughout the thesis. It was an educational and maturing experience to learn about the process of a successful research. Also, I want to thank Professor Anna Mikola, the thesis' supervisor, for professional guidance and entrusting me with this project. Last but not least, I'd like to thank Raed Al-Juboori and Timo Larsson for assistance with the theoretical aspect of emission calculations.

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Symbols and abbreviations

$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulfate
A	Open surface area (cm ²)
BES	Bio-electrochemical systems
BOD	Biochemical Oxygen Demand
C	NH ₃ concentration in liquid balanced state (mg/L)
$\text{Ca}(\text{OH})_2$	Calcium hydroxide
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
D	Diffusivity
FO	Forward osmosis
FTIR	Fourier-transform infrared spectroscopy
GHG	Greenhouse gas
GPHM	Gas permeable hydrophobic membrane
H_2O	Water
J	Diffusion flux
k	Henry's law constant ($\frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}$)
LCA	Life cycle assessment
LKD	Lime kild dust
M	Molar mass NH ₃ (g/mol)
Mg	Magnesium
$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	Magnesium ammonium phosphate
N	Nitrogen

N_2	Dinitrogen
NH_3	Ammonia
NH_4	Ammonium
NH_4Cl	Ammonium chloride
NO_3^-	Nitrate
P	Air pressure (Pa)
PAX	Polyaluminium chloride
$PM_{2.5}$	Particulate matter
PO_4^{3-}	Phosphate
PPM	Parts per million
SS	Suspended solids
Total-N	Total nitrogen
Total-P	Total phosphorus
WWTP	Wastewater treatment plant
X	Molar fraction of NH_3 in air balanced state
x	Position
Φ	Concentration

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1 Introduction

Ammonia's (NH_3) wide applicability as a fertilizer has ensured that its use has increased exponentially over the last century. Although the agricultural use has dramatically increased, recycling of ammonia has remained a subtle debate. Ever more, the importance of ammonia emissions has risen into an unignorable topic. Thus, mitigation of ammonia emissions is not only necessary but should be on the forefront of mitigation research. (Cabello et al., 2009; Fowler et al., 2013)

Ammonia as a fertilizer works phenomenally, but in excessive amounts, it increases the eutrophication and acidification of waterbodies. Creating a lot of waterbodies with oxygen depletion causes loss in water biodiversity. Furthermore, when enriched with a lot of nutrients, increased formation of algae in the waterbodies deteriorates the water quality for fish.

To mitigate environmental impacts of ammonia, technological improvements are required. Recently, nutrient recovery methods such as membrane extraction, struvite precipitation and microalgae formation that are suitable for different purposes have seen accelerated development. Generally, cost, recovery efficiency, and end-product are the main factors considered before implementation. Aalto University project, NPHarvest offers a solution in the wastewater treatment sector. Contaminants in the wastewater, mainly ammonia and phosphorus, are recycled back as fertilizers which is cost-efficient and environmentally friendly. This results in significantly lower energy consumption in producing fertilizer and less ecological impact in the form of eutrophication and acidification. (Al-Juboori et al., 2022; Koskue et al., 2021)

Ammonia and phosphorus are recovered using the NPHarvest technology as two separate products. Only the extraction and recycling of ammonia (ammonia salt fertilizer) is the focus of this thesis. The process starts with a pre-treatment that involves increasing pH with lime and recovering nitrogen with ammonia transfer through hydrophobic, gas-permeable membranes. To create fertilizer, gas permeable hydrophobic membrane (GPHM) repels water and infuses ammonia gas with acid. The potential of the technology is seen in its low energy needs and tolerance of high suspended solids levels. Recycling ammonia using NPHarvest technology has ecological and energy-efficient benefits for producing ammonia fertilizers in the future.

NPHarvest small-scale pilot was tested in Öresund WWTP, Sweden in 2021. It had promising results regarding ammonia recovery. Life cycle assessment (LCA) was conducted on NPHarvest to see what environmental impacts it creates through various tests including environmental impact categories

such as climate change, eutrophication, acidification. The magnitude of the impacts is similar between NPHarvest and alternative technology, except for eutrophication and acidification where the latter resulted in significantly higher ammonia levels. For NPHarvest to be viable for large-scale use, an assessment of the overall impact on the environment needs to be addressed. (Högstrand et al., 2023) Therefore, the goal of this thesis is to research mitigating factors and the magnitude of their impact on ammonia and methane emissions.

The study examines the magnitude of emissions caused by the design and materials of the pilot. To properly examine the leading causes of emissions, a lab-scale version of the pilot is created to test the factors in a supervised laboratory condition. According to Högstrand et al. (2023), the open surface area of the large-scale pilot is seen as the largest culprit in the magnitude of emissions thus this research mainly focuses on the open surface area's impact on the emissions. Thorough examination of the process and the impact of the different factors on emissions is necessary to not only find an answer to NPHarvest technology and the high emissions according to earlier research but also to overall mitigate the emissions for a greener environment. Furthermore, feasibility of emission mitigation technologies needs to be assessed and implemented for sustainability purposes. Human population growth must be met through sustainable development while preserving our irreversible virgin resources.

These are the research questions this thesis aims to answer:

- 1) What impact does ammonia emissions from the implementation of NPHarvest technology have on the environment?
- 2) Which factors are most impactful to ammonia emissions?
- 3) What are the most efficient mitigating procedures?

Literature review (chapter 2) focuses on ammonia and methane emissions, as well as their effects on human health and environment. Moreover, it contains an introduction for the impact of ammonia-containing fertilizers use on eutrophication and acidification, treatment of ammonia-containing wastewater, mitigation procedures, and effective nutrient (N and P) recovery technologies available. Additionally, the chapter contains a lead-in to theoretical diffusion calculation background which uses mathematical tools derived from Henry's and Fick's law to compute diffusion. Material and methods (chapter 3) describes the experimental tests' equipment, materials, and procedures. Conducted test layout and different factors are described concisely in this chapter. As well as, a clear summary of the test schedule, parameters, properties (wastewater and chemicals utilized), and analysis methods. Results (chapter 4) shows the results of the conducted tests. The results obtained of ammonia and methane emission rates with different parameters are displayed and described. This

chapter also computes the experimental and theoretical emissions. In addition, there is a description of mass balance measurement findings. Discussions (chapter 5) analyses the impact of the computed ammonia and methane results. Evaluation of the contribution of different factors effect on emissions is considered throughout chapter 5. Furthermore, there is suggestions of improvement and feasible harvesting methods for ammonia mitigation.

2 Literature review

2.1 Nitrogen cycle

Nitrogen (N) has a vital role in guiding diversity and running ecosystems. N is a significant component in the production of amino acids which are essential in building protein and chlorophyll in the photosynthesis process. Yet, it occurs mostly as unreactive dinitrogen gas (N_2). N_2 is an odorless and colorless gas, which presents itself in water, soil, and atmosphere. Animals and plants cannot utilize N_2 as it is in gaseous form. However, microorganisms can biologically convert the N_2 gas into reactive nitrogen compounds such as ammonia and nitrate which are vital for crop production. As a compound, reactive N is mostly the product of microbial activities. Before the Haber-Bosch process, all the reactive N compounds were formed and recycled by microorganisms. However, in the recent century the production of nitrogen-based chemicals and products for agricultural purposes has been accelerated. (Fowler et al., 2013)

The nitrogen cycle is described as a development of element from atmospheric nitrogen gas to reactive compounds such as ammonia and nitrates, then back to nitrogen gas through various nitrogen transformation processes such as ammonification ($N_2 \rightarrow NH_3$), nitrification ($NH_3 \rightarrow NO_3^-$), denitrification ($NO_3^- \rightarrow N_2$), as simplified in Figure 1. (Bicking et al., 2019; Stein & Klotz, 2016).

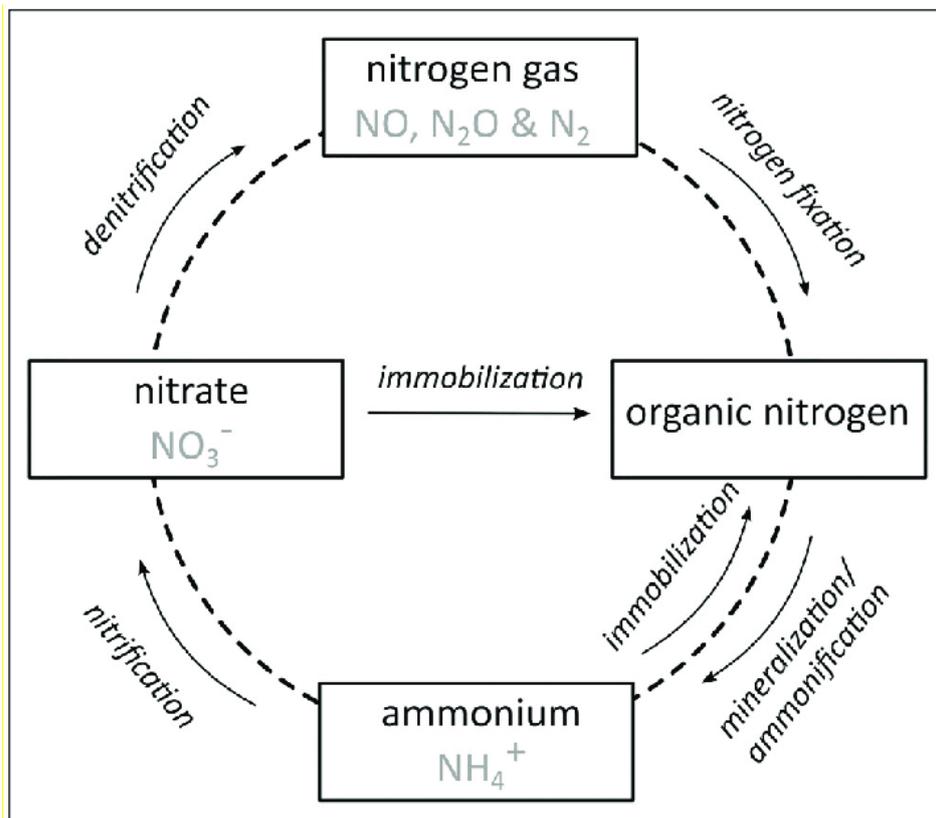


Figure 1. Nitrogen cycle (Bicking et al., 2019)

The global cycle of N has been heavily altered by human activities such as agriculture and use of fossil fuels which has increased N-based emissions impacting climate change. Fossil fuel combustion, fertilizer, and wastewater have been hot topics since having a direct link to the increase of emissions. The natural nitrogen cycle is changing rapidly, affecting biodiversity and human health. (Steffen et al., 2015)

2.2 Ammonia

NH_3 is the most widely produced inorganic chemical compound. NH_3 is a colorless and, in large concentrations, toxic gas with a distinct odor. It plays a significant role in food production since it is used as a fertilizer in the agriculture industry. Moreover, NH_3 is widely used in chemical products for industrial and household use. (Cabello et al., 2009)

Fertilizing has multiple applications such as improving plant growth, quality, and fertility. Ammonia fertilizer containing high nitrogen content is directly applied to the soil. It enriches the soil giving the plants the nutrients needed for growth. (Aziz et al., 2020; Fowler et al., 2013)

The solubility of ammonia depends on the temperature and pH of water. Ammonium (NH_4) is mostly encountered as an ion in liquids of pH 0-9. Higher than pH 9, ammonium in the liquid transforms into ammonia gas form (NH_3), as shown in Figure 2. (Cofie et al., 2016).

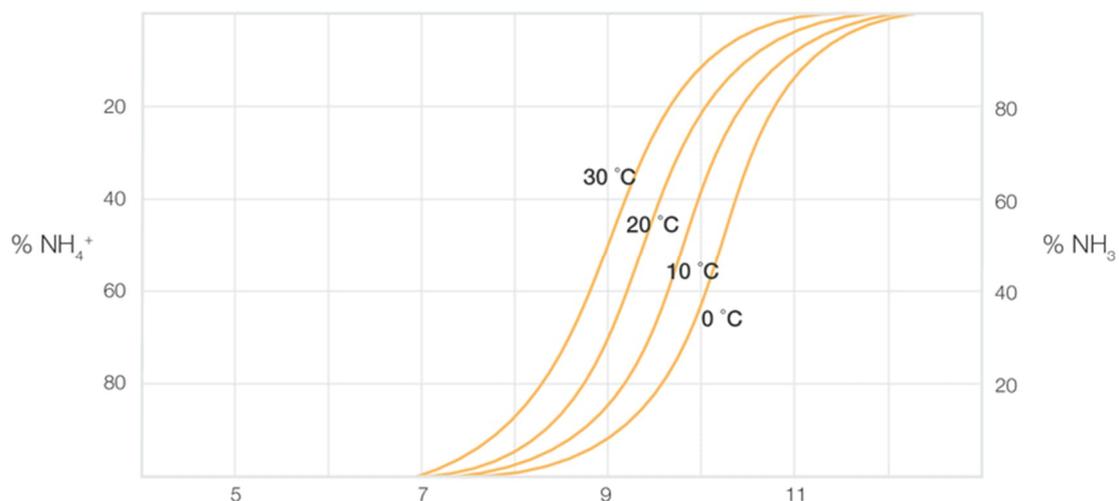


Figure 2. Ammonium ammonia equilibrium conversion. (Cofie et al., 2016)

Synthetic fertilizer production increased significantly after the 1960s. It is believed that this increase in fertilizer use is partly responsible for rapid world population growth. Currently, almost half of the

global population's food production is supported with synthetic fertilizers, as shown in Figure 3. (Erisman et al., 2008)

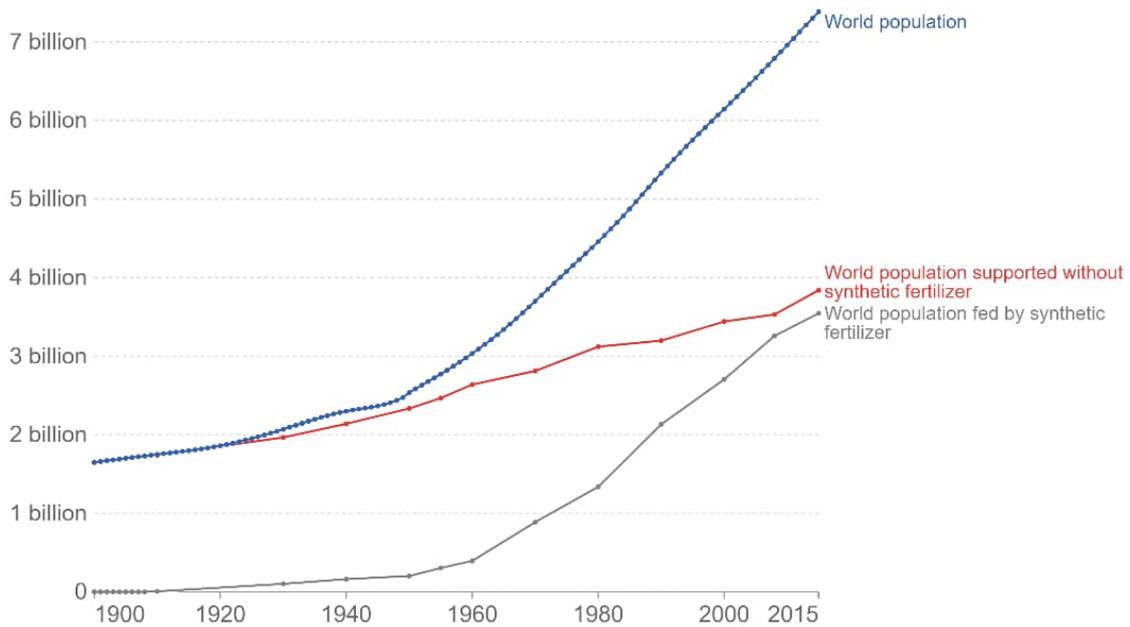


Figure 3. Nitrogen-based synthetic fertilizers support on world population growth (Erisman et al., 2008)

Ammonia is made from natural gas (methane), water steam (H_2O) and air. By removing water H_2O , CO_2 and other impurities, the extracted hydrogen and nitrogen gas are then carried to a reactor with high pressure and temperature where they form ammonia, as seen in Figure 4. In general, the Haber-Bosch process requires high temperature and pressure, following high energy consumption which impacts the environment.

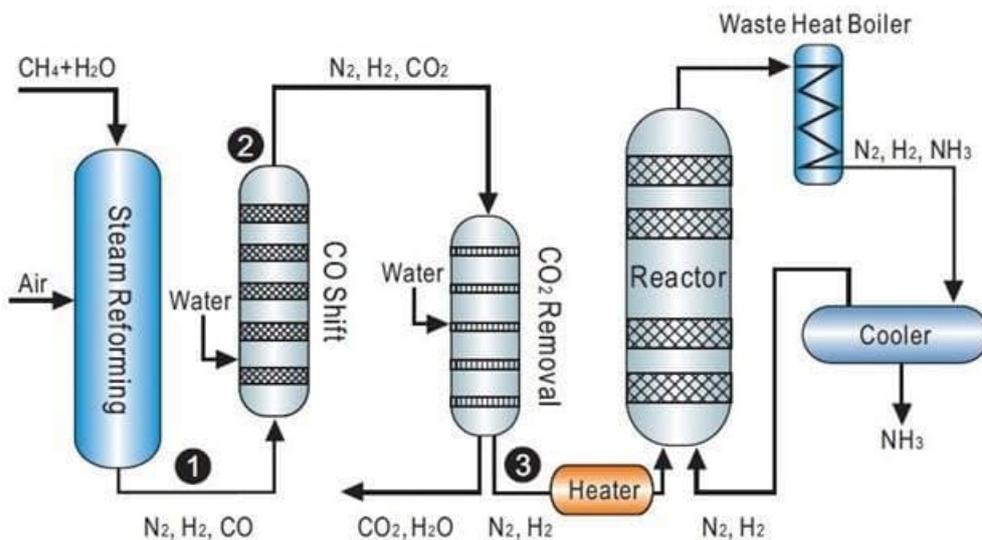


Figure 4. Ammonia production process (Ekejiuba, 2017)

Synthetic ammonia production was first properly implemented for commercial use in 1909 by Fritz Haber and Carl Bosch. This was a remarkable step for global ammonia production due to its simplicity and practicality. (Rouwenhorst et al., 2022)

The Haber-Bosch process revolutionized the industry of fertilizers. Not only did it increase the capacity to mass-produce fertilizers for crop production, but also commercialized the use of ammonia globally. However, this process emits a significant amount of greenhouse gases such as CO₂ relative to the product. (Rouwenhorst et al., 2022) Since Haber-Bosch process is highly dependent on high-energy consumption, which is derived from mainly fossil fuels, there is a rise of interest and need in alternative technologies that recycle ammonia to tackle the rising concern of climate change.

