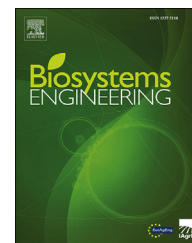


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Review

Reviewing the N-gap in livestock manure systems: Direct and indirect methods for measuring N losses and perspectives for quantifying N₂ emission



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The main objectives of this review were to: (1) review different methods/techniques to assess gaseous N-losses from manure (2) review N-gaps, attributed to dinitrogen loss as the difference between directly measured N compounds summed as total N loss and indirectly measured N loss through a mass balance in livestock manure systems, and (3) provide approaches to close the N-gap. In literature, N-gaps run up to 80% of total N loss, this undermines N emission assessments and leaves a huge part of the emission unexplained. However, studies that measure N-gaps are scarcely available or are limited in their evaluation, hence more study is needed. Three approaches are introduced to research N-gaps: (1) measure N₂ through a suggested Gas Flow Soil Core (GFSC) technique and compare the sum of all measured N losses with the indirect method, (2) assume N₂ loss as being the N-gap and (3) include N₂ as an estimate based on ratios from literature. In a hypothetical example for poultry manure, assumed values for measurement error of 50% and variance due to physical differences between the experimental units of 50% led to a total standard deviation of 131% in the N-gap. Variance of N-gap was reduced with 80% point when assuming 16 vessels compared to single vessel. Using literature-based-ratios to estimate losses of N compounds led to variation of N-gap from 0.06% initial N overestimation to 26% of initial N underestimation. Future research should address this variance and apply methods to measure N₂ to close N-gaps.

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1. Introduction

Today, agriculture is strongly affecting the nitrogen biogeochemical cycle. Globally 120 Tg N yr⁻¹ is anthropogenically introduced as synthetic fertiliser to sustain crop and grass production of which 50–70 Tg N is biologically fixed (Sutton, Bleeker, et al., 2013). Of all anthropogenic N, only 20–30% ends up in food for human consumption and the other part is lost to the environment, mainly in the form of ammonia (NH₃, 37 Tg N yr⁻¹) (Sutton, Reis, et al., 2013), N₂O (25 Tg N yr⁻¹) (Billen, Garnier, & Lassaletta, 2013), and leached or run-off as NO₃⁻ and NH₄⁺ (95 Tg N yr⁻¹) (Billen et al., 2013). In 2015, 94% of the NH₃ emission in the EU-28 was related to agricultural production (Eurostat, 2018). In agriculture, manure management (livestock) and agricultural soils accounted for 52% and 42% of total ammonia emission, respectively. Ammonia contributes to acidification and eutrophication, is a precursor of secondary particulate matter (Erismann & Schaap, 2004) and decreases biodiversity through deposition of nitrogen in the environment (Larios et al., 2016). Other nitrogen compounds inflict different impacts on the environment. For example, N₂O contributes to climate change and global warming and stratospheric ozone depletion (Ravishankara, Daniel, & Portmann, 2009). Another compound, NO, contributes to ozone production in the troposphere and is a precursor to acid rain (Williams, Hutchinson, & Fehsenfeld, 1992). Emissions from agriculture (livestock and soil) as well as other sources are regulated in the Nitrates Directive (1991) and the National Emission Ceilings Directives (NECD) (2001), the Gothenburg Protocol and worldwide with the Kyoto Protocol (1998) and the Paris Agreement (UNFCCC, 2015).

Typically, N emissions or gaseous losses from livestock manures (see section 2 for demarcation), and mainly solid poultry manure in barns and storages, range between 7% and 33% of the excreted N (Fig. 1). Based on Statistics Netherlands (CBS), up to 14% of this is determined as NH₃, up to 3% as N₂O and 3% as NO or NO₂ (van Bruggen & Geertjes, 2019). N₂ losses are not measured, but estimated because ambient air N₂ concentrations (approx. 80% of air) make measurement of net emission very hard. Depending on the abiotic conditions in the manure (temperature, water and oxygen availability and pH), which are influenced by the type of animal, housing and storage systems, the N-based ratio of NH₃, N₂O, NO and N₂ losses is estimated as 5:1:1:5 for solid manure and 10:1:1:10 for slurry (Oenema et al., 2000; van Bruggen & Geertjes, 2019). These ratios originate from soil studies, but have not been validated for manure and, therefore, are highly uncertain as we will address in Section 3.2. Of this review. In a recent report from the statistics bureau in the Netherlands it was reported that, when comparing directly measured and indirectly assessed N emissions, in some cases 80% of the indirectly assessed N loss remained unexplained (van Bruggen & Geertjes, 2019). Direct measurement of the total N loss is defined as measuring and summing all separate gaseous emissions of N compounds during a certain time interval. Gaseous N losses from manure mainly include NH₃, N₂O, NO and N₂ emissions. Indirect measurement of the total N loss is defined as assessment of the difference between the total N

inputs and outputs over time (a mass balance) (Groot Koerkamp et al., 1998; Hristov et al., 2009).

Comparing direct N losses with indirect N losses, the CBS study identified substantial differences in total N loss in poultry manure between both approaches (more in-detail information on the CBS report will follow in Section 4). Other comparative studies of direct and indirect methods are available in limited quantities only. This means that it is very difficult to verify a presumed missing amount of N from manure when comparing the direct and indirect method, or what we will further call 'the N-gap'. This huge N-gap undermines the current nitrogen emissions assessment and leaves a profound amount of emission unexplained. The N-gap can include N₂ losses, like in the CBS study calling the difference with indirect method 'remaining N', but can also be assumed to equal N₂ under the condition that no other than the forementioned gaseous N emissions occur. The N-gap poses several problems and questions: 1. How accurate are current emission measurements regarding NH₃, N₂O, NO and NO₂? 2. Have N₂ losses been adequately estimated? And if not, could they be underestimated and to what extent quantitatively? 3. What methods or approaches can be devised to assess the N-gap more accurately, and possibly close or reduce it? These questions directly bring us to the main objectives of this review.

- 1) Review different methods/techniques to assess gaseous N-losses from manure;
- 2) Review N-gaps, attributed to dinitrogen loss, as the difference between directly measured N compounds summed as total N loss and indirectly measured N loss through a mass balance in livestock manure systems;
- 3) Provide approaches to close the N-gap.

To understand the underlying processes that lead to N losses in livestock systems, we first give a concise overview of the main microbiological, physical and chemical processes related to the conversion and the volatilisation of N compounds. After that we address the specifics of current emission measurement techniques for N compounds and look at ways to measure N₂ losses from manure (objective 1). N-gaps in experiments and field studies will be reviewed (objective 2) followed by three recommendations to estimate/quantify N-gap and N₂ (objective 3). A quantitative example of estimating N₂ loss based on literature is provided to explore the potential of one of the proposed methods by comparing direct and indirect methods and their involved variances and uncertainties. In terms of type of manure, the main focus in this research will be on poultry/stackable manure.

2. Gaseous N losses in livestock barns and storages

2.1. Manure excretion

Cattle and pigs excrete (fresh) faeces and urine containing microbial protein and urea as the main nitrogenous compounds, respectively. In excreta of poultry and birds, faeces and urine are excreted together and undigested proteins and

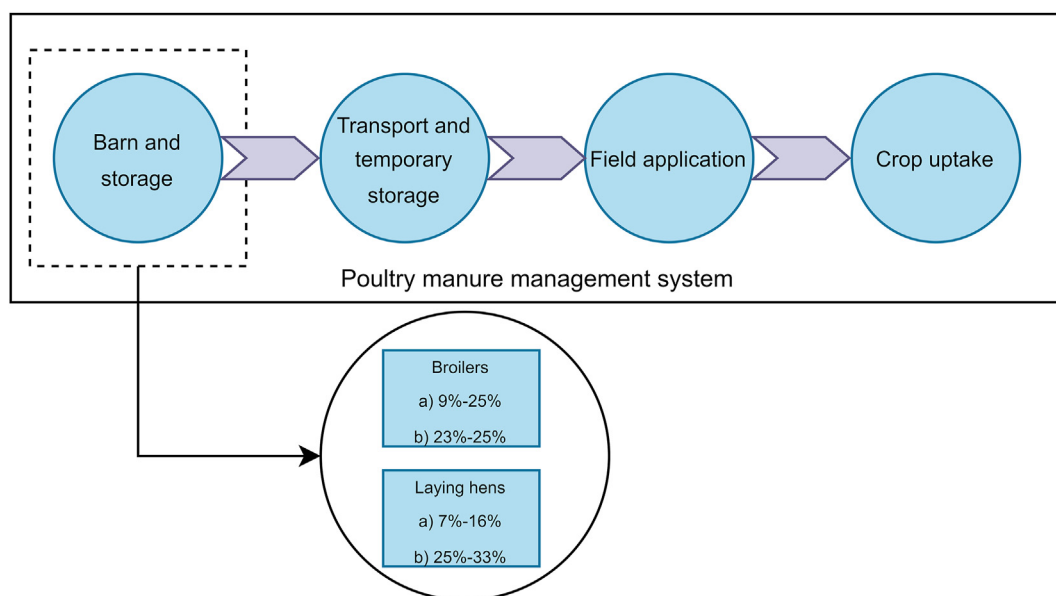


Fig. 1 – Range of variation for N losses in barn and storage for broilers and laying hens calculated by two different methods i.e. (a) direct (measuring $\text{NH}_3\text{-N}$, estimating $\text{N}_2\text{O-N}$, NO-N and $\text{NO}_2\text{-N}$) and (b) indirect: mineral ratio method (N/P ratio) (van Bruggen & Geertjes, 2019).

uric acid are the main nitrogenous compounds (Groot Koerkamp et al., 1998). We will use the term ‘manure’ in this review for faeces, urine, poultry excreta and mixtures thereof, possibly with other substances present in animal houses, such as straw, wood shavings/chips, sand, peat, manure fibre etc. It can either be in a liquid form which is often referred to as slurry and or in solid form, often referred to as farm yard manure or solid/stackable manure.

