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Review Article

A Review of Chamber and Micrometeorological Methods to Quantify NH_3 Emissions from Fertilisers Field Application

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Agriculture is mainly responsible for ammonia (NH_3) volatilisation. A common effort to produce reliable quantifications, national emission inventories, and policies is needed to reduce health and environmental issues related to this emission. Sources of NH_3 are locally distributed and mainly depend on farm building characteristics, management of excreta, and the field application of mineral fertilisers. To date, appropriate measurements related to the application of fertilisers to the field are still scarce in the literature. Proper quantification of NH_3 must consider the nature of the fertiliser, the environmental variables that influence the dynamic of the emission, and a reliable measurement method. This paper presents the state of the art of the most commonly used direct methods to measure NH_3 volatilisation following field application of fertilisers, mainly focusing on chamber method. The characteristics and the associated uncertainty of the measurement of the most widespread chamber types are discussed and compared to the micrometeorological methods.

1. Introduction

Agriculture represents the major emitter of ammonia (NH_3) and is responsible for the 94% of total emission in EU-28 in 2016 [1]. Among all the agricultural activities, livestock breeding contributes considerably to anthropogenic NH_3 emission in Europe [2, 3]. Even if each step of livestock manure management is characterised by a significant loss of ammonia [4, 5], the field application of slurry is responsible for 30–50% of total emissions [6, 7]. In recent years, an increase in animal manure use as fertiliser has been documented [8], with the aim of recovering manure nutrients to close the nutrient cycle of the agroecosystems and save fertilization costs [9]. Nevertheless, detailed knowledge of the amount of NH_3 lost during the application of different manure types is still lacking. This threatens both air and ecosystem quality [10] and often causes important economic farm losses due to the misestimation of real available N to plants [11, 12].

In the light of this, stricter regulations on the use of N in agriculture have been introduced over time. The last one, the National Emission Ceilings (NEC) Directive [13], establishes new national emission ceilings in Europe for five pollutants (sulphur dioxide, SO_2; nitrogen oxides, NO_x; non-methane volatile organic compounds, NMVOC; ammonia NH_3; and fine particulate matter ($PM_{2,5}$)) and compiles and checks the national emission inventories to compile with 2020 and 2030 reduction commitments. A common effort has been made in all European countries to produce reliable ammonia emission inventories. Despite that, there is still a lack of data regarding specific fertilisers (i.e., buffalo manure [14]) as well as the reference in various pedoclimatic conditions. In addition, data collection is affected by the heterogeneity of measurement methods, with a reduction of the accuracy of the total ammonia emission assessment [15].

Ammonia release into the atmosphere, known as the process of gaseous NH_3 transfer from the immediate surface of a solution with ammonium ion (NH_4^+), like slurry on soil surface, into a free airstream [11, 16], depends on several factors. First of all, it is affected by the concentration gradient of gaseous ammonia at the liquid surface and in the air boundary layer above it [17]. Thus, the greater the concentration of dissolved free ammonia $NH_3(aq)$ in a liquid solution, the higher the gaseous ammonia emission $NH_3(g)$. The total ammoniacal nitrogen (TAN) is the sum of $NH_3(aq)$ plus NH_4^+ deriving from the hydrolysis of urea, according to the following dynamic equations of ionisation (equation (1)) and liquid–gas equilibrium (equation (2)):

$$NH_4^+ + H_2O \overset{K_d}{\Longleftrightarrow} NH_3\,(aq) + H_3O^+ \quad (1)$$

$$NH_3\,(aq) \overset{K_H}{\Longleftrightarrow} NH_3\,(g) \quad (2)$$

NH_3 emissions depend on the dissociation of NH_4^+ [11, 18, 19] since only the free NH_3 in the liquid ($NH_3(aq)$) can directly volatilise into the atmosphere (equation (2); $NH_3(g)$). The pH of the ammoniacal solution and the soil matrix can be considered the most important driving force for ammonia release into the atmosphere, followed by the air temperature, on which K_d (the equilibrium constant) and K_H (the Henry law constant) depend [20]. Indeed, increasing pH in the ammoniacal solution moves the equilibrium to the right, thus increasing the concentration of NH_3-N in the liquid solution [9, 21]. In most cases, the current weather conditions affect the NH_3 emission rate as the air temperature which increases NH_3 concentration in the solution, while the rainfall dilutes the TAN and favours a rapid infiltration of the solution (i.e., slurry) in porous media (i.e., soil). Moreover, wind speed and solar radiation influence the ammonia gas transfer, increasing the turbulent transport at the emission surface [11]. The dynamic of the land–atmosphere emission over time is an important issue, since the highest ammonia fluxes are recorded in the first hours after manure spreading [9, 22, 23]. The interactions between soil conditions, chemical composition of animal slurry, and/or fertilisers characteristics together with amendment spreading techniques significantly influence ammonia volatilisation [9, 11, 12, 18]. As suggested in [24], surface spreading causes the major ammonia-volatilised amount, compared with a narrowband application or shallow injection.

A proper assessment of the ammonia volatilisation under field conditions depends on the measuring methods [25, 26]. In general, two different groups of methods can be identified: micrometeorological and chamber (enclosure) method. Micrometeorological methods are used for large fields (>0.5 ha) to small- and medium-scale fields (20–50 m on the side), whereas enclosures cover a confined portion of the surface (~0.1-2 m^2) [9, 27]. Generally, the chamber method is recommended for comparison studies, since the microenvironment inside them could be different from the ambient conditions [28].

Over the years, several studies focused on ammonia volatilisation assessment under various conditions highlighting the strengths and the limitations of different measurement methods. The most appropriate measurement method should be chosen according to the specific field conditions, type of fertiliser, and the agronomic practice used for the application [29], since dissimilar results can be produced due to the variability of the abovementioned process.

With this in mind, in this paper, the state of the art of the most widespread direct methods is reported to assess NH_3 emissions from fertiliser application to the field.

The characteristics and the uncertainties of the measurement techniques are considered and discussed through the results of the past 38 years literature (peer-reviewed papers from 1982 to 2020). Reviewed contributions have been selected among those who applied enclosure methods alone or in comparison with micrometeorological methods to assess NH_3 emissions from fertilizer application to the field. This allowed highlighting the strength and weak points, as well as the latest developments of each approach.

2. Chamber Method

2.1. Description of Method. The operating principle of chamber method consists of measuring the NH_3 that volatilises inside a hood, which is facing the emitting surface, during a given amount of time. Currently, different types of chambers, in terms of size and shape, have been used under both field condition and storage studies. In the present paper, only results from field trials were considered.

Compared to micrometeorological methods, chamber approach is simpler, as it allows replication and application to small experimental plots [27], as variety and agronomic trials. On the other hand, the shape of the chambers and the adopted operating conditions can introduce microclimate perturbation as radiation, evaporation, temperature, and wind speed, affecting transport of NH_3 [30]. This is the reason why they have been used for relative comparison of NH_3 emission from different fertilisation treatments. In fact, without an appropriate correction of collected data, these chambers could lead to inaccurate quantification of absolute field ammonia emissions [31, 32]. Nevertheless, the enclosure method is more flexible and easy to use for small-area sources compared to other methods; that is why more efforts have been made in the recent years to enhance the performance of this method and provide a suitable alternative to micrometeorological methods [32, 33].

Since the construction typologies of chambers have been classified in nonrigorous ways, to clarify and be effective, the classification operated by Matson and Harriss [34] was adopted. According to this, enclosures can be categorized by (i) operating conditions and (ii) construction (Figure 1). In the first case, it is possible to distinguish from "non-steady-state" and "steady-state" conditions belonging to static (or "closed") and dynamic chambers, respectively. The main difference between these categories is that in the closed chambers ammonia concentration gradient decreases during the measurement (Figures 1(a)–1(c)), while in the dynamic chambers, being connected to the atmosphere and equipped with a pump for constant forced air circulation, the inner gas concentration is lower or equal compared to the outgoing air (Figure 1(d)).

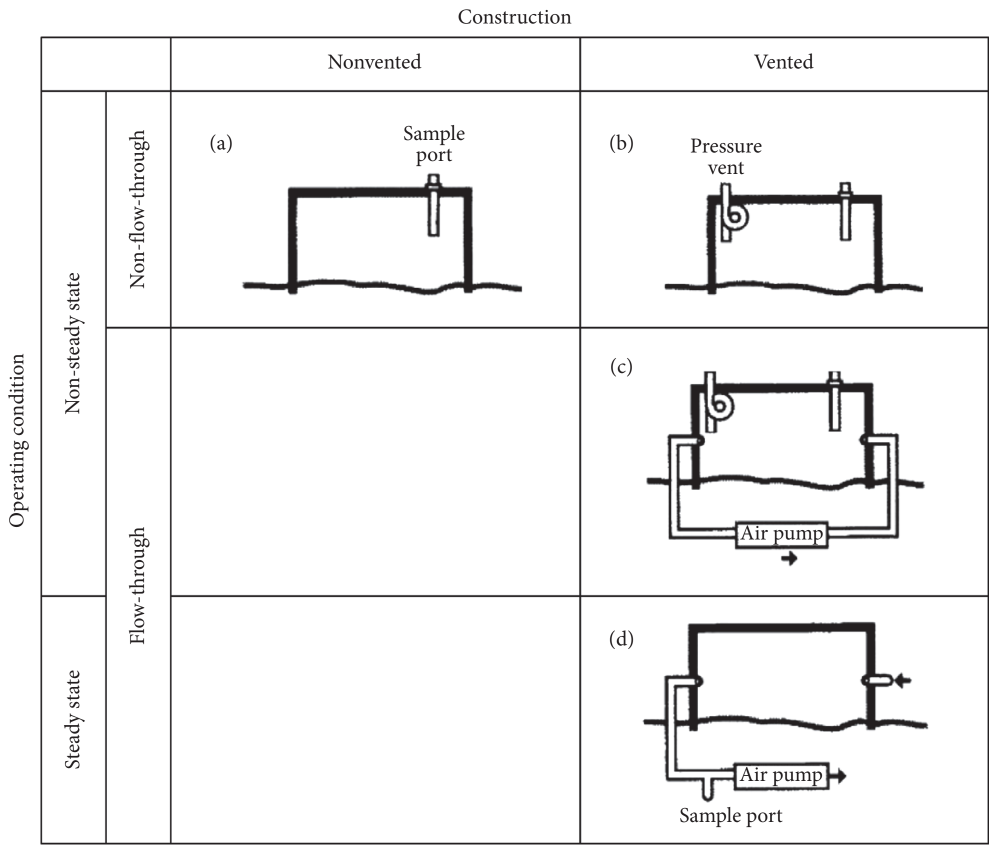


Figure 1: Chambers classification by Matson and Harriss [34].

Non-steady-state and steady-state chambers are discussed in the following paragraph, while specific types of dynamic chambers are described in separate paragraphs later: Dräger-Tube method and wind tunnel.

2.2. Non-Steady-State and Steady-State Chambers. Among non-steady-state chambers, the nonvented or "static chambers" (Figure 1(a)) are characterised from no forced air circulation in which the accumulation of ammonia emitted [35] is monitored, according to the variation of concentration within specific time intervals [5]. Static chambers prove to be the easiest and cheapest option to investigate the relative differences among different treatments [27]. Nômmik [36] used a simple static chamber, consisting in a metal cylinder with a 245 mm diameter and 150 mm height, for comparing emissions from different urea prills sizes (Figure 2). Two polyurethane plastic foam discs, previously treated with a solution of H_3PO_4 and glycerol, were placed at two different heights from the soil within each chamber, in order to absorb volatilized ammonia. The amount of ammonia trapped was then determined by titration and the cumulative emission was monitored replacing disks at scheduled time intervals during the sampling period. This simple system allowed comparing more treatments at the same time with low economic and labour costs, even if measured fluxes were affected by nonnegligible perturbation of soil temperature and moisture content due to the obstruction of the surface-to-atmosphere exchange.

On the basis of Nômmik [36], other studies have been conducted, adapting the construction material and the design to the circumstances. Grant et al. [42] and Rawluk et al. [43] used polyvinyl chloride cylinders with a diameter of 150 mm and a height of 200 mm, equipped with two ammonia absorbers polyfoam disc; these materials were tested in comparative field trials. Thereafter, Smith et al. [37] modified material and dimension of the closed static device using plexiglass 400 mm high and 200 mm wide. In this case, foam absorbers were placed in each chamber to discriminate between different ammonia sources: one was placed on the base of the chamber to monitor NH_3 volatilised from the soil, while the second was placed on a support device above the previous absorber to protect it from atmospheric NH_3, rainfall, and dust. Balsari et al. [38] used a PVC funnel covering 0.138 m^2 area, placed above the emitting surface. This system is usually equipped with a trap containing 1% boric acid solution to fix ammonia standing in the air over the funnel, during a fixed period of time (usually 24 h). Ammonia volatilisation is estimated by quantifying of NH_3 accumulated in the acid trap. This type of chamber is generally cheap and easy to manage. Nevertheless, "funnel system" is the less accurate method because of the slow accumulation of ammonia in the inner air within the chamber, due to a lowered emission rate [35] as a consequence of the small sampling area and the modifications of the boundary conditions [15]. To overcome the time resolution of measurements, but not the limits of this type of

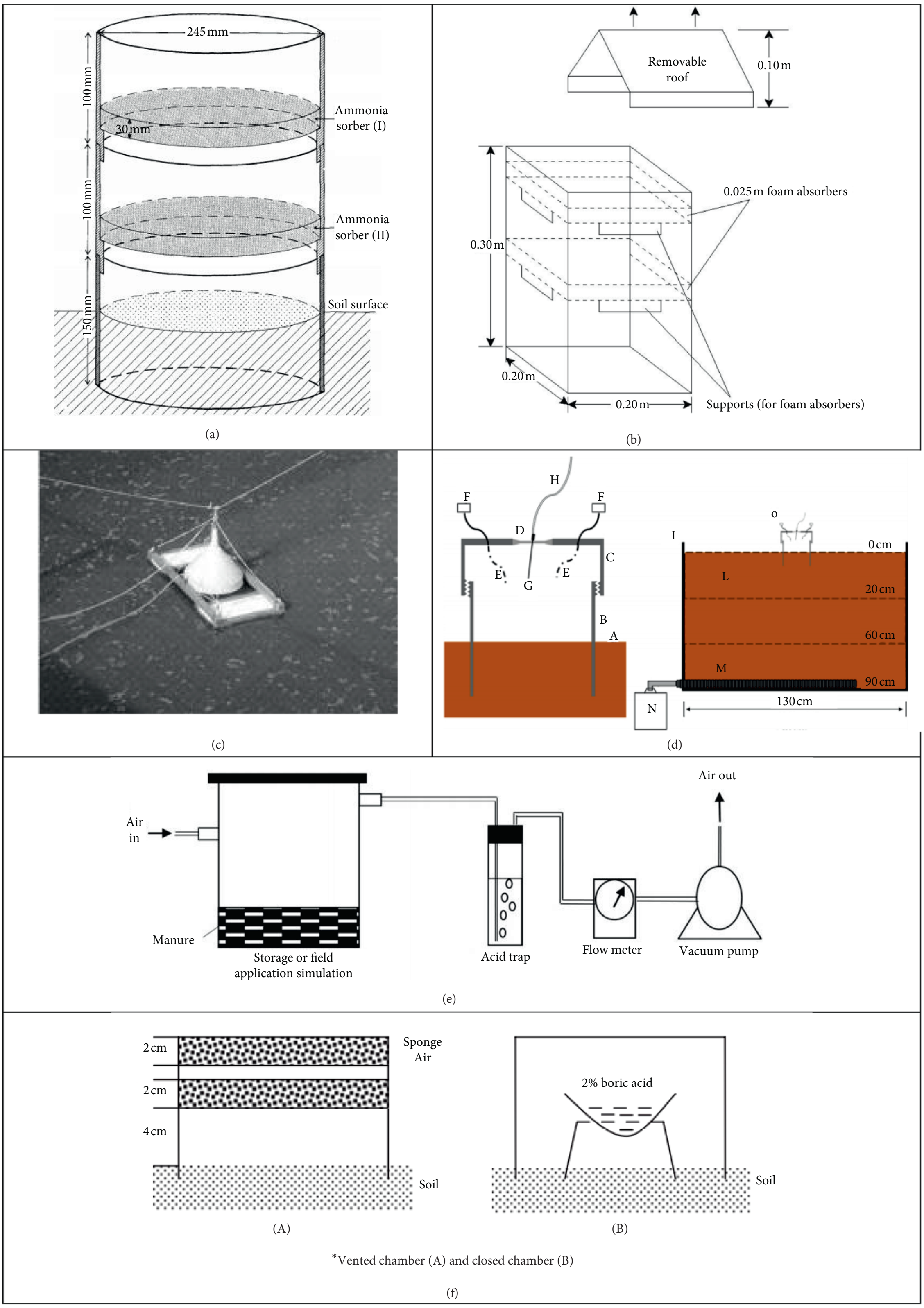


FIGURE 2: Some of the different chamber methods found in the literature. (a) Nômmik [36]. (b) Smith et al. [37]. (c) Balsari et al. [38]. (d) Verdi et al. [39]. (e) Ndegwa et al. [40]. (f) Wang et al. [41].

chamber, Verdi et al. [39] designed a circular PVC static chamber with a 20 cm diameter and 30 cm high headspace above soil, coupled with a portable gas analyser.

Vented chambers (Figure 1(b)) are not completely closed, since they allow an air exchange with the atmosphere through a pressure vent. Wang et al. [41] used the chambers described by Liao [44] made of a PVC tube with a diameter of 150 mm and a height of 100 mm, which contains two treated sponges, placed in two different positions, having the same functions of those described in the Nômmik [36] device, with the difference that a porous foam was adopted to allow the ventilation toward the atmosphere. Wang et al. [41] found that this system proved to be more reliable than static chambers in terms of ammonia emission assessment (about 30% bias). Steady-state flow-through and vented chambers were typically used in laboratory application, both applied to acid traps [45] and photoacoustic multigas [46] and portable analysers [47, 48] for comparison studies.

More efficient than previous chambers, closed-loop chambers (Figure 1(c)) are characterised by the circulation of the inner air containing emitted NH_3 within the inner space [35]. This type of chamber is generally characterised by a closed plastic container, which has one entry and one exit for headspace air. The exit is connected by means of Teflon tube to an acid trap, a flow meter to regulate the flow rate, and a vacuum pump to pull air through the system. Closed-loop chambers are used in many laboratory applications to simulate storage conditions or the spreading of fertilisers to the soil [40, 49–52]. Thanks to their construction features, they can offer the possibility to measure small variations in gas concentration [53]. In recent years, this type of chamber has been applied both in laboratory and field studies to compare anaerobic digestion and solid separation on ammonia emissions from stored and land applied dairy manure, as reported by Neerackal et al. [54]. The authors found significant differences between the two treatments using closed-loop chambers. Holly et al. [53] used an analogous closed-loop system for greenhouse gas and ammonia emission assessment from storage and field application of digested and separated dairy manure. They also found that closed-loop chambers can underestimate the cumulative NH_3 emissions after field application when TAN content in the fertilizer is low and the measurement period is too short.