Due to the increasing demand for food production, ammonia fertilizer production is on the rise despite the known consequences. Feeding people worldwide is dependent on fertilizers, however, now it is essential to emphasize the recycling of ammonia to divert CO₂ emissions and other environmental pollution. (Ma et al., 2021)

According to Natural resources institute of Finland, almost 90% of Finland's ammonia emissions come from agriculture. In 2020, ammonia emissions from agriculture contributed 27,5 Gg-NH₃ per year, totaling 30,5 Gg-NH₃ per year in all sectors. (Luke, 2021) Ammonia emissions from agriculture are mainly from manure and inorganic nitrogen fertilizers. Since inorganic fertilizer production and use contribute to a large amount of NH₃ emissions, nutrient recycling is seen as a promising solution to mitigate high emissions. Organic fertilizers offer an option to use nutrients from waste sources with high content in P and N, and transform it into a commercially viable product for agriculture use.

An alternate to tackle the issue of rising ammonia fertilizer use and its impact in the environment is to bypass the phases where most energy consumption is used such as extracting elements nitrogen and hydrogen, heating, and pressure. By mitigating the energy consumption of making fertilizers, climate change impact is controllable. Nitrogen recycling decreases emissions with a process that uses wastewater containing ammonia which contains multiple subprocesses that recover ammonia and binds it into acid, forming ammonia-based fertilizer for agricultural use. Consequently, solutions to skip steps in nitrogen ammonia cycle requiring energy demanding processes, as seen in Figure 5 displaying the shortcut of the cycle. NPHarvest technology portrays promising capabilities for future regarding its high ammonia recovery efficiency. Direct extraction of ammonia from wastewater and its transformation into a fertilizer has significant positive environmental and economic impacts.



Figure 5. NPHarvest solution principle (Uzkurt Kaljunen, 2018)

2.3 Methane

Methane (CH_4) is a chemical compound which represents the main component of natural gas. CH_4 is a powerful greenhouse gas that has a short lifespan compared to its counterpart carbon dioxide CO_2 . However, excessive CH_4 poses a large threat to global warming and climate change. Its capability to trap heat is significantly higher than CO_2 . As a concentration in air, CH_4 is regarded to have a global warming potential of 25 that of CO_2 . CH_4 has a remarkable impact on air quality and human health, and it is known to cause direct and indirect damage to biodiversity and ecosystems. (UNFCCC, 2022) Thus, it is important to emphasize and evaluate the role of its environmental impact combined with ammonia emissions. (Mar et al., 2022)

The concentration of CH_4 continues rising globally. In 2020, annual methane emissions contributed around 8 200 000 (kt of CO_2 equivalent). In Finland, this value is around 4 600 (kt of CO_2 equivalent). (World Bank, 2022; WRI, 2020)

According to the IPCC. (2021), third of recent global warming since industrialization started has been caused by CH_4 emissions. The most prominent sectors contributing to methane emissions are gas production/distribution, agriculture, and landfills. Therefore, it is necessary to consider the largest sectors contributing to CH_4 emissions to mitigate globally. (IEA, 2022)

2.3.1 Methane emissions from wastewater treatment

In 2010, wastewater-related methane emissions contributed around 7% of all methane emissions worldwide. Municipal wastewater is treated throughout treatment process emitting methane due to anaerobically decomposed organic material. For the collection and treatment of municipal

wastewater, most developed nations use centralized aerobic wastewater treatment facilities. The systems existing in underdeveloped nations with little wastewater collection and treatment tend to be anaerobic, which increases methane emissions. (GMI, 2013)

2.4 Theoretical diffusion calculations background

2.4.1 Diffusion

According to Henry's law, the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid. Henry's number can have different units depending on how the concentration of ammonia in the liquid phase is expressed. Usually, it is either expressed as a molar fraction or concentration (mg/L). The mole fraction is the result of the number of molecules of a certain component in a mixture and its total molecular weight. It is a means to convey how concentrated a solution is.

Henry's formula:

$$C = kP \tag{1}$$

Where,

C = Concentration of a dissolved gas

k = Henry's law constant

P = Partial pressure

M is the mass concentration of dissolved gas in the liquid, and C is the saturation concentration at equilibrium. A transfer term from the gas to the liquid causes a change in the oxygen content in the liquid phase over time. Only one equation is considered for the entire volume of liquid since it is assumed that the liquid is well mixed, and the parameters k and C are utilized as their average values in the column for computation. The oxygen molar fraction X can be used to calculate the oxygen concentration in the gas phase C using the ideal gas equation. (Larsson et al., 2022)

Mass transfer equation is a derived Henry's formula which combines the concentrations of the liquid and gas in the equilibrium state through Henry's constant, in more detail in Larsson et al. (2022). The

purpose of the mass transfer equation is to theoretically determine the saturated state concentration of ammonia emissions, seen in equation (2) as X. This enables us to calculate the theoretical emission rate of ammonia.

Mass transfer equation:

$$X = \frac{C}{k * P * M} \quad (2)$$

Where,

C = NH₃ concentration in liquid balanced state (mg/L)

k = Henry's law constant ($\frac{mol}{m^3 * Pa}$)

X = Molar fraction of NH₃ in air balanced state

M = Molar mass NH₃ (g/mol)

P = Air pressure (Pa)

This is a simplified equation lead from Henry's law which can be used to determine the ammonia concentration in air balanced state e.g., saturated state of ammonia in air.

Henry's law constant is the proportion of a compound's concentration in water at a particular temperature to its partial pressure in air, at equilibrium state. The constant depends on the nature of the gas, liquid, and temperature. The solubility of the gas in the liquid increases with an increase in Henry's law constant at a certain pressure. Literature indicates that Henry's constant for calculating the concentration of ammonia in balanced state depends widely on source used. Multiple Henry's law constants are in use depending on the source mostly ranging between 0.6-0.7 mol/(m³*Pa). This paper uses 0.74 as Henry's constant for ammonia value which is most suitable for conditions of NPHarvest technology. (Sander, 2015)

2.4.2 Theoretical diffusion

Theoretical diffusion is conducted as a revision to ensure correlation of experimental diffusion results. To calculate theoretical diffusion rate, Fick's law states that the solute moves from higher concentration to lower concentration across concentration gradient.

Fick's law connects the gradient of the concentration to the diffusive flow. It proposes that the flux moves across a concentration gradient from areas of high concentration to areas of low concentration,

with a magnitude that is proportional to the gradient (spatial derivative), or, put more simply, the idea that a solute moves from an area of high concentration to an area of low concentration.

$$J = -D \frac{d\phi}{dx} \tag{3}$$

J: diffusion flux

D: diffusivity

ϕ : concentration

x: position

The concentration gradient ($\text{mol/m}^3/\text{m} = \text{mol/m}^4$) is movement concentration (mol/m^3) from high concentration area to low concentration divided by the gradient length. Diffusion coefficient depends on the compound (ammonia and methane) and varies depending on the reference. Fick's law equation estimates the diffusion flux which calculates the rate of ammonia emissions per unit of time.

2.5 Effects of ammonia emissions

2.5.1 Eutrophication and acidification

Fertilizer production and usage creates a lot of environmental toxins such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). This has many effects such as decrease in aquatic biodiversity, reduced soil fertility, and global warming. (Kumar et al., 2023)

The process of eutrophication involves the gradual enrichment of a body of water with minerals and nutrients, especially nitrogen and phosphorus which is accelerated by fertilizer runoff. This nutrient pollution foster the growth of algae and aquatic plants. (Doster et al., 2013) Algae has a distinct smell, interferes with sunlight penetration, and releases toxins harming the wildlife of the aquatic habitat. After the algae is broken down by microorganisms, the waterbody becomes oxygen depleted. (Wagner et al., 2021)

Primarily, acidification occurs when acidifying gas oxides are absorbed into a waterbody. One of the main contributors for acidification is nitrogen (NO_x) oxides. Acidification threatens the aquatic ecosystem and affects populations which rely on it as a source of nutrition and income (EBS, 2022) When pH levels decrease, the higher acidity in the waterbodies affects biodiversity. This is seen in

weakening of coral reefs which affects the stability and sustainability of food chains in the aquatic ecosystems. (Wagner et al., 1053)

2.5.2 Health effects

Ammonia volatilization increases the risk of high concentration exposure that causes damage to human health. When exposed to NH_3 , the most common health issues are eye, nose, and throat irritation, nausea, cough, chest tightness. Long-term effects include impairment of respiratory and cardiovascular functions, even proved to cause premature death. (Aziz et al., 2020; Fowler et al., 2013)

Agricultural NH_3 can be harmful to human health when inhaled directly, but when considered as a precursor to particulate matter ($\text{PM}_{2.5}$), it has a considerably larger potential to do so. $\text{PM}_{2.5}$ has particles that, when breathed, can reach the thoracic area of the respiratory system. Exposure to $\text{PM}_{2.5}$ pollution increased the chance of early death and deteriorating health, as well as illnesses like asthma and heart disease. (Wyer et al., 2022)

2.6 Wastewater

Wastewater is water containing contaminants from municipal or industrial uses. Municipal wastewater contains high content of P and N which are derived mostly from feces and urea. The treatment process's purpose is to remove contaminants and prevent their entry to natural environment. These contaminants/pollutants include but are not limited to nutrients (N and P), BOD and TSS. Phase separation, biological, and chemical processes are utilized in the treatment of wastewater. The basic goal of wastewater treatment is to enable safe disposal or re-use of the treated wastewater. After the removal of contaminants from wastewater, effluent is recycled back into the water cycle. Effluent is treated so that it has a tolerable impact on the environment when disposed.

The solid or slurry residue material of the wastewater treatment is called sludge. Sludge is removed using various treatment processes which settle and separate sludge from wastewater. After the separation, sludge is either digested or otherwise stabilized. Digestion produces a digestate that is further separated into solid and liquid fractions. The liquid fraction is called reject water and it typically has high nutrient content. (Seruga et al., 2019)

Wastewater's NH_3 is carried down to the wastewater treatment plant (WWTP) for treatment. After the treatment process part of N is untreated which is then discharged to nature, causing acceleration of eutrophication, acidification in aquatic ecosystem, toxicity in waters, and even contamination of ground water. (Seruga et al., 2019) Thus, efficient removal of N in the WWTP processes is required not only to decrease climate change effects but also to mitigate impact on human health.

Blackwater

Blackwater contains contaminants from toilet such as feces, urine, and other compounds generated mainly from toilets and kitchen. Compared to reject water, blackwater has similar attributes like high nitrogen and organic matter concentration.

Reject water

Wastewater streams that are high in nitrogen result from the dewatering of anaerobically digested municipal sewage sludge. Due to the internal cycling inside treatment facilities, they represent up to 25% of the overall nitrogen burden of wastewater treatment. (Koskue et al., 2021) Dewatered digestate's solid portion is thought to have 7–20% of the nitrogen still present, with reject water holding the remaining 80%. About 2% of the influent flow of the wastewater treatment plant is made up of reject water. The recirculated reject water significantly increases the nitrogen load in the influent. (Janus & van der Roest, 1997) Reject water, seen in Figure 6, is the liquid fraction of the digestate that has been dewatered after anaerobic digestion of waste sludge. Due to its high N concentration, reject water is sometimes processed through biological processes to recover/remove N before being disposed of correctly.



Figure 6. Reject water in the bucket

2.7 Ammonia recovery methods

Recovery

The method of collecting nutrients from wastewater that would otherwise be wasted, such as nitrogen and phosphorus, and turning them into an environmentally acceptable fertilizer utilized for ecological and agricultural reasons is known as nutrient recovery. Nutrient recovery is beneficial for decreasing disturbance in the nutrient cycles and depletion of scarce virgin resources.

2.7.1 Recovery methods

N recovery from wastewater can be achieved using technological solutions, each having their advantages and disadvantages. Methods can be divided into two sections: physic-chemical and biological harvesting methods.

2.7.1.1 Physic-chemical methods

Ammonia stripping is mainly used for reject water treatment with high ammonia concentrations. Ammonium nitrogen transforms to its gaseous form when pH and temperature increases. Figure 7 demonstrates the process of ammonia stripping. NH_3 gas and air is segregated by the stripper to be transferred to ammonia scrubber with sulfuric acid (H_2SO_4) with a 90 % absorption rate, product being ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ fertilizer which is low in pH and suitable for agriculture use. Nevertheless, this technology is very energy demanding compared to other methods. (Capodaglio et al., 2015)

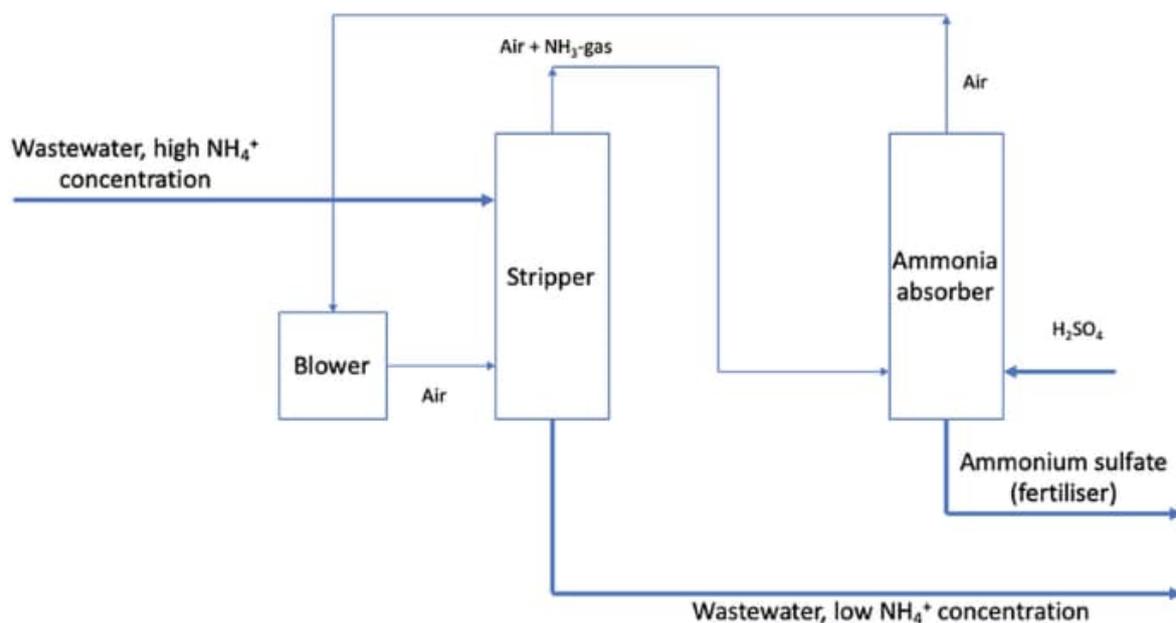


Figure 7. Ammonia stripping process (Lorick et al., 2020)

Struvite precipitation is known for P recovery. However, from the nitrogen perspective a large quantity of ammonium is recovered in this process. Struvite is a crystallized mineral which is composed of phosphate (PO_4^{3-}), ammonium (NH_4), and magnesium (Mg) with the chemical formula of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, also known as magnesium ammonium phosphate hexahydrate (MAP). The

process is highly dependent on the pH and ratio of PO_4^{3-} , NH_4 and Mg. However, enough Mg needs to be added to wastewater to get N:P:Mg molar ratio right for efficient struvite precipitation. Thus, by adding enough Mg the limiting factors depend on which of the concentrations of PO_4^{3-} and NH_4 are higher to limit the reaction. Struvite has a high ammonia nitrogen recovery rate and lower chemical price for harvesting than other methods. Struvite is a slow-release fertilizer with potential due to its mild contaminant rate. Recently, struvite's attributes as a fertilizer have been studied profoundly, finding promising results. The capability to replace phosphate rock is considered one of the main advantages due to its availability. (Lorick et al., 2020b)

Forward osmosis (FO) is one of the methods that can be applied to extract ammonia. FO is low-pressured membrane system process that can be used to separate neutral compounds such as ammonia from solutions. Nevertheless, this method requires the wastewater to be high in ammonia and low in organic matter concentrations. Human urine is the most suitable wastewater type, however, collection of urine alone as wastewater is rare. Moreover, at best, the recovery efficiency rate is about 50-86% depending on the method. The higher efficiency rate can be achieved with a proper pH level handling between the recovery barriers of both feed and draw containers, which add costs. Concisely, FO membrane recovery method has economic potential due to its low costs. (Ray et al., 2020)

Zeolite adsorption method involves an ion exchange process which removes NH_4 from wastewater. Ammonium recovery efficiency of about 80% can be achieved with optimal circumstances using wastewater streams. There are many applications for the product, main one being different fertilizer products and industrial cleaning gas. Zeolite technology, however, is highly advanced with a relatively high cost. (Manto et al., 2018)

2.7.1.2 Biological methods

Microalgae production recovers nutrients by growing in the wastewater. Nutrients such as ammonia and phosphorus are removed through the formation of microalgae in the wastewater. The generated microalgae biomass is utilized in fertilizer and biofuel production. The benefits of microalgae are rapid growth-rate, less greenhouse gas (GHG) emissions and binding of CO_2 . For this method to be applicable, it requires prerequisites of optimal warmer growth conditions and UV light which is challenging in the Nordics especially in winters. Furthermore, this technology is yet to be applied in large-scale application due to lack of development. (Brück et al., 2019)

Bio-electrochemical systems (BES) technical properties are based on the interaction of electron acceptors and the contaminants in wastewater. Electricity in the electrodes promote a chemical reaction where microorganisms degrade. There are two kinds of BES treatment methods: cathode-supported and cathode-stimulated treatment. The former is used to directly reduce compounds and

the other removal method accelerates the process algae growth or oxidant production for membrane treatment. (Jain & He, 2018)

BES is a successful technique for eliminating industrial wastewater's high concentrations of organic compounds and ammonium under ideal operating circumstances. The ammonium removal can achieve efficiency up to 94%. (Rahmani et al., 2020) However, BES alone has limited treatment efficiency for the effluent to be discharged. Therefore, this method is not widely used and practiced. Moreover, the process is highly dependent on high energy costs which decrease the viability of its use. (Jain & He, 2018)

2.8 Membrane-based technology

The Water and Environmental Engineering Research Group at Aalto University in Finland has created an innovative technique called NPHarvest that recovers N and P in distinct products, the first of which is a pure ammonium salt and the second is a P- and calcium-rich sludge-like product. The method relies on pre-treatment that involves P precipitation and pH elevation through lime addition which enables efficient ammonia recovery through gas-permeable hydrophobic membranes (GPHM). This works by repelling water and absorbing ammonia gas into acid as seen in Figure 8. The separated ammonia gas is carried to an acidic container in which ammonia gas binds with sulfuric acid forming ammonium sulfate. It has different applications but most notably used as a fertilizer in agricultural use. Although there are other technologies developed for similar membrane separation, NPHarvest process is comparably highly efficient and relatively fast process that has a recovery efficiency rate of about 80% in optimal circumstances. Furthermore, this process is very suitable for Nordic environments due to lack of warm temperatures requirements.