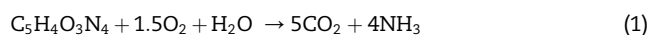
2.2. Conversion processes in manure

Nitrogen emissions occur in two main steps: (1) the conversion of nitrogenous compound to another compound, often done or supported by bacteria and enzymes, and (2) the volatilization of the nitrogenous compound, being transferred from the manure to air.

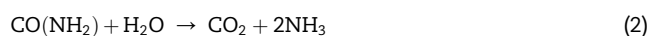
2.2.1. N conversions

In poultry manure, NH_3 is produced through a biochemical conversion of uric acid to NH_3 and follows three sub-steps (Carlile, 1984; Groot Koerkamp et al., 1998; Schefferle, 1965; Sousa et al., 2017).

- Biochemical degradation of uric acid to NH_3 ; which is positively affected by temperature, pH, moisture content and activity of the enzyme uricase (Eq. (1)):



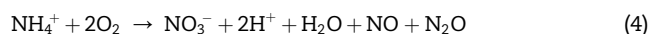
- Degradation process of urea to NH_3 ; which is affected by temperature, pH and enzyme urease activity (Eq. (2)):



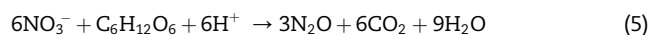
- Degradation of undigested protein by microbial conversion as a long-time process can be simplified as (Eq. (3)):



Nitrification is the microbial oxidation of NH_4^+ to NO_3^- that also produces NO and N_2O (Eq. (4)).



Denitrification is the microbial conversion of NO_3^- to the chemically inert and stable N_2 via NO_2^- , NO and N_2O (Eqs. (5) and (6)) (Oenema et al., 2000).



N_2O , NO and N_2 conversion and production processes depend on microbiological oxidation and nitrogenous reduction which is influenced by microbiological factors (bacteria population and activity), and chemical factors (pH, O_2 , NH_4^+ and NO_3^- concentration). Temperature and water activity have a marked influence on microbial and enzymatic activity, physical factors including air velocity and manure-to-air contact surface are of less importance (Granli & Bockman, 1994; Oenema et al., 2000; Seltzer, Moum, & Goldhaft, 1969).

The Anammox is another pathway of converting NH_4^+ to N_2 by using NO_2^- as an oxidant (Eq. (7)). Anammox is distinguishable from nitrification since N_2 is formed via pairing of the N atoms of NO_2^- and NH_4^+ (Oenema, Oudendag, & Velthof, 2007). This pathway was discovered for the first time in the 1990s and then distinguished as a dominant pathway for N loss in low-oxygen conditions (e.g. slurry and waste waters) and can represent up to 50% of total N loss (Arrigo, 2005).



2.2.2. Volatilisation

The second step in N emissions is the volatilisation of the N compounds. The volatilisation of N_2 , N_2O and NO includes transition of these gases from manure to the gaseous boundary layer followed by transport to the atmosphere. This volatilisation is linked to (1) rates of nitrification and denitrification, (2) the ratios of nitrification and denitrification end products and (3) diffusion and consumption of N gases prior to escape from manure to air (Davidson, 1991). The volatilisation of NH_3 differs from volatilisation of N_2 , N_2O and NO. The NH_3 volatilisation is a physio-chemical process in which the rate of mass transfer between manure and air is described by two known theories called ‘two-film theory’ and ‘boundary layer theory’. In the two-film theory, the rate of mass transfer is controlled by the rate of diffusion through the liquid and gas films. The boundary layer theory implies that there is a NH_3 concentration boundary layer between the puddle surface and flow of the air above (Ni, 1999). The volatilisation of NH_3 is mainly affected by physical (air velocity, manure-to-air contact surface, and temperature) and chemical (NH_4^+ concentration and pH) conditions (Snoek, Stigter, Ogink, & Groot Koerkamp, 2014).

3. Direct and indirect methods for assessing N losses

3.1. Direct measurement methods

The direct method of measuring N losses is aimed at measuring the gas flow of all compounds separately and summing them up to a total N loss. This means that for each compound, i.e. NH_3 , N_2O , NO and N_2 an assessment method is needed. The most commonly used methods measure the air flow rate through an enclosed volume and the concentration difference of the ingoing and outgoing air of the targeted nitrogen compound from time t_0 to t_{final} . The direct method can be expressed in the following equation (Eq. (8)):

$$[\text{N}]_{\text{loss}} = \int_{t_0}^{t_{\text{final}}} [Q] \times [\Delta n_1 + \Delta n_2 + \Delta n_3 + \dots] dt \quad (8)$$

where N_{loss} is the total N lost (g), Q is air flow rate (g/s) and Δn is the concentration difference of each nitrogen compound e.g. $\text{NH}_3\text{-N}$ (g/g) over time.

Table 1 provides a categorised and comprehensive overview of the different measurement approaches, methods and techniques to measure gaseous N compounds. The term approach was used in this table as a general term that includes a series of assumption to which one or more methods can be allocated. Three main approaches including gas concentration, air flow rate and in-field measurement are used in this table. Each measurement instrument has its own type of error. In this review, ‘error’, ‘uncertainty’, ‘uncertainty of measurement’, ‘accuracy’ and ‘precision’ are used as defined in the Joint Committee for Guides in Metrology (JCGM) (2008).

3.1.1. Ammonia – NH_3

Different techniques and methods have been used to measure NH_3 concentrations in the livestock sector, for instance, chemiluminescence, passive sampling, wet chemistry, photoacoustic, FTIR and electrochemical methods (Table 1). Chemiluminescence is a quick, robust and accurate approach with precision of 2%–5% (Ni et al., 1999; Oenema et al., 2000). Heber, Ni, Haymore, Duggirala, and Keener (2001) reported 0.5% precision with 0–90% response time of 120 s (average 10 s) when using chemiluminescence NO_x analyser to measure NH_3 (after conversion to nitric oxide) from swine finishing buildings. The passive flux sampler is cost effective, little training is required to handle the device and there is no need for a power source. However, sampling with this method is affected by wind velocity, relative humidity, radiation and temperature (Krupa & Legge, 2000) and has a reported accuracy of 5%–10% (Rabaud, James, Ashbaugh, & Flocchini, 2001). Wet chemistry is based on absorbing NH_3 to an acid aqueous and its conversion to ammonium; this method gives an average concentration over a certain period of time. The precision of this method is less than 5% (NEN 2826, 1999; Roadman, Scudlark, Meisinger, & Ullman, 2003). The photoacoustic method is cost effective and portable for continuous measurement with a precision of 2.5% (Hinz & Linke, 1998; Kang et al., 2014). Commercial FTIR devices (Gasmet CX4000) are available for measuring ammonia with the detection limit of 0.1 ppm and quantification limit of 0.3 ppm (Bobrowski et al., 2021). Electrochemical methods are portable and suitable for safety purpose in barns and industry (Kamieniak, Randviir, & Banks, 2015) and typically have a precision of 8% (Redwine, Lacey, Mukhtar, & Carey, 2002). The electrochemical sensors are sensitive to saturation when continuously exposed to NH_3 air and, therefore, are recommended for background NH_3 monitoring with little or no NH_3 in the environment (Gates, Xin, Casey, Liang, & Wheeler, 2005). More information on different methods and techniques to measure NH_3 can be found in Ni and Heber (2008).

3.1.2. Nitrous oxide – N_2O

N_2O concentrations in air can be measured by using Electron Capture Detectors (30 ppb limit of detection [LOD]) and precision of 0.18–0.4 ppb), Fourier transform infrared (precision of 0.1 ppb in 1 min and 0.03 ppb in 10 min), Lead Salt Lasers (precision <1 ppb in 5 s), Quantum Cascade Lasers (precision of 0.05 ppb) and Amperometric Microsensors (22 ppb LOD) (Rapson & Dacres, 2014). Photoacoustic Spectroscopy has been used for measuring N_2O concentration in animal buildings. Ngwabie, Jeppsson, Nimmermark, Swensson, and Gustafsson (2009) reported 2%–3% of measurement accuracy for a portable photoacoustic multi gas analyser. Cortus, Jacobson, Hetchler, Heber, and Bogan (2015) compared two methods i.e.: photoacoustic multi gas analyser (PAMGA) and gas-filter correlation analyser (GFC) to measure N_2O from a dairy free-stall barn. They reported precision of 2.4% and 8.3% for GFC and PAMGA methods, respectively, when comparing with a reference gas.