Among field applications, Yang et al. [55] use a steady-state flow-through and vented chamber (Figure 1(d)) on rice and wheat fields fertilised with urea. The shape of the chambers was a polymethylmethacrylate cylinder of 200 mm of diameter and 400 mm height. NH_3 was detected via a portable gas analyser. The authors compared the above-mentioned chamber design with other construction types, finding an underestimation of the fluxes, as discussed below in the text. In summary, chamber types analysed are reported in Table 1.

2.3. Dräger-Tubes. Dräger-tube method (DTM) [56–59] uses a different type of chamber for the monitoring of NH_3 volatilisation in field conditions, characterised by four chambers placed onto the emitting surface. It can be considered as a modified dynamic chamber, where air is sucked by means of a pump and the NH_3 concentration measured by a Dräger gas-analysis detector tube. The NH_3 flux is corrected by means of two calibration equations, for summer and winter experiments, to overcome the problem of the low air-exchange rate within the chambers (Table 2).

2.4. Wind Tunnels (WT). Wind tunnels are the enclosure technique generally preferred in field application for assessing fluxes from small emitting surface [65]. They are constituted by a chamber covering small area in which a fan forces an airflow inside them. The main advantage of this method is the opportunity to reproduce the field wind conditions, known as one of the main drivers affecting ammonia volatilisation. In these chambers, the emission rate is governed by the air velocity selected throughout the measurements and can be assessed as the product of the flow rate and the concentration of volatilized ammonia under the shelter, in which the aerodynamics and flow rates are controlled [64].

Previous researches have shown several examples of portable wind tunnels. Vallis et al.'s [60] study was the first to propose a wind tunnel characterised by a clear plastic cover 0.25 m^2 base and 150 mm height, open at one end.

The wind tunnel by Lindvall et al. [63] consisted of a rectangular measurement section, with contraction and expansion sections. Afterward, Lockyer [61] proposed a wind tunnel, 1 m^2 base and 450 mm height, made assembling two components: a tunnel made of transparent polycarbonate sheet and a steel circular duct, connected with an electrically powered fan.

All the other tunnel systems that have been used in later years were inspired by these two. The main chamber types studied over the years are summarised and reported in Table 2.

Bearing in mind that the tunnel system is constituted to reproduce the influence of environmental conditions, numerous issues emerged from monitoring campaigns in the literature. Table 3 summarizes the main studies focused on dynamic chamber method improvements.

Lockyer [61] highlighted that although his configuration system allowed for realistic wind speed conditions, condensation on the inner surface cover of the tunnel occurred during the night.

Many studies were conducted to assess the effects of the different tunnel geometries, since making a direct comparison among several emission rates measured by wind tunnels with different shapes' result is not easily practicable [69]. To this purpose, Saha et al. [69] showed that wind tunnel dimension and mainly chamber's height significantly affect ammonia emission. Smaller wind tunnels gave higher emission rate than the bigger ones, due to the different internal air velocity and turbulence profiles that are generated. Other studies [7] showed that during open-field monitoring, a higher air turbulence occurred in the first part of the tunnel due to the external wind action related to a wide inlet tunnel section.

Nevertheless, hood from Lindvall et al. [63] was tested in a research [64] who observed a rotation airflow generating around vertical axis. This phenomenon was called "jet effect" and it is due to the specific shape of the tunnel. In the same study, flow distribution devices were suggested to minimize this problem.

Since the aerodynamic performance of the tunnel is considered a critical parameter [64], in recent years few studies have been carried out to assess the airflow conditions

Table 1: Classification of chamber types according to [34].

Operating conditions		Construction	Measurement surface area (cm^2)	Chamber characteristics	Pros and cons	References
Non-steady state	*Non-flow-through*	*Nonvented*	314.2	Cylindric, PVC, portable gas analyser	Pros: (i) Multiple treatments (ii) Low economic cost (iii) Reduced field labour Cons: (i) Serious perturbation of boundary conditions (ii) Limited spatial representativeness (iii) "Memory effects" on the chamber walls	Verdi et al. [39]
			314.2	Cylindric, plexiglass, acid trap		Smith et al. [37]
			176.7	Cylindric, polyvinyl, acid trap		Rawluk et al. [43]
			176.7	Cylindric, polyvinyl, acid trap		Grant et al. [42]
			1380.0	Funnel shape, PVC, acid trap		Balsari et al. [38]
			471.4	Cylindric, metal body, acid trap		Nômmik [36]
			—	Cylindric, PVC, acid trap		Wang et al. [41]
			3000.0	Cylindric, IR spectroscopy		Holly et al. [53]
			324.0	Cylindric, IR spectroscopy		Neerackal et al. [54]
Steady state	*Flow-through*	*Vented*	314.2	Cylindric, polymethylmethacrylate, portable gas analyser		Yang et al. [55]

inside the tunnels and how much they affect ammonia emission rate. The most recent papers dealing with this topic involve the Computational Fluid Dynamics (CFD) simulation model and investigate the airflow characteristics above ammonia-emitting surfaces to better understand what is the effect of wind tunnel dimensions and shape on ammonia emission and the mass transfer process [68–71].

3. Micrometeorological Methods

Micrometeorological methods are generally preferred compared to enclosure one when the aim is to assess NH_3 volatilisation under medium and field scale conditions and over short-to-long integration time. Compared to chamber method, this approach limits the uncertainty in the measurement of NH_3 emissions since it is nonintrusive and barely disturbs the natural exchange between land surface and atmosphere [30, 72–74].

Moreover, these methods provide an integrated measure over the study plot area, resulting more representative of real conditions. In spite of that, micrometeorological methods suffer from many limitations due to the need of large, homogeneous monitoring areas as well as the great number of samples and analyses required [33].

Micrometeorological techniques include eddy covariance (EC), aerodynamic gradient method (AGM), inverse dispersions modelling (IDM), and mass balance techniques [74].

3.1. Eddy Covariance.

3.1. Eddy Covariance. Eddy covariance technique measures the turbulent transfer within the atmospheric boundary layer and it is considered the most direct and least error-prone approach for flux determination [73, 74]. In particular, this technique evaluates the gaseous exchange rate across the interface between the atmosphere and the emitting surface by measuring the covariance between fluctuations in vertical wind velocity and NH_3 mixing ratio. Indeed, it is considered that ammonia transport is given by eddying motion in the boundary layer over an extensive and uniform surface [27].

The requirement is to sample each eddy of air that contributes to the flux so that a fast instrument response time is necessary, typically 10 to 20 Hz [35, 74]; otherwise, fluxes can be underestimated [27]. The mean vertical flux density of the NH_3 is given by

$$F = \overline{w'c'}, \tag{3}$$

where w' is the instantaneous vertical velocity and c' is the instantaneous fluctuation of the NH_3 concentration of each eddy. The bar denotes an average across a sampling period of usually 30 minutes [75], in order to consider all eddy fluctuations affecting the flux [73]. The advantage of this technique is to perform continuous measurements over large areas, although it needs expensive equipment and some nonnegligible correction as a function of the source strength.

3.2. Aerodynamic Gradient Method. The aerodynamic gradient is a technique related to the concept that NH_3 emitted from a surface moves along the mean concentration gradient, thanks to the simultaneous presence of two processes, considered in the same way: turbulent transport and molecular diffusion. Moreover, the horizontal concentration gradient is assumed negligible with regard to vertical one, hypothesising a horizontal airflow uniformity and a constant vertical flux with height.

The aerodynamic gradient is one of the most commonly used techniques nowadays to measure ammonia emission, but it is a technique sensitive to advection of NH_3 affecting the flux measurement and requires sensors with high resolution. The most limiting parameter of this method is the possibility of having an undisturbed flow to avoid flux underestimation [27, 74].

Ammonia flux is calculated as follows:

$$F = -K\frac{dc}{dz}, \tag{4}$$

Table 2: Main dynamic chambers characteristics and reference studies.

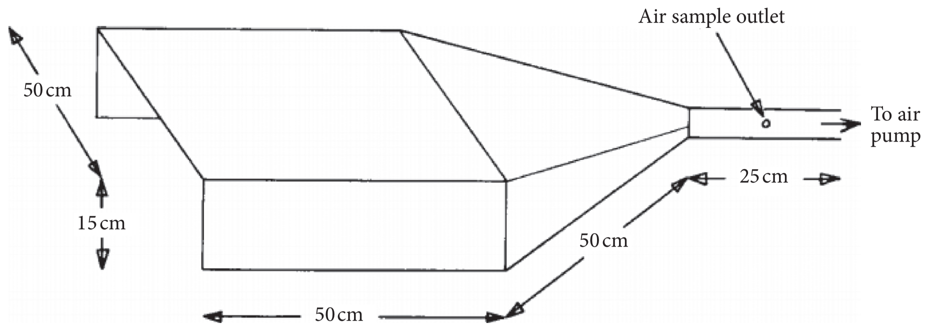
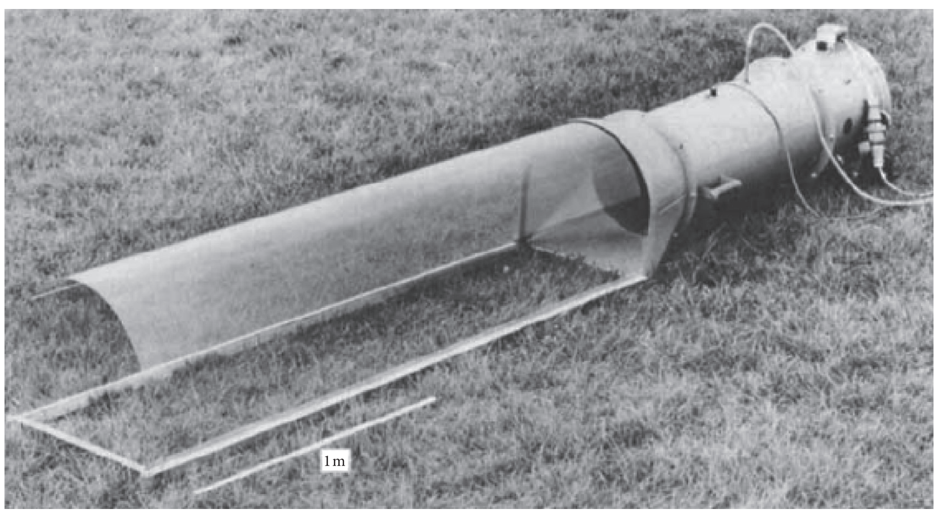
Chamber method	Measurement surface area (m)	Airspeed (m s^{-1})	Chamber characteristics	Pros and cons	Reference
	0.25^2	Variable (0.07 max)	It consisted of a polycarbonate chamber (50 cm by 50 cm) open to one side and the bottom.	(i) Minimizes the temperature and wind speed differences with outside. (ii) Simulates the natural wind speed. (iii) Condensation on the internal walls during the night.	Vallis et al. [60]
	1^2	0.04–3.77	Wind tunnel made of 2 parts: a tunnel formed from a transparent polycarbonate sheet and a steel circular duct, connected with the fan.	(i) Provides natural sward condition inside it. (ii) Obtains internal airspeed similar to outside one. (iii) Condensation inside of the tunnel occurs.	Lockyer [61]

Table 2: Continued.

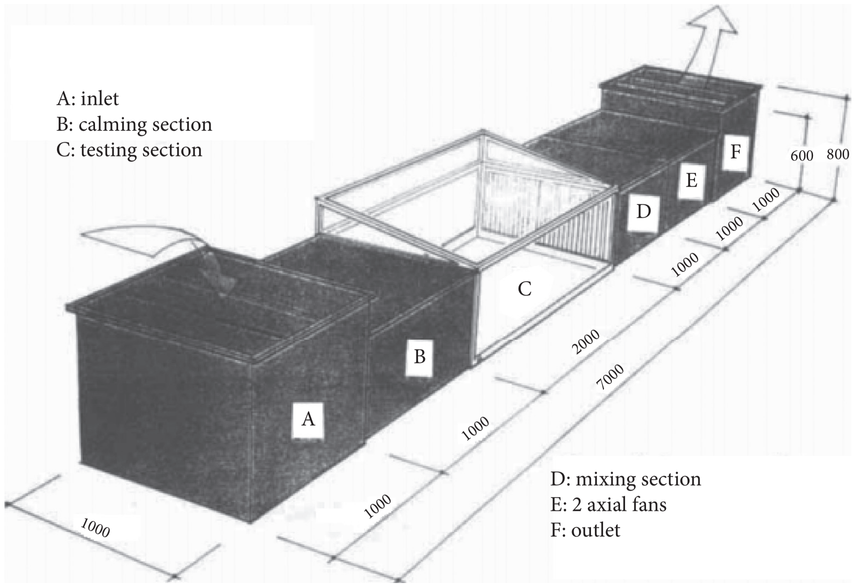
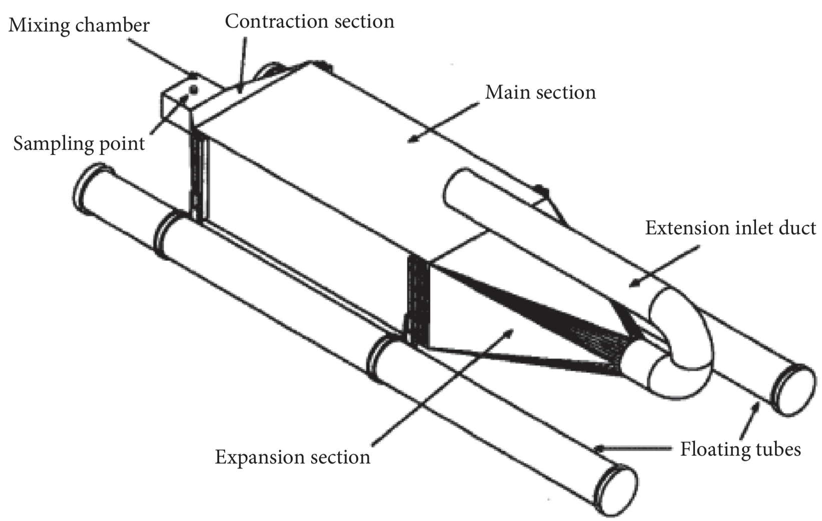
Chamber method	Measurement surface area (m)	Airspeed ($m\ s^{-1}$)	Chamber characteristics	Pros and cons	Reference
	2^2	0.3–3.5	Wind tunnel characterised by 6 following chambers: inlet, calming section, testing section, mixing section, 2 axial fans section, and outlet.	(i) Alteration of microclimatic conditions inside the chambers is avoided by automatic adjusting of inside air. (ii) The testing section is covered by a transparent foil to not alter the irradiation.	Braschkat et al. [62]
	0.32^2	0.33	Wind tunnel based on Lindvall [63] hood consists of an emission chamber 25 cm high, situated between a divergent diffuser and a convergent duct, respectively, 50 cm and 15 cm long.	(i) Aerodynamic disadvantages of the primal geometries are corrected, introducing some flow devices (flat vanes, perforated baffle, and extension duct).	Jiang et al. [64]

Table 2: Continued.

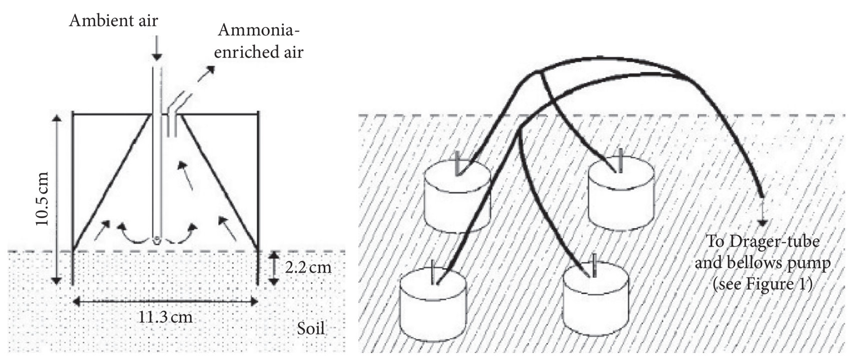
Chamber method	Measurement surface area (m)	Airspeed (m s^{-1})	Chamber characteristics	Pros and cons	Reference
 (a) (b)	415^2	Variable	Dynamic chamber characterised by 4 chambers placed onto the emitting surface. Air is sucked from them simultaneously by a pump and the ammonia concentrations are measured by a Dräger tube.	(i) High reliability of this method for comparative studies. (ii) No electricity and laboratory analysis. (iii) Low air exchange rate could lead to an underestimation of flow rate.	Roelcke et al. [56]

Table 3: Summary of main studies focused on dynamic chamber method improvements.

Lockyer (1984)	Jiang et al. [64]	Roelcke et al. [56]	Study conditions	Aim	Important improvements	Reference
X			(i) CO_2 was used instead of NH_3 (ii) 3 trials were carried out: two of them in a greenhouse and the other in the field	Testing the reliability of the conventional sampling system.	Introduction of 20 sampling points on 4 branches, to avoid underestimation of the actual gas flux.	Loubet et al. [7]
	X		(i) CO was used as a gas tracer (ii) It was introduced below a water surface, using a single point or a linear manifold	Determination and improvement of gas recovery rate.	The recovery rate was improved up to 92–102%, using a modified sampling chamber and tube configuration.	Wang et al. [66]
X			(i) 2 indoor experiments conducted at constant wind speeds of 0.5 and 1.0 m·s^{-1} (ii) An alkaline solution (3 L) containing ammonium sulphate was used as trap for each tunnel	Design, construction, and calibration of a revised wind tunnel	A new arrangement that allows each tunnel to be an independent unit, with an adjustable speed motor and a continuous air sampler.	Meisinger et al. [67]
		X	(i) 5 field experiments were carried out measuring NH_3 volatilisation with IHF and DTM, in winter and summer season (ii) Urea was used as fertiliser	Calibration of DTM by means of comparison with IHF results.	Two different calibration equations: $\ln(NH_3flux_{IHF}) = 0.444$ $\ln(NH_3flux_{DTM}) + 0.590 \ln(v_{2m})$ *(winter season)* $\ln(NH_3flux_{IHF}) = 0.456$ $\ln(NH_3flux_{DTM}) + 0.745 \ln(v_{2m}) - 0.280 \ln(v_{0.2m})$ *(summer season.)*	Pacholski et al. [57]
X			(i) Laboratory experiments were conducted with an NH_3 source tank (ii) Mean wind speed of 0.1–0.4 m·s^{-1}, while turbulence intensities of 11–33%	Studying and modelling the NH_3 mass transfer in the wind tunnel.	NH_3 mass transfer coefficient was modelled statistically, depending on wind velocity and turbulence intensity.	Saha et al. [68]
X			(i) 5 wind tunnel sizes were simulated using CFD (ii) Inlet air velocity range is 0.1–0.6 m·s^{-1}	Studying the effect of wind tunnel sizes on NH_3 emissions.	The effects of wind tunnel size were evaluated. In particular, wind tunnel height affects both velocity and concentration boundary layer thickness.	Saha et al. [69]
	X		(i) 4 flow distribution devices were designed and compared using CFD (ii) Inlet air velocities used were 1, 2.5, and 5 m·s^{-1}	Assessment of the best aerodynamic performances with different WT configurations.	The problem of air stagnation and flow recirculation inside the chamber could be solved introducing particular flow distribution devices.	Scotto di Perta et al. [70]

Notes. IHF = integrated horizontal flux; DTM = Dräger tube method; WT = wind tunnel; CFD = computational fluid dynamics.

where K (m^2 s^{-1}) is assumed to be equal to the eddy diffusivity for heat or transport coefficient of ammonia in atmosphere and z (m) is the height above the emitting surface at which concentration c (μg·m^{-3}) is measured.