Microporous gas-permeable membrane

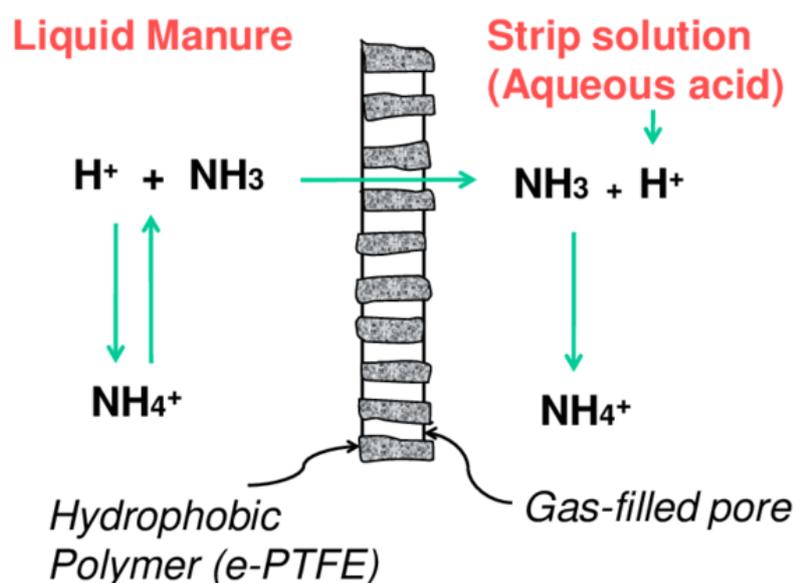


Figure 8. Ammonia gas harvesting through gas-permeable membrane principle (Vanotti & Szogi, 2011)

A more detailed description of the process is found in Al-Juboori et al. (2022), explaining the NPHarvest technology thoroughly.

pH has an important role in converting ammonium ions into ammonia in the water. As in Cofie et al. (2016), with normal room temperature of 20 degrees Celsius at pH 10 which were the conditions of the lab testing settings, about 80% of the ammonium has converted into ammonia. All the ammonium ions convert into ammonia over pH 11. To extract the ammonia through the membrane, ammonia needs to be in volatile form. This can be achieved by chemical procedure which increases the pH so that the ammonium in the liquid transform into ammonia gas. Soluble ammonia gas passively transitions through the membrane into an acid forming fertilizer.

3 Material and methods

3.1 Equipment

The tests are conducted in Water building laboratory of Aalto University, Espoo. The facility provides the optimal environment for small-scale laboratory testing that replicates NPHarvest pilot tank characteristics from which NH_3 and CH_4 emissions are released.

The large-scale NPHarvest pilot that was used in Viikinmäki and Sweden is displayed in Al-Juboori et al. (2022) and Högstrand et al. (2023). It processes roughly 100 L/h and includes various parts that treat wastewater, from tanks to centrifuges that work together to extract ammonia through GPHM. In the large-scale pilot system, largest tank's volume is roughly 500L which works as a slow mixing tank. Tank has an open surface area from where the emissions leak. Although the exact size of the open surface area is unknown, tests help to gain insight on the magnitude of emissions.

To simulate similar conditions as in the NPHarvest pilot in Sweden, a simplified version of the pilot was created to simulate the large tank from which the ammonia gas leakage occurs. The large tank is simulated with a bucket that mixes wastewater thoroughly throughout the process. The volume of air needs to be limited to efficiently measure the magnitude of emission and concentration leaking from the tank. Closed-vessel, container, is most suitable for this testing; it enables measuring and keeps the emissions in a closed space. This simplified small-scale test setup simulates the large tank and the air space that the air leaks.

The size of the container is 230L and inside it is 10L or 30L buckets which are filled with 5L of wastewater. Tests were executed inside the container that is put on top of the buckets to seal all the gases inside, as seen in Figure 9. This represents the equivalent of the large-scale tank from the pilot. Gas analyzer tubes measure gases such as ammonia and methane through a small hole seen on top of the container, seen in Figure 10. Creating similar conditions used in NPHarvest pilot in Sweden, is the key to obtain understanding of the magnitude of emissions and factors effect.

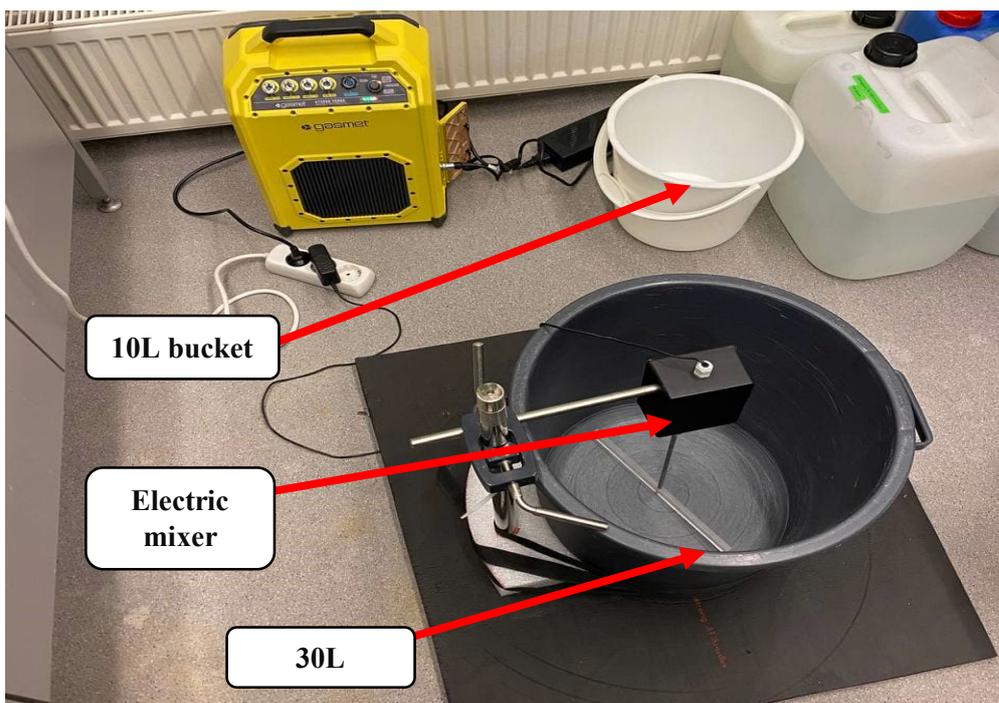


Figure 9. 30L grey bucket or 10L white bucket and electric mixer.

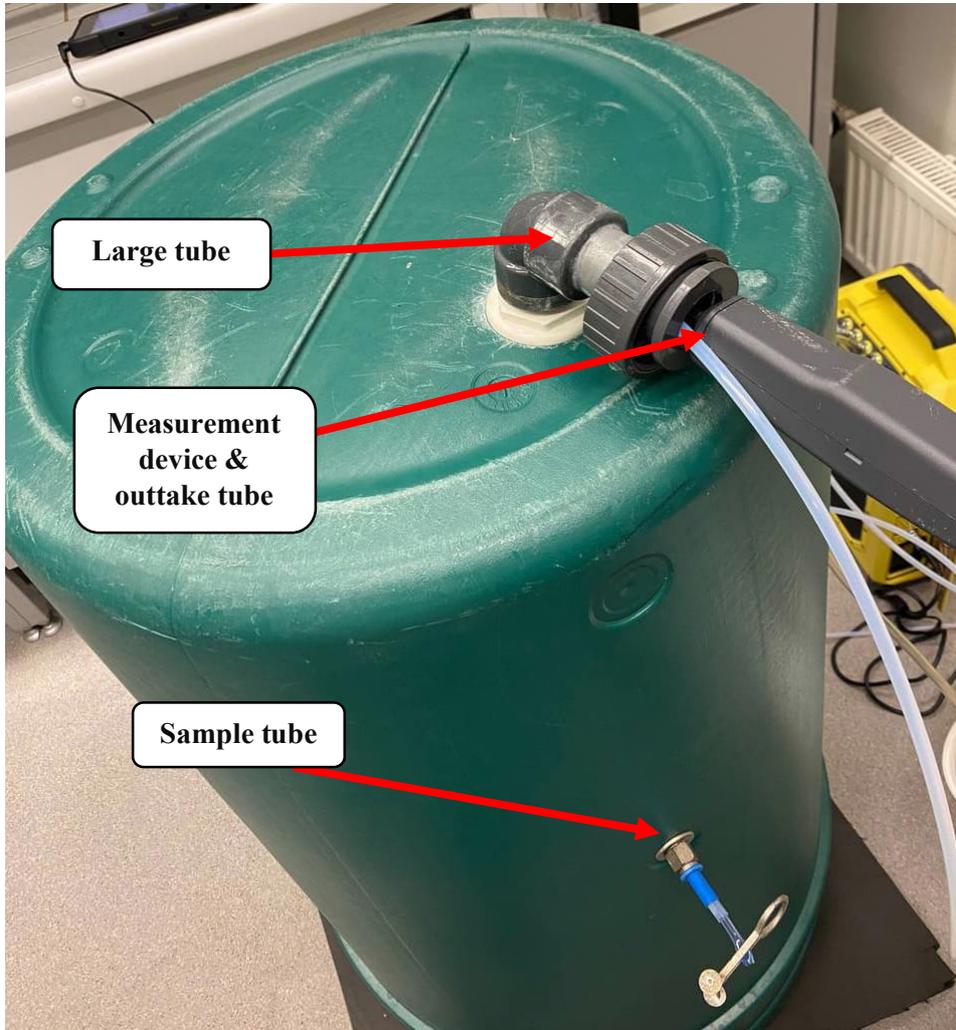


Figure 10. The container. Measurement device (capturing and carrying air samples to analyzer) and outtake tube (returning air samples back to container) are plugged airtight inside the large tube. Sample tube is squeezed airtight for sampling the wastewater.

By having a limited air volume as the container, the magnitude and rate of emission can be experimentally measured and theoretically calculated. The difference is that facility in which Sweden's pilot tests were conducted, emissions were ventilated with air conditioning which stopped the gases from accumulating and reaching a saturated state. This measurement method produces lower emission rates because the concentration of the gas phase increases. However, to properly measure the magnitude of emissions is to trap all the gases inside the container for measurement. The container is large enough to simulate the facility air space. Thus, the gas leakage that occurs in large-scale pilot is possible to be measured with the container in small-scale laboratory tests. For measuring the ammonia emissions rate and amount, Gaset, a gas analyzer is used for measuring

the gas concentration. This small-scale setup simply simulates the tank part of which the ammonia leaks outside in the large-scale process.

The main component of the system is the gas analyzer which has tubes (measurement device and outtake tube) installed in the large tube, as seen in Figure 10. There is a measurement tube that intakes the air and carries it to the analyzer which analyzes the sample of air consisting of different compounds. When analyzed inside the Gasmeter analyzer, it sends back the gas to the container via outtake tube, keeping the gas pressure balanced and possible to reach saturated state. This ensures that minimal to no gas leaking occurs.

Chemical dosing is conducted using different sizes of syringes and cups. A weight scale is utilized to ensure the chemical dosing is precise. The wastewater dosage of 5L is verified and transferred using a graduated cylinder. For mixing, the wastewater is mixed with a magnetic mixer in 10L bucket and larger electric mixer for 30L bucket due to the size different. These two different mixers are used to ensure good quality mixing throughout the bucket. The mixing speeds are matched for both buckets for consistency and simplicity in the results.

3.2 Parameters

NPHarvest's ammonia emissions are impacted by the following factors: wastewater (reject water & ammonia water), chemicals, mixing speed and surface area exposed. Testing how these parameters affect emissions helps with understanding the mitigation process and should give indication on the amount of emission each factor contributes in the larger-scale pilot to mitigate emissions. For the tests to be consistent, other factors like temperature, liquid density, humidity, pressure, surface area must be constant.

To efficiently simulate the conditions in the NPHarvest pretreatment phase where the ammonia emission leakage occurs, it is necessary to create a similar environment. All the possible factors that affect the amount of emissions should be considered in testing. The measurement is executed with 10L and 30L buckets to help us analyze whether dimensions of the bucket influence the magnitude of emissions. Inside the container, a bucket filled with 5L of wastewater (reject water or ammonia water) is constantly stirred with the mixer. Chemicals are added to the wastewater mixing in the bucket upon which the container is placed to seal the gases inside for measurement. Simultaneously, the analyzer starts its measuring process. Figure 11 displays the layout of the test process. The data of emissions are collected into the software of the Gasmeter portable tablet. This data is available to be analyzed with computer software such as Excel for further detailed analysis.

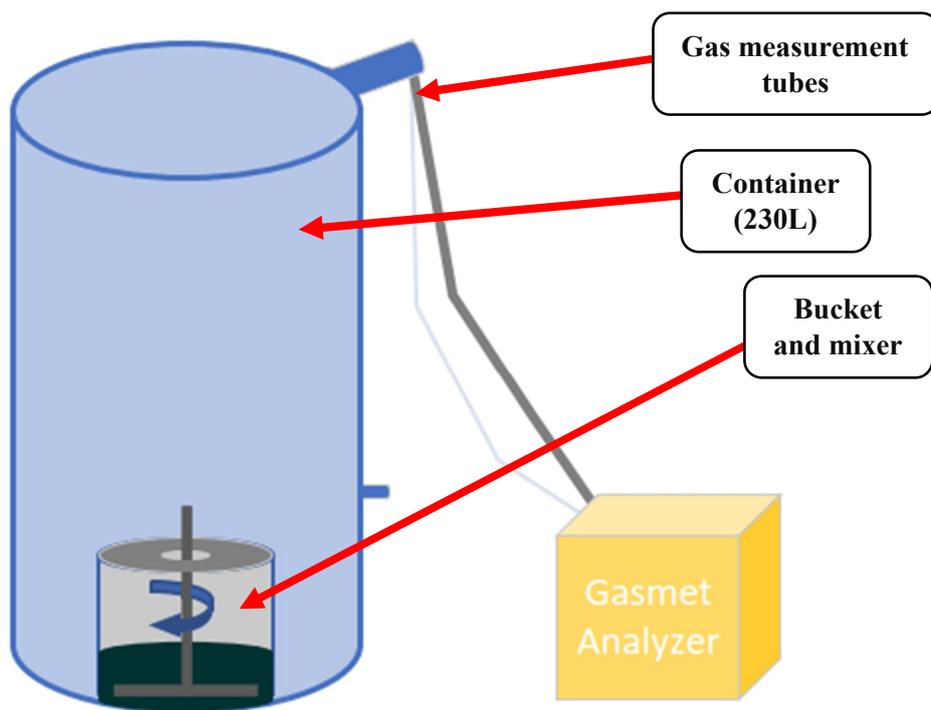


Figure 11. Water lab test layout.

Although many factors are considered to affect the magnitude of emissions, open surface area is seen as the largest emission contributor due to it being a limiting factor which adjusts the possible gas magnitude escaping outside of the tank. Thus, the tests focus on the open surface area's effect on the rate of ammonia and methane emissions. Consequently, surface area was monitored very closely and emphasized on all tests. Different surface area sizes are tested to find out their correlation to emission rate. The surface areas in the first tests include 1017 cm^2 (36cm diameter), 530 cm^2 (26cm diameter) and with a lid on top 3.1 cm^2 (2cm diameter) open surface areas. The 30L bucket has a 36cm diameter open surface area and with a lid on top, 2cm diameter hole. 10L bucket has a 26cm diameter open surface area and a lid with a lid on top, 2cm diameter hole. The 2cm closed lid test, seen in Figure 12, allows us to obtain data on the magnitude difference in ammonia emissions for smaller open surface areas.