Table 1 – Comprehensive overview of the different measurement approaches, methods and techniques to measure N compounds.

| Approach | Method | Technique | Comment | Detected gas | Precision | Literature | |
|-------------------|---|---|--|---|---|---|---------------------------|
| Gas Concentration | Electrochemical | Sensor/analyser | Pros: Portable, suitable for safety reasons (industry) and low concentrations. Cons: Sensitive to saturation when exposed to NH ₃ -laden air. | NH ₃ | 8% | (Gates et al., 2005; Redwine et al., 2002) | |
| | Cumulative: passive sampling ^a | Badge, surface absorbent/packed diffusion tubes, cartridge, chemical absorption | Pros: Cost effective, little training needed, no need for power source. Cons: Affected by environmental condition (wind, radiation, temperature, etc.). | NH ₃ and N ₂ O | N.A. ^b | Krupa and Legge (2000) | |
| | Cumulative: active sampling | | Pros: Continuous measurement, longer measurement period is possible. Cons: Sensitive to water condensation when using automatic sampling units. | NH ₃ and N ₂ O | N.A. | Larios et al. (2016) | |
| | Chamber | Open-path | | Pros: Longer measurement period is possible, similar environmental condition for inside gas and ambient. Cons: Less sensitive technique (suitable for low concentrations), gas diffusion from substrate may be stimulated. | NH ₃ and N ₂ O | N.A. | Granli and Bockman (1994) |
| | | | Closed-path | Pros: Simple instrumentation, high sensitivity. Cons: Ventilation is needed to control intrinsic temperature rise, gas diffusion may be hampered by high partial pressure above the substrate, labour demanding. | NH ₃ and N ₂ O | N.A. | Granli and Bockman (1994) |
| | Gas chromatography (GC) | Flame Ionisation Detector (FID), Electron Capture Detector (ECD), Thermal Conductivity Detector (TCD) | GC combines unmatched high separation ability with sensitivity, ease of use and relatively low cost as a tool for complex environmental applications and premier technique for the separation of thermally stable, volatile organic compounds in analytical laboratories worldwide. Cons: not mobile. | N ₂ O and NH ₃ | 3% for N ₂ O by ECD. 4%–15% for NH ₃ by GC. | (Katlie, Simon, & De Greeff, 2019; Larios et al., 2016; Rapson & Dacres, 2014) | |
| | Spectroscopy | Fourier Transform Infrared (FTIR) | Pros: Higher signal-to-noise ratio than dispersive spectroscopy, less sensitive to stray light, wide spectral range, portable. Cons: Unable to detect diatomic or noble gases. | NO, NO ₂ , N ₂ O, NH ₃ | 2%–5% | Singh, Singh, Beg, and Nishad (2019) | |
| | | Chemiluminescence | Rapid response, robust and high sensitivity. | NH ₃ and NO _x | 2–5% for NH ₃ and 0.5–4.6% for NO _x . | (Maeda et al., 1980; Ni, Hendriks, Coenegrachts, & Vinckier, 1999; Oenema et al., 2000) | |
| | | Photoacoustic | Pros: Portable, continuous measurement Con: Expensive | N ₂ O and NH ₃ | 1.12% for N ₂ O | Vovk and Prosek (2000) | |

(continued on next page)

Table 1 – (continued)

| Approach | Method | Technique | Comment | Detected gas | Precision | Literature |
|----------------------|-----------------------------|--|---|--------------------------------------|---|--|
| | | Cavity ring-down laser absorption | Pros: Super sensitive at a ppt ^c level due to the multipass nature of the detection cell (long pathlength), measurement is not affected by laser intensity fluctuations, wide range of use for a given set of mirrors, commercially available and high throughput on the millisecond for each individual ring down event. Cons: Expensive, spectra cannot be quickly achieved when using monochromatic laser source, limited availability of tuneable laser at appropriate wavelength and availability of high reflectance mirrors at the same wavelengths. | NH ₃ and N ₂ O | At ppbv ^d level | (Shadman, Rose, & Yalin, 2016; Stelmaszczyk et al., 2009; Tang, Li, & Wang, 2019) |
| Air exchange rate | Anemometer | Hot wire anemometer | Ventilation rate measuring technique affected by non-uniform distribution of the velocity profile in inlet and outlet openings. | NH ₃ | 25% | Ouwerkerk (1993) |
| | | Fan-wheel anemometer | Reference method to measure the ventilation rate from mechanically ventilated livestock houses. The fan-wheel anemometer must cover the entire area of exhaust and with sufficient distance from ventilator. | NH ₃ | 5% (except for low flow velocities) | (VERA, 2018) |
| | Tracer gas | SF ₆ | Straightforward calculation for balance equation needed and the method determines overall ventilation rate through system. | NH ₃ | 10%–15% | van Buggenhout et al. (2009) |
| | Balance | Heat balance, moisture balance and CO ₂ balance | Assumption of perfect mixing and measurement errors from unknown sources prevents wide application of these methods. | N.A. | (31%–101%) (5%–40%) 15%–40% respectively | van Buggenhout et al. (2009) |
| | 3D spatio-temporal model | Computational fluid dynamics (CFD) | Complex method with errors up to 65%. This method requires practical verification. | N.A. | 35% | Molina-Aiz, Valera, and Álvarez (2004) |
| In-field measurement | Gas flux chamber | Steady-state, non-steady-state and tunnel | Pro: Accurate measurement of gaseous emissions from animal housing. Cons: Suitable for small scale, interfere with normal production of gases, chambers create artificial environment and may induce animal stress. | NH ₃ | 5%–10% | Raubaud et al. (2001) |
| | Micrometeorological methods | Mass balance, vertical flux, inverse dispersion analysis, boundary layer budgeting | Pros: Suitable for measuring animal housing, without animal handling or altering animal behaviour. Measurement possibility for large scale. Cons: Dependency of measurement on wind direction, large uniform area needed for open field measurements, unable to separate various emitting sources on a farm. | NH ₃ and N ₂ O | 8% for NH ₃ via mass balance | (Harper, Denmead, & Flesch, 2011; Huijsmans, Hol, & Vermeulen, 2003; Zhu et al., 2014) |

| | | | | | |
|--------|-----------------------|--|-----------------|--|--|
| Remote | Tracer gas dispersion | Pros: Suitable for whole-farm emission measurement, reduces measurement uncertainty by sufficient mixing and emission source simulation through far enough emission source measurement and providing multiple complete plume transects. Cons: Perfect mixing is required, building effects are important close to animal house, measurements should be carried out outside the building resulting in underestimation of the emission for measurements far from animal house and when local deposition is important. | NH ₃ | 2% with conductivity detector (AMANDA) | (Erisman et al., 2001; Mosquera, Monteny, & Erisman, 2005; Vecchi, Mellqvist, & Scheutz, 2022) |
|--------|-----------------------|--|-----------------|--|--|

^a Active and passive samplings are not limited to the gas concentration measurements and may be applied for flow or in-filed measurements as well.
^b Not available.
^c Part per trillion.
^d Part per billion by volume.

3.1.3. Nitrogen dioxide/nitric oxide – NO₂ and NO
 Maeda, Aoki, and Munemori (1980) reported that the relative standard deviation of the chemiluminescence method for measuring NO₂ concentration in samples with 3.8 ppm and 5.5 ppb varied between 0.54% and 4.6%, respectively. Fibiger, Hastings, Lew, and Peltier (2014) measured NO and NO₂ by isotopic analysis with 1.5% precision. Gas Chromatography (GC) with a Chemiluminescence detector was used by Molstad, Dörsch, and Bakken (2007) to measure nitric oxide. This technique has an absolute detection limit for NO of 0.2 ppm and is a simple solution for analysing small gas samples. Isotopic analysis was suggested as inexpensive and easily adjustable for passive samplers to collect NO₂ (Felix & Elliott, 2014). Noto, Murayama, Tosaka, and Fujiwara (1999) suggested Flame Ionisation Detector (FID) to measure NO_x in small magnitudes of sample gas (1 ppm).

3.1.4. Nitrogen gas – N₂
 Methods and techniques for measuring N₂ are mainly developed in soil science and are of great interest for this paper to understand the N related processes and emissions from manure. The main reason is that soil structure can be fairly similar to manure structure, especially solid manure. From the literature, all attempts to measure N₂ focused on soil or water (aqueous) environment. Table 2 presents an overview of different research conducted in order to measure N₂ in soil and water condition. The Gas Flow Soil Core (GFSC) technique and membrane inlet mass spectroscopy are two commonly and most used techniques to measure N₂ concentrations and fluxes from soil. Tuneable diode-laser spectrometer, gas ratio (N₂/Ar), stable isotope and gas tension device (GTD) are common techniques that have been used in recent decades to measure N₂ from aqueous circumstances like ocean water.

Dannenmann, Butterbach-Bahl, Gasche, Willibald, and Papen (2008) measured N₂ emission and N₂:N₂O emission ratios from soil based on the Gas Flow Soil Core (GFSC) technique. Liao et al. (2013) developed the GFSC technique by adding a chemiluminescent detector and a gas chromatograph detector to measure N₂, N₂O, NO, CO₂ and CH₄ gas concentrations from soil automatically and online to overcome the drawbacks described by Wang et al. (2011), such as low frequency of measurement, low accuracy in N₂ detection and intensive manual operation. Dissolved N₂ in rivers was directly measured by the gas ratio (N₂/Ar) technique (Wu et al., 2013). Measurements of N₂ were also carried out by stable N and O isotope methods (Peters et al., 2018). N₂ fluxes (in aquatic circumstance) were measured using a gas trapping device method (GTD) and membrane inlet mass spectroscopy method; the two methods showed quite similar results under same conditions (Liu et al., 2016).