3.3. Inverse Dispersion Modelling. Inverse dispersion modelling relates one or more concentrations measured in the plume to the atmospheric turbulent characteristics to obtain the emission rate of the corresponding source. The underlying hypotheses are that the studied tracer should be conservative over the measurement integration time and the volatilisation flux should be spatially homogeneous [76]. This technique provides a prediction of emitted ammonia from a surface of any geometry and size. Ammonia emission, in a single source configuration, is determined as follows:

$$F = \frac{\left(C - C_{\mathrm{bgd}}\right)}{D}, \tag{5}$$

where C and C_{bgd} are, respectively, the concentrations (μg·m^{-3}) measured downwind from the source and the background; D is the transfer coefficient ($m \cdot s^{-1}$) calculated by the dispersion model from the turbulence parameters.

The most common dispersion models used to estimate NH_3 emission in short range are the backward Lagrangian stochastic (bLS) [77] and the Eulerian [78].

The advantage of this method is the independence from any confined surface geometry and the reduced number of inputs required. Another limitation is linked to the time resolution and the sensitivity of the concentration measurement downwind of an emitting surface [27, 74, 77, 79].

Recently, Loubet et al. [78] adopted this method to monitor multisource experimental units, as agronomic plots (25 to 200 m side), having several and simultaneously small- and medium-size emitting sources. This method consists in the measure of concentration with time-averaged acid traps and the study of the turbulence parameters with a three-dimensional ultrasonic anemometer. This nonintrusive application is a low-cost solution to estimate NH_3 emissions that does not bias volatilisation estimates, with an uncertainty less than 10%. IDM accuracy has been confirmed for short times measurement (e.g., 30 min) [31].

3.4. Mass Balance or "Integrated Horizontal Flux" Method. Conversely to the above-described methods, the *integrated horizontal flux* (*IHF*) technique requires a small experimental circular area with fetch ranging from 15 to 20 and up to 50 m, as long as there are almost uniform wind conditions. For this reason, IHF method is commonly adopted [30], being applicable for measuring gas emission from a spatially inhomogeneous nonplanar source. Due to its flexibility, it is considered the most representative technique and, for this reason, it is the reference method to validate new methods for assessing ammonia emission from the field [27, 31, 80].

It allows the calculation of vertical flux from measurements of horizontal fluxes across downwind and upwind boundaries of the emitting source. The technique is robust and needs no further chemical or physical assumption for the estimation of vertical fluxes.

Based on the conservation of mass, the general method equates the vertical ammonia flux emitted from the treated plot with the net horizontal flux at a known downwind distance.

The horizontal flux density at any height is the product of horizontal wind speed u and gas concentration c_g. The total horizontal flux is obtained by integrating that product over the depth of the modified layer z. The average surface flux density is given by

$$F_{\text{vertical}} = \frac{1}{x}\left[\int_0^z uc_{\text{downwind}} \cdot \mathrm{d}z - \int_0^z uc_{\text{upwind}} \cdot \mathrm{d}z\right], \quad (6)$$

where x is the radius of the circular source (m). The integration is calculated over 0, that is the roughness length (height where the wind speed is 0) and z that corresponds to the maximum height of the emission plume where the concentration equals c_{upwind}.

Concentrations are measured by means of a mast placed in the centre of the source, or multiple masts upwind or downwind from the source; each mast is equipped with air samplers disposed to different heights [35]. In particular, among the various types of NH_3 samplers and analytical techniques studied, the most used are "Leuning et al.'s samplers" [81] and glass tubes [82].

The IHF system proposed by Leuning et al. [81] is equipped with passive NH_3 samplers consisting of a cone and a pipe made with PVC, able to point always toward the wind direction. The airstream enters in the device through an orifice and leaves it from the bottom. Inside each sampler, there is a stainless complex surface coated with a thin film of oxalic acid, which traps ammonia contained in the airstream. In this context, a number of samplers are mounted on a measurement mast that is placed in the centre of the treated plot to sample air at different heights (usually 5) and obtain the vertical profile of the horizontal ammonia flux [83].

The IHF system proposed by Schjoerring et al. [82] uses passive flux samplers consisting of two pairs of *glass tubes* (each tube 100 mm long, 10 mm outer diameter, and 7 mm inner diameter) with a coating of oxalic acid on their inner surfaces. Two tubes are connected by means of a piece of silicone tubing. One side of the tube is connected to a steel disc with a hole, in which the airstream enters. These devices are nonrotating samplers so that two units of samplers must be mounted at four heights on four masts placed on the perimeter of the circular plot to trap ammonia in the four wind directions.

Compared with Leuning et al.'s samplers, the glass tubes are easier to manage and cheaper. The sole disadvantage is the need of a great number of glass tubes. To solve this problem, an improved glass tube method was proposed by Wood et al. [84]. Instead of using four masts, a rotating mast centred in the circular plot was associated with the glass tubes. This system allowed reducing cost, labour, and analytical requirement considering the qualities of the previous flux methods. Moreover, results showed that the improved method increased the accuracy of ammonia volatilisation measurement. The ZINST method [85] is a particular case of IHF, where a single measurement of u and c_g is required to estimate the emission. This measurement height represents the point where the ratio of horizontal to vertical fluxes are relatively unaffected by atmospheric stability conditions. ZINST, as well as IHF, requires flat and uniform areas to be applied, but with the advantage of further reducing costs due to a single measurement point [80].

Recently, IHF method has been recently questioned [86] for systematic overestimation of the flux, since in theory it does not consider the turbulent horizontal transport ($u'c'$, or the fast fluctuating components around that average value). Sintermann et al. [6] suggested that this correction could vary between 5 and 20% depending on atmosphere stability, except for samplers like "Leuning et al.'s samplers" [81] and glass tubes [82], which captured NH_3 proportional to the horizontal wind speed.

4. Comparison of Ammonia Fluxes Measurement Methods

Several studies reported results of ammonia volatilisation from field experiment by using and comparing enclosure

Table 4: Comparison of ammonia cumulative emission in kg N ha^{-1} and % applied N determined by different measurement methods.

Ammonia cumulative emission kg·N·ha^{-1} (% applied N) Micrometeorological methods	*Ammonia cumulative emission* kg·N·ha^{-1} (% applied N) Chambers methods	Source type	Reference crop	Important findings	Reference
49.1^{f} (24.55%)^{f}	30.2^{h} (15.1%)^{h}	Exp 1 (1 m·s^{-1}) 200 kg·Urea-N·ha^{-1}	Cut sward	Rain leads to overestimating the NH_3 losses with the wind tunnel. Wind tunnel efficiency could enhance with automatic control of airspeed inside the tunnel, according to ambient wind speed.	Ryden et al. [87]
96.9^{f} (48.45%)^{f}	101^{h} (50.5%)^{h}	Exp 2 (1–3 m·s^{-1}) 200 kg Urea-N·ha^{-1}			
10.8^{f} (41.7%)$^{f, +}$	10.7^{g} (41.4%)^{g}	Pig and cattle slurry 24 kg TAN·ha^{-1}	Bare soil	Good accordance in the results between both methods under standard conditions in field applications.	Mannheim et al. [88]
15.6^{f} (77.4%)$^{f, +}$	15.2^{g} (74.4%)^{g}	12.3 kg TAN·ha^{-1}			
3.4^{f} (27.2%)$^{f,+}$	4.3^{g} (35.2%)^{g}	20.4 kg TAN·ha^{-1}			
1.9^{f} (7.3%)$^{f, +}$	11.2^{g} (42.1%)^{g}	26.6 kg TAN·ha^{-1}			
(75%)^{a,*}	(71%)^{h}	Cattle slurry: 127.25 kg·N·ha^{-1}	Bare soil	Wind tunnels are preferred to make small plot comparative studies.	Misselbrook et al. [89]
(54%)^{a,*}	(21%)^{h}	Poultry manure: 613.74 kg·N·ha^{-1}			
(29%)^{a,*}	(39%)^{h}	Poultry wetted manure: 316.2 kg·N·ha^{-1}			
32.7^{a} (43.6%)^{a} 45.6^{c} (60.8%)^{c}	26.8–30.6^{d} (35.5%)^{d}	75 kg Urea-N·ha^{-1}	Bare soil	IHF(GT) tends to underestimate or overestimate ammonia flux (12.5 to 64%), while dynamic chambers and IHF(L) have a similar ammonia loss kinetic.	Pacholski et al. [58]
21.6^{a} (1.8%)^{a} 8.2^{c} (4.1%)^{c}	22.2^{d} (11.1%)^{d}	200 kg Urea-N ha^{-1}			
23.9^{a} (19.9%)^{a} 21^{c} (17.5%)^{c}	25–29.8^{d} (20.8%)^{d}	120 kg Urea-N ha^{-1}			
18.8^{a} (12.5%)^{a} 8.6^{c} (5.7%)^{c}	51–59.8^{d} (34%)^{d}	150 kg Urea-N ha^{-1}			
9.9 (4.9%)^{b}	7.4 (3.7%)^{m}	Urea: 200 kg·N·ha^{-1}	Bare soil	WT measurements are affected by frequent sampling activities, but that correlation between WT and IHF method could be improved with 3 h of minimum sampler exposition time.	Scotto di Perta et al. [14]
46.8 (11.7%)^{b}	26.5 (6.63%)^{m}	Buffalo slurry: 400 kg·N·ha^{-1}			
49.2 (27.95%)^{b}	26.4 (15%)^{m}	Buffalo digestate: 176 kg·N·ha^{-1}			

Notes. Data in round brackets "( )"are expressed in % applied N. IHF = integrated horizontal flux; IHF(GT) = integrated horizontal flux with glass tubes, IHF(L) = integrated horizontal flux with Leuning et al.'s samplers, DTM = Dräger tube method; WT = wind tunnel; TAN = total ammoniacal-N; UAN = uric acid and ammoniacal-N. [a]IHF method by Leuning et al. [81]; [b]IHF method by Wood et al. [84]; [c]IHF method by Schjoerring et al. [82]; [d]DTM; [e]ZINST; [f]IHF method by Denmean [90]; [g]WT by Braschkat et al. [62]; [h]WT by Lockyer [61]; [m]WT by Jiang et al. [64]. [+]As % of applied TAN; [*]as % of applied of UAN.

and micrometeorological methods; thus, it is possible to make a cross-comparison among them in the various situations (see Table 4).

Dynamic chambers together with micrometeorological methods have been used in several studies (Table 4) using different fertilisers under different pedoclimatic conditions.

Compared to the chamber method, wind tunnels proved to be the best approach to minimize the discrepancy between the environmental conditions from inside to outside the chamber [25]. As a consequence, in the studies which compared NH_3 emissions from static and dynamic chambers, those measured using wind tunnels are always higher. Balsari et al. [91] found that NH_3 losses measured with the funnel-shaped static chamber, after manual application of raw cattle slurry to alfalfa grassland, is about 16% lower than those measured by wind tunnels (with an air velocity of 0.6 m·s^{-1}), both during summer and autumn. Moreover, both methods proved to be useful in comparing different fertilisers; indeed, they were sensitive to treatments and temperature variation of the season.

Unlike dynamic chambers, static ones are associated with a general underestimation of the emissions due to the higher resistance to atmospheric vertical transfer in absence or under low headspace air turbulence [92]. Miola et al. [65] compared NH_3 emission measured by static chambers and wind tunnel after field application of different manures. They found a large underestimation of the static chambers up to 80% (23% on average), regardless of the source strength, motivating this discrepancy as a consequence of low air movement that increases the resistance to NH_3 atmospheric transfer in static chambers. Furthermore, they found an indirect and time-related bias linked to the impact of chamber environment on the ammonification of organic N supplied by "manure amendment."

With regard to comparison between static and dynamic systems, as also suggested by Balsari et al. [2], NH_3 emission measurements performed on the same source and environmental conditions with the "funnel system" and wind tunnel were significantly different. The main reason for this difference is the constant airflow recirculation inside the wind tunnel over the emitting surface and the absence of this in the "funnel system." In particular, the ammonia emission rate evaluated with the wind tunnel was higher than the one measured by means of the "funnel system." Thus, this static chamber did not allow obtaining comparable data to those of real environmental conditions, but it can be used only as comparison system. Instead, the results obtained by the wind tunnel can be considered closer to the real emission phenomenon.

Yang et al. [55] compared different chamber types, a steady-state flow-through and vented chambers, with a vented and a closed chamber in a lab experiment, finding a severe underestimation of NH_3 quantification with all the chamber designs, due to large and negative variances, as also found by Wang et al. [41]. According to these results, the authors proposed that all the researchers adopting chamber methods declare the underestimation without applying any empirical correction of measured emissions, which can be source-strength dependent.

Finally, other studies, such as that of Pacholski et al. [58], reported the comparison of micrometeorological methods and dynamic chamber methods on urea emissions (Table 4). The authors used an IHF method equipped with Leuning et al.'s [81] passive samplers (IHF(L)) and an IHF equipped with glass tubes [82] (IHF(GT)) and a DTM. The results showed that IHF(GT) tends to underestimate or overestimates ammonia losses probably due to the different responsiveness of the samplers to the wind speed or the choosing of a smaller diameter pot (12.5 m), as well as the introduction of plastic-cover roof for the rain. On the other hand, DTM presented a good agreement with IHF(L) results in terms of ammonia loss kinetic, since only a qualitative comparison could be made.

Another comparison between static chambers and IHF method proposed by Bittman et al. [93] and Shah et al. [94] confirms the underestimation of static chambers such as those reported by Verdi et al. [39], Smith et al. [37], Rawluk et al. [43], Grant et al. [42], Balsari et al. [38], Nômmik [36], and Wang et al. [41], compared to the micrometeorological method. In addition, static chambers should not be chosen to perform ammonia emission measurements in field application of fertilisers because the enclosure affects heat transfer inside the chamber, whereas wind tunnels better mimic natural airflow. In most parts of them, except for Mannheim et al. [88], wind tunnels underestimate NH_3 emissions if compared with IHF method. In particular, the main parameters affecting the wind tunnel efficiency is the air velocity inside the dynamic chamber [87]. Indeed, as reported by Misselbrook et al. [89], comparable results with the IHF method can be achieved when the inner air velocity corresponds with the ambient wind speed.

In conclusion, a nonnegligible aspect in the selection of the proper measurement method is the consideration of many factors, including the resources and objective of the research. To this purpose, some parameters (e.g., replication, land area requirement, labour costs, analytical costs, reliability of technique, duration of measurement, and intrusiveness) should be taken into account. [89, 94].

5. Conclusions

Different aspects of ammonia measurement methods have been considered and discussed. Overall, the chambers method can be a viable option when it is not possible to apply micrometeorological methods. IHF micrometeorological technique is considered as a reference for quantifying NH_3 emission after manure field application, even if some corrections have been lately proposed. Compared to chamber method, wind tunnels proved to be the most suitable technique to mimic wind conditions, thus reducing the uncertainty with ammonia fluxes, as supported by the latest improvements on this technique. Finally, this literature review reported the strength and the weak points of the method nowadays used to assess ammonia emission in the field. The conclusion is that enclosure methods, as well as the dynamic chambers like the wind tunnels, are a reliable tool for a relative comparison of the emissions, when their limits and uncertainties are considered to choose the most suitable technique for specific experimental conditions.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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References

[1] C. Guerreiro, A. G. Ortiz, F. M. de LeeuwViana, and J. Horálek, "Air quality in Europe-2016 report," Publications Office of the European Union, Brussels, Belgium, 2016.

[2] P. Balsari, G. Airoldi, E. Dinuccio, and F. Gioelli, "Ammonia emissions from farmyard manure heaps and slurry stores-effect of environmental conditions and measuring methods," *Biosystems Engineering*, vol. 97, no. 4, pp. 456–463, 2007.

[3] L. Clarisse, C. Clerbaux, F. Dentener, D. Hurtmans, and P.-F. Coheur, "Global ammonia distribution derived from infrared satellite observations," *Nature Geoscience*, vol. 2, no. 7, pp. 479–483, 2009.

[4] S. Pindozzi, S. Faugno, C. Okello, and L. Boccia, "Measurement and prediction of buffalo manure evaporation in the farmyard to improve farm management," *Biosystems Engineering*, vol. 115, no. 2, pp. 117–124, 2013.

[5] J. E. Olesen and S. G. Sommer, "Modelling effects of wind speed and surface cover on ammonia volatilization from stored pig slurry," *Atmospheric Environment. Part A. General Topics*, vol. 27, no. 16, pp. 2567–2574, 1993.

[6] J. Sintermann, A. Neftel, C. Ammann et al., "Are ammonia emissions from field-applied slurry substantially over-

estimated in European emission inventories?" *Biogeosciences*, vol. 9, no. 5, pp. 1611–1632, 2012.

[7] B. Loubet, P. Cellier, D. Flura, and S. Génermont, "An evaluation of the wind-tunnel technique for estimating ammonia volatilization from land: Part 1. Analysis and improvement of accuracy," *Journal of Agricultural Engineering Research*, vol. 72, no. 1, pp. 71–81, 1999.

[8] FAOSTAT, *FAO Statistics, Food and Agriculture Organization of the United Nations*, FAOSTAT, Rome, Italy, 2019, http://www.fao.org/faostat/en/#data.

[9] M. Rostami, S. Monaco, D. Sacco, C. Grignani, and E. Dinuccio, "Comparison of ammonia emissions from animal wastes and chemical fertilizers after application in the soil," *International Journal of Recycling of Organic Waste in Agriculture*, vol. 4, no. 2, pp. 127–134, 2015.

[10] C. A. Rotz, F. Montes, S. D. Hafner, A. J. Heber, and R. H. Grant, "Ammonia emission model for whole farm evaluation of dairy production systems," *Journal of Environmental Quality*, vol. 43, no. 4, pp. 1143–1158, 2014.

[11] S. G. Sommer and N. J. Hutchings, "Ammonia emission from field applied manure and its reduction-invited paper," *European Journal of Agronomy*, vol. 15, no. 1, pp. 1–15, 2001.

[12] J. Martínez-Lagos, F. Salazar, M. Alfaro, and T. Misselbrook, "Ammonia volatilization following dairy slurry application to a permanent grassland on a volcanic soil," *Atmospheric Environment*, vol. 80, pp. 226–231, 2013.

[13] EC, Directive 2016/2284 of the European Parliament and of the Council of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending directive 2003/35/EC and repealing directive 2001/81/EC, EC Official Journal of the European Union L. 344 of 17.12.2016, 2016.

[14] E. Scotto di Perta, N. Fiorentino, L. Gioia, E. Cervelli, S. Faugno, and S. Pindozzi, "Prolonged sampling time increases correlation between wind tunnel and integrated horizontal flux method," *Agricultural and Forest Meteorology*, vol. 265, pp. 48–55, 2019.

[15] S. Minoli, M. Acutis, and M. Carozzi, "NH_3 emissions from land application of manures and N-fertilisers: a review of the Italian literature," *Italian Journal of Agrometeorology*, vol. 3, pp. 5–24, 2015.

[16] J. Ni, "Mechanistic models of ammonia release from liquid manure: a review," *Journal of Agricultural Engineering Research*, vol. 72, no. 1, pp. 1–17, 1999.