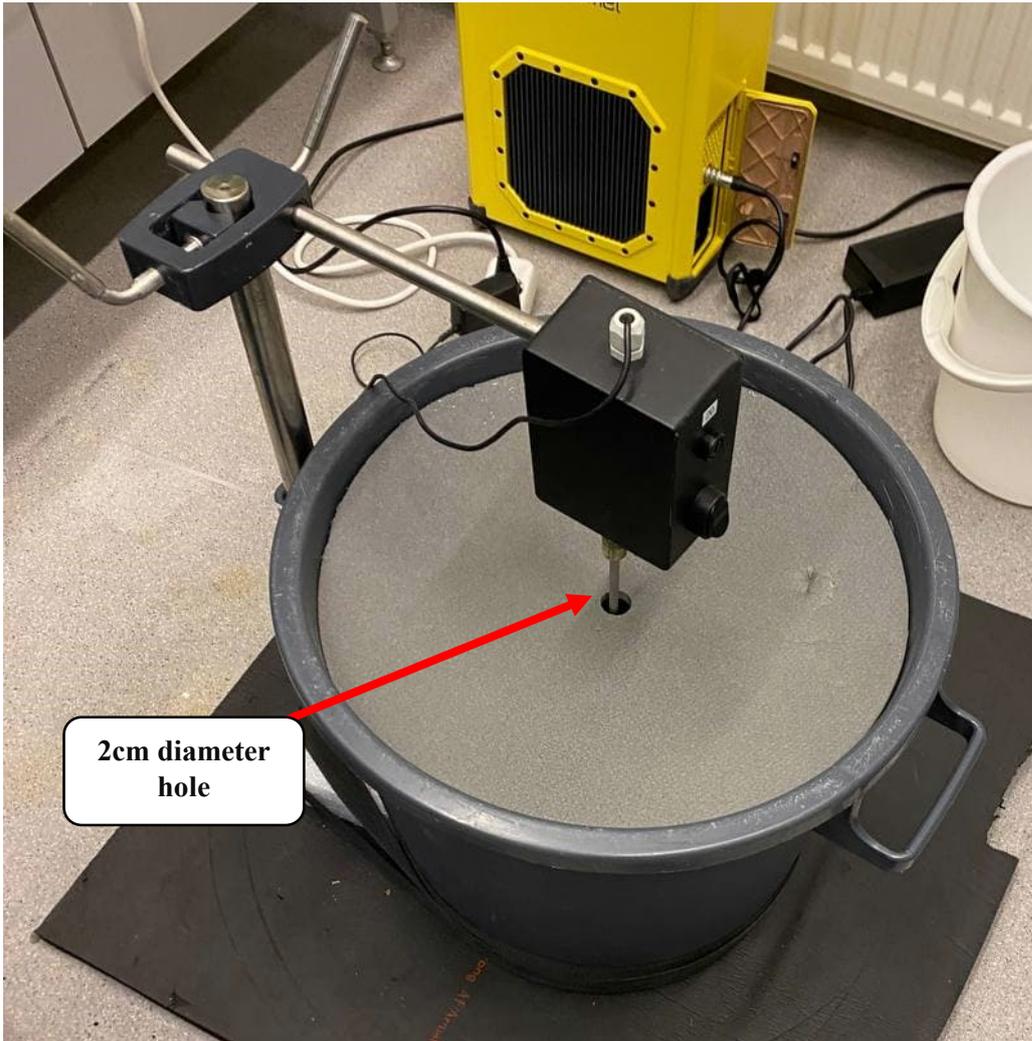


Figure 12. Closed lid (2cm) test.

Tests are run with same parameters of pH, reject water, and chemical mix. The saturation tests are performed with 200cm^2 (16cm diameter), 50cm^2 (8cm diameter), and 3.1cm^2 (2cm diameter) open surface areas. These surface areas were adjusted with measuring tape and cropped accordingly forming a lid with different open surface area holes as in figure 12. Testing with different open surface areas may offer an explanation whether air volume for saturation has significant differences in emission levels. The realistic open surface area of the large-scale NPHarvest pilot tank has a hole between the size of 2cm to 16cm diameters. If the lid of the large-scale pilot is sealed properly, the only open surface area is in between the mixer rod and the gap. The gap is a maximum of 16cm diameter hole inside of which the mixer rod rotates. This decreases the open surface area for emissions to escape. Thus, testing the 16cm diameter hole in small-scale tests is done to find out the worst-case scenario of magnitude of emissions although realistically the surface area is smaller.

In Figure 2 displaying the equilibrium of NH_4 and NH_3 , higher pH ensures that most of the ammonium has converted to ammonia. In the large-scale pilot the pH runs between pH 10 and pH

11. According to the Cofie et al. (2016) however, higher level than pH 11 is not necessary since all the ammonium has converted to ammonia. Thus, pH 10 and pH 11 are both tested in the tests to discover the effect on the magnitude of magnitude and rate of emissions.

Wastewater types (reject water and ammonia water) are tested for comparing the wastewater's effect on the emissions. Reject water was brought from Viikinmäki WWTP in Helsinki. Ammonia water was produced in the laboratory by adding ammonium chloride (NH_4Cl) in sufficient amount for the NH_4 concentration to match reject water NH_4 concentration. This is done to ensure simplicity in the result analysis. 3.8 g/L of NH_4Cl is added to tap water to produce ammonia water of 800 mg/L NH_4 concentration. The ammonium concentration in both reject water and ammonia water is 800 mg/L.

Wastewater samples are gathered and analyzed to provide data of ammonia concentration in the liquid. These wastewater samples were collected with a syringe from a tube connected to the bucket inside the container, as seen in Figure 10. Samples should provide data of the correlation with the ammonia concentration in the air. Logically, the more ammonia concentration is dissolved into the air in the system the less it should be in the liquid. Results of the samples can ensure accurate information of the amount of ammonia emitted.

3.3 Schedule

All the tests performed included either reject water or ammonia water and the correct chemical mix. 2-hour tests contained 4 types of variables in the open surface area that are mentioned in Table 1 to 3 for comprehension.

2-hour tests open surface area:

Table 1. bucket diameter, closed lid.

30L bucket (36cm diameter)
30L bucket (36cm diameter), closed lid (2cm diameter)
10L bucket (26cm diameter)
10L bucket (26cm diameter), closed lid (2cm diameter)

Ammonia water tests

Table 2. Ammonia water, ammonia emissions tests.

Parameters	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
<i>Diameter (cm)</i>	36	36	36	36	26	26	26	26
<i>pH</i>	10	11	10	11	10	11	10	11
<i>Lid open/close</i>	open	open	closed	closed	open	open	closed	closed

Reject water tests

Table 3. Reject water, ammonia emissions tests.

Parameters	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
<i>Diameter (cm)</i>	36	36	36	36	26	26	26
<i>pH</i>	10	11	10	11	10	11	11
<i>Lid open/close</i>	open	open	closed	closed	open	open	closed

The tests are run for 2-hour period from which the wastewater samples are taken every 30 minutes from every test conducted. Overall, 4 samples were taken in the 2-hour test period.

24-hour saturation tests:

Table 4. Reject water 24-hour saturation tests.

1. 30L bucket: pH11: Closed lid (16cm diameter)
2. 30L bucket: pH11: Closed lid (8cm diameter)
3. 30L bucket: pH11: Closed lid (2cm diameter)

Three saturation tests are performed with reject water. Same factors (chemical mix, pH and 30L bucket) are applied except open surface area size which is modified accordingly seen as diameters in table 4. This helps to gain insight of the rate of emissions and the saturated state emission curve.

Samples of gas are taken for measuring in sufficient intervals, every 4 minutes for 24 hours. Unlike the 2-hour tests, 3 liquid samples are taken in the 24-hour run, 2 in the first hours and one in the last hour for gaining insight on the consistency of concentration.

3.4 Properties

Chemical used for wastewater pH adjustment is calcium hydroxide Ca(OH)_2 . Ca(OH)_2 is the only chemical used in ammonia water tests. The tests performed with reject water were carried out with a chemical mix which includes Ca(OH)_2 + LKD (Lime kild dust) + PAX (polyaluminium chloride) + SuperFloc A120 due to solid matter content. 0.4 mg/L of Superfloc A120 is mixed with water (H_2O) to create a solution from which 4 mL/L is added into the chemical mix. Large-scale processes use this chemical mix to flocculate solid matter and separate the mix into phases, high solid content and other with high liquid content. Chemicals were added at the same time. Thus, adding all the chemicals consecutively to the wastewater simplifies our small-scale testing.

In order for the NH_4 to transform into NH_3 , the pH-level needs to be around 10-11. Determining the proper dosing to obtain optimum pH-level requires testing beforehand. Lab analysis was conducted to test the right amount of chemical to reach pH 10 and pH 11 in both blackwater and reject water. The main chemical that controls the pH is Calcium hydroxide Ca(OH)_2 thus the dosing was primarily focused on the dosing of Ca(OH)_2 . The dosing is based on the average of the tests performed to determine the average dosing needed to reach pH 10 and pH 11. Other chemical such as Superfloc, PAX, and LKD for the flocculation were used in Viikinmäki NPHarvest pilot for reject water tests. The dosages of these chemicals are applied to our reject water tests according to the operation process documents that were used while piloting in Viikinmäki. Chemical dosages can be seen below in Table 5.

Chemical dosages

Table 5. Chemical dosages.

Chemicals	Ammonia water	Reject water
Ca(OH)_2	2.2 g/L=pH10 : 2.8 g/L=pH11	5 g/L=pH10 : 5.4 g/L = pH11
LKD (Lime kild dust)	-	1.0 g/L
PAX (polyaluminium chloride)	-	1.8 g/L

Superfloc A120	-	4 mL/L of solution (0.4 mg/L of A120 mixed with H ₂ O in the solution)
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Ammonia water properties

Reject water properties:

Table 6. Reject water properties. Reject water collected from Helsinki's Viikinmäki WWTP.

pH	8.03
Alkalinity (mmol/L)	72
Total-P (mg/L)	11.7–15.8
Total-N (mg/L)	861
NH ₄ -N (mg/L)	816
SS (mg/L)	1460–1670
BOD (mg/L)	706–381
COD (mg/L)	2523

3.5 Analysis methods

List of standards used as analyzing methods.

Table 7. List of standards used.

pH	SFS-EN ISO 10523, v. 2012
Alkalinity	SFS-EN ISO 9963-1, v. 1996
Total-P	21 st edition, 2005, 4500-P E
Total-N	Total organic carbon analyzer with total nitrogen measuring unit, Shimadzu TOC-L + TNH-L + autosampler (Shimadzu TOC-LCSH/CSN)
NH ₄ -N	SFS ISO 15923-1:2018 Water quality. Equipment used: NH ₄ analyzer & BluVision analyzer (Skalar)
SS	SFS-EN 872, v.2005
BOD	OxiTop manual, SFS-EN 1899,1, v. 1998

COD	SFS 5504, v. 1988
pH	SFS-EN ISO 10523, v. 2012

3.5.1 Differences in ammonia analysis methods

BluVision analyzer (Skalar) is an automatic analyzer which produces accurate results. The BluVision Discrete Analyzer offers total automation for colorimetric tests of ammonia, nitrate, nitrite, ortho phosphate, sulfate, chloride, and many more chemicals. This unique idea incorporates automatic reanalysis of samples with concentrations that are below or above the range. The NEN-ISO 15923-1, CMA/2/I/C.8, EPA, and BluVision analytical procedures are compliant. Low detection limits, good accuracy, and a big sample capacity are the main advantages of this technology.

NH₄ analyzer is a manual sensor -type. The process includes adding a chemical to the measured sample which allows the analyzer to efficiently measure the ammonium concentration. However, manual testing of the samples tends to have inaccuracies compared to the automatic analyzer.

3.5.2 Gasmet analyzer

Gasmet analyzer GT5000 is a portable multigas Fourier-transform infrared spectroscopy (FTIR) analyzer, seen in Figure 13. The analyzer enables simultaneous gas measurements, up to 50 gases at the same time. It is a state-of-the-art technological gadget which is reliable and accurate for multipurpose application in all terrains. Gasmet analyzer turned out to carry all the tests without any technical difficulties in the conducted tests.

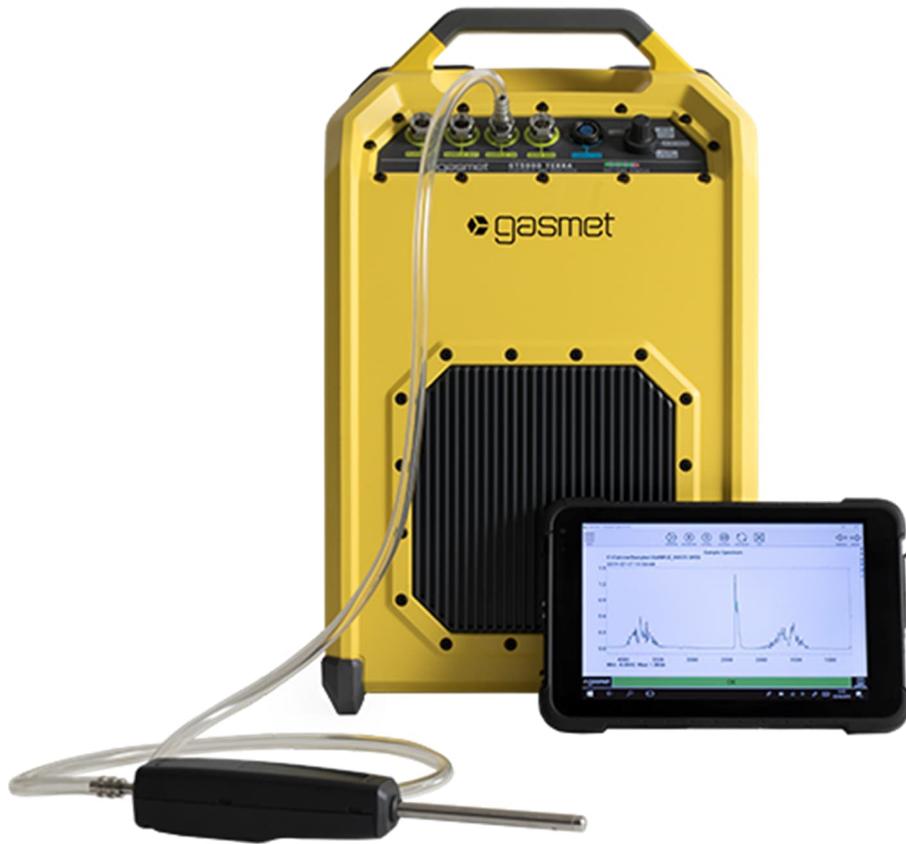


Figure 13. Gasmeter GT5000 analyzer system. Contains analyzer, tube measurement device and tablet for data.

4 Results

The results are presented as concentrations of ammonia and methane emissions, saturation tests emissions, sample concentrations, theoretical emissions, and effect of factors. The concentration results are visualized and descriptively analyzed.

4.1 Ammonia emission rates

The test results of the first tests with ammonia water were as expected: with open lid tests ammonia concentration is significantly higher. This applies to 1017cm² (36cm diameter) and 530cm² (26cm diameter) surface areas and their different emission rates in 2 hours run. However, theoretically, both surface areas have same factors of initial NH₄ concentration in the wastewater, chemicals, and liquid volume which in a longer testing results in same equilibrium.

Nonetheless, ammonia water emissions displayed a peculiar and unexpected phenomenon. Open lid pH 10 tests seemed to have a higher rate of ammonia emission than pH 11 tests. Logically, it should be other way around since by pH 11, all the ammonium is converted into ammonia. Although it was not clear what lead to this observation, its relevance is low since NPHarvest is designed for wastewaters, like reject water, where this phenomenon was not observed.

Closed lid tests are seen in the bottom of Figure 14, as tests 4,7,3, and 8. Emission rate was low in all closed lid tests. Concluding that the difference of ammonia emissions in open and closed lid is significant thus surface area has most impact on the emissions regardless of other factors.

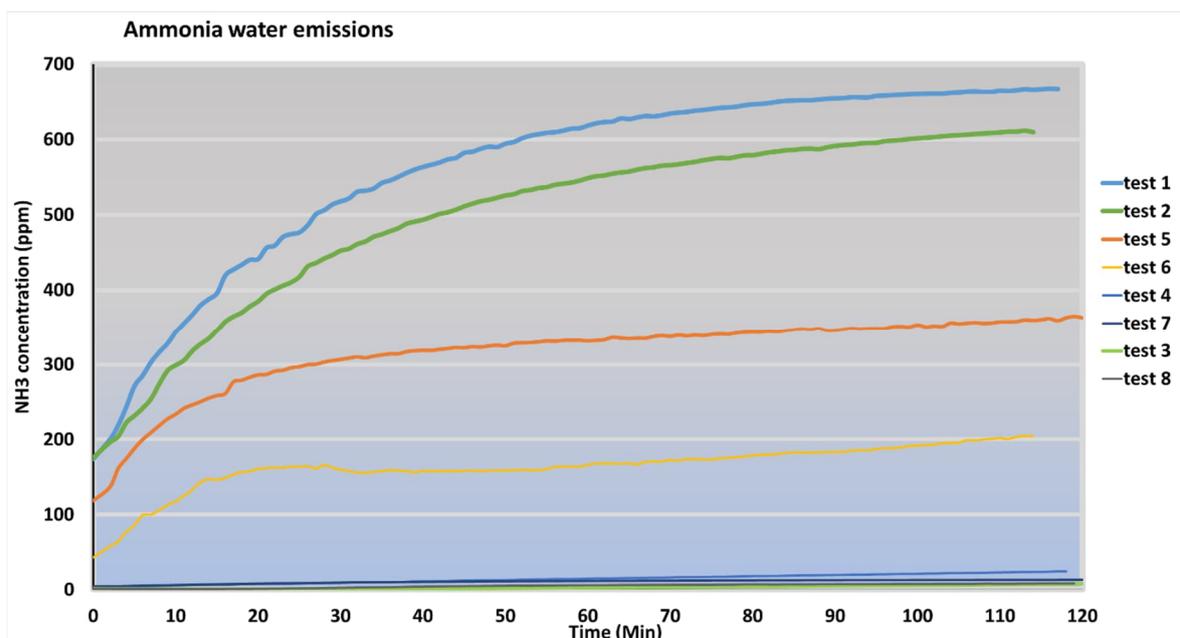


Figure 14. Ammonia water, ammonia emissions (2-hour test). Table 2 for tests details.