Of the methods used for measuring N₂ emission from terrestrial and aquatic environments, the GFSC techniques may be the most compatible with manure samples. The GFSC technique is a technique in which the soil atmosphere is replaced by an N₂-free atmosphere to allow direct measurement of N₂ from the soil. This method was first introduced in the 1970s for anaerobic conditions to measure N₂O and N₂ from soil samples in a helium/argon atmosphere. Later it was developed to measure emitted N₂ by denitrification processes

Table 2 – Overview on dinitrogen (N₂) measurement techniques applied in terrestrial and aquatic environments.

| Title of research | Techniques and Methods | Description | Result(s) | Literature |
|--|---|---|--|--|
| Automated online measurement of N ₂ , N ₂ O, NO, CO ₂ , and CH ₄ emissions based on a gas-flow-soil-core technique | Gas Flow Soil Core (GFSC) technique, chemiluminescent detector, gas chromatograph detector | GFSC system updated by using both a chemiluminescent detector and a gas chromatograph detector to measure NO, synchronizing the measurements of N ₂ , NO, N ₂ O, CO ₂ and CH ₄ . | Fully automating the sampling/analysis of all measured gases. These technical modifications significantly reduced labour demands by at least a factor of two, increased the measurement frequency from 3 to 6 times per day and resulted in remarkable improvements in measurement accuracy (with detection limits of 0.5, 0.01, 0.05, 2.3 and 0.2 µg N or C h ⁻¹ kg ⁻¹ ds, or 17, 0.3, 1.8, 82, and 6 µg N or C m ⁻² h ⁻¹ , for N ₂ , N ₂ O, NO, CO ₂ , and CH ₄ , respectively). | Liao et al. (2013) |
| Gaseous nitrogen emissions from anaerobic swine lagoons: ammonia, nitrous oxide, and dinitrogen gas | Thermal conductivity detector | Gas bubbles emitted from the lagoons were collected using floated collars equipped with evacuated sample lines and evacuated SUMA canisters. | NH ₃ and N ₂ were registered to be 12 ± 17 kg NH ₃ -N ha ⁻¹ d ⁻¹ and 37 ± 25 kg ha ⁻¹ d ⁻¹ respectively. | Harper, Sharpe, and Parkin (2000) |
| Dinitrogen emissions and the N ₂ :N ₂ O emission ratio of a Rendzic Leptosol as influenced by pH and forest thinning | Gas Flow Soil Core (GFSC) technique | 1-day flushing time for soil cores were executed. N ₂ , N ₂ O emissions and N ₂ :N ₂ O emission ratio were determined. | N ₂ emission showed a huge variability (range: 161 ± 64–1070 ± 499 µgNm ⁻² h ⁻¹), so that potential effects of microclimate or silvi-cultural treatment on N ₂ emission could not be identified with certainty. | Dannenmann et al. (2008) |
| Diode-laser measurements of N ₂ -broadening coefficients in the ν ₁₀ band of allene at low temperatures | Tuneable diode-laser spectrometer | N ₂ -broadening coefficients of Allene for 5 lines in the ν ₁₀ fundamental band near 11 µm at five low temperatures ranging from 167.7 K to 259.7 K were measured | n parameter (order of power) of the temperature dependence for the N ₂ -broadening of Allene lines was obtained | Fissiaux, Blanquet, and Lepère (2013) |
| Direct measurement of dissolved dinitrogen to refine reactive modelling of denitrification in agricultural soils | Simulation technique, Membrane inlet mass spectrometry (MIMS) | The USGS geochemical speciation model PHREEQC was used to simulate the titration and subsequent complete degradation of acetate under NO ₃ ⁻ reducing conditions | Modelling of nitrate degradation processes as a whole, using geochemical datasets and codes, will improve the estimates of agricultural landscapes denitrification and support better nitrogen management | Mastrocicco, Colombani, and Castaldelli (2019) |
| Direct measurement of dissolved N ₂ and denitrification along a subtropical river-estuary gradient, China | Gas ratio (N ₂ /Ar) measurement | Concentration of dissolved N ₂ (µmol L ⁻¹) and N ₂ O (nmol L ⁻¹) in surface or bottom water were determined. | The results showed that excess dissolved N ₂ ranged from 9.9 to 76.4 µmol L ⁻¹ . | Wu et al. (2013) |
| Estimating fixed nitrogen loss and associated isotope effects using concentration and isotope measurements of NO ₃ , NO ₂ , and N ₂ from the Eastern Tropical South Pacific oxygen deficient zone | Nutrient concentration measurement, Gas ratio (N ₂ /Ar) measurement, Stable N and O isotopes in NO ₃ , NO ₂ , and N ₂ | Stable isotopic measurements of NO ₂ , NO ₃ and N ₂ were used to calculate N and O isotope effects for NO ₃ reduction and N isotope effects for dissolved inorganic nitrogen (DIN) removal. | Concentration recognizing in different area and depth of ocean. N ₂ :Ar measurements allowed estimates of biologically produced N ₂ . Estimating of ocean nitrogen budget. | Peters et al. (2018) |

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|---|---|---|--|--|
| In-situ O ₂ and N ₂ measurements detect deep-water renewal dynamics in seasonally-anoxic Saanich Inlet | Gas tension device (GTD) | N ₂ excess was derived by combining measurements of total dissolved gas pressure from a (GTD) with dissolved oxygen measurements and comparing to expected equilibrium concentrations. Measurements of N ₂ broadening coefficients for transitions of the ν_6 band. J- and K-rotational quantum number dependences of the N ₂ -broadening coefficient were studied. GTD and MIMS methods were compared for measuring N ₂ flux from water under similar conditions | High rates of denitrification in the bottom waters over most of the year have provided the N ₂ excess. | Hamme, Berry, Klymak, and Denman (2015) |
| Measurements and modelling of N ₂ broadening coefficients for the ν_6 band of CH ₃ F, comparison with CH ₃ Cl and CH ₃ Br molecules | Fourier transform spectroscopy | | J- and K-rotational model applied to CH ₃ Cl, CH ₃ Br and CH ₃ F in this study had similar results in comparison of empirical model in literature. | Ramchani, Jacquemart, Soulard, and Guinet (2017) |
| Supplemental tests of gas trapping device for N ₂ flux measurement | Gas trapping device method (GTD), Membrane inlet mass spectrometry (MIMS) | | N ₂ fluxes from water measured by GTD and MIMS methods are quite similar under all three concentrations of nitrate (5.30, 10.55 and 17.25 mg L ⁻¹) and two levels of temperature (20 and 30 °C). GTD method offers a reliable alternative method to estimate N ₂ flux rate in aquatic ecosystem. | Liu et al. (2016) |

under aerobic conditions (Wang et al., 2011). Compared to other available methods and techniques such as isotope labelling and acetylene inhibition, the GFSC technique has some advantages e.g. (a) it has the ability to directly measure N₂ emission by applying inert gas to flush the soil core (Liao et al., 2013); (b) it is non-destructive, because no inhibitors or labels are being applied into soil (Swerts, Uytterhoeven, Merckx, & Vlassak, 1995); (c) it can be done by an automated set-up and online analysis (Liao et al., 2013) and has the possibility of measuring other nitrogenous and non-nitrogenous compounds alongside N₂. A drawback of the method is that, compared to the $\delta^{15}\text{N}$ tracer technique, it does not allow to distinguish between different process sources of N₂, e.g. classic denitrification versus heterotrophic and autotrophic nitrifier denitrification (Chapuis-lardy, Wrage, Metay, Chotte, & Bernoux, 2007; Poth, 1986) as well as anaerobic NH₃ oxidation (Thamdrup & Dalsgaard, 2002). Another drawback of the method is that the required replacement of the soil atmosphere by flushing is a time-consuming process.

3.2. N₂:N₂O ratios in soil literature

The current N emission ratios used in manure studies originate from soil literature. The earlier mentioned CBS ratios for solid manure and slurry have been derived from one study (Oenema et al., 2000). From a review of the distribution of N compound losses in soil and manure, they formulated the N₂ emissions to be 90% of the total N loss as a result of both nitrification and denitrification processes. As N₂O is another product of nitrification and denitrification, the ratio of 10:1 was estimated for N₂:N₂O (Oenema et al., 2000). Robertson (1991) reported that animal manure anthropogenically contribute to on average 6.1% N₂O–N emission. However, more supporting data is needed to establish a ratio between N₂ and N₂O. Granli and Bockman (1994) stated that N₂ and N₂O emission are totally dependent on interactive factors including soil water content, temperature, pH, availability of NO₃⁻ and presence/lack of O₂. Availability of mineral N (NH₄⁺ and NO₃⁻) to bacteria is an important factor for the microbial process that produces N₂O (Granli & Bockman, 1994). It was also found that as temperature increases, the N₂O/N₂ ratio declines. In addition to N₂, N₂O is also a considerable contributor to nitrification and denitrification processes. Mosier, Parton, and Hutchinson (1983), found that the N₂O production and evolution may be greater in less anoxic environments while the N₂ production predominates in more anoxic sites. Although the significance of N₂O remains obscure in nitrification and denitrification processes largely because it may further be reduced to N₂ (Focht, 1974), Stefanson (1973) showed that the ratio of N₂:N₂O gases in soils treated by ¹⁵NO₃⁻ and NH₄ varied from 0.1:1 to 6:1 and 3.5:1 to 133:1, respectively, depending on the soil water potential, pasture soil or crop soil and soil with or without plant conditions. Davidson (1991) reviewed that in soil studies, the prediction of gas fluxes is expressed through water-filled pore space (WFPS). Denitrification becomes increasingly important when WFPS exceeds 60%. They indicated that as WFPS reaches 80%, N₂O consumption occurs, and N₂ becomes the major final product. Mosier et al. (1983) outlined that at NO₃⁻ levels less than 10 ppm, 70% of N from denitrification is lost as

N_2 . As the NO_3^- levels increase, the N_2 decreases to less than 40% at 30 ppm of NO_3^- . Firestone, Firestone, and Tiedje (1980) showed similar results indicating that about 20% of the NO_3^- denitrified in soil with 20 ppm NO_3^- -N evolved as N_2O and 80% as N_2 , yet at 2 ppm NO_3^- approximately 5% was evolved as N_2O and 95% as N_2 .

To sum up, there is no consensus concerning a constant ratio for N_2O and N_2 in soil studies, as the ratio between N_2O and N_2 may change depending on different biotic-abiotic conditions. This requires further investigation in manure studies in order to define a range of ratios for N_2 and N_2O under different biotic-abiotic conditions. Additionally, the intrinsic characteristics of manure, specifically in terms of composition and physical structure, require compatibility verification with the soil-based knowledge.