[17] Z. Ye, G. Zhang, B. Li, J. Søberg Strøm, G. Tong, and P. J. Dahl, "Influence of airflow and liquid properties on the mass transfer coefficient of ammonia in aqueous solutions," *Biosystems Engineering*, vol. 100, no. 3, pp. 422–434, 2008.

[18] S. Génermont and P. Cellier, "A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil," *Agricultural and Forest Meteorology*, vol. 88, no. 1–4, pp. 145–167, 1997.

[19] S. D. Hafner, F. Montes, and C. Alan Rotz, "The role of carbon dioxide in emission of ammonia from manure," *Atmospheric Environment*, vol. 66, pp. 63–71, 2013.

[20] D. Beutier and H. Renon, "Representation of NH_3-H_2S-H_2O, NH_3-CO_2-H_2O, and NH_3-SO_2-H_2O vapor-liquid equilibria," *Industrial & Engineering Chemistry Process Design and Development*, vol. 17, no. 3, pp. 220–230, 1978.

[21] V. K. Vaddella, P. M. Jiang, and A. Jiang, "An empirical model of ammonium ion dissociation in liquid dairy manure," *Transactions of the ASABE*, vol. 54, no. 3, pp. 1119–1126, 2011.

[22] Z. Yang, H. Niimi, K.-i. Kanda, and Y. Suga, "Measurement of ammonia volatilization from a field, in upland Japan, spread with cattle slurry," *Environmental Pollution*, vol. 121, no. 3, pp. 463–467, 2003.

[23] M. Carozzi, R. M. Ferrara, M. Fumagalli et al., "Field-scale ammonia emissions from surface spreading of dairy slurry in Po Valley," *Italian Journal of Agrometeorology*, vol. 3, pp. 15–24, 2012.

[24] J. F. M. Huijsmans, J. M. G. Hol, and M. M. W. B. Hendriks, "Effect of application technique, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to grassland," *NJAS-Wageningen Journal of Life Sciences*, vol. 49, no. 4, pp. 323–342, 2001.

[25] H. T. Søgaard, S. G. Sommer, N. J. Hutchings et al., "Ammonia volatilization from field-applied animal slurry—the ALFAM model," *Atmospheric Environment*, vol. 36, no. 20, pp. 3309–3319, 2002.

[26] P. Gostelow, P. Longhurst, S. A. Parsons, and R. M. Stuetz, "Sampling for measurement of odours," Scientific and Technical Report No. 17, IWA Publishing, London, UK, 2003.

[27] L. A. Harper, "Ammonia: measurement issues," in *Micrometeorology in Agricultural Systems*, J. L. Hatfield and J. M. Baker, Eds., vol. 47, pp. 345–379, ASA, CSSA, and SSSA, Madison, WI, USA, 2005.

[28] S. G. Sommer and T. H. Misselbrook, "A review of ammonia emission measured using wind tunnels compared with micrometeorological techniques," *Soil Use and Management*, vol. 32, pp. 101–108, 2016.

[29] M. Ferm, B. Galle, L. Klemedtsson, A. Kasimir-Klemedtsson, and D. W. T. Griffith, *Comparison of different Techniques to Measure Ammonia Emission after Manure Application*, Swedish Water and Air Pollution Research Laboratory-Publications-IVL B, Gothenburg, Sweden, 2000.

[30] J. S. Schepers and W. Raun, Eds., *Nitrogen in Agricultural Systems. No. 49*, ASA-CSSA-SSSA, Madison, WI, USA, 2008.

[31] S. G. Sommer, S. M. McGinn, and T. K. Flesch, "Simple use of the backwards Lagrangian stochastic dispersion technique for measuring ammonia emission from small field-plots," *European Journal of Agronomy*, vol. 23, no. 1, pp. 1–7, 2005.

[32] D. Parker, J. Ham, B. Woodbury et al., "Standardization of flux chamber and wind tunnel flux measurements for quantifying volatile organic compound and ammonia emissions from area sources at animal feeding operations," *Atmospheric Environment*, vol. 66, pp. 72–83, 2013.

[33] R. R. Sharpe and L. A. Harper, "Soil, plant and atmospheric conditions as they relate to ammonia volatilization," in *Nitrogen Economy in Tropical Soils*, pp. 149–158, Springer Netherlands, Dordrecht, Netherlands, 1996.

[34] P. A. Matson and R. C. Harriss, *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, John Wiley & Sons, Hoboken, NJ, USA, 2009.

[35] FAO, *Global Estimates of Gaseous Emissions of NH_3, NO and N_2O from Agricultural Land*, International Fertilizer industry Association/Food and Agricultural Organization of the United Nations, Rome, Italy, 2001.

[36] H. Nômmik, "The effect of pellet size on the ammonia loss from urea applied to forest soil," *Plant and Soil*, vol. 39, no. 2, pp. 309–318, 1973.

[37] E. Smith, R. Gordon, C. Bourque, and A. Campbell, "Comparison of three simple field methods for ammonia volatilization from manure," *Canadian Journal of Soil Science*, vol. 87, no. 4, pp. 469–477, 2007.

[38] P. Balsari, G. Magrini, and R. Pons, "Ammonia losses from pig slurry storage: first results of field tests," in *Proceedings of the 5th Technical consultation on the ESCORENA*, Rome, Italy, 1994.

[39] L. Verdi, P. J. Kuikman, S. Orlandini, M. Mancini, M. Napoli, and A. Dalla Marta, "Does the use of digestate to replace mineral fertilizers have less emissions of N_2O and NH_3?" *Agricultural and Forest Meteorology*, vol. 269-270, pp. 112–118, 2019.

[40] P. M. Ndegwa, V. K. Vaddella, A. N. Hristov, and H. S. Joo, "Measuring concentrations of ammonia in ambient air or exhaust air stream using acid traps," *Journal of Environmental Quality*, vol. 38, no. 2, pp. 647–653, 2009.

[41] Z. H. Wang, X. J. Liu, X. T. Ju, F. S. Zhang, and S. S. Malhi, "Ammonia volatilization loss from surface-broadcast urea: comparison of vented-and closed-chamber methods and loss in winter wheat–summer maize rotation in North China Plain," *Communications in Soil Science and Plant Analysis*, vol. 35, no. 19-20, pp. 2917–2939, 2004.

[42] C. A. Grant, K. R. Brown, L. D. Bailey, and S. Jia, "Short communication: volatile losses of NH_3 from surface-applied urea and urea ammonium nitrate with and without the urease inhibitors NBPT or ammonium thiosulphate," *Canadian Journal of Soil Science*, vol. 76, no. 3, pp. 417–419, 1996.

[43] C. D. L. Rawluk, C. A. Grant, and G. J. Racz, "Ammonia volatilization from soils fertilized with urea and varying rates of urease inhibitor NBPT," *Canadian Journal of Soil Science*, vol. 81, no. 2, pp. 239–246, 2001.

[44] X. L. Liao, "The methods of research of gaseous loss of nitrogen fertilizer," *Progress in Soil Science*, vol. 11, pp. 49–55, 1983.

[45] S. Monaco, D. Sacco, S. Pelissetti et al., "Laboratory assessment of ammonia emission after soil application of treated and untreated manures," *The Journal of Agricultural Science*, vol. 150, no. 1, pp. 65–73, 2012.

[46] E. Dinuccio, W. Berg, and P. Balsari, "Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation," *Atmospheric Environment*, vol. 42, no. 10, pp. 2448–2459, 2008.

[47] E. Scotto di Perta, E. Cervelli, S. Faugno, and S. Pindozzi, "Monitoring of NH_3 and CH_4 emissions from dairy cows under storage conditions," in *Proceedings of the 2019 IEEE International Workshop on Metrology for Agriculture and Forestry (MetroAgriFor)*, pp. 35–39, Naples, Italy, October 2019.

[48] E. Scotto di Perta, A. Mautone, M. Oliva, E. Cervelli, and S. Pindozzi, "Influence of treatments and covers on NH_3 emissions from dairy cow and buffalo manure storage," *Sustainability*, vol. 12, no. 7, pp. 1–11, 2020.

[49] D. R. Chadwick, J. Martinez, C. Marol, and F. Béline, "Nitrogen transformations and ammonia loss following injection and surface application of pig slurry: a laboratory experiment using slurry labelled with 15N-ammonium," *The Journal of Agricultural Science*, vol. 136, no. 2, pp. 231–240, 2001.

[50] Y. Shi, D. B. Parker, N. A. Cole, B. W. Auvermann, and J. E. Mehlhorn, "Surface amendments to minimize ammonia emissions from beef cattle feedlots," *Transactions of the ASAE*, vol. 44, no. 3, p. 677, 2001.

[51] T. H. Misselbrook, J. M. Powell, G. A. Broderick, and J. H. Grabber, "Dietary manipulation in dairy cattle: laboratory experiments to assess the influence on ammonia emissions," *Journal of Dairy Science*, vol. 88, no. 5, pp. 1765–1777, 2005.

[52] V. K. Vaddella, P. M. Ndegwa, and H. Joo, "Ammonia loss from simulated post-collection storage of scraped and flushed dairy-cattle manure," *Biosystems Engineering*, vol. 110, no. 3, pp. 291–296, 2011.

[53] M. A. Holly, R. A. Larson, J. M. Powell, M. D. Ruark, and H. Aguirre-Villegas, "Greenhouse gas and ammonia emissions from digested and separated dairy manure during storage and after land application," *Agriculture, Ecosystems & Environment*, vol. 239, pp. 410–419, 2017.

[54] G. M. Neerackal, P. M. Ndegwa, H. S. Joo et al., "Effects of anaerobic digestion and solids separation on ammonia emissions from stored and land applied dairy manure," *Water, Air, & Soil Pollution*, vol. 226, no. 9, p. 301, 2015.

[55] Y. Yang, X. Ni, B. Liu et al., "Measuring field ammonia emissions and canopy ammonia fluxes in agriculture using portable ammonia detector method," *Journal of Cleaner Production*, vol. 216, pp. 542–551, 2019.

[56] M. Roelcke, S. X. Li, X. H. Tian, Y. J. Gao, and J. Richter, "In situ comparisons of ammonia volatilization from N fertilizers in Chinese loess soils," *Nutrient Cycling in Agroecosystems*, vol. 62, no. 1, pp. 73–88, 2002.

[57] A. Pacholski, G. Cai, R. Nieder et al., "Calibration of a simple method for determining ammonia volatilization in the field-comparative measurements in Henan province, China," *Nutrient Cycling in Agroecosystems*, vol. 74, no. 3, pp. 259–273, 2006.

[58] A. Pacholski, G.-X. Cai, X.-H. Fan et al., "Comparison of different methods for the measurement of ammonia volatilization after urea application in Henan province, China," *Journal of Plant Nutrition and Soil Science*, vol. 171, no. 3, pp. 361–369, 2008.

[59] D. Gericke, A. Pacholski, and H. Kage, "Measurement of ammonia emissions in multi-plot field experiments," *Biosystems Engineering*, vol. 108, no. 2, pp. 164–173, 2011.

[60] I. Vallis, L. Harper, V. Catchpoole, and K. Weier, "Volatilization of ammonia from urine patches in a subtropical pasture," *Australian Journal of Agricultural Research*, vol. 33, no. 1, pp. 97–107, 1982.

[61] D. R. Lockyer, "A system for the measurement in the field of losses of ammonia through volatilisation," *Journal of the Science of Food and Agriculture*, vol. 35, no. 8, pp. 837–848, 1984.

[62] J. Braschkat, T. Mannheim, D. Horlacher, and H. Marschner, "Measurement of ammonia emissions after liquid manure application: I. Construction of a windtunnel system for measurements under field conditions," *Zeitschrift für Pflanzenernährung und Bodenkunde*, vol. 156, no. 5, pp. 393–396, 1993.

[63] T. Lindvall, O. Thyselius, and L. Thyselius, "Odor reduction for liquid manure systems," *Transactions of the ASAE*, vol. 17, no. 3, pp. 508–512, 1974.

[64] K. Jiang, P. J. Bliss, and T. J. Schulz, "The development of a sampling system for determining odor emission rates from areal surfaces: Part I. Aerodynamic performance," *Journal of the Air & Waste Management Association*, vol. 45, no. 11, pp. 917–922, 1995.

[65] E. C. C. Miola, C. Aita, P. Rochette et al., "Static chamber measurements of ammonia volatilization from manured soils: impact of deployment duration and manure characteristics," *Soil Science Society of America Journal*, vol. 79, no. 1, pp. 305–313, 2015.

[66] X. Wang, J. Jiang, and R. Kaye, "Improvement of a wind-tunnel sampling system for odour and VOCs," *Water Science and Technology*, vol. 44, no. 9, pp. 71–77, 2001.

[67] J. J. Meisinger, A. M. Lefcourt, and R. B. Thompson, "Construction and validation of small mobile wind tunnels for studying ammonia volatilization," *Applied Engineering in Agriculture*, vol. 17, no. 3, pp. 375–381, 2001.

[68] C. K. Saha, G. Zhang, and J.-Q. Ni, "Airflow and concentration characterisation and ammonia mass transfer modelling in wind tunnel studies," *Biosystems Engineering*, vol. 107, no. 4, pp. 328–340, 2010.

[69] C. K. Saha, W. Wu, G. Zhang, and B. Bjerg, "Assessing effect of wind tunnel sizes on air velocity and concentration boundary layers and on ammonia emission estimation using computational fluid dynamics (CFD)," *Computers and Electronics in Agriculture*, vol. 78, no. 1, pp. 49–60, 2011.

[70] E. Scotto di Perta, M. A. Agizza, G. Sorrentino, L. Boccia, and S. Pindozzi, "Study of aerodynamic performances of different wind tunnel configurations and air inlet velocities, using computational fluid dynamics (CFD)," *Computers and Electronics in Agriculture*, vol. 125, pp. 137–148, 2016.

[71] L. Rong, B. Elhadidi, H. E. Khalifa, P. V. Nielsen, and G. Zhang, "Validation of CFD simulation for ammonia emissions from an aqueous solution," *Computers and Electronics in Agriculture*, vol. 75, no. 2, pp. 261–271, 2011.

[72] M. Ferm, J. K. Schjørring, S. G. Sommer, and S. B. Nielsen, "Field investigation of methods to measure ammonia volatilisation," *Odour and Ammonia Emissions from Livestock Farming*, pp. 148–155, Elsevier Science Publishers Ltd., Barking, Essex, UK, 1991.

[73] T. P. Meyers and D. D. Baldocchi, "Current micrometeorological flux methodologies with applications in agriculture," *Micrometeorology in Agricultural Systems*, vol. 47, pp. 381–396, 2005.

[74] A. N. Hristov, M. Hanigan, A. Cole et al., "Review: ammonia emissions from dairy farms and beef feedlots," *Canadian Journal of Animal Science*, vol. 91, no. 1, pp. 1–35, 2011.

[75] R. M. Ferrara, G. Rana, and N. Martinelli, "Caso studio: approccio micrometeorologico per il monitoraggio continuo dei flussi di ammoniaca in ambiente semi-arido," in *Proceedings of the XII National Conference of Agrometeorology, Climate and Agriculture: Adaptation and Mitigation Strategies*, pp. 134-135, Sassari, Italy, 2009.

[76] M. Carozzi, B. Loubet, M. Acutis, G. Rana, and R. M. Ferrara, "Inverse dispersion modelling highlights the efficiency of slurry injection to reduce ammonia losses by agriculture in the Po Valley (Italy)," *Agricultural and Forest Meteorology*, vol. 171-172, pp. 306–318, 2013.

[77] T. K. Flesch, J. D. Wilson, and E. Yee, "Backward-time Lagrangian stochastic dispersion models and their application to estimate gaseous emissions," *Journal of Applied Meteorology*, vol. 34, no. 6, pp. 1320–1332, 1995.

[78] B. Loubet, M. Carozzi, P. Voylokov, J.-P. Cohan, R. Trochard, and S. Génermont, "Evaluation of a new inference method for estimating ammonia volatilisation from multiple agronomic plots," *Biogeosciences*, vol. 15, no. 11, pp. 3439–3460, 2018.

[79] P. Robin, G. Amand, C. Aubert et al., *Reference Procedures for the Measurement of Gaseous Emissions from Livestock Houses and Stores of Animal Manure*, Institut National de la Recherche Agronomique (INRA), Paris, France, 2010, https://www6.rennes.inra.fr/umrsas/content/download/4310/46810/version/1/file/rapport_final_ADEME_AnimalEmissionProcedures2010.pdf.

[80] S. V. Pedersen, E. Scotto di Perta, S. D. Hafner, A. S. Pacholski, and S. G. Sommer, "Evaluation of a simple, small-plot meteorological technique for measurement of ammonia emission: feasibility, costs, and recommendations," *Transactions of the ASABE*, vol. 61, no. 1, pp. 103–115, 2018.

[81] R. Leuning, J. R. Freney, O. T. Denmead, and J. R. Simpson, "A sampler for measuring atmospheric ammonia flux," *Atmospheric Environment*, vol. 19, no. 7, pp. 1117–1124, 1967.

[82] J. K. Schjoerring, S. G. Sommer, and M. Ferm, "A simple passive sampler for measuring ammonia emission in the field," *Water, Air, and Soil Pollution*, vol. 62, no. 1-2, pp. 13–24, 1992.

[83] J. Laubach, A. Taghizadeh-Toosi, R. R. Sherlock, and F. M. Kelliher, "Measuring and modelling ammonia emissions from a regular pattern of cattle urine patches," *Agricultural and Forest Meteorology*, vol. 156, pp. 1–17, 2012.

[84] C. W. Wood, S. B. Marshall, and M. L. Cabrera, "Improved method for field-scale measurement of ammonia volatilization," *Communications in Soil Science and Plant Analysis*, vol. 31, no. 5-6, pp. 581–590, 2000.

[85] J. Lavrsen Kure, J. Krabben, S. Vilms Pedersen, M. Carozzi, and S. G. Sommer, "An assessment of low-cost techniques to measure ammonia emission from multi-plots: a case study with urea fertilization," *Agronomy*, vol. 8, no. 11, p. 245, 2018.

[86] A. Hensen, A. Neftel, D. Famulari et al., in *Proceedings of the International Workshop on Ammonia Measurements (IWAM)*, Ras al Khaimah, UAE, 2015.

[87] J. C. Ryden and D. R. Lockyer, "Evaluation of a system of wind tunnels for field studies of ammonia loss from grassland through volatilisation," *Journal of the Science of Food and Agriculture*, vol. 36, no. 9, pp. 781–788, 1985.

[88] T. Mannheim, J. Braschkat, and H. Marschner, "Measurement of ammonia emission after liquid manure application: II. Comparison of the wind tunnel and the IHF method under field conditions," *Zeitschrift für Pflanzenernährung und Bodenkunde*, vol. 158, no. 3, pp. 215–219, 1995.

[89] T. H. Misselbrook, F. A. Nicholson, B. J. Chambers, and R. A. Johnson, "Measuring ammonia emissions from land applied manure: an intercomparison of commonly used samplers and techniques," *Environmental Pollution*, vol. 135, no. 3, pp. 389–397, 2005.

[90] O. T. Denmead, "Micrometeorological methods for measuring gaseous losses of nitrogen in the field," in *Gaseous loss of Nitrogen from Plant-Soil Systems*, pp. 133–157, Springer, Dordrecht, Netherlands, 1983.