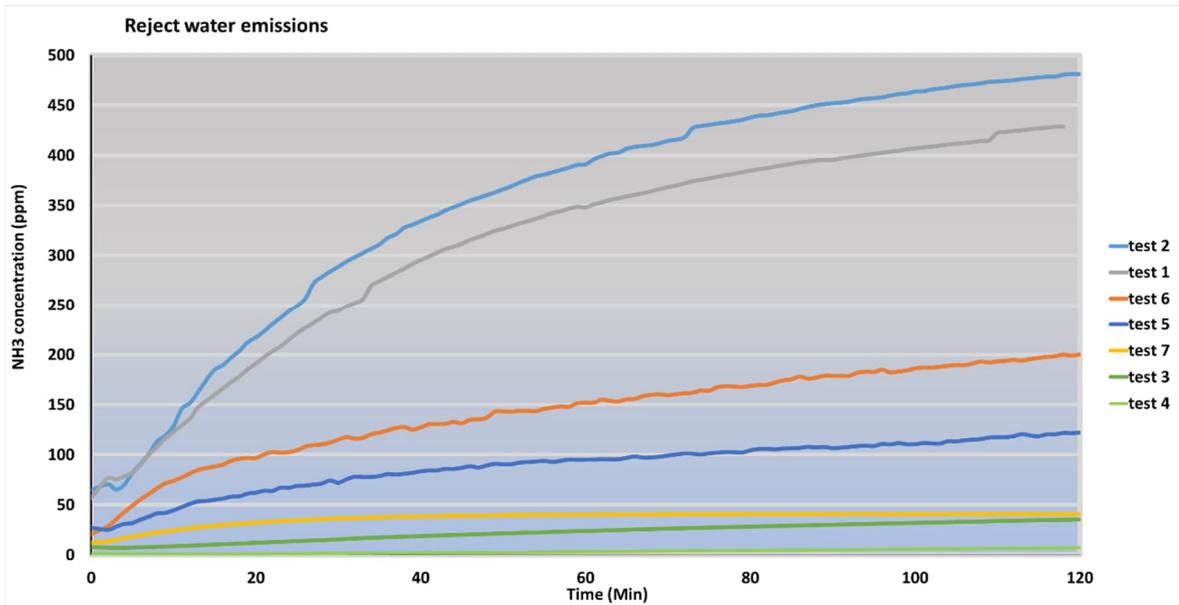


Figure 15. Reject water, ammonia emissions (2-hour test). Table 3 for tests details.

Reject water tests showed promising and expected result. Comparing both Figures 14 and 15, reject water reaches lower ammonia concentration levels. The hypothesis of increased surface area and pH-level effecting emission rate has clear evidence based on the test results. Surface area has the largest effect in the emission rate. However, pH is notably affecting the emission rate. As expected, pH 10 tests show that not all ammonium transforms to ammonia as fast as pH 11. Moreover, 10L bucket size influences the magnitude of ammonia emissions significantly.

Closed lid tests emissions rates showed similar low emission rate pattern regardless of wastewater, pH-level, or bucket size. Part of closed lid tests resulted in relatively high ammonia emissions rate. Most probably, leaking of ammonia emission outside the bucket occurred from improper installation of the lid or delayed installation of container setup. Theoretically, all the closed lid test should roughly have same shape of the graph.

4.1.1 Ammonia saturation emission rates

In saturation tests, surface area was the key variable that focused on to examine the rate of ammonia emissions. Open surface area was set, and emission rates calculated from the beginning part of the test (from 0h-1h average): 201cm² (16cm diameter) has 320 ppm/h, 50cm² (8cm diameter) has 62 ppm/h and 3.1cm² (2cm diameter) has 2.5 ppm/h. Emission rates tend to follow logarithmic curve pattern. For 3.1cm² (2cm diameter) open surface area 24-hour run is not sufficient to display logarithmic pattern. However, over time, it should follow similar logarithmic curvature and reach the saturated state concentration of 550 ppm as tests 2 and 3.

As seen in Figure 16, the larger the surface area the faster the system reaches its saturated state. 201cm² (16cm diameter) has had the fastest saturation rate following by 50cm² (8cm diameter) both reaching saturation concentration of 550 ppm. Logarithmic curvature sharpness is dependent on the surface area of the system e.g., larger surface area tends to reach saturated state in a faster rate than smaller surface area.

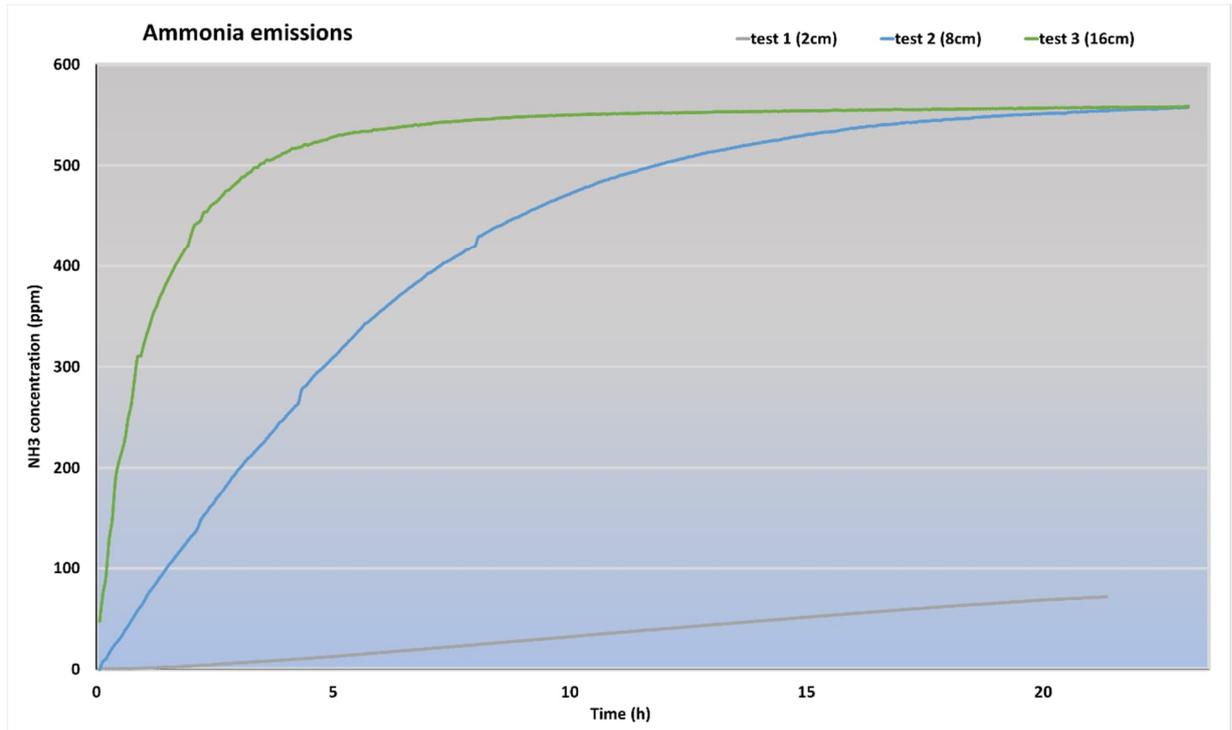


Figure 16. Ammonia emissions saturation tests (24h run). Open surface area diameter indicated as cm.

Closed lid hole of 3.1cm² (2cm diameter) displays linear curve. This indicates that the logarithmic growth effect is not applied in small open surface areas. Saturation tests need 24h before reaching saturated state. This finding is important when comparing the tests to the NPHarvest pilot which has a small open surface area. Emissions escape through the open surface area. This is compared to simulate the overall emissions large-scale pilot produces.

Henry's law is applied for comparing whether experimental tests ammonia concentration in the air correlates with the theoretically based value. To determine the theoretical Henry's law ammonia concentration value for the reject water, Henry's formula (1) and mass transfer equation (2) is used. The ammonia concentration using Henry's law resulted in 625 ppm while in the experimental tests showed 550 ppm in the saturated state. The values are relatively close, however, Henry's value is based on clean water. Uncertainties regarding Henry's law's use in wastewater is likely possible due

to the wastewater characteristics effects on the value. Uncertainties such as setup leakage, concentration differences and chemical dosing can decrease the concentration value as well.

4.2 Methane emission rates

Apart from the ammonia emissions in the reject water tests, methane compound was found to form in the reject water tests as well. Unlike logarithmic ammonia emissions rate, methane emission showed a steadily rising emission rate pattern of 60 ppm in an hour which are seen in Figure 17. Closed lid tests, tests 3 and 4, are seen as a lower amount of concentration and emission rate naturally. However, surprisingly test 7 contributed to a lot of emissions although the lid was closed with no direct explanation. Leakage or installation issue is probably the reason behind it. Most of the results of open surface area had roughly same slope and emission rate.

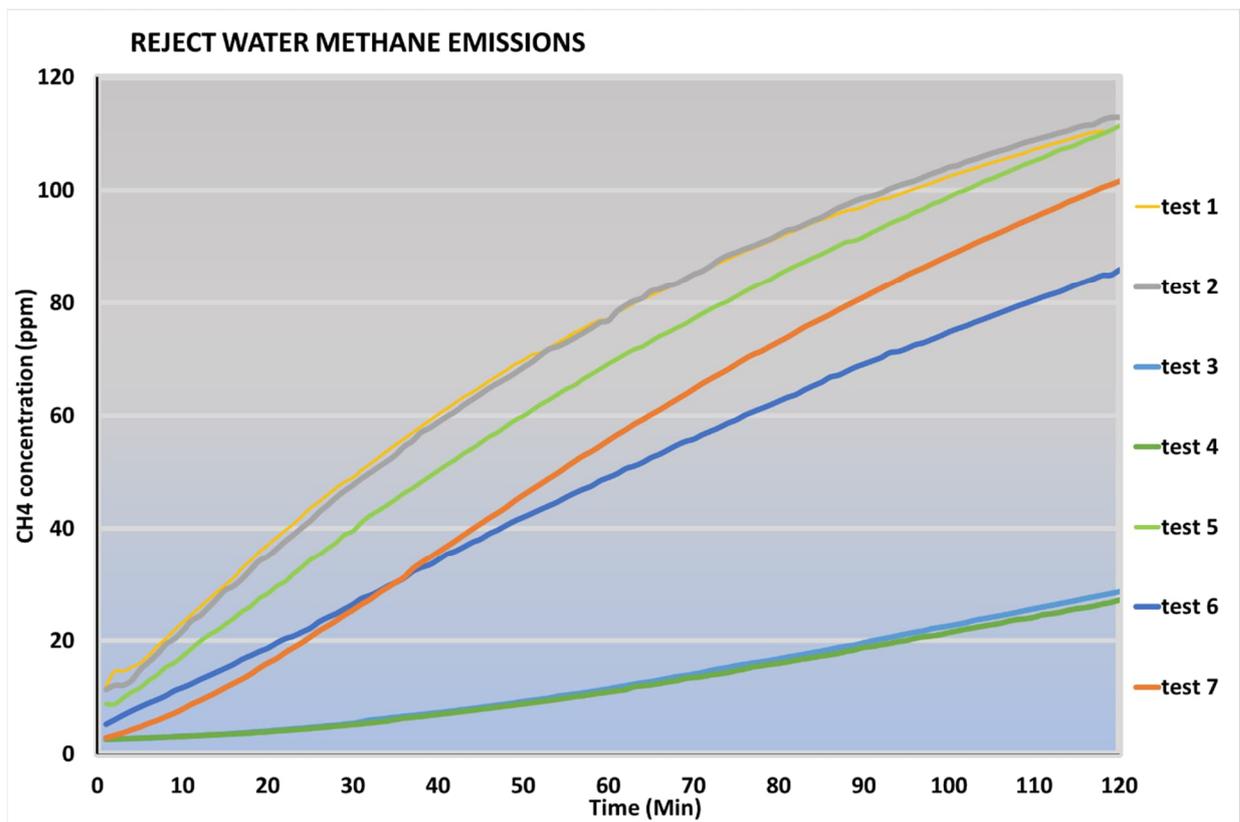


Figure 17. Reject water methane rate (2-hour run), Table 2 for test parameters.

4.2.1 Methane saturation emission rates

The reject water tested in the 24 hours testing resulted up to 320 ppm of concentration levels in its saturated state seen in Figure 18. This is comparable to half the ammonia emissions concentration. Methane saturation test runs were the same as ammonia saturation tests that were run for 24 hours.

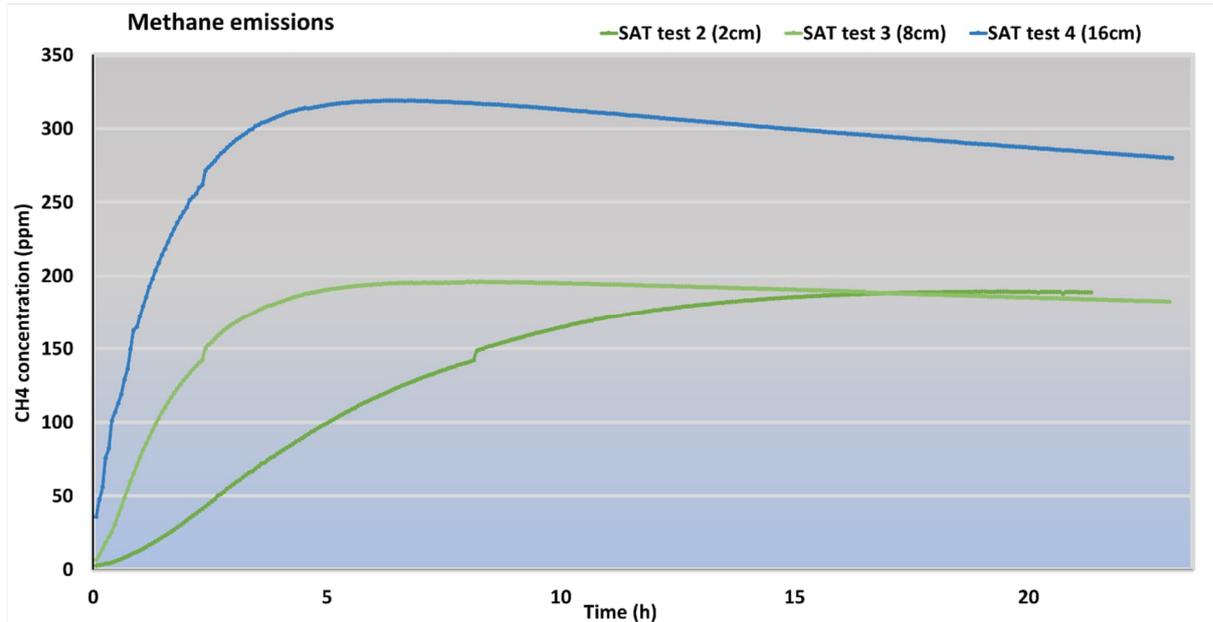


Figure 18. Methane emissions saturation tests (24h run)

Larger surface area had an impact on reaching higher concentration level in the air unlike ammonia emissions which achieved the same concentration after time when comparing Figures 16 and 18. The larger the surface area the faster the saturated state was reached. Another exceptional finding is saturated state in all testing should reach the same concentration of CH₄. However, this didn't happen. Methane emissions in the saturated state concentration seem to be proportionate to the open surface area. Test with the largest diameter of 16cm reached significantly higher concentrations in its balanced state compared to the other two tests.

Additionally, strange phenomenon occurred when the tests were run for 24 hours. After methane concentration reached its peak, the saturated concentration levels started to decrease gradually over time. Ammonia emissions results showed no decrease in the concentration which makes this finding strange to comprehend. The reason for the decrease of methane may be methane compound's ability to dissolve back into the liquid in a faster rate in larger surface areas as seen in the curves of Figure 18. Another hypothesis is that the methane gas can infiltrate and escape the plastic interior of the container although this is considered highly unlikely. Perhaps the balance of methane changes in the process. Further research is needed for understanding factors effecting methane emissions.

4.3 Emissions calculation results

The focus of these calculations is to determine the concentrations of ammonia in balanced state reached in the tests. Moreover, these calculations help backup the results of the experimental findings. According to the Henry's law, dissolved ammonia concentration in the liquid is directly proportionate to the concentration of ammonia in air balanced state. Henry's constant is the proportionate factor in the equation. Dissolved gas in the liquid system is ammonia where ammonium is transformed to ammonia gas form when pH has reached sufficiently high level after adding chemicals.

The wastewater liquid used in the test was ammonia and reject water containing 800 mg/L of NH_4 concentration. By knowing the concentration of NH_4 in liquid, determining the concentration in the air is theoretically calculated with Henry's law equation.

According to the result of the mass transfer equation (2) the concentration of NH_3 in air balanced state is 625 ppm.

Theoretical calculations of NH_3 in the air balanced state are calculated assuming a pressure of 1 atmosphere and a temperature of 25 degrees Celsius. The following calculation can be used for these circumstances to convert the concentration of ammonia in parts per million (ppm) to the concentration in milligrams per cubic meter (mg/m^3).

T (K)	298.15
R (J/mol/K)	8.31446
V (L)	230
p (Pa)	101325
R (J/mol/K)	8.3145
M(NH_3) (g/mol)	17.03
Air molar volume (L/mol)	24.055
m (NH_3) in 230 L (g)	0.097697693
Ammonia mass concentration (g/m^3)	0.409

Ammonia mass calculations

$m(\text{NH}_3) \rightarrow \text{Molar fraction} * (\text{Volume of container} / \text{Air molar volume}) * \text{Ammonia molar mass} =$
 $(600\text{ppm} / 1000000) * (230\text{L}/24.055) * 17.03 = 0.09769 \text{ g}$

$$\frac{V}{n} = \frac{RT}{p}$$

(4)

V/n converts mg/m^3 to ppm. Since our results are in form of ppm displayed in the Gasmeter analyzer as ppm. To convert other way around, molar volume is switched to n/V to convert ppm to mg/m^3 .

Conversion formula

Concentration rate ($\text{mg/m}^3/\text{h}$) = Ammonia molar volume (mg/m^3) x concentration rate (ppm/h) x molecular weight (M)

Conversion formula is in cubic meters; thus, volume of container (230 L) is necessary to include in the equation to determine the experimental tests concentration in cubic meters. This is included in the conversion formula by converting the container volume into cubic meters.

When performing the conversion, it is important to note that the cubic meter is calculated in cubic meters of air. However, in the Sweden's report it was calculated per cubic meters of liquid wastewater which differentiates the answers. Thus, conversion to same metric volume is necessary for concentration calculations.

Ideal gas law equation (4) helps determine the molar volume of ammonia which is used in the conversion equation. Conversion equation converts ppm concentration into mg/L which enables to calculate the magnitude of emissions per cubic meter of wastewater.

The large-scale NPHarvest pilot treats 500L of wastewater in the large tank with a retention time of 6 hours. Therefore, pilot processes a cubic meter of wastewater in 12 hours. (Högstrand et al., 2023) This enables the calculation of hourly rate of the ammonia emissions in a certain open surface area.

The emission rate is calculated from the highest slope of ammonia saturation tests which occurs in the beginning 15 minutes of the test. Highest slope is due to the pH increase that transforms ammonium into ammonia immediately after chemicals are added to the wastewater.