3.3. Indirect measurement methods

Indirect measurement of N loss assesses the mass and N concentration change from the start to the end of an experiment or measuring sequence (Eq. (9)).

$$[N]_{\text{loss}} = (W \times [n])_{\text{initial}} - (W \times [n])_{\text{final}} \quad (9)$$

where $[N]_{\text{loss}}$ is total nitrogen loss (g), W is the manure mass (g), $[n]$ is nitrogen concentration (g N/g mass). Experimentally, this can be done by weighing the whole mass of the material at the start and end of an experiment. A N balance is capable of providing a clear picture of total N loss when there are numerous input and output pathways containing N (Shah, Grimes, Oviedo-Rondón, Westerman, & Campeau, 2013). However, applying this method in commercial farming conditions is rather impractical, which can be overcome to add another reference component to the mass balance. Normally, this reference is a non-volatile substance in the manure, e.g. P, K or ash. In such environments, the mass balance can be constructed by for example using the N/P ratio in which the mass of the non-volatile element, in this case P, is assumed to be constant during the time interval (as P is found mostly in the form of P_2O_5 , this ratio is often presented N/P_2O_5). The N loss can be presented as either an absolute (Eq. (10)) or a relative loss (Eq. (11)).

$$[N]_{\text{loss}} = \left[\left(\frac{N}{P} \right)_{\text{initial}} - \left(\frac{N}{P} \right)_{\text{final}} \right] \times P_{\text{initial}} \quad (10)$$

$$[N]_{\text{rel.loss}} = \frac{\left(\frac{N}{P} \right)_{\text{initial}} - \left(\frac{N}{P} \right)_{\text{final}}}{\left(\frac{N}{P} \right)_{\text{initial}}} \quad (11)$$

in which $[N]_{\text{rel.loss}}$ is relative N loss in manure, $(N/P)_{\text{initial}}$ and $(N/P)_{\text{final}}$ are the N/P ratios at the start and end of the experiment, and P is the amount of phosphorus in the mass(g). The pro of this approach is that one can assess total N loss without a high demand of technical devices and labor. A con of the N/P balance is that it is challenging to gather a representative sample because of the inhomogeneous composition of manure, and it is almost impossible to achieve high temporal resolution of N losses. Another con is that one cannot determine the form in which the N is lost. Hence, for experimentation and assessing practical N losses application of both the direct and indirect method is required.

4. Direct and indirect measurement methods of N loss for poultry manure: N-gaps in experimental and field studies

Simultaneous use of direct and indirect methods of measuring N compounds in poultry manure has been reported in a limited number of studies only. In most studies, only NH_3 -N emissions were directly measured, whereas other N-compounds were estimated from literature or considered negligible when comparing N-balance results with emission measurements. In general, there is lack of consistency in the results when comparing N emissions with N loss in balances. Table 3 provides an overview of poultry studies under practical barn conditions that include both direct and partly indirect measurement of N loss.

In a study with 9 flocks with broilers Shah et al. (2013) estimated the loss of NH_3 -N and N_2O -N to be 29.2% of N-input. Keener and Zhao (2008) observed NH_3 -N emission magnitudes from laying hens 25–250% greater than the N balance method, but reported that their NH_3 -N measurements were not reliable and should not be used for calculating absolute N losses. Coufal, Chavez, Niemeyer, and Carey (2006) measured N-balances in 18 consecutive flocks of broilers without gaseous emission measurements. They partitioned N input between output of carcass, mortality, litter, and the remaining part being loss, where N loss on average amounted 21% of N-input. They reported huge differences in N losses between flocks, varying from 18 to 82% of excreted N. Rosa, Arriaga, and Merino (2020) compared NH_3 emissions from a manure-belt laying hen facility, accumulated over 15 months, with the N loss calculated from the nitrogen balance over the same period, and found a close agreement between both, amounting to 93.8 and 98.4 mg $NH_3 \text{ d}^{-1} \text{ hen}^{-1}$ respectively. In an experimental study with 66 samples of poultry litter gathered from 12 commercial aviary houses (Groot Koerkamp et al., 1998), compared NH_3 -N emission measured by the impinger method (during 60 h) and total initial N content. The NH_3 -N emission measured by the impinger method varied from 0.3 to 22% (mean 4.0) of total initial nitrogen. Wang, Liu, Beasley, Munilla, and Baughman (2006) estimated total N loss from broiler litter by measuring NH_3 -N emissions through two different direct methods (acid scrubber method and Chemiluminescence (Thermo Environmental Instrument (TEI)) and N balance method. For a substrate with moisture content of 17.8%, acid scrubber and TEI methods measured 138 mg and 160 mg total N loss respectively, whereas, the N balance method registered 994 mg over the same period. This study showed a substantial difference between the direct and indirect method. Moreover, a significant difference was reported between direct methods, requiring further investigations to explain the differences.

Besides field studies information on N loss from manure can also be derived from data that are collected for regulatory reasons. The national statistical bureau in the Netherlands, Statistics Netherlands, (CBS) published in 2019 an analysis of N losses from animal manure that was based on a database containing the N- and P-content of all manure samples that farmers need to report to account for the yearly N and P balance of their farm (van Bruggen & Geertjes, 2019). For this

Table 3 – Overview of studies comparing N losses from poultry manure and housing systems by direct and indirect assessment methods.

| Title of research | Case study | Methodology/assumption | Results | Comment | Reference |
|--|---|--|--|--|--|
| Degradation of nitrogenous components in and volatilization of ammonia from litter in aviary housing systems for laying hens | 66 samples of litter taken from 12 commercial aviary houses for laying hens. | NH ₃ measurement: <ul style="list-style-type: none"> ➤ Two impingers each containing 70 ml HNO₃ (0.5 M) ➤ NH₃ concentration was measured according to NEN 6472, 1983. ➤ Measurement duration was 60 h. <p>The total initial nitrogen content was measured according to Kjeldahl method.</p> | The amount of volatilised NH ₃ caused a decrease in bulk TAN of the litter about 5–145 mmol/kg (mean 55). This amount was 5–110% (mean 31%) of initial TAN and 0.3–22% (mean 0.4) of total initial nitrogen concentration. | Other N compounds were not included. The NH ₃ –N emission only was compared with initial N content and not with the difference of initial and final N content. There is also high variation of NH ₃ –N magnitudes compared to initial N content. | Groot Koerkamp and Elzing (1996) |
| Nitrogen emissions from broilers measured by mass balance over eighteen consecutive flocks | Broilers reared to 40–42 d of age | <ul style="list-style-type: none"> ➤ Only NH₃ was considered as dominant compound in the emission. ➤ Total N loss was considered approximately equal to NH₃ loss. | – | No comparison was made between direct and indirect method. The emission contribution of other nitrogen compounds was omitted. | Coufal et al. (2006) |
| Measuring NH ₃ emissions from broiler litter | Litter samples at age of one-year, two-year, four-year, five-flock, eight-flock and twelve-flock were treated | <ul style="list-style-type: none"> ➤ Chemiluminescence method: Thermo Environmental Instruments (TEI) (Model 17C) (real-time NH₃ concentration measurements in ppm); ➤ Acid scrubber (final analytical results of time-weighted average mass concentration of NH₃); ➤ Nitrogen mass balance approach | The average NH ₃ concentration measured by TEI was significantly higher than when measured by scrubber. At litter moisture content of 17.8% and 33.0%, TEI measured the average NH ₃ at 24 ppm and 59 ppm while scrubber registered 21 ppm and 38 ppm. N mass balance had a significant greater magnitude than other methods (e.g. at moisture content of 17.8% the NH ₃ –N concentrations was 994 mg, 160 mg and 138 mg for N mass balance, TEI and scrubber methods respectively. | Other N compounds were not included and the results between direct methods (TEI and scrubber) and indirect method (N mass balance) revealed substantial N-gap. | Wang, Zifei, Beasley, Munilla, and Baughman (2006) |
| A modified mass balance method for predicting NH ₃ emissions from manure N for livestock and storage facilities | laying hens | <ul style="list-style-type: none"> ➤ NH₃ was measured through airflow/gas concentration ➤ N-balance applied to estimate NH₃ based on N/ash ratios | NH ₃ emission magnitude measured by flow rate/gas concentration was 25%–250% greater than N balance method. | The measured NH ₃ -emission is indicative and should not be taken as prediction of absolute loss. | Keener and Zhao (2008) |
| Nitrogen mass balance in commercial roaster houses receiving different acidifier application rates | 9 flocks of roasters | <ul style="list-style-type: none"> ➤ Limited N₂O emission monitoring (40 days) with Photo-acoustic sensor. ➤ NH₃–N was collected through 250 ml boric acid (2% vol/vol) scrubbers at the end of ventilation fans and concentration (mg l⁻¹) was analysed via colorimetry. | NH ₃ –N emission accounted for 17.3% of the total N input. Extrapolating findings from published research on NH ₃ –N emissions during layout and limited N ₂ O–N emission monitoring accounted for up to 29.2% of the total N input, whereas 13.7% of the N-balance could not be accounted for. | Uncertainty of input and output measurements, N ₂ O emissions and soil N leaching were not provided. | Shah et al. (2013) |

(continued on next page)

Table 3 – (continued)

| Title of research | Case study | Methodology/assumption | Results | Comment | Reference |
|--|------------|--|---|---|--------------------|
| NH ₃ emission from a manure-belt laying hen facility equipped with an external manure drying tunnel | laying hen | <p>NH₃ emission were continuously measured from building and drying tunnel by a photo-acoustic multi gas analyser.</p> <p>N mass balance was carried out to estimate NH₃ loss from the building.</p> | <p>Mean NH₃ emission rate from the building was 93.8, whereas NH₃-loss estimated as N loss in the nitrogen mass balance amounted 98.4</p> | <p>No obvious seasonal differences were observed in the NH₃ estimation by N balance. N balance was incapable of reflecting the variations between short period of times.</p> | Rosa et al. (2020) |

purpose all manure transports off-farms were weighed, sampled and analysed by certified laboratories in line with regulatory protocols, and results were reported to the national agency supervising the mineral accounting regulations. The CBS analysed and reported data of 3 years (2015–2017), each year containing about 90,000 manure samples originating from 8000 farms. Per animal category and housing type, the relative N loss was estimated by using the principle of decrease in N/P ratios after animal excretion as expressed in Eq. (11). Information on N/P-initial in this equation was based on default values that are used in the national mineral accounting system, derived from excretion studies and yearly surveys of feed composition in farm practice. The N/P-final in Eq. (11) was based on the reported N/P ratios in the samples from transported manure. CBS compared the mean relative N loss within each animal/housing type category with the loss based on their assigned NH₃/N₂O/NO/N₂-emission factors, which in theory should end up in the same total N loss. Emission factors were derived from the National Emission Model for Agriculture (NEMA) in the Netherland used to provide national inventory reports on national N emissions and other emissions from livestock production (Zee et al., 2019). In the NEMA model, the NH₃ emission factors are based on extensive measurement campaigns within each animal category/housing type combination, whereas the other N emissions due to nitrification and denitrification are mainly based on IPCC guidelines and estimated N₂O–NO–N₂ ratios provided by Oenema et al. (2000) as earlier outlined in Section 3.2.