[91] P. Balsari, E. Dinuccio, E. Santoro, and F. Gioelli, "Ammonia emissions from rough cattle slurry and from derived solid and liquid fractions applied to alfalfa pasture," *Australian Journal of Experimental Agriculture*, vol. 48, no. 2, pp. 198–201, 2008.

[92] K. Jiang and R. Kaye, "Comparison study on portable wind tunnel system and isolation chamber for determination of VOCs from areal sources," *Water Science and Technology*, vol. 34, no. 3-4, pp. 583–589, 1996.

[93] S. Bittman, L. J. P. van Vliet, C. G. Kowalenko, S. McGinn, D. E. Hunt, and F. Bounaix, "Surface-banding liquid manure over aeration slots: a new low-disturbance method for reducing ammonia emissions and improving yield of perennial grasses," *Agronomy Journal*, vol. 97, no. 5, pp. 1304–1313, 2005.

[94] S. B. Shah, P. W. Westerman, and J. Arogo, "Measuring ammonia concentrations and emissions from agricultural land and liquid surfaces: a review," *Journal of the Air & Waste Management Association*, vol. 56, no. 7, pp. 945–960, 2006.

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Research Article

Aerial Nitrogen Fluxes and Soil Nitrate in response to Fall-Applied Manure and Fertilizer Applications in Eastern South Dakota

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Manure and inorganic fertilizer help to meet crop nitrogen demand by supplementing soil nitrogen (N). However, excessive N losses reduce soil fertility and crop yield and can impair water and air quality. The objectives of the research were to compare different forms of fall-applied N for (1) the change in soil nitrate (NO_3-N) over the growing season and (2) the aerial ammonia (NH_3) and nitrous oxide (N_2O) fluxes during the fall and early growing season. Treatments included solid beef cattle manure with bedding (BM), solid beef cattle manure only (SM), urea (UO), and no fertilizer (NF). The two-year plot-scale study took place in Brookings County, South Dakota, under rain-fed conditions in a silty clay loam. Manure and urea were applied at equal plant-available N rates of 130 and 184 $kg \cdot N \cdot ha^{-1}$ in Y1 and Y2, respectively, according to the South Dakota nutrient management planning process. The average total (i.e., 0–0.60 m soil depth) soil NO_3-N for Y1 (83 $kg \cdot ha^{-1}$) was significantly higher than Y2 (67 $kg \cdot ha^{-1}$), whereas surface (i.e., 0–0.15 m soil depth) soil NO_3-N was not significantly different between years. The average surface soil NO_3-N (33.5 $kg \cdot ha^{-1}$) and total soil NO_3-N (105.0 $kg \cdot ha^{-1}$) for UO were significantly higher than the remaining treatments ($P < 0.05$). Soil water NO_3-N concentrations, leaf-N, corn-grain-N, and yield measurements did not indicate any significant differences between treatments. Based on the two-year average, the highest NH_3-N flux occurred from the BM (3.4 $g \cdot ha^{-1} \cdot h^{-1}$); however, this flux was only significantly higher than NF (1.4 $g \cdot ha^{-1} \cdot h^{-1}$). The NH_3-N fluxes from UO (2.2 $g \cdot ha^{-1} \cdot h^{-1}$) and SM (1.7 $g \cdot ha^{-1} \cdot h^{-1}$) were similar to both BM and NF. The N_2O-N flux from UO (0.79 $g \cdot ha^{-1} \cdot h^{-1}$) was significantly greater than NF (0.25 $g \cdot ha^{-1} \cdot h^{-1}$), while BM- (0.49 $g \cdot ha^{-1} \cdot h^{-1}$) and SM-produced (0.33 $g \cdot ha^{-1} \cdot h^{-1}$) N_2O-N fluxes were not significantly different than neither UO nor NF. The three fall-applied N sources had similar aerial-N fluxes even though urea application resulted in significantly higher soil nitrate.

1. Introduction

Soil nitrogen (N) is critical for crop yield [1, 2]. As an N source, manure can also increase soil organic matter and improve soil health [3, 4], which translates to higher productivity. However, an excess amount of soil N loss can lessen nutrients for crop production and pollute surrounding air and water bodies. Over application or mismanagement of manure and N fertilizer sources can promote N losses from the soil [5, 6] through volatilization, denitrification, leaching, runoff, and erosion [7–10]. Nitrous oxide (N_2O) loss to the atmosphere contributes to global warming as well as depletion of the ozone layer [11–14]. EPA [13] indicated that agricultural activities including manure/fertilizer application and cropping practices were responsible for about 79% of total United States (US) N_2O emissions in 2014. European studies suggest 10 to 50% of total agricultural ammonia (NH_3) loss is from land-applied manure fertilizers [15, 16]. Ammonia has a wide variety of environmental impacts including soil acidification, acid rainfall, and eutrophication of ecosystems [17]. Also, aerial-NH_3 can react with atmospheric gases such as sulfur dioxide or nitrogen oxides (in the presence of water) to form fine particulate matter that is very harmful for human and animal health and the environment [18, 19]. In order to reduce aerial and other N losses, we must first understand the conditions that promote N loss to the environment.

Eastern South Dakota is part of the Northern Great Plains and the Upper Missouri River Basin, with a semiarid climate [20]. In 2012, 22% of the US beef cows and 20% of corn production occurred in the Northern Great Plains [20], with many producers integrating livestock manure and crop production management decisions.

Previous studies have demonstrated the effect of land application of solid manure regarding nutrient availability [21], greenhouse gas emission [22–24], NH_3 emission [22, 23], and leachate concentrations [25]. Several studies have also compared the effects of slurry or liquid manure application of different manure types (swine, dairy, poultry, feedlot, etc.) for similar factors [8, 9, 26–34].

Bedding is used on animal farms for animal comfort, to reduce animal injury and to aid in manure handling [35, 36]. Corn or soybean stover, wheat straw, or corn cobs are common bedding materials for beef cattle in the Midwest and Northern Great Plains because they are locally available [37]. Bedding with manure may impact soil properties, N and phosphorus (P) uptake, and N mineralization rates [4, 9, 28, 38, 39]. Carbon-rich bedding can temporarily immobilize manure N in the soil, delaying the release of plant-usable forms of N. However, as soil microbes use carbon as an energy source, they also help N mineralization [40]. Miller et al. [28] found that soil inorganic N, soil P, and soil mineralizable N were significantly affected by manure applications and the effects changed with year, bedding, rate of application, and their interactions.

In the Northern Great Plains, fall application of manure is a common practice—this allows emptying of manure storages prior to the winter period and avoids soil compaction associated with manure application during the often wet spring season. A study by Loecke et al. [8] reported that N use efficiency on corn was higher for fall-applied manure than spring-applied manure. Also, manure has sufficient time to decompose while it is applied in the fall and make nutrients more available for crop uptake in the spring [41]. Best management practices recommend fall application of fertilizers once the soil temperature is less than 10°C to limit N losses [42].

The objectives of the research were to compare different forms of fall-applied N (solid beef cattle manure with bedding, solid beef cattle manure only, and urea) and no fertilizer for (1) the change in soil nitrate (NO_3-N) over the growing season and (2) the aerial ammonia (NH_3) and nitrous oxide (N_2O) losses during the fall and early growing season. This study was conducted near Brookings, South Dakota, following a nutrient management plan guide for the area. This study does not account for all N losses from the crop system, but these data add to the understanding of factors affecting aerial nitrogen losses. In conjunction with other research, this type of data helps in the future refinement of management and nitrogen loss factors used in manure nutrient management planning tools. Similarly, concurrent research occurred in North Dakota [23, 43] and Nebraska under different climatic and soil conditions.

2. Materials and Methods

2.1. Site Description. The research was conducted at the South Dakota Felt Farm in Brookings County (44°22′07.5″N and 96°47′35.7″W, and 516 m above mean sea level) between October 2015 and October 2017. The research site area was 0.11 ha (45.7 × 24.7 m) with average slope <1%. The soil was silty clay loam, classified as *Udic Haploborolls* [44]. Daily temperature and precipitation records for the research site were collected from the South Dakota State University Climate and Weather Station located about 7 km from the site.

2.2. Experimental Design. The experimental design was a randomized complete block design (RCBD). The four treatments included solid beef cattle manure with bedding (BM), solid beef cattle manure without bedding (SM), urea (UO), and no fertilizer/control (NF). There were four blocks with four plots (experimental units; 3.3 m × 9.1 m) per block. A plot was assigned in each block to each treatment (Figure 1). The project periods from nitrogen application in November of 2015 and 2016 to harvest in October of 2016 and 2017 were designated as Year 1 (Y1) and Year 2 (Y2), respectively.

Based on soil and manure tests, N-based application rates were determined using the South Dakota Fertilizer Recommendations Guide EC-750 [45] (Table 1) for a corn yield goal of 11.3 $Mg{\cdot}ha^{-1}$ (180 $bu{\cdot}ac^{-1}$). There was no credit prescribed for the soybean crop preceding Y1. Aggregated soil samples (0–0.6 m) from the research site area showed an average soil nitrate nitrogen concentration of 113 $kg\,ha^{-1}$ prior to Y1 application, and the postharvest soil nitrate nitrogen levels in Y1 (Table 2) were used for Y2 application rates (methodology described in Soil Parameters). Manures and urea were manually applied to each plot in November each project year. The entire research site was tilled within 24 h of nitrogen application with two passes of a disk plow. There was no irrigation. In Y1, the corn plant date was May 2. In Y2, corn was first planted on May 6 and replanted on June 2 following insufficient seed emergence.

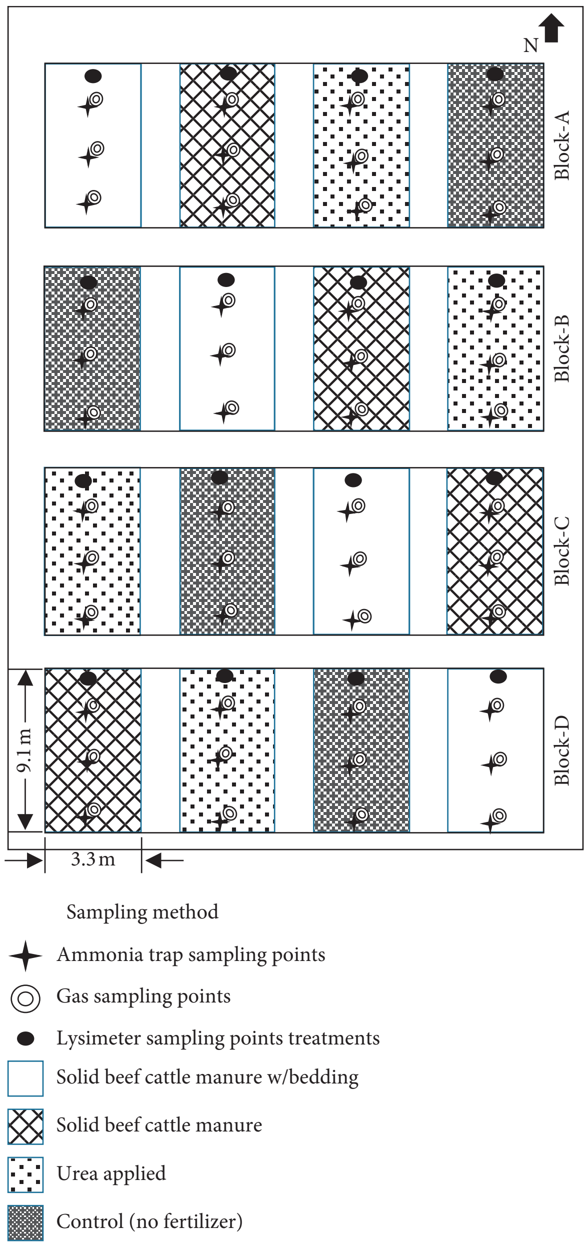

Figure 1: Layout of the experimental site at the South Dakota State University Felt Farm (Brookings County).

2.3. Sample Collection and Analysis

2.3.1. Manure Parameters. The SM and BM were from beef cattle manure stockpiles at the South Dakota State University Ruminant Nutrition Center, Brookings, SD. The BM included corn stover bedding. Prior to application, ten random shovel samples of manure were collected from stockpiles of each type in a pail and mixed thoroughly and a subsample used for manure characterization following recommended practices by Peters et al. [46]. Total N analysis was by dry combustion Dumas method, ammonium-N (NH_4-N) analysis was by distillation, and phosphate (P_2O_5), potassium oxide (K_2O), sulfur (S) were determined using microwave-assisted digestion and inductively coupled plasma spectroscopy.

2.3.2. Soil Parameters. Soil samples were collected prior to manure application and prior to planting, six-leaf vegetative stage (V6), and postharvest stage from each plot. On each sampling day, composite soil samples were collected for 0–0.15 m (0–6 in.) and 0.15–0.60 m (6–24 in.) depths in each plot using a probe auger. Shallow soil sample (0–0.15 m) analyses included ammonium nitrogen (NH_4-N), electrical conductivity (EC), organic matter (OM), phosphorus (P) concentration, total N, total C, and pH. The NO_3-N for the 0.15–0.60 m deep sample in each plot was added to the shallow sample measurement for total soil NO_3-N. The pH, EC, and OM were analyzed using North Central Extension Research Activities guidelines [47]. Soil NO_3-N and NH_4-N were analyzed using the flow injection analysis QuikChem method 12-107-04-1-B with 2 M KCl extraction [48]. Similarly, Olsen-P was determined by the sodium bicarbonate method [49], whereas ammonium and total N and C in the soil samples were analyzed using the QuikChem method 12-107-06-2-F [50] and Dumas method [51], respectively.

A suction lysimeter (1270 mm in length and 22 mm diameter; Irrometer Company, Inc., CA, USA) was installed at 1200 mm soil depth in the north end of each plot (Figure 1). Soil water samples were collected on 17, 23, 31, 35, 44, and 50 d after planting in Y1 and 16, 24, 33, 39, 48, and 53 d after planting in Y2. The number of soil water sampling days depended on rainfall events and soil water availability. During sample collection, a hand pump applied a vacuum pressure between −60 and −70 kPa and the vacuum was maintained for 4 hours. Soil water collected in the lysimeters was extracted using a 60 mL polypropylene syringe, collected into a 50 mL polypropylene vial, and transferred to the laboratory for analyses. In the laboratory, NO_3-N concentration in collected water was determined using an Automated Timberline TL2800 ammonia analyzer (Timberline Instruments, Boulder, CO).

The Aridlands Ecology Lab Protocol (modified 2009.01.19, S. Castle) was used to measure bulk density of the top 50 mm of soil. Soil surface (0–50 mm) samples were collected from each plot using the AMS bulk density soil sampling mini kit (50 mm dia. × 50 mm stainless steel ring). A composite soil sample was used for mechanical texture analysis.

2.3.3. Crop Parameters. The six most recently unfurled leaves below the whorl at the six-leaf vegetative stage (V6) and six leaves below the corn ear at tasseling (VT) and physiological maturity stage (R6) were collected and composited from six plants in each plot. We collected yield and corn-grain nitrogen concentration measurements during the Y1 harvest.

After drying and grinding, total N concentration of the plant and grain samples were measured using the micro-Kjeldahl procedure [52].

2.3.4. Ammonia Flux. The NH_3 gas flux was collected at three locations in each plot using semistatic chambers with acidified (0.5 M H_3PO_4) foam strips as described by Jantalia et al. [53]. In Y1, flux was measured −4, 3, 7, and 13 d from the day of fall N-application, and −6, 10, and 30 d from the day of planting. In Y2, flux was measured −7, 1, 6, and 15 d from the day of fall N-application, and −35, 7, and 42 d from

Table 1: Physical characteristics and application rates of manure and urea fertilizers for experiment site.

Variable	Year	Treatment[z] Manure with bedding	Manure only	Urea
Crop nitrogen requirement[y] ($kg{\cdot}ha^{-1}$)	1 & 2		242	
Soil nitrate nitrogen (0–60 cm; pre-N application; $kg{\cdot}ha^{-1}$)	1		113	
	2	57.3 ± 7.5	44.5 ± 5.9	63.7 ± 8.4
Plant available nitrogen recommendation[x] ($kg{\cdot}ha^{-1}$)	1		130	
	2		183	
Manure moisture content ($g{\cdot}kg^{-1}$)	1	742	723	—
	2	691	530	—
Manure/urea total nitrogen ($g{\cdot}kg^{-1}$)	1	8.5	8.2	460
	2	8.5	11.5	460
Manure/urea[w] ammonium nitrogen ($g{\cdot}kg^{-1}$)	1	1.85	1.77	460
	2	1.62	1.16	460
Plant available nitrogen in manure[v]/urea ($g{\cdot}kg^{-1}$)	1	4.0	3.8	460
	2	4.9	6.2	460
Manure/urea application rate ($Mg{\cdot}ha^{-1}$)	1	32.5	33.8	0.28
	2	37.7	29.5	0.40

[y]South Dakota Fertilizer Recommendations Guide EC-750 [45] recommends 1.2 times corn-grain yield goal (11.3 $Mg{\cdot}ha^{-1}$). [x]Plant-available nitrogen recommendation = crop nitrogen requirement – soil nitrate nitrogen [45]. [w]Assumes all urea-based nitrogen will hydrolyze to ammonium nitrogen in soil. [v]Plant-available nitrogen in manure = (application loss factor) ∗ (manure ammonium nitrogen) + (mineralization factor) ∗ (manure total nitrogen – manure ammonium nitrogen); application loss factor = 0.9 for incorporation within 24 h; mineralization factor = 0.35 for first year of manure (Y1) and 0.5 for second year of manure (Y2).

the day of replanting. Collection periods ranged from 1 to 2 d before fall N-application, 2 to 8 days after fall N-application, and 3 to 8 days in the spring. After each collection period, we transferred the acidified foam strips to a freezer. We extracted the acid trap solution from thawed sample traps with 250 mL of 2 M KCL solution. A subsample of the extraction solution was analyzed for ammonia using automated methods (Model TL2800 ammonia Analyzer, Timberline Instruments, Boulder, CO).

Ammonia concentration was obtained in $g{\cdot}N{\cdot}ha^{-1}$ by multiplying NH_3 concentration ($\mu g{\cdot}mL^{-1}$) and the total volume of solution (250 mL) and then dividing by the surface area of the soil covered by the respective chamber (79 cm^2). The ammonia flux ($g{\cdot}N{\cdot}ha^{-1}{\cdot}h^{-1}$) for each plot was determined by dividing ammonia concentration by elapsed time from installation to the removal of the NH_3 traps.

2.3.5. Nitrous Oxide Flux. In this study, the static chamber method was used described by Parkin and Venterea [54] to measure N_2O flux. Each chamber consisted of a polyvinyl chloride (PVC) collar (254 mm internal dia. × 150 mm) and a vented PVC cap. Each collar was installed 10 cm into the soil. The average headspace height was 142 mm with the cap in place.