Calculating the increase in concentration divided by the time passed totals timely rate of ammonia emission, slope e.g., emission rate. Emissions of a large-scale tank of 500 L is equivalent to the laboratory scale if similar surface area opened in both. Due to the fact of surface area effecting the

total emissions regardless of tank size, emissions of NPHarvest technology are estimated based on laboratory tests that simulate the emission process in the tank. 2cm and 8cm holes are tested for an estimation of the annual emissions which are both experimentally tested and theoretically calculated.

Test data

- 2cm diameter hole -> 2.5 ppm per hour rate in 230 L
- 8cm diameter hole -> 62 ppm per hour rate in 230 L
- 16cm diameter hole -> 330 ppm per hour rate in 230L

To convert the emission rate data into a comparable ammonia emission value to the Sweden's pilot results, assumptions are necessary for proper conversion. Open surface area is the determining factor which is accountable for the magnitude of emissions. Thus, the magnitude of emission rate is constant regardless of wastewater volume e.g., pilot tank and test bucket emit similar magnitude of emissions when similar open surface area is applied. These conversion assumptions are based on diffusion law which applies when other factors are constant such as no leaks or pressure shifts. Furthermore, there are uncertainties and inaccuracies in data and the conversion assumptions/equations due to inconsistent factors.

Calculations of data

- Concentration rate ($\text{mg}/\text{m}^3\text{-air}/\text{h}$) = $0.0409 \times$ concentration rate (ppm/h) \times molecular weight (M)
- Mass flow rate (mg/h) = concentration rate ($\text{mg}/\text{m}^3\text{-air}/\text{h}$) \times volume of container (m^3)

Assumptions

- 1 m^3 of wastewater is processed in 12 hours in the tank
- Magnitude of ammonia emission is based on open surface area regardless of wastewater volume

Ammonia emissions in cubic meter of wastewater (mg/m^3) = mass flow rate (mg/h) \times 12 h

- 3.1 cm^2 (2cm diameter) surface area: $0.406 \text{ mg}/\text{h} \times 12 \text{ h} = 0.0049 \text{ g}/\text{m}^3$ *in cubic meter of wastewater*
- 50 cm^2 (8cm diameter) surface area: $10.089 \text{ mg}/\text{h} \times 12 \text{ h} = 0.1211 \text{ g}/\text{m}^3$ *in cubic meter of wastewater*
- 200 cm^2 (16cm diameter) surface area: $53.705 \text{ mg}/\text{h} \times 12 \text{ h} = 0.6445 \text{ g}/\text{m}^3$ *in cubic meter of wastewater*

4.3.1 Ammonia and methane emissions

WWTPs ventilation system works by ventilating the air inside and running various processes to clean the air. Generally, WWTPs ventilation system's ability to reduce emissions from getting to the nature is considered nonexistent. Therefore, we can generalize that all the emissions that escapes the pilot are calculated in the emission calculations.

The results of the ammonia and methane emissions in a period needs to be investigated properly to find out its full environmental impact in large-scale use. Viikinmäki WWTP, situated in Helsinki, is largest of its kind in the Nordics. It handles averagely about 280 000 m³/d, from which collected 2 500 m³/d is reject water. WWTP treats the wastewater of 800 000 people. This information is crucial to determine total contribution to emissions NPHarvest process emits per person. This result is compared to the total emissions from all sectors to determine the effect in larger picture. (HSY, 2021)

Both experimental and theoretical calculation results of ammonia and methane emissions from a cubic meter of wastewater were relatively similar. Thus, this paper uses the experimental results in the calculations of the average ammonia and methane emissions. The average ammonia and methane emissions from Finnish wastewaters can be roughly estimated through emissions per person, as follows.

Calculations of the emissions use 200 cm² (16cm diameter) open surface area. This is chosen to realistically simulate the pilot's open surface area design. Although the open surface area of the large-scale pilot ranges from 8cm to 16cm in diameter, it is reasonable to make conclusions based on larger surface area due to inaccuracies.

NPHarvest pilot emissions:

- Ammonia emissions: 0.6445 g/m³
- Methane emissions: 0.3114 g/m³

Viikinmäki WWTP parameters:

- Reject water: 2 500 m³/d
- Population: 800 000

Calculations

Total emissions in Viikinmäki:

- Ammonia: $0.6445 \text{ g/m}^3 * 2\,500 \text{ m}^3/\text{d} = 1611.25 \text{ g/d} * 365 \text{ d} = 590 \text{ kg-NH}_3 \text{ per year}$
- Methane: $0.3114 \text{ g/m}^3 * 2\,500 \text{ m}^3/\text{d} = 778.5 \text{ g/d} * 365 \text{ d} = 285 \text{ kg-CH}_4 \text{ per year}$

Per person:

- Ammonia: $588.106 \text{ kg} / 800000 = 0.735 \text{ g}/(\text{PE, year})$ of NH_3
- Methane: $284.152 \text{ kg} / 800000 = 0.355 \text{ g}/(\text{PE, year})$ of CH_4

In Finland:

Finnish Population: 5 540 000

- Ammonia: $0.735 \text{ g} * 5\,540\,000 = 4\,071\,900 \text{ g} = 4.1 \text{ ton-NH}_3$ per year
- Methane: $0.355 \text{ g} * 5\,540\,000 = 1\,966\,700 \text{ g} = 2.0 \text{ ton-CH}_4$ per year

Calculations indicate the total ammonia emissions using the NPHarvest technology would accumulate to roughly 4.1 ton- NH_3 per year, 0.735 g/(PE, year) of NH_3 . According to Högstrand et al. (2023), ammonia emissions were remarkably higher, 0.44 kg/(PE, year). Compared to Sweden's pilot results, emissions are about 600 times higher. This is a significant finding for NPHarvest, considering ecological viability.

4.3.2 Experimental methane emissions calculations

Methane emissions occurred only with reject water tests. However, experimental results of methane emissions were highly inconsistent. Compared to ammonia emissions, methane emissions rate performed quite differently making methane emissions hard to predict. The saturated state seemed to be determined by the surface area open. At most, with a 16cm diameter surface area, the tests reached the highest concentration at around 300 ppm of methane emissions which decreased steadily with time unexpectedly. The methane concentration in the reject water was never measured due to difficulty and unavailability of the proper analyzing equipment. Thus, the calculations of the possible methane emissions are only based on the findings of gas analyzer. These results are indicative and should be considered with caution.

Using Fick's law in methane emissions to determine the methane emissions rate. Same process as in earlier ammonia calculations are implemented in this study as well. Methane emission rate is averagely 170 ppm per hour in laboratory conducted tests.

T (K)	293.15
R (J/mol/K)	8.3145
V (L)	230
p (Pa)	101325
R (J/mol/K)	8.3145

M(NH ₃) (g/mol)	16.04
Air molar volume (L/mol)	24.055
Molar volume (mg/m ³)	0.0409

Concentration rate

- Concentration rate (mg/h) = Molar volume (mg/m³) x concentration rate (ppm/h) x molecular weight (M) * container volume (m³) = 25.9527 mg/h

Multiplying by 12 hours to determine emissions per cubic meter of wastewater.

- 25.9527 mg/h * 12 h = 0.3114 g-CH₄/m³

4.4 Theoretical calculation results

Purpose of this section is to see whether theoretically calculated emission rate is in a similar range with experimental emission rate. This increases credibility of the results. With equation (3), Fick's law can be utilized to theoretically calculate the emission rate as follows.

$$x = \text{Gradient length (m)} \quad 0.02$$

$$d\phi / dx = \text{Concentration gradient (mol/m}^4) \quad 1.2471303$$

$$D = \text{Ammonia diffusion coefficient in air (m}^2/\text{s)} \quad 0.0000228$$

$$J = \text{Diffusion flux (mol/m}^2/\text{s)} \quad 2.84346\text{E-}05$$

From the earlier calculations of the tests, pilot handles a cubic meter of wastewater in 12 hours. Then transforming the result from g/h to g/m³ multiplying by 12 hours.

Surface area is regarded as a circle in this thesis, thus, to determine the surface area using equation of $A = \pi r^2$, which diameter $d = r/2$. The gradient length (m) is hypothetically set to 0.02 m which would be reasonable regarding the tank structure.

$$A = \text{open surface area (m}^2)$$

$$t = \text{time (s), } 12 \text{ h} = 12 * 60 * 60 = 43200\text{s}$$

$$M(\text{NH}_3) = 17.03 \text{ g/mol}$$

4.4.1 Theoretical emissions rate calculations

Ammonia gas emissions per cubic meter of wastewater (g/m^3) = $J * A * M(\text{NH}_3) * t$

- Transfer through 3.1cm^2 (2cm diameter) open surface area:
 $J * A * M(\text{NH}_3) * 12 \text{ h} = 0.006276 \text{ (g/m}^3\text{)}$
- Transfer through 50cm^2 (8cm diameter) open surface area:
 $J * A * M(\text{NH}_3) * 12 \text{ h} = 0.104596 \text{ (g/m}^3\text{)}$
- Transfer through 200cm^2 (16cm diameter) open surface area:
 $J * A * M(\text{NH}_3) * 12 \text{ h} = 0.418384 \text{ (g/m}^3\text{)}$

The results indicate that the larger the open surface area, the greater the magnitude of emissions. Moreover, compared to the experimentally calculated emissions rate results, theoretical emissions rates were fairly similar. This increases the credibility of the experimental findings that were conducted.

Theoretical result calculated from the equation determines the absolute balanced state where variables are constant and other components are not considered such as the possibility of reject water binding some of the ammonia, all ammonium converted to ammonia and thorough mixing of the liquid (for the ammonia gas to be in contact with the surface for evaporation). Realistically, unconsidered components in theoretical calculations affect the balanced state concentration in the experimental testing, hence the results are expected to be lower.

4.5 Mass balance measurement

Samples were taken to provide us data of ammonia concentration in the liquid. Sample results provide additional evidence of ammonia concentration in the air. Logically, more ammonia concentration is emitted into the air in the system means less in the liquid.

The ammonia concentration of the samples was first tested using manual NH_4 -analyzer which turned out to give inaccurate and unrealistic ammonia concentrations exceeding the initial wastewater concentration of 800 mg/L. Afterwards the tests were performed with an automatic measurement device, BluVision analyzer. As seen in the Figures 19 and 20, results of the concentrations were ranging high and low with a lot of inconsistency in both analysis methods.

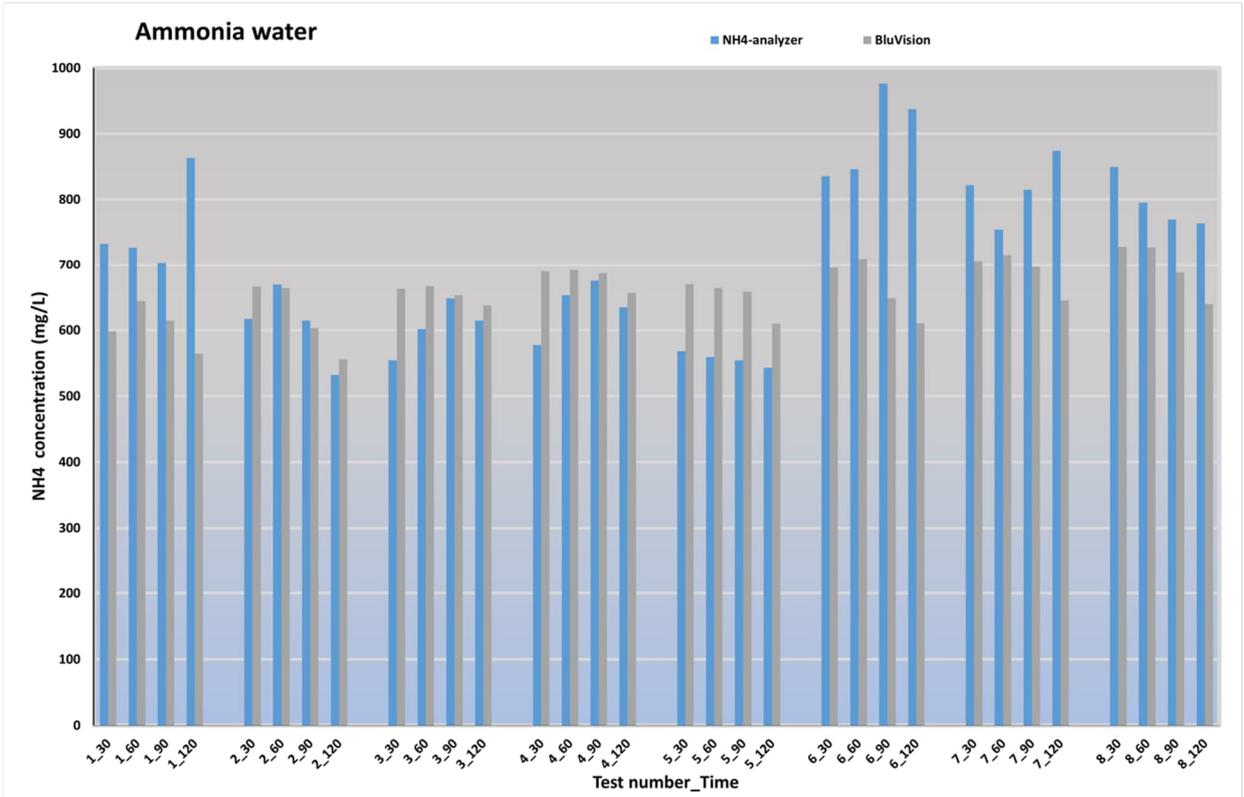


Figure 19. Ammonia water samples 30-minute interval, see Table 1 for test parameters.

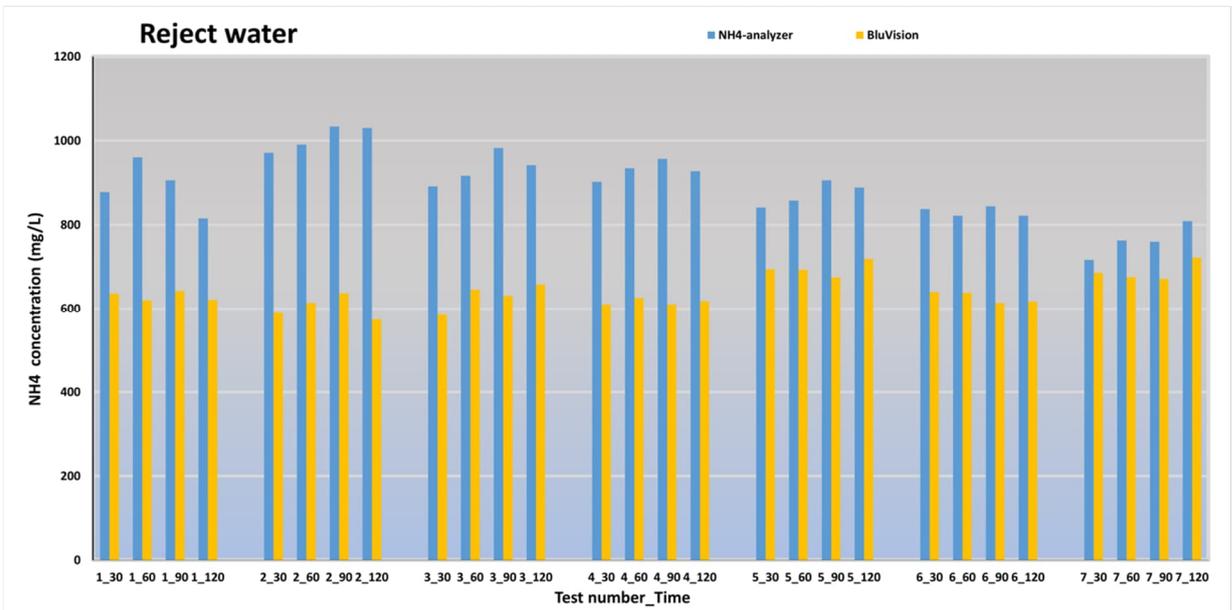


Figure 20. Reject water samples 30-minute interval, Table 2 for test parameters.

Same testing of the ammonia concentration in the liquid was also conducted with a reliable analyzer called BluVision analyzer. After analyzing the samples with the BluVision, results were more accurate and realistic than the NH₄-analyzer results. The BluVision results show that reject water's ammonia concentration scaled between 700-550 mg/L which seem quite reasonable. The difference

in the concentration of dissolved ammonia is probably due to factors of experimental uncertainty. In some of the samples, concentration increased unexpectedly mid-testing, showing either inaccurate results from the analyzer or error in the sample. According to the BluVision analyzer manual, error of 5-10 percent in concentration values are possible. Generally, the results were far more accurate and consistent than NH_4 -analyzer thus the final reflection is based on BluVision analyzer results. Altogether, ammonia concentration results showed significant consistency and deviation was subtle.

5 Discussion

5.1 Calculated results

Calculations of the emissions were based on 200 cm² (16cm diameter) open surface area which is chosen to realistically simulate the pilot's open surface area size. Although the open surface area of the large-scale pilot ranges between 8cm to 16cm in diameter, it is reasonable to make conclusions based on larger surface area due to inaccuracies.

According to Högstrand et al. (2023), emissions amounted from Sweden's WWTP pilot resulted to an average of 0.2 kg NH₃/m³ of WW. It was calculated that for the yearly amount of wastewater processed, a person produces approximately 0,44 kg/(PE, year). However, this is compared to Sweden's usage average which is different than Finland's average. Imperfect sealing of the pilot has a significant importance in article's magnitude of emission. Furthermore, unknown information of pilot's exact open surface area size in Sweden WWTP testing should be considered accordingly. (Högstrand et al., 2023) In comparison with this paper's results, the amount of ammonia emissions calculated in Sweden's test results are remarkably high although performed with unreliable mass balance calculation.

The calculated results show that the ammonia emissions are 0.735 g/(PE, year) which is substantially lower than previously measured in Sweden's pilot tests. Order of magnitude emissions difference is a factor of 1000 compared to the results of Sweden's pilot. Moreover, it is mentioned that the emission is comparable to 8.6% of the total Swedish NH₃ emissions. This percentage is significantly high for wastewater treatment pilot process only to contribute to this extent. (Högstrand et al., 2023)

Ammonia emissions

According to Natural resources institute of Finland, total ammonia emission is about 30.5 Gg-NH₃ per year in Finland (Luke, 2021). If used to treat all the reject water of Finland, NPHarvest technology would contribute an average of 4.1 ton-NH₃ per year emissions which is about 0.01% of the annual total ammonia emissions contributed by Finland. This percentage is significantly lower than previously thought. Compared to Högstrand et al. (2023) who mentioned 8.6% of the total Swedish NH₃ emissions per capita, 0.01% annual total ammonia emissions on Finnish national level seems significantly lower impact due to NPHarvest technology use.