Figure 2 shows the results of the CBS-analysis, showing the N losses expressed as percentage of N excretion in poultry, pig and cattle production, depicting the losses according to the emission factors and the difference with the N loss according to the N/P ratio method. In cases where the total N loss from the emission factors is lower than estimated from N/P ratios this unexplained percentage is indicated as ‘remaining N’. The overall picture from gap in Fig. 2 is that, with a few exceptions, the relative N loss estimated from the reported N/P ratios cannot be fully explained by the gaseous N emission based on emission factors, demonstrating an N gap between the indirect (N/P ratio) and direct (measured NH₃-emission factors and other N-emissions derived from N-ratios) method in the majority of animal category/housing combinations. CBS also reported that generally the N-gap is higher for solid manure than slurry systems.

5. Approaches to investigate N-gaps

N-gap can be investigated by three approaches.

- 1) Measure all gaseous N losses (NH₃-N, N₂O-N, NO-N, NO₂-N) including N₂-N loss and compare the sum to the indirect N loss. This approach gives insight into what extent the N-gap can be closed or reduced by including N₂ and how variance in sampling and emission measurements contributes to this.
- 2) Assume that N₂ equals the N-gap and compare the sum of directly measured NH₃-N, N₂O-N, NO-N and NO₂-N with the indirect N loss. This approach will provide insight into the accuracy of predicting N₂ loss as the N-

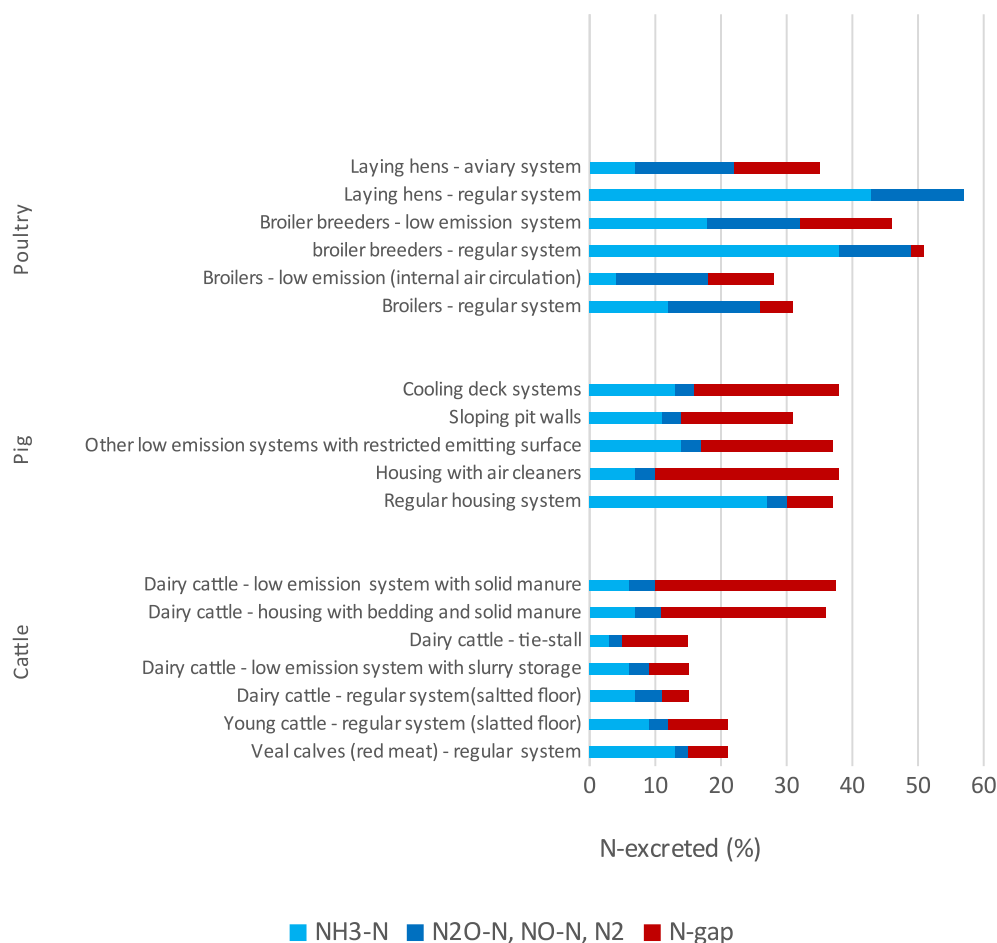


Fig. 2 – Average nitrogen loss (%), relative to excreted amount of nitrogen, per type of animal category and housing system for the period 2015–2017 in the Netherlands. Bars in light blue (NH₃-N) and dark blue (N₂O-N, NO-N and N₂) represent N losses based on emission factors. Red bars indicate the difference between the sum of N-losses by emission factors and the N loss assessed by the N/P ratio method (see Section 4 for details). Data adopted from CBS report (van Bruggen & Geertjes, 2019). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

gap and how variance in sampling and emission measurements contributes to this.

- As in 1, but estimating N₂ loss based on currently used ratio's from literature instead of measuring N₂ (method in CBS report). This approach will give insight into how well the ratio's predict the closure/reduction of the N-gap and how variance in sampling and emission measurements contributes to this.

The first approach is based on direct measurement of all N losses including N₂. In theory this would give the best comparison between the direct and indirect methods. However, a technical limitation is in place as no available set-up has been developed yet to measure N₂ emissions from manure under lab or barn conditions. An outline of a potential set-up regarding to approach 1 is provided in paragraph 5.1. Given its complexity and the lack of experience, the second and third approach are pragmatic ones. Measuring losses of all N compounds, except N₂, can provide a better insight into N compound losses than studies based on only measuring NH₃-N as more N compounds are directly measured. It also

provides a methodological approach for indirectly measuring N₂ loss, because this loss can be calculated as the remaining unexplained part of the N balance equalling the N-gap (approach 2) or be estimated based on ratios from literature (approach 3). In Section 5.2 we present a hypothetical measurement example to explore the potential of this approach to accurately determine all N losses including an estimate N₂ being equal to the N-gap. In Section 5.3, N₂ loss will be included in the N-gap based on range of possible ratios in order to understand the effect of these ratios on the N-gap.

5.1. Measurement set-up to measure N₂ loss from manure samples (approach 1)

Determining the magnitude of N₂ loss from manure plays a pivotal role in closing or reducing the N-gap. The challenge here is to reduce or eliminate the interference of background concentrations of N₂ in the atmosphere. To overcome this problem, various methods and techniques from other fields of science including terrestrial and aquatic environments were reviewed (Table 2). The GFSC technique is projected to be able

Table 4 – A hypothetical experiment to compare the total N losses from solid manure (laying hens) calculated by direct and indirect methods in order to estimate N₂ loss from their difference, including types and estimations of measurands in the direct and indirect methods, measurement techniques, assumed (italics) and calculated (underlined) standard deviation (S.D.) of relative errors, and range of variation for the estimated measurands in grams (estimated mean ± S.D. %).

| Measurement method | Measurand | Estimated magnitude | Unit | Measurement technique(s) | Assumptions | Assumed or calculated S.D. | Range of variation | Literature |
|--------------------|--|--------------------------|-------------------|---|---|----------------------------|-------------------------------------|---|
| Indirect | N _{initial} | <u>25</u> ^{a,b} | g/kg (fresh mass) | Chemical decomposition | N _{initial} concentration is assumed to be 25 g/kg | 5% ^c | | NEN 7433 (2020) |
| | N _{final} | <u>22.5</u> | g/kg (fresh mass) | Chemical decomposition | Total N loss of 10% is assumed to be within 7 days | 5% | | NEN 7433 (2020) |
| | W _{initial} | 100 | g | | Initial substrate mass is assumed to be 100 g | 0% | | |
| | W _{final} | <u>85</u> | g | | Substrate mass loss assumed to be 15% during the trial | 0% | | |
| | $[N]_{\text{loss-indir.}} = (W_{\text{initial}} \times [N]_{\text{initial}}) - (W_{\text{final}} \times [N]_{\text{final}})$ | <u>0.59</u> | g | | | <u>30%</u> | <u>0.59 ± 0.177</u> g | |
| Direct | NH ₃ -N | 0.25 | g | Impinger | NH ₃ -N loss is assumed to be 1% of N _{initial} | 5% | <u>0.25 ± 0.0125</u> g | (Mosquera, Ploegaert, & Kupers, 2019; NEN 2826, 1999; Neysari, Ogink, De Vries, & Groot Koerkamp, 2021) |
| | N ₂ O-N | <u>0.05</u> | g | Infrared photoacoustic spectroscopy/Gas Chromatography (GC) | N ₂ O-N:NH ₃ -N ratio is presumed to be 1:5 | 1% | <u>0.05 ± 5 × 10⁻³</u> g | (Rapson & Dacres, 2014, van Bruggen & Geertjes, 2019) |
| | NO-N | <u>0.05</u> | g | Chemiluminescence | NO-N:NH ₃ -N ratio is presumed to be 1:5 | 3% | <u>0.05 ± 0.0015</u> g | (Sanhueza, Plum, Pitts, 1984, van Bruggen & Geertjes, 2019; Winer, Peters, Smith, & Pitts, 1974) |
| | NO ₂ -N | <u>0.05</u> | g | Chemiluminescence | NO ₂ -N:NH ₃ -N ratio is assumed to be 1:5 | 3% | <u>0.05 ± 0.0015</u> g | (Sanhueza et al., 1984, van Bruggen & Geertjes, 2019; Winer et al., 1974) |