Three collars on each plot ($n = 48$) were installed. In Y1, flux was measured −4, 7, and 13 d following fall N-application and −7, 1, 6, and 15 d following N-application in Y2. Flux measurements were collected −7 d in Y1 and −38 and −17 d in Year 2 relative to corn planting and subsequently at monthly intervals in both years. For each flux measurement, 10 mL gas samples were withdrawn from each chamber using a syringe after 0, 30, and 60 min of cap placement. We transferred samples to 12 mL preevacuated glass vials. A sample of ambient air during the sampling time for each block was collected to capture the ambient N_2O concentration, and all samples were collected between 930 and 1600 h. The N_2O concentrations in the vials were measured using gas chromatography (Model 14B, Shimadzu Corporation, Japan). Air and soil temperature (Model 00641W, AcuRite, Lake Geneva, WI) and soil moisture (Model ML2x, Delta-T Devices, Cambridge, England) were monitored in the vicinity of each chamber on each sampling day.

The average ambient concentration measurement was used in place of the 0 min samples for each sampling day. The N_2O fluxes were determined from N_2O concentrations relative to elapsed time. Flux calculations were not performed if (a) the 30 min (T30) and/or 60 min (T60) concentration(s) were less than (1 – error) ∗ ambient concentration and (b) the quadratic curve through the 3 data points was concave down and T60 ∗ (1 + error) was less than T30 ∗ (1 – error) or (c) the quadratic curve through the 3 data points was concave up and a linear slope fit through the 3 points was not significantly different than zero. If the quadratic curve through the 3 points was concave down, the slope at time zero (the first-order coefficient of the quadratic equation fits through the 3 data points) was used to calculate the flux. If the quadratic curve through the 3 points was concave up, but the linear slope through the 3 points was significantly different than zero, the linear slope was used to calculate the flux. The allowable error (proportional to concentration) was 20%. Evaluated N_2O fluxes were then converted into μg N_2O-N $m^{-2}{\cdot}h^{-1}$ using the ideal gas law equation. The resulted fluxes were corrected using soil properties (bulk density, clay fraction, pH, moisture content, and soil temperature) using the method of Venterea [55].

2.4. Statistical Analysis. PROC GLIMMIX procedure [56] was used for mixed model analyses with repeated measures for all variables except corn yield and corn-grain nutrients.

Table 2: Soil, leaf, grain, and yield measurements (±standard error)[z] based on treatment, year, and growth stage.

Parameter / Year	Growth stage	Treatment: Manure with bedding	Manure only	Urea	No fertilizer	Mean	
Total soil nitrate nitrogen in the top 0–60 cm of soil ($kg \cdot ha^{-1}$)							
Y1	Preplant	153.3 ± 19.5	155.1 ± 19.8	304.1 ± 38.7	151.9 ± 19.4	181.2 ± 14.5	a
	V6	67.3 ± 16.6	50.2 ± 12.4	109.7 ± 27.1	57.5 ± 14.2	66.5 ± 8.8	b
	Postharvest	57.3 ± 7.5	44.5 ± 5.9	63.7 ± 8.4	34.8 ± 4.6	48.5 ± 4.0	bc
	Mean	83.2 ± 9.9	69.7 ± 8.3	127.5 ± 15.2	66.6 ± 8.0	83.4 ± 5.8	aa
Y2	Preplant	182.7 ± 23.3	172.2 ± 21.9	422.3 ± 53.8	159.7 ± 20.3	213.6 ± 17.1	a
	V6	39.2 ± 9.7	38.7 ± 9.7	43.4 ± 10.7	44.7 ± 11.1	40.6 ± 5.3	bc
	Postharvest	34.3 ± 4.5	35.2 ± 4.6	37.5 ± 4.9	38.8 ± 4.8	35.7 ± 2.9	c
	Mean	62.1 ± 7.4	61.2 ± 7.3	87.5 ± 10.5	63.5 ± 7.6	67.5 ± 4.7	bb
Y1Y2	Mean	71.7 ± 6.3 b	65.1 ± 5.7 b	105.3 ± 9.2 a	64.9 ± 5.7 b		
Surface soil nitrate nitrogen in the top 0–15 cm of soil ($kg \cdot ha^{-1}$)							
Y1	Preplant	40.8 ± 6.6	41.7 ± 6.8	116.3 ± 18.9	35.0 ± 5.7	55.9 ± 4.9	a
	V6	14.4 ± 2.3	7.7 ± 1.2	16.8 ± 2.7	7.5 ± 1.2	10.8 ± 1.0	cd
	Postharvest	28.5 ± 4.6	21.2 ± 3.4	26.4 ± 4.3	17.4 ± 2.8	22.8 ± 2.2	b
	Mean	25.4 ± 2.5	18.8 ± 1.9	36.9 ± 3.7	16.5 ± 1.6	23.1 ± 1.3	
Y2	Preplant	67.1 ± 10.9	55.1 ± 8.9	189.0 ± 30.7	45.7 ± 7.4	74.5 ± 7.1	a
	V6	11.7 ± 1.9	8.6 ± 1.4	9.8 ± 1.6	8.7 ± 1.4	9.6 ± 0.9	d
	Postharvest	14.6 ± 2.4	13.3 ± 2.2	15.7 ± 2.6	15.4 ± 2.5	14.6 ± 1.4	c
	Mean	22.4 ± 2.2	18.4 ± 1.8	30.5 ± 3.0	18.2 ± 1.8	21.8 ± 1.3	
Y1Y2	Mean	23.8 ± 1.7 b	18.5 ± 1.3 bc	33.5 ± 2.4 a	17.3 ± 1.2 c		
Soil water nitrate nitrogen concentration at 120 cm soil depth between planting and V6 growth stages ($mg \cdot L^{-1}$)							
Y1		9.0 ± 3.2	16.6 ± 3.2	12.1 ± 3.2	12.4 ± 3.2	12.5 ± 3.2	a
Y2		3.7 ± 3.4	9.1 ± 3.3	8.5 ± 3.4	4.5 ± 3.3	9.5 ± 3.3	b
Y1Y2	Mean	6.35 ± 3.3	12.85 ± 3.3	10.3 ± 3.3	8.45 ± 3.3		
Corn leaf nitrogen concentration, $g \cdot kg^{-1}$							
Y1	Preplant	29.3	29.9	31.3	27.7	29.6 ± 0.8	a
	V6	27.9	27.2	29	28.4	28.1 ± 0.8	a
	Postharvest	15.0	14.5	14.5	12.6	14.2 ± 0.8	b
	Mean	24.1 ± 0.9	23.9 ± 0.9	25.0 ± 0.9	22.9 ± 0.9	23.9 ± 0.5	aa
Y2	Preplant	28.5	27.3	31	26.4	28.3 ± 0.8	a
	V6	17	16.9	20.6	15.6	17.5 ± 0.8	b
	Postharvest	10.6	10.8	10.3	10.4	10.5 ± 0.8	c
	Mean	18.7 ± 0.9	18.3 ± 0.9	20.6 ± 0.9	17.5 ± 0.9	18.8 ± 0.5	bb
Y1Y2	Mean	21.4 ± 0.7	21.1 ± 0.7	22.8 ± 0.7	20.2 ± 0.7		
Corn grain nitrogen concentration, $g \cdot kg^{-1}$							
Y1		13.3 ± 0.6	12.2 ± 0.4	13.6 ± 0.7	11.9 ± 0.2	12.8	
Corn yield, $Mg \cdot ha^{-1}$							
Y1		12.0 ± 1.0	10.8 ± 1.0	12.5 ± 0.5	10.8 ± 0.5	11.5	

[z]Mean ± SE = estimated mean ± standard error obtained from least squared means table. Different letters in means among the treatments indicate significant difference at $P < 0.05$ within a variable type. Double letters indicate significant differences between yearly means. The absence of letters indicates $P > 0.05$ between means.

Treatment (BM, SM, UO, and NF) and growth stage (stages differed for the various dependent variables) were considered fixed factors for surface and total soil NO_3-N and leaf-N concentration data, but time (sampling day) was considered a random factor for soil water NO_3-N concentration, NH_3 flux, and N_2O flux data. Year was considered a fixed effect and block considered as a random replication factor for all variables. The normality of the residuals was reviewed using Q-Q plots, and if residuals were not normal, different distribution options (e.g., lognormal, exponential, and Poisson) available in PROC GLIMMIX were tested. Different covariance structures were used to assess the repeated measure data, including covariance component (VC), compound symmetry (CS), autoregression (AR (1)), unstructured (UN), and Toeplitz (TOEP). The covariance structure selected for each variable was based on the smallest Akaike information criterion (AIC) value. Table 3 summarizes the fixed and random effects, distribution type, and covariance structure used for each variable. Significant differences were considered at $P < 0.05$.

The obtained least squared means (LSMeans) from the lognormal distributions were back transformed for reporting purposes. For post hoc tests, Tukey's honest significant difference (HSD) was used. We used correlation analyses to investigate relationships between yield, leaf-N, and soil nitrate data.

3. Results and Discussion

Herein, data for weather, soil, and crop data that relate to aerial N_2O and NH_3 fluxes for the experimental period were

Table 3: Summary of statistical tests and model factors.

Descriptor	Total soil nitrate in the top 0–60 cm of soil	Surface soil nitrate in the top 0–15 cm of soil	Olsen-P	Soil OM	Soil pH	Soil EC	Soil K	Corn leaf nitrogen concentration	Total N	Total C	Ammonium	Corn yield	Corn grain nitrogen concentration	Nitrous oxide	Ammonia flux	Soil water nitrate concentration
Fixed effects	Trt, Y, GS							Trt, Y, GS	Trt, GS			Trt		Trt, Y		
Random effects	Block							Block	Block			Block		Date, block		
Distribution type	Log	Log	Log	Nor	Nor	Log	Log	Nor	Log	Exp	Log	Nor	Nor	Log	Log	Nor
Covariance structure	UN	AR(1)	VC	VC	VC	CS	VC	AR(1)	AR(1)	AR(1)	AR(1)			VC	VC	AR(1)
Effects	Type III tests of fixed effects *P* value															
Trt	**0.0009**	**<0.0001**	**0.001**	0.058	0.241	**0.002**	**0.0002**	0.0802	0.28	0.999	0.232	0.58	0.098	**0.0106**	**0.0185**	0.1989
Y	**0.0331**	0.4575	0.132	0.809	0.793	**0.002**	0.168	**<0.0001**						0.3204	0.4245	**0.0305**
GS	**<0.0001**	**<0.0001**	**0.017**	**0.004**	**0.032**	**<0.0001**	**0.0006**	**<0.0001**	**0.005**	0.97	0.22					
Trt * GS	0.1157	**0.0001**	**0.082**	0.309	**<0.0001**	**<0.0001**	**0.012**	0.5657	0.1	1	0.219					
Trt * Y	0.4603	0.4136	0.771	0.411	0.95	0.455	0.985	0.8584						0.1712	0.1921	0.8708
Y * GS	**0.0114**	**0.0018**	0.109	0.679	**0.062**	**<0.0001**	**<0.0001**	**0.0001**								
Trt * Y * GS	0.3077	0.2078	**0.0005**	0.214	0.243	0.118	**0.0004**	0.2351								

All statistical tests were performed using PROC GLIMMIX and included interactions among fixed and random effects. Abbreviations for fixed effects: Trt = treatment; Y = year; GS = growth stage. Abbreviations for distribution type: Log = lognormal; Nor = normal or Gaussian; Exp = exponential. Abbreviations for covariance structure: UN = unstructured; AR(1) = first-order autoregression; VC = variance components.

presented. Additional supporting data collected during the experiment are in Table 4, Mehata [57], and Mehata et al. [58] for future reference or modeling purposes.

3.1. Weather Conditions. Daily mean air temperatures were 13°C in Y1 and 7°C in Y2 on the day of manure/fertilizer application (Figure 2). In Y1, there was no rainfall for 12 d after N-application; however, light rainfall (1 mm) occurred 2 d after N-application in Y2. Annual precipitation in 2016 and 2017 was 5.3% higher and 3.9% lower, respectively, compared to average annual precipitation between 1981 and 2010 (618 mm). Wet and cool weather in May of 2017 contributed to poor emergence and the need for replanting in Y2. The 530 mm of precipitation received during Y1 during the corn growth period (May through October 2016) was 17% higher than the 442 mm received during the Y2 growing season (June to October 2017).

3.2. Soil Nitrogen. All fertilized plots received equal amounts of plant-available nitrogen, which includes ammonium-N and mineralized organic N from the manure (Table 1). Treatment significantly affected the total soil NO_3-N (0 to 0.60 m) and surface soil NO_3-N (0 to 0.15 m) during the project (Table 2). The mean surface soil NO_3-N (33.5 kg·ha^{-1}) and mean total soil NO_3-N (105.3 kg·ha^{-1}) for UO were significantly higher than manure and no-fertilizer plots ($P < 0.05$, Table 2). The average surface soil NO_3-N between Y1 (23.1 kg·ha^{-1}) and Y2 (21.8 kg·ha^{-1}) was not significantly different, but total soil NO_3-N was significantly greater in Y1 (83.4 kg·ha^{-1}) compared to Y2 (67.5 kg·ha^{-1}). It is possible more soil NO_3-N moved from the lower depths by leaching in Y2 because rainfall in Y2 (preplanting to V6 stage) was 226 mm, compared to 172 mm for Y1.

For the surface soil nitrate, the interaction between treatment and growth stage was significant. Carbon and organic matter can reduce N mineralization in manure plots, influencing soil nitrate. Qian and Schoenau [21] found that N mineralization decreases significantly with an increase in the C/N ratio in cattle manure.

The interaction between year and growth stage was a significant effect for surface and total soil NO_3-N ($P < 0.05$, Figure 3). Nominally, but not significantly, the Y2 preplant surface and total nitrate-N were 25 and 18% greater than Y1, respectively. In this study, the recommended soybean credit [45] of 44.8 kg·ha^{-1} was neglected in the Y1 nitrogen application rate calculations (Table 1). Nitrogen fixation in the soil likely increased the Y1 preplant soil nitrate levels. The Y2 preplant nitrate-N concentration for the NF, BM, and SM treatments increased approximately 125 kg·N·ha^{-1} from the postharvest levels; the UO treatment showed a similar increase in addition to the urea-N applied in the fall. Mineralization of organic N in the research site area over winter and spring could account for some of the additional nitrate-N. Mineralization of N from soil organic matter and residual nitrogen immobilized from different fertilizer sources after snow melt may have contributed to the increased nitrate level preplant. The wet spring conditions and soil moisture levels may have also promoted upward movement of nitrate from lower soil profiles. Despite the higher Y2 preplant levels for all treatments though, nitrate-N levels decreased faster between preplant and V6. Surface nitrate decreased between preplant and V6 each year and increased between V6 and postharvest. The decrease in Y2 between preplant and V6 was more significant than Y1. The significant effect of growth stage between Y1 and Y2 on soil NO_3-N may be related to the replanting of the crop in Y2 and differences in precipitation during the growing seasons between Y1 and Y2. Wetter conditions during early spring in Y2 may have promoted nitrate loss via erosion and leaching prior to the growing season measurements.

Other soil parameters such as average total N concentration (0.2%), ammonium concentration (22.68 kg·ha^{-1}), and total carbon (2.2%) were not significantly different among treatments for Y2 (Y1 data not available) (Table 4).

3.3. Soil Water Nitrate Concentration. Soil water samples from each plot between corn planting and the V6 stage in both Y1 and Y2 growing seasons were indicators of leachate concentration under the root zone. Treatment was not a significant factor ($P > 0.05$; Table 2). The average soil water NO_3-N concentration was significantly greater in Y1 compared to Y2. This difference may be due in part to soil nitrate and rainfall differences. The total soil NO_3-N was higher at preplanting time but lower at the V6 stage in Y2 compared to Y1 at the same stages (Figure 3). The 148 mm of rainfall in Y1 between planting and V6 stage was greater than the 108 mm of rainfall in Y2 during the same period of corn growth. Allaire-Leung et al. [59] found a positive correlation between nitrate leaching and soil NO_3-N. Nitrate leaching from soil also depends on soil type, N-application rate, types of N sources, cover crops cropping intensity, and crop N uptake [60–62], and these factors influence translation of these research results to other fields and crop systems.

3.4. Crop Response. The average leaf-N concentration significantly differed based on year and growth stage (V6, VT, and R6; $P < 0.05$; Figure 4). The leaf-N concentration at the V6 stage was higher in both years of study and the concentration of N in leaves decreased with corn growth stage. The N uptake from soil peaks between the vegetative and tasseling stages [63, 64]. The mean leaf-N concentration at the V6 stage was not significantly different between Y1 and Y2, whereas at VT and R6 stages, average leaf-N was significantly greater in Y1 compared to Y2 (Figure 4). The variation in leaf-N concentration over the growing stages may relate to differences in soil NO_3-N over the corn growth period. The average leaf-N was 23.9 g·kg^{-1} for the Y1, whereas for Y2, it was 18.8 g·kg^{-1}. The significant variation in leaf-N concentration among two years may be due to rainfall, soil moisture, and soil-available N for late corn planting in the Y2. Leaf-N has also been linked to rainfall during the growing season, and low rainfall can affect nutrient availability [65].

Yield and grain-N concentrations in Y1 did not differ based on treatment, including NF, despite differences in soil N. The BM and UO corn yields greater than 12.0 Mg·ha^{-1}

Table 4: Average supporting surface soil (top 0–0.15 m) test data (± standard error)[z] for the four treatments in Year 1 (Y1) and Year 2 (Y2).