This paper's results have showed significantly lower emission impact that are minor compared to the mass balance calculation results conducted in Sweden's findings. NPHarvest technology possesses significantly smaller threat to eutrophication and acidification than previously thought. Nonetheless, consideration of the mitigation procedures is recommended although the total ammonia emissions

are considerably lower than previously thought. Thus, all factors, most notably surface area, need proper installation and examination before large-scale implementation.

Methane emissions

Waste, agriculture, and energy sector are the largest contributors of CH₄, in Finland, totaling 300 Gg-CH₄ per year in 1990. Methane emissions in Finland have decreased substantially. Between the years 1990-2010, third of annual methane emissions decreased. Waste sector was responsible for the most CH₄ emissions, especially landfills. However, energy use and recovery of waste has decreased the CH₄ emissions drastically. (Rautalahti & Kupiainen, 2016)

In 2019, the total methane emissions in Finland were about 185 Gg-CH₄ per year (World Bank, 2022). If the whole Finnish population's wastewater was processed with NPHarvest technology, the annual methane emissions would add up to an average of 2.0 ton-CH₄ per year. This amount is remarkably low, about 0.001%, compared to the total methane emissions of all sectors in Finland. Thus, it is safe to assume that the implementation of NPHarvest technology poses insignificant threat to climate change. In fact, the pros of NPHarvest technology outweigh the cons significantly considering other advantages of the technology such as energy consumption in nutrient recovery and the economic benefits of nutrient commercialization.

Methane emissions results are based on the theoretical and experimental calculations. There is a certain degree of uncertainties in the result that is considered in overall assessment of the emission impact both in ammonia and methane emissions. Lastly, further research is recommended for both ammonia and methane emissions if precise emission calculations are needed.

Compared results

When comparing calculated theoretical and experimental results, the values were comparable in magnitude which indicate that experimental tests were executed well. Furthermore, confirming that the theoretical and experimental results are in same magnitude raises a question of Sweden's pilot significantly high ammonia gas emissions. Specifically, factors leading to high amounts of ammonia emissions require reviewing of method of calculation and pilot process factors.

Pilot process factors such as the imperfect sealing of the tank, physical factors (wastewater type, chemical etc.), and testing environment are most likely the reason for high ammonia results. Although the largest culprit of high emissions, imperfect sealing of the pilot, has a large contribution to the amounts of ammonia emitted, exemption of this degree is still unordinary.

In Sweden's pilot, method of calculation was based on mass balance calculations which usually has issues regarding the accurate loss that considers total process. Mass balance equation states that total mass in all systems is preserved. That is, Total mass in = Total mass out + Total mass loss. Total mass loss should reveal the amount of ammonia compound that is emitted. In the LCA of Högstrand et al. (2023), there was not an exact description of how the mass balance calculations was performed and thus its reliability is not to be counted on with certainty. Since there is no certainty about the LCA process, possibility of uncertainty in results are highly probable. The difference between the two results is highly significant so an accurate analysis of the possible factors remains unsolved.

5.2 Effects of different factors

Effects of different factors are mostly seen in ammonia emissions point of view. Emphasis was put to examine magnitude of ammonia emissions. Since Högstrand et al. (2023) never mentioned methane emissions in its calculations, its effects are lightly mentioned in the following discussion. Nevertheless, further research needs to be performed for better understanding of how different factors affect the magnitude of methane emissions.

5.2.1 Effect of surface area

When open surface area increases, more surface is exposed with open air resulting in higher amounts of molecules possibility to escape. Since all the other factors are constant, determining the rate of emission and different surface area behaving is linked with the speed of ammonia evaporation rate.

The system strives to reach its balanced state e.g., saturated state which is limited to the volume of air inside the closed space. Also, ammonia emission rate is dependent on the volume of air surrounding it. The less volume of air in the closed state with same volume of liquid, the faster it reaches saturated state e.g., ratio of liquid and air volume in a closed state is dependent on the rate of evaporation.

Open surface area size has a large effect on logarithmic curvature. Larger surface areas have a steeper curve which reaches saturated state significantly faster as seen in Figures 20 and 22. On the other hand, smaller surface area takes longer time to reach saturated state and thus has a steady linear curve.

Furthermore, closed lid surface tests (2cm) indicated similar patterns of steady evaporation rate regardless of factors like pH, mixing speed, bucket size when reaching its saturated state. Thus, surface area has most impact on emission rate of ammonia emissions. The impact of other factors has minor effect on the speed of evaporation rate. Importantly, calculating ammonia emissions from

the NPHarvest pilot is very useful to determine which settings and factors need to be accounted for in mitigation of the ammonia emissions.

5.2.2 Effect of mixing speed

High mixing speed and mix rod proportionate to the size of the bucket (80-60% of the bucket diameter) increases the dissipation of ammonium into ammonia gas e.g., it reaches the saturated state faster.

Mixing speed and 10L bucket was stirred with a magnetic stirrer which is not as efficient due to its size and the height of the wastewater. Mixing speed was adjusted so that the wastewater had an even thorough mix in both buckets, so the assumption is that both buckets are mixed well enough. Although the mixing speed was matched so that both buckets seem to have efficient and thorough mixing inside the bucket. Nevertheless, tests with similar factors showed difference in emission rate which indicate that mixing speed and height of the bucket causes disruption in the emission release process. Thus, the mixing speed and height plays a role in the sufficient thorough mixing of wastewater which decreases emission rates. However, the focus of the tests was never conducted to find out the correlation between mixing speed and its effect on emission rate. So, comparing these results with the large-scale NPHarvest pilot is not of great importance due to the pilots closed lid characteristic. These findings are based on the test results so there are multiple uncertainties to note such as the inaccuracy in matching mixing efficiency.

Although the mixing speed's effect on the magnitude of emissions was not specifically tested, it is seen to have a degree of impact. Concluding that the emissions are affected by higher mixing efficiency of the wastewater. In an optimal solution, lower mixing efficiency has decreasing emission effect. However, in a large-scale pilot process, the proper mix of chemicals is necessary for efficient nutrient recovery. Mitigating emissions with mixing speed seem to not be suitable for NPHarvest pilot.

5.2.3 Effect of pH

The way to compare ammonium-ammonia equilibrium is to only consider open lid tests due to faster rate of achieving saturated state than closed lid tests. Furthermore, it is easier to compare open lid test between each other due to surface area having a large impact on reaching saturated state.

Test results of reject water show cohesiveness with the ammonium ammonia equilibrium in Figure 2. The saturated state of the pH 11 tests contained higher concentration of emissions than pH 10 tests. Unexpectedly, some tests were applied with ammonia water and the results contradicted the equilibrium with pH 10 resulting in higher amounts of ammonia emissions than pH 11. Various factors may cause this such as the change of water type (Ammonia water not containing other compounds or solid matter like reject water), chemical (only $\text{Ca}(\text{OH})_2$ was used as chemical for test)

or technical inaccuracies that led to these differences. Nevertheless, choosing pH 10 is preferable since it reduces the need for chemical use (when there is no significant difference between pH 11 and pH 10).

According to the ammonium-ammonia equilibrium seen in Figure 2, pH 10 is sufficient for efficient nutrient recovery and would decrease the ammonia emissions slightly. pH higher than 10 is unnecessary due to increased expenses on chemicals and its effect on the fast emission rate. However, NPHarvest process is economically viable when ammonium transforms into ammonia fully in the process which requires no more than pH 10. pH has an effect momentarily on emission rate like mixing speed. However, after reaching saturated state, in which the large-scale pilot is continuously operating on, both pH and mixing speed have insignificant role in the magnitude of emissions.

5.2.4 Effect of wastewater type

The main difference in the wastewater type is the concentration of ammonia saturated in the air. Ammonia water had higher concentration of 650 ppm while reject water has 550 ppm. According to the Henry's law, the saturated state should have a concentration of around 625 ppm range when liquid contains 800 mg/L concentration of NH_4 . Direct explanation of the reject water saturated concentration level can be explained by the binding of ammonia in the reject water flocculation process or the analyzer's incapability to precisely detect the concentrations of many compounds at once. However, this is based on speculation of the possible reasons leading to the difference in the concentration of the saturated state.

Wastewater type with high concentration of NH_4 increases saturated state NH_3 concentration (ppm). This results in an increase in magnitude of emissions which is unwanted. However, from a recovery point of view, a higher concentration of NH_4 in the wastewater is better for the commercial viability of the technology. Pilot design is paramount as the most crucial factor that affects the emissions. However, besides the design, wastewater itself has a clear impact, although it is mitigated by good design. Economic viability is seen as more important than minor increase in the magnitude of emissions.

This paper had not the chance to perform tests with blackwater which was used in Sweden's pilot. Although reject water and blackwater have similar nutrient properties, solid matter content and compounds are different which may change the concentration of saturated state. Notably, when the concentration of the saturation state increases, also does the emission rate escaping e.g., magnitude of emissions. Further analysis of the effects of wastewater type is interesting to investigate specifically to properly find out the emissions characteristics in NPHarvest pilot process.

5.3 Uncertainties in results

The tests have uncertainties regarding its entire process, from materials to methods of use. Spillages, inaccuracies in dosing, mixing of the liquid, analytical inaccuracies and gas leakages can occur throughout the testing phase which can affect the accuracy of the results

The exact moment the chemicals are mixed with the wastewater, equilibrium of ammonium begins to transform into ammonia gas form. Sealing the container as fast as possible is crucial for all the emitted ammonia gas to be sealed inside. However, executing this procedure fast is difficult due to the delay in proper installation of the container. This causes a decrease in the overall concentration of ammonia. It could explain the lower saturation state value of 550 ppm rather than the theoretical value of 625 ppm in the 800 mg/L-NH₃ concentrated liquid.

Container use can possibly cause inconsistency in the results. Procedures to decrease inconsistency and inaccuracy includes sealing of the container when the chemicals are added, ensuring minor escape of emissions from the container for accurate measurement.

In our tests conducted in Aalto University's water building lab, ammonia and reject water was used for testing the ammonia emission levels. In Sweden's WWTP, blackwater was used for performing the tests of LCA-analysis. Reject water is closer to the composition of blackwater although having differences in solid matter and compound content. This is a difference that needs to be noted due to the content differences in these wastewater types which may cause difference in ammonia and methane concentration levels. (Högstrand et al., 2023)

Methane emissions occurred only in reject water tests. It is difficult to determine the concentration of methane in reject water due to inconsistency of this paper's results. There is a decrease of concentration when reaching saturated state which is strange due to this not occurring for ammonia concentration in the same tests 1, 2, and 3, seen in Figures 20 and 22. Furthermore, surface area determines the saturated state concentration level of methane unlike ammonia, displayed in Figure 22. The emission rate pattern between ammonia and methane gas is very different as well. Methane tends to have a relatively high emissions rate compared to ammonia even at smaller open surface areas. Further research is recommended for methane concentration comprehension.

Liquid samples of the ammonia concentration taken have uncertain results due to inconsistent values in the concentration. Although the BluVision analyzer showed more reliable results, inconsistency was present. Decision was made to only include samples tested with BluVision analyzer. Importance was placed on experimental gas emissions measured by Gasmeter analyzer and theoretical calculations results to decrease inaccuracy in ammonia and methane emission results,

The largest uncertainty lies in the amount of ammonia emissions found in Sweden's pilot. Although many factors contributed to the high emissions, the difference in magnitude is remarkably high. Mass balance calculations and improper sealing of the pilot's tank has a significant role in the difference in magnitude between this paper's and Högstrand et al. (2023), article's results.

5.4 Suggestions for improvement

There are few core differences when comparing the tests done in the lab to the pilot trial. Tank's air phase reaches and maintains saturated state due to the volume differences between liquid and air. Even when the water changes in the pilot tank (retention time) constantly the balanced state remains due to the high wastewater liquid to air ratio. Importance of pH-level and mixing speed in the assessment of the large-scale pilot is different comparing it to the small-scale tests. Inside the large-scale pilot tank, saturated state is constant from which the ammonia escapes from the saturated air inside the tank to outside of the tank evenly throughout the process, regardless of pH and mixing speed. Thus, it can be stated that pH-level and mixing speed overall effects on emission mitigation is insignificant in the large-scale NPHarvest pilot tank. As earlier mentioned, large-scale pilot tank's restrictive factor for emissions control is the open surface area.

Large-scale pilot is sufficient with minimal air effluent hole to discharge thus design should be altered to create a closed system. The results indicate that sealing the lid tightly with less open surface areas exposed decreases the amount of leakage certainly regardless of other factors. However, design of installed mixer rod in the large-scale pilot tank needs space in between the gap hole to rotate. Emission mitigation solutions are reducing the open surface area to decrease emissions, or alternatively integrate the mixer as part of the tank attached from the bottom so that there is not open surface area exposed. Suggestion to decrease the open surface area would substantially lower the emission rate. The surface area open in the pilot has the most impact on the emission rate. It should be important for any pilot to be sealed properly before implementation. Tests are recommended to conduct for proper checkup of any sources of open area leakages.

According to NJDH. (2016), threshold limit concentration of ammonia gas is 25 ppm in an 8-hour working shift. When a worker is exposed to higher concentrations continually, health symptoms arise such as risk of lung damage and even cancer. Up to several hours, respiratory ammonia concentrations of up to 100 ppm are readily tolerated. However, in about 30 minutes, concentrations of 2500 to 4500 ppm can be lethal. (Birken et al., 1981) In NPHarvest technologies case, the maximum concentration of ammonia reaches 600 ppm inside the pilot's tank which worse-case scenario can cause severe health damage if exposed for too long. However, this can be easily avoided by preventive exposure actions such as taking a distance from the tank and immediate retreatment when ammonia gas is smelled. In a normally functioning pilot process however, the escaped

ammonia gas never reaches threshold concentrations due to air conditioning which makes working near the pilot safe.

Different factors cause an effect on the emissions rate. Performed test consisted of three main factors that contributed to emissions: pH-level, wastewater type and open surface area. According to result analysis, optimal design for the setup is pH 10, slow mixing speed, reject water, small as possible surface area exposed, and higher ratio of liquid to air volume in the tank of the pilot. This design and process setup minimizes emissions in NPHarvest wastewater treatment process.

5.5 Ammonia gas emissions harvesting methods

Wastewater treatment processes emit significant amount of ammonia and methane to the air. (Vanotti & Szogi, 2011) There are two different options of decreasing the magnitude of the emissions which includes capturing emissions or applying mitigating procedures. Most viable option for NPHarvest is to concentrate its assets on the mitigation of emissions by implementing mitigating procedures to the design and process. However, emission capture can potentially be another option to decrease the emissions. Although emission harvesting increases the costs of the process, it has great advantages in the mitigation of ammonia of the process. Ammonia harvesting technologies capture and recover gas emissions for further processing to fertilizers or chemical use. (Brück et al., 2019; Capodaglio et al., 2015; Jain & He, 2018; Vanotti & Szogi, 2011) These technologies can be applied as part of the NPHarvest pilot by integrating it as part of the system.

Ammonia emissions can be harvested by a variety of technologies in different sectors of gas refineries, agriculture, and landfills. These technologies can easily be included in a wastewater treatment process. Ammonia gas emission harvesting technologies have advantages and disadvantages depending on the process such as recovery efficiency, costs of use, lifespan, and applicability. According to Harihastuti et al. (2021), adsorption methods reduce and recover ammonia gas more efficiently than other available technologies.

Nonetheless, few factors determine whether application of these technologies are profitable in large-scale process, design feasibility, financial viability, and environmental benefits. Depending on the magnitude of emission and its impact to the environment, it is possible to determine whether available harvesting technologies are viable for NPHarvest process. However, these technologies vary in their recovery efficiency, costs of use, lifespan, and applicability which important to consider thoroughly before use. Other limiting factor is the suitability of the technology for the large-scale pilot design. Further research is recommended for the assessment of which harvesting technology method is most suitable for NPHarvest process.

5.5.1 Emission capture technologies

Emission capture technologies and their suitability for NPHarvest technology.

Acid scrubbers

Scrubbers use a liquid-based solvent to absorb pollutants. Before the gas leaves the scrubber, it travels through a mist eliminator to catch any droplets. The contaminants are caught in the solvent droplets. The droplets are collected and used, for instance, for production of fertilizer.

Acid scrubber removes ammonia from air-streams and absorbs it to a solution that binds ammonia into ammonium sulphate which is converted to commercialized product fertilizer afterwards. (Ray et al., 2020) Wet acid scrubbers have demonstrated exceptionally effective ammonia recovery, between 91 and 99%. (Melse & Ogink, 2005)

Wet scrubbers frequently have larger potential costs. This is mostly since wet scrubbers need to be made of stainless steel since liquid solutions are corrosive. Energy expenses are also larger with a wet system. Strong fans must be used to apply sufficient mechanical force to mix the exhaust emission gas with the water. Further research is required for the comprehension of full expenses if used in NPHarvest technology.

Acid scrubbers can be made applicable to NPHarvest with few alterations to the design. Mainly the installation of a pipe directing emissions to acid scrubber. Generally, acid scrubbers are the most suitable option for gas harvesting considering the removal efficiency and cost from the available technologies.

Acid tank

Another similar solution of ammonia gas harvesting is an acid tank from which ammonia gas goes through binding it into the acid. The method is directing the ammonia gas to the bottom of another tank filled with sulphuric acid. When the gas bubbles through the liquid, ammonia compound binds into the acid forming ammonium sulphate. Ammonium sulphate has a lot of commercialization potential and is marketed as a fertilizer after processing.

Directly acid tank technology has no records of being applied. However, theoretically it can be designed as a solution. Compared to acid scrubbers, acid tank can be potentially a cheaper option due to only directing the gas to the bottom of sulfuric acid which would cut on the energy expenses a lot. NPHarvest pilot has an acid tank integrated as a part of the system which is why acid tank technology would be the most attractive for ammonia gas recovery. Nevertheless, this needs proper engineering to implement it in a way that would be feasible and viable.