| | | | | | |
|--|---|------|---|---|--|
| Indirect and direct | $\frac{[N]_{\text{total-dir.}} - [N]_{\text{total-indir.}}}{r}$ | 0.4 | g | 5% | 0.4 ± 0.02 g |
| $[N]_{\text{total-dir.}} = \text{NH}_3\text{-N} + \text{N}_2\text{O-N} + \text{NO-N} + \text{NO}_2\text{-N}$ | $\bar{N}_2 = \sum_{i=1}^r N_2$ | 0.19 | g | For r vessels $\sigma_{N_2}^2 = \frac{\sigma_a^2 + \sigma_m^2}{r}$, $\sigma_m^2 = 0.03$ (one vessel, single sample) and $\sigma_a^2 = 0.03$ and b) $\sigma_a^2 = 0.17$ | a) S.D. $\bar{N}_2 = \frac{131\%}{\sqrt{r}}$, b) S.D. $\bar{N}_2 = \frac{236\%}{\sqrt{r}}$ a) 0.19 ± $\frac{131\%}{\sqrt{r}}$ (S.D.) g (total N loss indirect); b) 0.19 ± $\frac{236\%}{\sqrt{r}}$ (S.D.) g (total N loss indirect) |

Neysari, Ogink, De Vries, & Groot Koerkamp, 2021

a A manure substrate of 100 g was assumed to contain 25 g/kg of N. The NH₃-N emission magnitude was estimated as a percentage of N_{initial}. Other N compounds were estimated by using the NH₃-N emission magnitude and the CBS ratio for solid manure (NH₃-N:N₂O-N:NO-N:NO₂-N to be 5:1:1:1). The difference between the summed magnitudes of N compounds (direct) and the total N loss calculated by N balance (indirect) was used to estimate N₂ at single vessel level and multiple-vessel level. $\sigma_{N_2}^2$ is the variance of N₂ at single vessel level, σ_a^2 is the variation source for N₂ resulting from substrate composition/conversion differences between the vessels and can be calculated through $\sigma_a^2 = \sigma_{N-gap}^2 - \sigma_m^2$, σ_m^2 is the variation resulting from measurement and can be calculated through all underlying measurement error components: $\sigma_m^2 = \frac{\sigma_{N_{\text{initial}}}^2}{s} + \frac{\sigma_{N_2\text{O-N}}^2}{v} + \frac{\sigma_{N_2\text{O-N}}^2}{u} + \frac{\sigma_{N_2\text{O-N}}^2}{t} + \frac{\sigma_{N_{\text{final}}}^2}{t} + \frac{\sigma_{N_2\text{O-N}}^2}{v} + \frac{\sigma_{N_2\text{O-N}}^2}{w} + \frac{\sigma_{NO_2-N}^2}{z}$ where $\sigma_{N_{\text{initial}}}^2$, $\sigma_{N_{\text{final}}}^2$, $\sigma_{NH_3-N}^2$, $\sigma_{N_2\text{O-N}}^2$, σ_{NO-N}^2 and $\sigma_{NO_2-N}^2$ are the variation sources related to initial N content, final N content, NH₃-N, N₂O, NO-N and NO₂-N, respectively and s, t, u, v, w and z are the number of measurements per vessel for initial N content, final N content, NH₃-N, N₂O, NO-N and NO₂-N respectively.

b Calculated.

c Assumed.

d When σ_m^2 and σ_a^2 are assumed to contribute a) 50% and 50%, respectively and b) 15% and 85%, respectively to total error (S.D. \bar{N}_2).

to measure N₂ loss from manure. The technique is able to measure different gaseous N compounds simultaneously and online which will give more precise measurement of all N compounds as well as N₂. In this set-up, the sample is kept sealed (controlled aerial condition) and under controlled temperature conditions.

The set-up of GFSC consists of three main parts including a water bath, valve control unit and sensors/detectors unit. The water bath controls the temperature of surrounding water around the vessels and provides sealing conditions to avoid inevitable interference caused by atmospheric compounds (for N₂). The valve control unit is used to control the gas flow rate and gas direction towards the sensors. Gas concentration measurement of each N compound is performed in the sensor/detector part through corresponding detectors or analysers. Both on-line and accumulated gas concentration of each target gas are accessible in this set-up using a data-logger and monitor.

The GFSC technique however needs some adjustments for manure studies, as it has been developed for soil samples. For lab-scale measurements, N₂, N₂O and NO_x sample containers (vessels) need to be treated differently than the one for NH₃. The NH₃ emission from manure, as stated previously, is abiotic-dependent and flushing the samples may perpetuate its emission. However, the other gases can be flushed when using tracer gases. This techniques is projected to have serious barriers for field-scale measurements due to its complex structure of measuring gases simultaneously and flushing obligation for especially N₂ gas.

5.2. Hypothetical experiment to explore the accuracy of determining N₂ loss as the N-gap (approach 2)

In this approach, the N₂ loss is considered equal to the N-gap (approach 2). The directly and indirectly calculated total N losses are compared based on a hypothetical experiment in which the underlying error/uncertainty components of each method and their propagation were included (Table 4). The experiment is based on the principle of a laboratory set-up in which the N losses from solid manure (of laying hens) is measured during a week in a series of small sample containers (vessel) with controlled ventilation in the headspace. In the example, the theoretical accuracy of estimating N₂ loss as the difference between direct measurements of N compounds and total N from a N balance is explored by estimating variances of measurement and sampling errors and composition/conversion-based variance components. Assumptions of N losses during 1 week of testing are hypothetical, but their order of magnitude is based on real laboratory trials with poultry manure (Neysari, Ogink, De Vries, & Groot Koerkamp, 2021).

In the example, an amount of 100 g of a poultry manure in a vessel is assumed to contain initially 25 g N/kg manure. Total N loss over one week amounts 10% of initial N and for total mass loss 15% of initial mass, mainly related to evaporation of water. Total N loss is assigned to specific N compounds as follows:

NH₃-N loss is estimated to be 1% N_{initial}, for the other N compounds, N₂O-N, NO-N and NO₂-N losses are calculated by using a ratio for solid manure (NH₃-N:N₂O-N:NO-N:NO₂-N

to be 5:1:1:1) based on the premise that NH₃-N is basis for estimation. The N₂ loss at single vessel level was calculated (Eq. (12)) as:

$$N_2 = [N_{total-indir.}] - [N_{total-dir.}] \tag{12}$$

where N_{total-indir.} is the total N loss calculated through the indirect method (g) and N_{total-dir.} is the N loss measured through the direct measurement method (g). The average N₂ loss determined in r vessels was calculated using Eq. (13):

$$\bar{N}_2 = \frac{\sum_{i=1}^r ([N_{total-indir.}] - [N_{total-dir.}])_i}{r} \tag{13}$$

where \bar{N}_2 represents the average N₂ loss per vessel, and r is the number of experimental units (vessels).

After this, the variance related to measurement uncertainty was determined in order to estimate the overall certainty by which the emission of N₂ can be determined. The variance related to uncertainty in measured mean N₂ loss ($\sigma_{\bar{N}_2}^2$) in an experiment with r vessels can be calculated through Eq. (14):

$$\sigma_{\bar{N}_2}^2 = \frac{\sigma_v^2 + \sigma_m^2}{r} \tag{14}$$

where σ_v^2 is the variance in N emission between the vessels caused by (small) differences in manure composition and resulting conversion process, σ_m^2 is the variance related to measurement uncertainty at (single) vessel level, and r is the number of vessels. The measurement uncertainty (σ_m^2) can be further elaborated as Eq. (15):

$$\sigma_m^2 = \frac{\sigma_{N_{initial}}^2}{s} + \frac{\sigma_{N_{final}}^2}{t} + \frac{\sigma_{NH_3-N}^2}{u} + \frac{\sigma_{N_2O-N}^2}{v} + \frac{\sigma_{NO-N}^2}{w} + \frac{\sigma_{NO_2-N}^2}{z} \tag{15}$$

where the variances $\sigma_{N_{initial}}^2$, $\sigma_{N_{final}}^2$, $\sigma_{NH_3-N}^2$, $\sigma_{N_2O-N}^2$, σ_{NO-N}^2 and $\sigma_{NO_2-N}^2$ are related to measurement uncertainty at vessel level of initial total N mass, final total N, and loss of NH₃-N, N₂O, NO-N and NO₂-N, respectively. The parameters s, t, u, v, w and z are the number of measurements per vessel for the measured variables. Table 4 lists the assumed values of mass and N-concentrations in the poultry manure at the start and end of the experiment, the assumed and calculated variance components, N₂ loss (Eqs. (13) and (14)) and the calculated uncertainty in N₂ loss as a function of the number of vessels (Eqs. (14) and (15)).

The N₂ loss from laying hen manure within a time of 7 days was estimated to be 32% of total N loss (N balance) or 0.19 g ± $\frac{131\%}{\sqrt{r}}$ (±S.D.) when σ_m^2 and σ_v^2 contribute equally (50% and 50%) to total error (S.D. \bar{N}_2) and 0.19 g ± $\frac{236\%}{\sqrt{r}}$ (±S.D.) when σ_m^2 and σ_v^2 contribute as 15% and 85%, respectively to total error with r being the number of vessels. This means that reducing the variance of physical differences by increasing the number of vessels is most effective in reducing the variance of the N-gap.