Parameter Year	Growth stage	Treatment Manure with bedding	Manure only	Urea	No fertilizer	Mean	
Soil Olsen test phosphorus (ppm)							
Y1	Preplant	15.3 ± 3.1	20.0 ± 4.0	11.5 ± 2.3	10.7 ± 2.1	13.8 ± 1.6	ab
	V6	18.1 ± 3.6	15.9 ± 3.2	7.8 ± 1.6	7.4 ± 1.5	11.2 ± 1.3	ab
	Postharvest	17.1 ± 3.4	15.1 ± 3	7.2 ± 1.4	7.5 ± 1.5	10.7 ± 1.3	ab
	Mean	16.7 ± 2.7	16.8 ± 2.7	8.6 ± 1.4	8.3 ± 1.3	11.8 ± 1.0	b
Y2	Preplant	38.6 ± 7.7	36.4 ± 7.3	8.9 ± 1.8	11.3 ± 2.3	19.2 ± 2.3	a
	V6	14.5 ± 2.9	10 ± 2	8.8 ± 18	10.1 ± 2	10.5 ± 1.3	b
	Postharvest	18.3 ± 3.7	16.7 ± 3.3	10.4 ± 2.1	13.3 ± 2.7	14.1 ± 1.7	ab
	Mean	21.6 ± 3.5	18.1 ± 2.9	9.3 ± 1.5	11.4 ± 1.8	14.1 ± 1.3	a
Y1Y2	Mean	18.9 ± 2.3 a	17.3 ± 2.1 a	8.9 ± 1.1 b	9.7 ± 1.2 b		
Soil pH							
Y1	Preplant	7.7 ± 0.2	7.7 ± 0.2	7.4 ± 0.2	7.7 ± 0.2	7.6 ± 0.1	b
	V6	7.9 ± 0.2	8 ± 0.2	7.8 ± 0.2	7.9 ± 0.2	7.9 ± 0.1	a
	Postharvest	7.8 ± 0.2	7.8 ± 0.2	7.7 ± 0.2	7.8 ± 0.2	7.8 ± 0.1	ab
	Mean	7.8 ± 0.2	7.8 ± 0.2	7.6 ± 0.2	7.8 ± 0.2	7.8 ± 0.1	a
Y2	Preplant	7.8 ± 0.2	7.8 ± 0.2	7.4 ± 0.2	7.8 ± 0.2	7.7 ± 0.1	ab
	V6	7.7 ± 0.2	7.9 ± 0.2	7.7 ± 0.2	7.8 ± 0.2	7.8 ± 0.1	ab
	Postharvest	7.8 ± 0.2	7.9 ± 0.2	7.9 ± 0.2	7.9 ± 0.2	7.9 ± 0.1	ab
	Mean	7.8 ± 0.2	7.9 ± 0.2	7.7 ± 0.2	7.8 ± 0.2	7.8 ± 0.1	a
Y1Y2	Mean	7.8 ± 0.1	7.9 ± 0.1	7.7 ± 0.1	7.8 ± 0.1		
Total N ($g{\cdot}kg^{-1}$)							
Y2	Preplant	2.5 ± 0.17	2.42 ± 0.17	2.3 ± 0.16	2.19 ± 0.15	2.3 ± 0.1	a
	V6	2.11 ± 0.15	1.66 ± 0.12	1.93 ± 0.13	2.40 ± 0.17	2.0 ± 0.1	b
	Postharvest	2.14 ± 0.17	2.34 ± 0.16	2.35 ± 0.16	2.30 ± 0.16	2.3 ± 0.1	a
	Mean	2.3 ± 0.1	2.1 ± 0.1	2.2 ± 0.1	2.3 ± 0.1		
Ammonium ($kg{\cdot}ha^{-1}$)							
Y2	Preplant	20.7 ± 4.11	18.06 ± 3.58	18.91 ± 3.75	17.65 ± 3.5	18.57 ± 2.25	a
	V6	20.44 ± 4.09	17.49 ± 3.5	28.06 ± 5.62	40.69 ± 8.15	24.98 ± 3.13	a
	Postharvest	21.59 ± 4.27	25.67 ± 5.18	26.87 ± 5.42	26.49 ± 5.35	24.76 ± 3.11	a
	Mean	20.63 ± 2.26	19.83 ± 2.22	23.93 ± 2.68	26.34 ± 2.96		
Soil carbon ($g{\cdot}kg^{-1}$)							
Y2	Preplant	23.4 ± 11.7	22.9 ± 11.4	22.5 ± 11.2	21.8 ± 10.9	22.6 ± 5.7	a
	V6	21.2 ± 10.6	19.7 ± 9.9	20.8 ± 10.4	21.3 ± 10.7	20.7 ± 5.2	a
	Postharvest	22.6 ± 11.3	22.2 ± 11.1	21.8 ± 10.9	21.5 ± 10.8	22.0 ± 5.5	a
	Mean	22.4 ± 6.5	21.5 ± 6.2	21.7 ± 6.3	21.5 ± 6.2		

[z]Mean ± SE = estimated mean ± standard error obtained from least-squared means table; different letters in the overall mean among the treatments indicate the vales are significantly different at $P < 0.05$ within a variable type. The absence of letters indicates $P > 0.05$ between means.

exceeded the yield goal of 11.3 $Mg{\cdot}ha^{-1}$, whereas the SM and NF plots were 96% of the yield goal. Voss et al. [66] and Kovács and Vyn [67] found that ear-leaf-N concentration and corn yield were significantly correlated. The Y1 data showed that yield and leaf-N concentration for each plot at the corn tasseling stage ($N = 16$) were significantly related ($r = 0.70$, and $P < 0.05$). The yield ($r = 0.68$) and grain-N ($r = 0.71$) also correlated with the average Y1 total NO_3-N present in the soil ($N = 16$). The correlation result indicated that yield and grain-N are dependent on available soil N. These correlations suggest lower yield and grain-N concentrations in Y2 compared to Y1 were likely based on lower soil nitrate and leaf-N levels in Y2.

Crop response differences between manure- and urea-N sources were not expected because of the common plant-available N-application rates. However, differences in response between fertilized and NF treatments were expected. Limited replications and lack of Y2 yield data do not allow us to validate the nitrogen application recommendations as they pertain to corn growth.

3.5. Aerial Nitrogen Fluxes

3.5.1. Ammonia Flux. Table 5 shows the average NH_3 fluxes for sampling days after N-application for Y1 and Y2. The measurements showed NH_3 fluxes increased on the first sampling day after N-application in the fall for Y1 and Y2 relative to preapplication, and then decreased over the remainder of the fall sampling days (Table 5). Over the project, the analysis showed a significant effect of treatment on NH_3 flux ($P < 0.05$) but no significant effect of year or treatment by year interaction. The average NH_3 flux from BM (3.4 ± 0.9 $g{\cdot}ha^{-1}{\cdot}h^{-1}$) was only significantly higher than NF (1.4 ± 0.4 $g{\cdot}ha^{-1}{\cdot}h^{-1}$), whereas SM and UO were not significantly different than either BM or NF. In the companion study by Niraula et al. [43] in North Dakota,

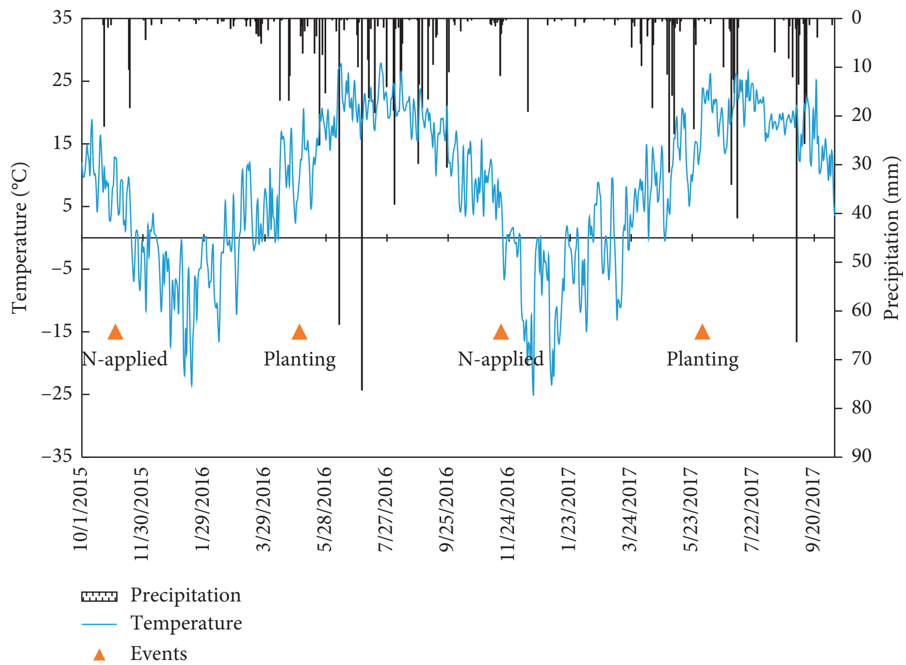

Figure 2: Daily average air temperature, daily precipitation totals, and plot management events during the project period.

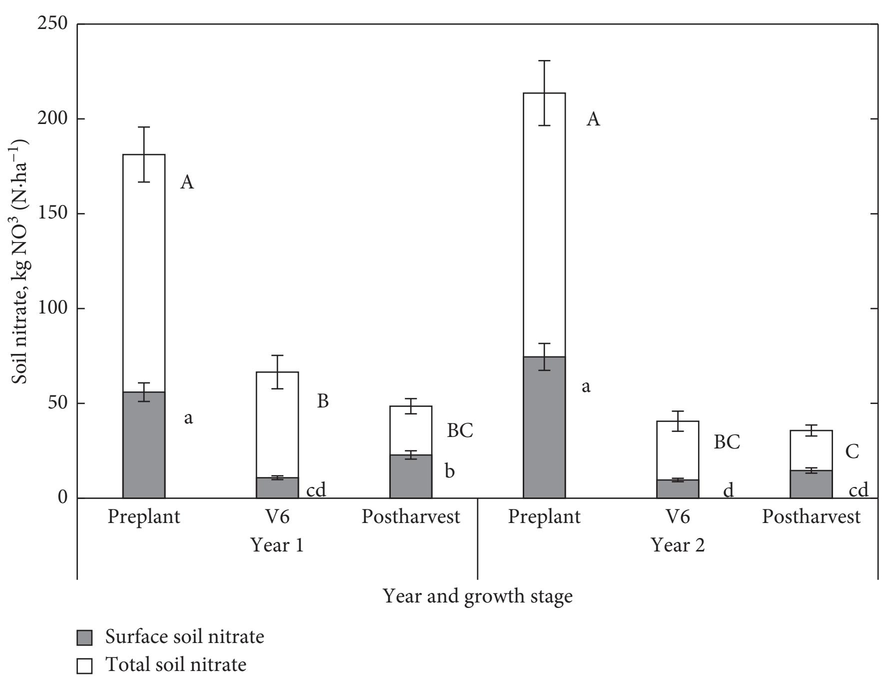

Figure 3: Mean soil nitrate with standard error (vertical lines) for growth stage by year. Significant differences ($P < 0.05$) are indicated by lowercase (surface, 0–0.15 m depth) and uppercase (total, 0–0.60 m depth) letters.

the average NH_3 loss rate from N-applied plots (solid beef manure with and without bedding and urea) was not significantly different, similar with the current study's result. The daily mean NH_3 loss rates measured in North Dakota ranged from 1.8 to 32.0 $g{\cdot}N{\cdot}ha^{-1}{\cdot}h^{-1}$. Adviento-Borbe et al. [31] reported peaks as high as 15 $g{\cdot}N{\cdot}ha^{-1}{\cdot}h^{-1}$ during manure application that decreased within 24 h, with fluxes typically below 1.07 $g{\cdot}ha^{-1}{\cdot}h^{-1}$ from liquid dairy manure and fertilizer N-treated plots under corn-corn and corn-alfalfa rotation. They stated that decreasing NH_3 flux might be due to decreased total ammoniacal nitrogen at the soil surface, infiltration of slurry into the soil profile, and a drop in pH due to NH_3 volatilization. The pattern of NH_3 fluxes in this study was

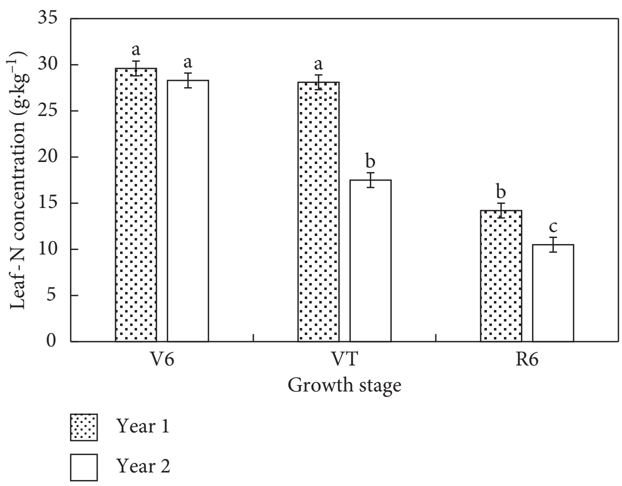

Figure 4: Mean leaf N concentration with standard error (vertical bars) for Y1 and Y2 based on growth stage. (V6, VT, and R6 are a six-leaf stage, tasseling stage, and maturity stage of corn, respectively; different letters above the bars indicate significant differences ($P < 0.05$)).

similar to their observation after N-application. Application timing, methods, N sources, and bedding material also affect reported soil NH_3 flux data compared to this study. Within our study, the higher NH3 fluxes from BM treatment could be due to higher ammonium-N (NH_4^+-N) (Table 1) in the manure with bedding compared to the manure only (SM). Huijsmans et al. [68] observed that soil NH_3 flux increased with an increase TAN in manure.

Lab-scale studies suggest bedding material can influence ammonia volatilization from stored manure with bedding (i.e., bedded pack manure). Ayadi et al. [69] found NH_3 volatilization increased when corn stover bedding is used compared to soybean stubble during warmer weather because of rapid urea and protein hydrolysis and higher moisture content in corn stover. The simulation study by Spiehs et al. [70] showed using corn stover and different woodchip bedding produced a higher NH_3 compared to green and dry cedar chips; the difference was associated with pH levels of the bedding materials. This study did not detect different ammonia losses between the bedded and non-bedded manure once land-applied and using data collected over multiple seasons.

The present study suggests that when manure or urea is applied to silty clay loam soils in late fall at agronomic rates based on plant-available nitrogen and incorporated within 24 hours, ammonia loss can increase slightly compared to no nitrogen application, but the source of nitrogen is not significant.

3.5.2. Nitrous Oxide Flux. The theoretical flux underestimation method as described by Venterea [71] used an average soil bulk density of 1.3 g·cm^{-3}, a clay fraction of 18%, the measured surface soil pH (Table 4), and the soil temperature and moisture content (Table 6).

Table 6 shows the average nitrous oxide fluxes for each sampling day during Y1 and Y2. Treatment significantly affected the overall combined N_2O fluxes. Year and interaction of year with treatment did not show any significant effects on N_2O fluxes. The average (±SE) N_2O flux from UO was 0.78 (±0.25) g N_2O-N·ha^{-1}·h^{-1} and significantly higher than the flux from NF of 0.25 (±0.08) g N_2O-N·ha^{-1}·h^{-1}. The average flux (±SE) from manure treatments BM and SM were 0.49 (±0.15) and 0.33 (±0.10) g N_2O-N·ha^{-1}·h^{-1}, respectively. The N_2O fluxes from manure-treated plots were not significantly different from UO and NF (Table 6).

For the two-year study, the average (±SE) N_2O flux was 0.44 (±0.14) g N_2O-N·ha^{-1}·h^{-1} for the silty clay loam soil plots. Miller et al. [4] compared the long-term land application of stockpiled feedlot beef manure with bedding (barley straw and woodchips) on C/N ratio, denitrification, and carbon dioxide emission in southern Alberta, starting in 1998. They annually applied stockpiled feedlot manure with bedding at the rate of 77 Mg (dry weight) ha^{-1}·yr^{-1} for 13 to 14 years to a clay loam soil. The measurement of denitrification fluxes were taken in 2011 and 2012 (every 2 weeks between May and August). They found mean N_2O fluxes for manure with straw bedding were between 0.04 and 44.92 g N_2O-N·ha^{-1}·h^{-1} (0.9 and 1078 g N_2O-N·ha^{-1}·d^{-1}), from 0.03 to 13.58 g N_2O-N·ha^{-1}·h^{-1} (0.8 to 326 g N_2O-N·ha^{-1}·d^{-1}) for manure with woodchip bedding, and 0.03 and 10.42 g N_2O-N·ha^{-1}·h^{-1} (0.6 to 250 g N_2O-N·ha^{-1}·d^{-1}) for control. However, they observed that total N, daily denitrification flux, and daily carbon dioxide flux were not affected by bedding materials. The maximum mean N_2O flux (0.80 (±0.25) g N_2O-N·ha^{-1}·h^{-1} in this study was very low compared to the maximum fluxes reported by [4]; it might be because of lower rate of solid beef manure application (about half application rate), different bedding materials used (corn stover vs. barley straw and woodchips), gas sampling techniques/methods, and weather conditions. Akiyama and Tsuruta [72] measured N_2O flux for poultry manure (PM), swine manure (SM), and urea applied to soil using an automated flux monitoring system. They found the total fluxes were 0.21, 0.07, and 0.05 g N_2O-N·ha^{-1}·h^{-1} (184, 61.3, and 44.8 Mg N_2O-N·m^{-2}·y^{-1}) from PM, SM, and urea, respectively. This study showed higher N_2O fluxes than the fluxes reported by Akiyama and Tsuruta [72]; this difference likely can be attributed to soil properties (silty clay loam vs. Andisol (volcanic ash soil)), types and rate of N sources, sampling method, and different climatic conditions. In contrast, the N_2O flux obtained for broadcast-incorporated N placement by Engel et al. [73] was similar to N_2O fluxes from urea-treated plots from this study. Engel et al. [73] studied the effect of urea placements (broadcast, band, and nest) on N_2O emission from a silt loam soil. The rate of urea application was 200 kg·N·ha^{-1}. They found maximum N_2O fluxes for the broadcast surface, broadcast incorporated, band, nest, and control were 0.62, 0.55, 1.03, 1.17, and 0.13 g N_2O-N·ha^{-1}·h^{-1} (14.8, 13.2, 24.1, 28.1, and 3.1 g N_2O-N·ha^{-1}·d^{-1}), respectively. In the Red River Valley, North Dakota, Niraula et al. [43] found the N_2O fluxes varied from 0.022 (NF) to 1.91 (UO) g·N·ha^{-1}·h^{-1} (2.2 to 191 μg·N·m^{-2} hr^{-1}). They did not find any significant difference between N-applied plots, which was similar to the current study. However, they observed very high N_2O flux

Table 5: Average ammonia nitrogen fluxes (±standard error)[z] for the four treatments based on time (sampling day) for Year 1 (Y1) and Year 2 (Y2).

Date	Ammonia nitrogen flux ($g \cdot ha^{-1} \cdot hr^{-1}$)				
	Manure with bedding	Manure only	Urea	No fertilizer	Mean
10/30/2015	0.61 ± 0.21	0.59 ± 0.07	0.67 ± 0.07	0.89 ± 0.10	0.69 ± 0.06
11/3/2015	Y1 manure application				
11/6/2015	10.41 ± 0.73	1.84 ± 0.59	2.09 ± 0.28	0.64 ± 0.06	3.74 ± 1.03
11/10/2015	8.74 ± 1.83	1.76 ± 0.21	1.7 ± 0.19	1.23 ± 0.06	3.36 ± 0.9
11/16/2015	5.23 ± 1.32	1.32 ± 0.10	1.83 ± 0.23	1.16 ± 0.13	2.39 ± 0.52
4/26/2016	1.44 ± 0.02	1.36 ± 0.07	1.57 ± 0.18	1.49 ± 0.15	1.46 ± 0.06
5/2/2016	Y1 corn planting				
5/12/2016	1.39 ± 0.04	1.36 ± 0.09	1.26 ± 0.05	1.21 ± 0.05	1.31 ± 0.03
6/1/2016	1.62 ± 0.07	1.46 ± 0.04	1.36 ± 0.09	1.59 ± 0.06	1.51 ± 0.04
Y1	3.87 ± 1.28	1.49 ± 0.49	1.63 ± 0.54	1.17 ± 0.39	1.79 ± 0.47
11/9/2016	3.12 ± 0.56	2.92 ± 0.36	3.22 ± 0.29	3.92 ± 0.77	3.3 ± 0.26
11/16/2016	Y2 manure application				
11/17/2016	14.59 ± 1.57	6.12 ± 0.77	4.74 ± 0.22	5.17 ± 0.5	7.65 ± 1.12
11/22/2016	5.87 ± 1.96	3.58 ± 1.02	9.84 ± 2.76	1.70 ± 0.19	5.25 ± 1.11
12/1/2016	2.98 ± 1.76	0.65 ± 0.05	4.06 ± 2.08	0.64 ± 0.04	2.08 ± 0.72
4/28/2017	1.49 ± 0.31	1.22 ± 0.22	1.14 ± 0.08	1.45 ± 0.14	1.32 ± 0.10
5/6/2017	Y2 corn planting				
5/16/2017	1.69 ± 0.07	1.67 ± 0.14	1.60 ± 0.34	1.57 ± 0.12	1.63 ± 0.09
6/2/2017	Y2 corn replanting				
6/9/2017	1.37 ± 0.03	1.35 ± 0.03	1.40 ± 0.06	1.38 ± 0.07	1.38 ± 0.02
7/14/2017	2.13 ± 0.32	2.14 ± 0.12	1.94 ± 0.22	1.98 ± 0.18	2.05 ± 0.10
Y2	3.11 ± 1.03	1.99 ± 0.66	3.03 ± 1.01	1.79 ± 0.59	2.36 ± 0.63
Y1Y2	3.40 ± 0.89 a	1.69 ± 0.44 ab	2.18 ± 0.57 ab	1.42 ± 0.37 b	

[z]Mean ± SE = estimated mean ± standard error obtained from least squared means table. Different letters in overall mean among the treatments indicate significant difference at $P < 0.05$. The absence of letters indicates $P > 0.05$ between means.