Bio-filtration

Bio-filtration works with a porous organic layer of different material mainly wood and compost creating a biofilm. Facilities ventilated air flows through the porous layer is converted into carbon dioxide and water. Airborne substances like ammonia and methane bond to form a biofilm that develops on the material layer. Ammonia emissions can be reduced via biofiltration by 65% (Kavyashree et al., 2015).

Bio filters last up to 10 years depending on the design of the ventilation system. For facilities with mechanically ventilated system bio-filtration method is an excellent option due to its price-quality ratio and lifespan. (Moines et al., 2008) For NPHarvest technology bio-filtration is a long-term viable technology. However, it poses difficulties regarding its relatively low removal efficiency compared to other technologies.

For NPHarvest, bio-filtration to be implemented as part of the process requires installation of a pipe directing emission gas to the bio filter. Thus, integration of bio-filtration is theoretically possible although not implemented in similar processes.

Activated carbon

Activated carbon is very efficient method of emissions gas removal and the technology is utilized in many processes of different energy sectors. The activated carbon has porous element that binds different compounds into it. Filtering method has recently been applied in various purification methods. Advantages of activated carbon is easy maintenance and high absorption efficiency. Absorption efficiency of activated carbon is around 80-95% (Harihastuti et al., 2021). Nevertheless, the price of this technology is significantly higher than to the other ammonia gas harvesting methods.

Activated carbon has a high removal efficiency. However, for NPHarvest technology, activated carbon is not a viable method due to inability to economically recover ammonia gas. Unlike other technologies this captured emissions cannot be utilized for fertilizer production. Furthermore, activated carbon is significantly more expensive compared to other emission removal methods due to material cost.

5.6 Sweden's case analysis

According to the Sweden's LCA the ammonia emissions were significantly higher than this paper's results. The tests conducted in Water lab indicate that the ammonia emissions noticed in Sweden could have been over-estimated. Reason for high emissions calculated is assumed to be imperfect sealing of the pilot, and mass balance measurement method performed in Sweden's LCA to calculate ammonia emissions. Since this was performed by the difference in the ammonia concentration in wastewater, the exact amount of ammonia gas cannot be accurately calculated. Whereas in the closed environment gas analyzer efficiently calculates ammonia emission that is emitted to the air.

Högstrand et al. (2023) mentioned that the lid of the pilot tank was imperfectly sealed which resulted in $0.2 \text{ kg-NH}_3/\text{m}^3$. According to the results of lab tests, when the lid of the pilot tank is sealed properly the amount of ammonia emissions resulted experimentally and theoretically around $0.735 \text{ g}/(\text{PE}, \text{ year})$. The surface area of the pilot plays a huge role in the ammonia emissions rate. It is important to emphasize that when the pilot setup is imperfectly sealed, magnitude of emissions increase significantly. For NPHarvest pilot to emit $0.2 \text{ kg-NH}_3/\text{m}^3$ is highly improbable when comparing to this paper's results. However, imperfect sealing of the pilot and mass balance measurement method are possible reasons for the results of LCA calculations.

Since the testing was performed in Aalto Water lab with reliable equipment and under surveillance of professional lab technicians, experimental results backed up with theoretical calculations are a solid source of pilot's magnitude of emission. Moreover, the results were measured with the gas analyzer, this is a significantly more reliable way to calculate the emissions than with the mass balance calculations due to emissions measured in a closed system.

6 Conclusions

The aim of this thesis was to find which factors contributed to ammonia and methane emissions. This was tested creating a simplified miniature laboratory scale system that simulates large-scale pilot.

According to Högstrand et al. (2023), mitigation of ammonia emissions in the NPHarvest pilot process was recommended, thus the factors contributing to emissions were closely studied. Factors effecting the magnitude of emissions such as the design and factors (wastewater type, chemicals, mixing speed, pH-level, and open surface area) of the large-scale pilot were tested and analyzed. However, focus of the research was put on the open surface area due to having the largest contribution on the magnitude to emissions. It is an important step to prioritize open surface area in the future NPHarvest pilot processes for ammonia mitigation.

Ammonia and methane emissions were calculated both experimentally in the laboratory simulating large-scale pilot process and theoretically using gas law's to certify the results. According to the results, the experimental findings were very close to the theoretical findings which increase the credibility of experimental results. Findings showed that the emission rate grows linearly depending on the open surface area. Limiting the size of the open surface area and sealing pilot system properly is seen as best solutions for emission mitigation. Although the findings of this thesis indicate significantly lower impact on eutrophication and acidification, emission mitigation procedures are necessary for environmentally viable wastewater nutrient recovery process.

The ammonia emissions findings deviated significantly from Högstrand et al. (2023) results. This paper's experimental and theoretical calculations results showed that ammonia emissions are 0.735 g/(PE, year), whereas in Högstrand et al. (2023), ammonia emissions were about 0.44 kg/year (PE, year). The magnitude of ammonia emissions is substantially lower than in Sweden's pilot findings. Additionally, if employed to treat all of Finland's wastewater, NPHarvest technology would contribute an average of 4.1 ton-NH₃ per year emissions, which is 0.01% of Finland's annual total ammonia emissions. Lower ammonia emissions increase the ecological viability of NPHarvest technology. (Rautalahti & Kupiainen, 2016; World Bank, 2022)

Definite answers of high emission results in Sweden's pilot are unknown. However, clear indication of the methods used is needed, and mass balance equation and improper sealing of the pilot have an effect on the Högstrand et al. (2023) results.

References

- Al-Juboori, R. A., Uzkurt Kaljunen, J., Righetto, I., & Mikola, A. (2022). Membrane contactor onsite piloting for nutrient recovery from mesophilic digester reject water: The effect of process conditions and pre-treatment options. *Separation and Purification Technology*, 303. <https://doi.org/10.1016/j.seppur.2022.122250>
- Aziz, M., Wijayanta, A. T., & Nandiyanto, A. B. D. (2020). Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies*, 13(12), 3062. <https://doi.org/10.3390/en13123062>
- Bicking, S., Burkhard, B., Kruse, M., & Müller, F. (2019). Bayesian Belief Network-based assessment of nutrient regulating ecosystem services in Northern Germany. *PLoS ONE*, 14(4). <https://doi.org/10.1371/JOURNAL.PONE.0216053>
- BIRKEN, G. A., FABRI, P. J., & CAREY, L. C. (1981). Acute Ammonia Intoxication Complicating Multiple Trauma. *The Journal of Trauma: Injury, Infection, and Critical Care*, 21(9), 820–822. <https://doi.org/10.1097/00005373-198109000-00015>
- Brück, T. B., Balasubramaniam, A., Brück, W. M., Ahmadzadeh, H., Molazadeh, M., Pourianfar, H. R., Lyon, S., & Rampelotto, P. H. (2019). The Use of Microalgae for Coupling Wastewater Treatment With CO₂ Biofixation. *Frontiers in Bioengineering and Biotechnology | Www.Frontiersin.Org*, 1, 42. <https://doi.org/10.3389/fbioe.2019.00042>
- Cabello, P., Roldán, M. D., Castillo, F., & Moreno-Vivián, C. (2009). Nitrogen Cycle. *Encyclopedia of Microbiology*, 299–321. <https://doi.org/10.1016/B978-012373944-5.00055-9>
- Capodaglio, A. G., Hlavínek, P., & Raboni, M. (2015). Physico-chemical technologies for nitrogen removal from wastewaters: A review. *Revista Ambiente e Agua*, 10(3), 481–498. <https://doi.org/10.4136/AMBI-AGUA.1618>
- Cofie, O., Nikiema, J., Impraim, R., Adamtey, A., Paul, J., & Kone, D. (2016). *Co-composting of solid waste and fecal sludge for nutrient and organic matter recovery*. <https://doi.org/10.5337/2016.204>
- Doster, E., Zitomer, R., & Chislock, M. F. (2013). *Eutrophication: Causes, consequences, and controls in aquatic ecosystems Use of metagenomic shotgun sequencing technology to detect foodborne pathogens within their microbiome in beef production chain View project Large effects of consumer offense on ecosystem structure and function View project*. <https://www.researchgate.net/publication/285683019>
- EBS. (2022). *Maintaining Nitrification During Cold Weather*. Maintaining Nitrification During Cold Weather. <https://www.ebsbiowizard.com/articles/maintaining-nitrification-cold-weather/>
- Ekejiuba, A. (2017). *Evaluation of the Exact Production Quantity of Nitrogen Fertilizer in Real-Time from any Particular Associated Gas Flare Volume in Nigeria*.
- Erismann, J. W., Sutton, M. A., Galloway, J., Klimont, Z., & Winiwarter, W. (2008). How a century of ammonia synthesis changed the world. *Nature Geoscience* 2008 1:10, 1(10), 636–639. <https://doi.org/10.1038/ngeo325>
- Fowler, D., Coyle, M., Skiba, U., Sutton, M. A., Cape, J. N., Reis, S., Sheppard, L. J., Jenkins, A., Grizzetti, B., Galloway, J. N., Vitousek, P., Leach, A., Bouwman, A. F., Butterbach-Bahl, K., Dentener, F., Stevenson, D., Amann, M., & Voss, M. (2013). *The global nitrogen cycle in the twenty-first century*. <https://doi.org/10.1098/rstb.2013.0164>

- GMI. (2013). *The Global Methane Initiative*. www.globalmethane.org
- Harihastuti, N., Djayanti, S., & Sari, I. R. J. (2021). Dry filtration technology application with activated carbon media to remove odor ammonia emissions from production process feed mill industry. *IOP Conference Series: Earth and Environmental Science*, 896(1). <https://doi.org/10.1088/1755-1315/896/1/012047>
- Helsinki Region Environmental Services Authority. (2021). *Viikinmäki wastewater Treatment Plant*. <https://julkaisu.hsy.fi/jatevedenpuhdistus-paakaupunkiseudulla-2021.html#>
- Högstrand, Juho Uzkurt Kaljunen, Raed Al-Juboori, Karin Jönsson, Hamse Kjerstadius, Anna Mikola, Greg Peters, & Magdalena Svanström. (2023). *Life cycle assessment of reject water treatment with nutrient recovery for a novel, membrane-based technology*.
- IEA. (2022). *Global Methane Tracker 2022 – Analysis*. Global Methane Analysis. <https://www.iea.org/reports/global-methane-tracker-2022>
- Jain, A., & He, Z. (2018). *Cathode-enhanced wastewater treatment in bioelectrochemical systems*. <https://doi.org/10.1038/s41545-018-0022-x>
- Janus, H. M., & van der Roest, H. F. (1997). Don't reject the idea of treating reject water. *Water Science and Technology*, 35(10), 27–34. [https://doi.org/10.1016/S0273-1223\(97\)00220-5](https://doi.org/10.1016/S0273-1223(97)00220-5)
- Kavyashree, A., N, R., M, S. U., B, C., & S, S. (2015). Ammonia Gas Removal using Biofilter. *IARJSET*, 2(7), 110–114. <https://doi.org/10.17148/IARJSET.2015.2724>
- Koskue, V., Freguia, S., Ledezma, P., & Kokko, M. (2021). Efficient nitrogen removal and recovery from real digested sewage sludge reject water through electroconcentration. *Journal of Environmental Chemical Engineering*, 9(5), 106286. <https://doi.org/10.1016/J.JECE.2021.106286>
- Kumar, A., Mishra, S., Bakshi, S., Upadhyay, P., & Thakur, T. K. (2023). Response of eutrophication and water quality drivers on greenhouse gas emissions in lakes of China: A critical analysis. *Ecohydrology*, 16(1). <https://doi.org/10.1002/eco.2483>
- Larsson, T., Duran Quintero, C., Gillot, S., Cockx, A., & Fayolle, Y. (2022). Development and validation of a comprehensive 1-D model to simulate gas hold-up and gas–liquid transfer in deep air–water bubble columns. *Chemical Engineering Science*, 248. <https://doi.org/10.1016/j.ces.2021.117210>
- Lorick, D., Macura, B., Ahlström, M., Grimvall, A., & Harder, R. (2020a). Effectiveness of struvite precipitation and ammonia stripping for recovery of phosphorus and nitrogen from anaerobic digestate: a systematic review. *Environmental Evidence*, 9(1). <https://doi.org/10.1186/S13750-020-00211-X>
- Lorick, D., Macura, B., Ahlström, M., Grimvall, A., & Harder, R. (2020b). Effectiveness of struvite precipitation and ammonia stripping for recovery of phosphorus and nitrogen from anaerobic digestate: a systematic review. In *Environmental Evidence* (Vol. 9, Issue 1). BioMed Central Ltd. <https://doi.org/10.1186/s13750-020-00211-x>
- Ma, R., Li, K., Guo, Y., Zhang, B., Zhao, X., Linder, S., Guan, C. H., Chen, G., Gan, Y., & Meng, J. (2021). Mitigation potential of global ammonia emissions and related health impacts in the trade network. *Nature Communications*, 12(1). <https://doi.org/10.1038/s41467-021-25854-3>

- Manto, M. J., Xie, P., Keller, M. A., Liano, W. E., Pu, T., & Wang, C. (2018). Recovery of ammonium from aqueous solutions using ZSM-5. *Chemosphere*, *198*, 501–509. <https://doi.org/10.1016/J.CHEMOSPHERE.2018.01.126>
- Mar, K. A., Unger, C., Walderdorff, L., & Butler, T. (2022). Beyond CO₂ equivalence: The impacts of methane on climate, ecosystems, and health. *Environmental Science and Policy*, *134*, 127–136. <https://doi.org/10.1016/j.envsci.2022.03.027>
- Melse, R. W., & Ogink, N. W. M. (2005). AIR SCRUBBING TECHNIQUES FOR AMMONIA AND ODOR REDUCTION AT LIVESTOCK OPERATIONS: REVIEW OF ON-FARM RESEARCH IN THE NETHERLANDS. *Transactions of the ASAE*, *48*(6), 2303–2313.
- Moines, D., Muhlbauer, E., Moody, L., & Burns, R. (2008). *Mitigating air Emissions from aniMal fEEding opErations*. www.mwps.org
- Natural resources institute of Finland. (2021). *Ammonia emissions from agriculture*. <https://www.luke.fi/en/ammonia-emissions-from-agriculture#description-of-the-indicator>
- NJDH. (2016). *Hazardous Substance Fact Sheet*. <http://nj.gov/health/workplacehealthandsafety/right-to->
- Rahmani, A. R., Navidjouy, N., Rahimnejad, M., Nematollahi, D., Leili, M., Samarghandi, M. R., & Alizadeh, S. (2020). Application of the eco-friendly bio-anode for ammonium removal and power generation from wastewater in bio-electrochemical systems. *Journal of Cleaner Production*, *243*, 118589. <https://doi.org/10.1016/J.JCLEPRO.2019.118589>
- Rautalahti, E., & Kupiainen, K. (2016). *REPORTS OF THE MINISTRY OF THE ENVIRONMENT 19en | 2016 Emissions of Black Carbon and Methane in Finland 2015 National Submission to the Arctic Council MINISTRY OF THE ENVIRONMENT*.
- Ray, H., Perreault, F., & Boyer, T. H. (2020). Ammonia Recovery from Hydrolyzed Human Urine by Forward Osmosis with Acidified Draw Solution. *Environmental Science & Technology*, *54*(18), 11556–11565. <https://doi.org/10.1021/acs.est.0c02751>
- Rouwenhorst, K. H. R., Travis, A. S., & Lefferts, L. (2022). 1921–2021: A Century of Renewable Ammonia Synthesis. *Sustainable Chemistry*, *3*(2), 149–171. <https://doi.org/10.3390/suschem3020011>
- Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, *15*(8), 4399–4981. <https://doi.org/10.5194/acp-15-4399-2015>
- Seruga, P., Krzywonos, M., Pyzanowska, J., Urbanowska, A., Pawlak-Kruczek, H., & Niedźwiecki, Ł. (2019). Removal of ammonia from the municipal waste treatment effluents using natural minerals. *Molecules*, *24*(20). <https://doi.org/10.3390/molecules24203633>
- Steffen, W., Richardson, K., Rockström, J., Cornell, S. E., Fetzer, I., Bennett, E. M., Biggs, R., Carpenter, S. R., de Vries, W., de Wit, C. A., Folke, C., Gerten, D., Heinke, J., Mace, G. M., Persson, L. M., Ramanathan, V., Reyers, B., & Sörlin, S. (2015). Planetary boundaries: Guiding human development on a changing planet. *Science*, *347*(6223). <https://doi.org/10.1126/science.1259855>
- Stein, L. Y., & Klotz, M. G. (2016). The nitrogen cycle. *Current Biology*, *26*(3), R94–R98. <https://doi.org/10.1016/J.CUB.2015.12.021>

- UNFCCC. (2022). UNITED NATIONS CLIMATE CHANGE ANNUAL REPORT 2021. *UNITED NATIONS CLIMATE CHANGE*. <https://unfccc.int/annualreport>
- Uzkurt Kaljunen, J. (2018). *Nitrogen harvesting from liquid waste streams using hydrophobic gas permeable membranes*. <http://urn.fi/URN:NBN:fi:aalto-201806293775>
- Vanotti, M., & Szogi, A. A. (2011). Use of Gas-Permeable Membranes for the Removal and Recovery of Ammonia from High Strength Livestock Wastewater. *Proceedings of the Water Environment Federation, 2011*, 659–667. <https://doi.org/10.2175/193864711802867405>
- Wagner, C., Nyord, T., Vestergaard, A. V., Hafner, S. D., & Pacholski, A. S. (2021). *Acidification Effects on In Situ Ammonia Emissions and Cereal Yields Depending on Slurry Type and Application Method. 11*, 1053. <https://doi.org/https://doi.org/10.3390/agriculture11111053>
- World Bank. (2022). World emission data, Methane. *World Bank*. climatewatchdata.org/ghg-emissions
- WRI. (2020). Climate Watch, GHG emissions. *Washington, DC: World Resources Institute*. <https://www.climatewatchdata.org/ghg-emissions>
- Wyer, K. E., Kelleghan, D. B., Blanes-Vidal, V., Schaubberger, G., & Curran, T. P. (2022). Ammonia emissions from agriculture and their contribution to fine particulate matter: A review of implications for human health. In *Journal of Environmental Management* (Vol. 323). Academic Press. <https://doi.org/10.1016/j.jenvman.2022.116285>