The overall propagated error of the sum of directly measured N compounds amounted 5%, whereas the magnitude of propagated error was 30% of indirectly calculated N loss (N balance method) based on the assumed underlying errors (Table 4). One plausible reason for the higher propagated error for the N balance is that the corresponding relative

Table 5 – Estimates of variances and standard deviations related to N₂ measurement uncertainty based on a hypothetical experimental setup (Table 4) using different assumed numbers of vessels and sample replicate(s) per vessel.

| No. of vessels | Replicate ^a (s) of samples (per vessel) | σ_m^2 | σ_v^2 | $\sigma_{\bar{N}_2}^2$ | S.D. \bar{N}_2 (g) | S.D. decrease ^c (%) |
|----------------|--|-------------------|--------------|------------------------|----------------------|--------------------------------|
| 4 | Single | 0.03 ^b | 0.03 | 0.015 | 0.12 | 51 |
| 6 | Single | 0.03 | 0.03 | 0.010 | 0.10 | 60 |
| 8 | Single | 0.03 | 0.03 | 0.008 | 0.09 | 65 |
| 10 | Single | 0.03 | 0.03 | 0.006 | 0.08 | 69 |
| 12 | Single | 0.03 | 0.03 | 0.005 | 0.07 | 72 |
| 14 | Single | 0.03 | 0.03 | 0.004 | 0.07 | 74 |
| 16 | Single | 0.03 | 0.03 | 0.004 | 0.06 | 76 |
| 4 | Duplicate | 0.02 | 0.03 | 0.011 | 0.11 | 58 |
| 6 | Duplicate | 0.02 | 0.03 | 0.008 | 0.09 | 65 |
| 8 | Duplicate | 0.02 | 0.03 | 0.006 | 0.08 | 70 |
| 10 | Duplicate | 0.02 | 0.03 | 0.005 | 0.07 | 73 |
| 12 | Duplicate | 0.02 | 0.03 | 0.004 | 0.06 | 76 |
| 14 | Duplicate | 0.02 | 0.03 | 0.003 | 0.06 | 77 |
| 16 | Duplicate | 0.02 | 0.03 | 0.003 | 0.05 | 79 |
| 4 | TriPLICATE | 0.01 | 0.03 | 0.010 | 0.10 | 60 |
| 6 | TriPLICATE | 0.01 | 0.03 | 0.007 | 0.08 | 67 |
| 8 | TriPLICATE | 0.01 | 0.03 | 0.005 | 0.07 | 72 |
| 10 | TriPLICATE | 0.01 | 0.03 | 0.004 | 0.06 | 75 |
| 12 | TriPLICATE | 0.01 | 0.03 | 0.003 | 0.06 | 77 |
| 14 | TriPLICATE | 0.01 | 0.03 | 0.003 | 0.05 | 79 |
| 16 | TriPLICATE | 0.01 | 0.03 | 0.003 | 0.05 | 80 |

^a s, t, u, v, w and z as the number of measurement replicates for initial N content, final N content, NH₃-N, N₂O, NO-N and NO₂-N per vessel, respectively, were considered to be equal.

^b Calculated based on assumed values for $\sigma_{N_{initial}}^2$, $\sigma_{N_{final}}^2$, $\sigma_{NH_3-N}^2$, $\sigma_{N_2O-N}^2$, σ_{NO-N}^2 and $\sigma_{NO_2-N}^2$ to be 0.005 each.

^c Standard deviation decrease (%) relative to the estimated S.D. of N₂ loss for one vessel and single sample per vessel (S.D. of a: 131%, Table 4).

Table 6 – N-gap variation caused by the use of ratios of N compounds including N₂ derived from literature at single vessel level and single sample replicate.

| Ratio (NH ₃ -N:N ₂ O-N:NO-N:NO ₂ -N:N ₂) | Literature | NH ₃ -N (g) | N ₂ O-N (g) | NO-N (g) | NO ₂ -N (g) | N ₂ (g) | Total N loss (direct) (g) | Total N loss (indirect) (g) | N-gap (g) | N-gap (% of initial N) |
|---|---|------------------------|------------------------|----------|------------------------|--------------------|---------------------------|-----------------------------|-----------|------------------------|
| <u>5:1:1:1:5</u> | (Oenema et al., 2000, van Bruggen & Geertjes, 2019) | 0.25 | 0.05 | 0.05 | 0.05 | 0.25 | 0.65 | 0.59 ^a | -0.06 | -0.24 |
| <u>10:1:1:1:10</u> | (Oenema et al., 2000, van Bruggen & Geertjes, 2019) | 0.25 | 0.03 | 0.025 | 0.025 | 0.25 | 0.58 | 0.59 | 0.01 | 0.06 |
| <u>10:10:10:10:1</u> | Stefansson (1973) | 0.25 | 0.25 | 0.25 | 0.25 | 0.03 | 1.03 | 0.59 | -0.44 | -1.74 |
| <u>5:1:1:1:133</u> | Stefansson (1973) | 0.25 | 0.05 | 0.05 | 0.05 | 6.65 | 7.05 | 0.59 | -6.46 | -25.8 |
| <u>5:1:1:1:6</u> | Stefansson (1973) | 0.25 | 0.05 | 0.05 | 0.05 | 0.30 | 0.70 | 0.59 | -0.11 | -0.44 |

Caveat: the underlined ratios are derived from literature and the ratios in italic are assumed.

^a Fixed assumed value for total N loss taken from Table 4.

measurement errors are multiplied by a substantially bigger N content than the fractions of N (N compounds) in the direct method, resulting in a larger impact on the uncertainty of their difference. Table 5 illustrates the estimated N₂ variances based on different number of vessels and sample replicates per vessel. Results show that as the number of vessels increase, the variation of the average N₂ loss decreases. Likewise, it was revealed that the number of sample replicates per vessel is linked to a decline in the average N₂ loss. For example, increasing the number of vessels to 16 with a single sample, declines the overall variation of estimated N₂ by 76% point compared to a single vessel. This reduction can be further increased up to 80% by triplicate sampling. Summarising, accuracy of the N₂ loss as the N-gap can be empowered by conducting an experiment with at least 4 vessels with single sample replicates.

5.3. Estimate N₂ loss using ratios from literature (approach 3)

In this section, N₂ was included in the estimate of the direct measurements based on ratios from literature (approach 3). A starting amount of 25 g N/kg fresh was assumed with 1% NH₃-N emission as in Section 5.2. Following ratios were defined based on literature. When compounds were not included in the ratios in literature, they were assumed as shown in Table 6. Following, all N losses were calculated and added up to a total N loss. This directly measured/estimated N loss was subtracted from the indirectly measured N loss taken from Table 4. This led to the given N-gap in Table 6. Adjusting the assumed ratios between the N compounds had a strong impact on overall variation of estimated N-gap (Table 6). Results showed that the N-gap ranged from 0.06% to 26% of initial N depending different assumed ratios between the N compounds. These ratios, therefore, highly affect the estimate of directly calculated N losses and incorporate a considerable variance and uncertainty. In order to make more useful estimates, it is required to have more insight under which conditions which ratios apply. This will require research considering various conditions and manure types to understand how N₂ is linked to the other N losses.

6. Conclusions and directions for future research

Research on the N-gap as the difference between direct and indirect methods of measuring N losses was reviewed in livestock manure systems with focus on solid poultry manure. N-gaps ran up to 80% difference between direct and indirect measurement of N loss, but varied greatly. Variability depended on the measured N compounds and the assumed loss ratios of N₂O, N₂, NO and NH₃. Different methods and techniques for measuring N compounds were reviewed including their pros and cons, as well as precision/accuracy of each method/technique. Generally, 5%–10% of the uncertainty in measurements can be attributed to the measurement technique.

The use of loss ratios of N compounds was studied from literature, mainly with attention to N₂ losses. Current ratios

used in manure systems originate from soil studies and varied greatly, e.g. from 1:10 to 133:1 for $N_2:N_2O$ and factors underlying this variability are not well understood. This means that estimates of the total N loss in manure systems, based on fixed ratios have a high uncertainty and will propagate when being used for calculations and estimations.

Measuring N_2 has been done in other fields of science, e.g. terrestrial and water environments, reviewed here. Of the methods and techniques, the Gas Flow Soil Core (GFSC) technique is considered to be the best suited approach to measure N_2 from manure, amongst other N compounds.

Three approaches were recommended to close or reduce N-gaps in different manure/housing systems i.e. (1) measure all N compounds including NH_3-N , N_2O-N , $NO-N$, NO_2-N and N_2 , (2) assume that N_2 equals the N-gap and compare the sum of directly measured NH_3-N , N_2O-N , $NO-N$ and NO_2-N with the indirect N loss and as in 1, but estimating N_2 loss based on currently used ratios from literature. The first approach is based on direct measurement of all specific N loss compounds. In theory this would give the best comparison between the direct and indirect methods. However, N_2 has not yet been measured from manure systems due to its complexity. The second and third approaches are more practical as N_2 is estimated and the other N compounds can be measured by current technologies preferably simultaneously in a set-up. A hypothetical experiment showed how accurately the N_2 loss can be estimated with the third approach. The example showed that N_2 can be estimated more accurately by increasing the number of vessels and reducing the variation caused by measurement and physical differences between the experimental units; standard deviation was reduced up to 80% point when including 16 vessels and triplicate measurement compared to one vessels and single measurement. Adjusting the ratios between the N compounds using ratios determined in different studies derived from literature showed a profound variation of estimated N_2 ranged from 0.06% overestimation to 26% underestimation of initial N for one vessel and single measurement.

We conclude that the use of the currently available loss ratios is a weak scientific principle to estimate N loss, especially from manure, as different biotic-abiotic conditions can affect these ratios greatly. Further research is needed to address issues and uncertainties in these ratios and application of methods/techniques to measure N_2 to further understand and close these N-gaps in livestock manure systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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