Table 6: Average nitrous oxide nitrogen fluxes (±standard error)[z] for the four treatments based on time (sampling day) for Year 1 (Y1) and Year 2 (Y2).

Date	Soil temp. (°C)	m	Corrected nitrous oxide nitrogen fluxes ($g \cdot ha^{-1} \cdot hr^{-1}$)					
			Manure with bedding	Manure only	Urea	No fertilizer	Mean	
10/30/2015	n/a							
11/3/2015	Y1 manure application							
11/10/2015	8.6 ± 1.1	18.4 ± 3.8	1.23 ± 0.26	0.97 ± 0.17	1.06 ± 0.09	0.77 ± 0.11	1.01 ± 0.09	
11/16/2015	9.1 ± 0.2	22.1 ± 2.4	0.86 ± 0.43	0.26 ± 0.11	0.77 ± 0.11	0.54 ± 0.42	0.61 ± 0.15	
4/24/2016	14.4 ± 1.2	24.4 ± 2.2	5.81 ± 4.68	0.66 ± 0.11	2.69 ± 0.69	1.04 ± 0.27	2.55 ± 1.18	
5/2/2016	Y1 corn planting							
5/9/2016	14.2 ± 0.5	19.7 ± 3.9	1.39 ± 0.80	0.36 ± 0.09	0.43 ± 0.20	0.51 ± 0.29	0.68 ± 0.23	
6/1/2016	17.9 ± 0.8	25.1 ± 2.5	1.10 ± 0.58	0.05 ± 0.03	0.82 ± 0.42	0.46 ± 0.23	0.61 ± 0.20	
7/7/2016	20.2 ± 0.7	30.9 ± 4.2	1.02 ± 0.16	0.97 ± 0.13	1.07 ± 0.19	0.90 ± 0.12	0.99 ± 0.07	
8/2/2016	24.2 ± 1.4	20.8 ± 2.0	−0.03 ± 0.03	0.07 ± 0.07	−0.02 ± 0.05	0.01 ± 0.06	0.01 ± 0.03	
Y1			0.85 ± 0.39	0.34 ± 0.15	0.79 ± 0.37	0.43 ± 0.20	0.54 ± 0.18	a
11/9/2016	7.8 ± 0.2	28 ± 0.4	−0.55	−3.08	−8.73	6.02	−1.59	
11/16/2016	Manure application							
11/17/2016	5.7 ± 0.2	32.5 ± 2.4	0.40 ± 0.17	0.40 ± 0.23	0.1 ± 0.07	0.01 ± 0.03	0.23 ± 0.08	
11/22/2016	1.4 ± 0.4	36.9 ± 3.5	0.46 ± 0.21	0.14 ± 0.06	0.19 ± 0.14	0.09 ± 0.12	0.22 ± 0.08	
12/1/2016	0.8 ± 0.3	42.6 ± 2.2	0.49 ± 0.31	1.11 ± 0.67	0.54 ± 0.28	0.01 ± 0.02	0.54 ± 0.21	
4/25/2017	5.9 ± 0.3	27.8 ± 3.2	0.58 ± 0.25	0.11 ± 0.08	2.84 ± 1.68	0.09 ± 0.11	0.91 ± 0.48	
5/6/2017	Y2 corn planting							
5/16/2017	17 ± 0.8	31.6 ± 4.2	3.35 ± 2.24	1.97 ± 1.33	4.16 ± 0.89	2.89 ± 2.54	3.09 ± 0.86	
6/2/2017	Y2 corn replanting							
6/9/2017	25.5 ± 1.3	19.8 ± 3.9	0.35 ± 0.22	0.35 ± 0.22	1.1 ± 0.62	0.52 ± 0.43	0.58 ± 0.2	
7/10/2017	29.6 ± 1.6	22.6 ± 3.0	0.7 ± 0.35	0.79 ± 0.24	2.96 ± 1.31	0.62 ± 0.38	1.27 ± 0.41	
8/10/2017	20 ± 1.4	38.3 ± 1.5	0.16 ± 0.12	0.12 ± 0.13	0.55 ± 0.3	0.54 ± 0.51	0.34 ± 0.15	
Y2			0.31 ± 0.13	0.36 ± 0.16	0.88 ± 0.39	0.15 ± 0.07	0.34 ± 0.11	a
Y1Y2			0.49 ± 0.15 ab	0.33 ± 0.10 ab	0.79 ± 0.25 a	0.25 ± 0.08 b		

[z]Mean ± SE = estimated mean ± standard error obtained from least squared means table. Different letters in overall mean among the treatments indicate significant difference at $P < 0.05$. The absence of letters indicates $P > 0.05$ between means.

from the urea-treated plot, which was more than 2-fold as compared to our study. This may be due to urea application timing (spring versus fall), soil characteristics, and local weather conditions.

The literature suggests N_2O flux normally varies strongly with the degree of water-filled porosity [74, 75], but this relationship was not apparent in this study. This may be, in part, because the flux correction method [71] reduces the influence of soil moisture on estimated flux rates in treatment comparisons. Nominally, the N_2O fluxes generally decreased between preplant and the growing season which may due to the active crop N uptake and N losses, similar to Niraula et al. [43].

Our study suggested that application of solid beef manure with or without corn stover bedding can reduce the potential N_2O release from the soil, but other parameters such as methane emission or capture, carbon dioxide emission, and nitrate leaching also need consideration when investigating nitrogen fertilizer sources.

4. Conclusion

In this study, manure and urea were applied to plots at equal plant-available N rates using nutrient management planning guide recommended rates. Fall application of beef manure with and without bedding and no fertilizer produced significantly lower soil nitrate levels compared to urea application during a two-year plot-scale study with the silty clay loam soil type in the Northern Great Plains region. No treatment differences in soil water nitrate concentration or corn leaf-N were observed. However, there were differences between years and growth stages for soil nitrate and leaf-N. Numerically, soil N_2O and NH_3 fluxes from applied N sources were UO > SM > BM and BM > UO > SM, respectively. The form of N-applied did not significantly affect fluxes. The UO and BM treatments produced significantly higher N_2O and NH_3 fluxes compared to NF, respectively. Because gas flux rates can vary by soil type, weather, and management practices, these data add to the body of knowledge for future modeling efforts and manure management decisions. Further study is required to refine N-application recommendations appropriate for increasing crop yield while minimizing soil N losses based on weather and soil characteristics.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Additional Points

Highlights. (i) Fall application of manure (with and without bedding) or urea did not result in different ammonia or nitrous oxide fluxes for the silty clay loam soil. (ii) Fall-applied urea produced significantly higher soil nitrate concentrations; however, crop response variables were statistically similar for all N source. (iii) Nitrate concentration in soil water differed between years, but not among N sources.

Disclosure

Any opinions, finding, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the view of the U.S. Department of Agriculture.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References

[1] B. Borghi, "Nitrogen as determinant of wheat growth and yield," in *Wheat: Ecology and Physiology of Yield Determination*, pp. 67–84, Food Products Press, New York, NY, USA, 1999.

[2] D. W. Lawlor, "Carbon and nitrogen assimilation in relation to yield: mechanisms are the key to understanding production systems," *Journal of Experimental Botany*, vol. 53, no. 370, pp. 773–787, 2002.

[3] M. S. Clark, W. R. Horwath, C. Shennan, and K. M. Scow, "Changes in soil chemical properties resulting from organic and low-input farming practices," *Agronomy Journal*, vol. 90, no. 5, pp. 662–671, 1998.

[4] J. J. Miller, B. W. Beasley, C. F. Drury, X. Hao, and F. J. Larney, "Soil properties following long-term application of stockpiled feedlot manure containing straw or wood-chip bedding under barley silage production," *Canadian Journal of Soil Science*, vol. 94, no. 3, pp. 389–402, 2014b.

[5] D. L. Dinnes, D. L. Karlen, D. B. Jaynes et al., "Nitrogen management strategies to reduce nitrate leaching in tile-drained Midwestern soils," *Agronomy Journal*, vol. 94, no. 1, pp. 153–171, 2002.

[6] J. Hatfield and C. Cambardella, "Nutrient management in cropping systems," in *Integrated management of land application of animal waste*, American Society of Agricultural and Biological Engineers, St. Joseph, MI, USA, 2001.

[7] J. A. Lamb, F. G. Fernandez, and D. E. Kaiser, *Understanding Nitrogen in Soils*, University of Minnesota Extension, St Paul, MN, USA, 2014.

[8] T. D. Loecke, M. Liebman, C. A. Cambardella, and T. L. Richard, "Corn response to composting and time of application of solid swine manure," *Agronomy Journal*, vol. 96, no. 1, pp. 214–223, 2004.

[9] J. J. Miller, B. W. Beasley, C. F. Drury, and B. J. Zebarth, "Barley yield and nutrient uptake for soil amended with fresh and composted cattle manure," *Agronomy Journal*, vol. 101, no. 5, pp. 1047–1059, 2009.

[10] S. Paramasivam, K. Jayaraman, T. C. Wilson, A. K. Alva, L. Kelson, and L. B. Jones, "Ammonia volatilization loss from surface applied livestock manure," *Journal of Environmental Science and Health, Part B*, vol. 44, no. 3, pp. 317–324, 2009.

[11] International Fertilizer Industry Association, *Global Estimates of Gaseous Emissions of NH_3, NO and N_2O from Agricultural Land*, Food and Agriculture Organization of the United Nations, Rome, Italy, 2001.

[12] EPA, "Global mitigation of non-CO2 greenhouse gases: 2010-2030," EPA Technical Report-430-R-13-011, 2013, http://www.epa.gov/climatechange/EPAactivities/economics/nonco2projections.html.

[13] EPA, *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2014*, U.S. Environmental Protection Agency, Washington, DC, USA, 2016.

[14] EPA, *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2015*, U.S. Environmental Protection Agency, Washington, DC, USA, 2017.

[15] J. Sintermann, A. Neftel, C. Ammann et al., "Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories?," *Biogeosciences*, vol. 9, no. 5, pp. 1611–1632, 2012.

[16] S. G. Sommer and N. J. Hutchings, "Ammonia emission from field applied manure and its reduction-invited paper," *European Journal of Agronomy*, vol. 15, no. 1, pp. 1–15, 2001.

[17] International Plant Nutrition Institute, *A Global Framework for Fertilizer BMPs*, International Plant Nutrition Institute, Saskatoon, Canada, 2011.

[18] S. Bittman, J. R. Brook, A. Bleeker, and T. W. Bruulsema, "Air quality, health effects and management of ammonia emissions from fertilizers," in *Air Quality Management: Canadian Perspectives on a Global Issue*, E. Taylor and A. McMillan, Eds., pp. 261–277, Springer Netherlands, Dordrecht, Netherlands, 2014.

[19] W. Hodan and W. R. Barnard, *Evaluating the Contribution of PM2. 5 Precursor Gases and Re-entrained Road Emissions to Mobile Source PM2. 5 Particulate Matter Emissions*, MACTEC Federal Programs, Research Triangle Park, NC, USA, 2004.

[20] R. T. Conant, D. Kluck, M. T. Anderson et al., "Northern great plains," in *Proceedings of the Fourth National Climate Assessment, US Global Change Research Program*, pp. 941–986, November 2018.

[21] P. Qian and J. J. Schoenau, "Availability of nitrogen in solid manure amendments with different C:N ratios," *Canadian Journal of Soil Science*, vol. 82, no. 2, pp. 219–225, 2002.

[22] R. Awale and A. Chatterjee, "Enhanced efficiency nitrogen products influence ammonia volatilization and nitrous oxide emission from two contrasting soils," *Agronomy Journal*, vol. 109, no. 1, pp. 47–57, 2017.

[23] S. Niraula, S. Rahman, and A. Chatterjee, "Temperature response of ammonia and greenhouse gas emission from manure amended silty clay soil," *Acta Agriculturae Scandinavica, Section B-Soil & Plant Science*, vol. 68, no. 8, pp. 663–677, 2018.

[24] P. Rochette, D. A. Angers, M. H. Chantigny, B. Gagnon, and N. Bertrand, "N2O fluxes in soils of contrasting textures fertilized with liquid and solid dairy cattle manures," *Canadian Journal of Soil Science*, vol. 88, no. 2, pp. 175–187, 2008.

[25] R. Thapa, A. Chatterjee, J. M. F. Johnson, and R. Awale, "Stabilized nitrogen fertilizers and application rate influence nitrogen losses under rainfed spring wheat," *Agronomy Journal*, vol. 107, no. 5, pp. 1885–1894, 2015.

[26] H. G. Adegbidi, R. D. Briggs, T. A. Volk, E. H. White, and L. P. Abrahamson, "Effect of organic amendments and slow-release nitrogen fertilizer on willow biomass production and soil chemical characteristics," *Biomass and Bioenergy*, vol. 25, no. 4, pp. 389–398, 2003.

[27] A. A. Ahmad, A. Fares, F. Abbas, and J. L. Deenik, "Nutrient concentrations within and below root zones from applied chicken manure in selected Hawaiian soils," *Journal of Environmental Science and Health, Part B*, vol. 44, no. 8, pp. 828–843, 2009.

[28] J. J. Miller, B. W. Beasley, C. F. Drury, and B. J. Zebarth, "Available nitrogen and phosphorus in soil amended with fresh or composted cattle manure containing straw or wood-chip bedding," *Canadian Journal of Soil Science*, vol. 90, no. 2, pp. 341–354, 2010.

[29] S. I. Ahmed, S. K. Mickelson, C. H. Pederson et al., "Swine manure rate, timing, and application method effects on post-harvest soil nutrients, crop yield, and potential water quality implications in a corn-soybean rotation," *Transactions of the ASABE*, vol. 56, no. 2, pp. 395–408, 2013.

[30] M. E. Amiri and E. Fallahi, "impact of animal manure on soil chemistry, mineral nutrients, yield, and fruit quality in 'golden delicious' apple," *Journal of Plant Nutrition*, vol. 32, no. 4, pp. 610–617, 2009.

[31] M. A. A. Adviento-Borbe, J. P. Kaye, M. A. Bruns, M. D. McDaniel, M. McCoy, and S. Harkcom, "Soil greenhouse gas and ammonia emissions in long-term maize-based cropping systems," *Soil Science Society of America Journal*, vol. 74, no. 5, pp. 1623–1634, 2010.

[32] G. Hernandez-Ramirez, S. M. Brouder, D. R. Smith, and G. E. Van Scoyoc, "Greenhouse gas fluxes in an eastern corn belt soil: weather, nitrogen source, and rotation," *Journal of Environment Quality*, vol. 38, no. 3, pp. 841–854, 2009.

[33] A. P. Mallarino and D. J. Wittry, "Crop yield and soil phosphorus as affected by liquid swine manure phosphorus application using variable-rate technology," *Soil Science Society of America Journal*, vol. 74, no. 6, pp. 2230–2238, 2010.

[34] E. C. C. Miola, P. Rochette, M. H. Chantigny et al., "Ammonia volatilization after surface application of laying-hen and broiler-chicken manures," *Journal of Environment Quality*, vol. 43, no. 6, pp. 1864–1872, 2014.

[35] R. Bey, J. K. Reneau, and R. J. Farnsworth, "The role of bedding management in udder health," *Annual Meeting-National Mastitis Council Incorporated*, vol. 41, pp. 45–55, 2002.

[36] K. L. Smith and J. Hogan, "Bedding counts in manure solids," in *Proceedings of the National Mastitis Council Annual Meeting*, Ecolab, Inc., St. Paul, MN, USA, January-February 2006.

[37] B. Doran, R. Euken, and M. Spiehs, "Hoops and mono-slopes: what we have learned about management and performance," in *Feedlot Forum*, Iowa State University Extension, Ames, IA, USA, 2010.

[38] R. B. Ferguson, J. A. Nienaber, R. A. Eigenberg, and B. L. Woodbury, "Long-term effects of sustained beef feedlot manure application on soil nutrients, corn silage yield, and nutrient uptake," *Journal of Environment Quality*, vol. 34, no. 5, pp. 1672–1681, 2005.

[39] J. J. Miller, B. W. Beasley, C. F. Drury, F. J. Larney, and X. Hao, "Nitrogen budgets following land application of composted or stockpiled feedlot manure containing wood-chips or straw bedding to barley silage for 12 years," *Compost Science & Utilization*, vol. 22, no. 2, pp. 57–67, 2014a.

[40] D. Crohn, "Nitrogen mineralization and its importance in organic waste recycling," in *Proceedings, National Alfalfa Symposium*, San Diego, CA, USA, December 2004.

[41] A. Lewandowski, *Manure Management (BU-7401)*, University of Minnesota, St. Paul, MN, USA, 2000, https://conservancy.umn.edu/bitstream/handle/11299/51796/BU-7401-S.pdf;jsessionid=50981D32932A9267B35639BA4DD2370F?sequence=1.

[42] D. L. Beck, D. E. Clay, and K. D. Reitsma, "Tillage, crop rotations and cover crops," in *Best Management Practices for Corn Production in South Dakota, 21-30*, D. Clay, K. Reitsma, and S. Clay, Eds., South Dakota State University, Brookings, SD, USA, 2009.

[43] S. Niraula, S. Rahman, A. Chatterjee, E. L. Cortus, M. Mehata, and M. J. Spiehs, "Beef manure and urea applied to corn show variable effects on nitrous oxide, methane, carbon dioxide, and ammonia," *Agronomy Journal*, vol. 111, no. 3, pp. 1448–1467, 2019.

[44] W. T. Schaefer, *Soil Survey of Brookings County, South Dakota*, 2005.

[45] SDSU, "South Dakota fertilizer recommendations guide EC-750," in *SDSU Extension Circulars*, vol. 28, South Dakota State University, Brookings, SD, USA, 2005.

[46] J. Peters, S. M. Combs, B. Hoskins et al., *Recommended Methods of Manure Analysis. Publication A3769*, University of Wisconsin-Extension, Madison, WI, USA, 2003.

[47] NCERA-13, *Recommended chemical soil test procedures for the North Central Region. Missouri Agricultural Experiment Station: I. Agricultural Experiment Stations of Illinois, Iowa, and M. Kansas, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota and Wisconsin*, Missouri Agricultural Experiment Station, Columbia, MO, USA, 2015.

[48] K. Knepel, *Determination of Nitrate in 2M KCl Soil Extracts by Flow Injection Analysis. QuikChem Method 12-107-04-1-B*, Lachat Instruments, Loveland, CO, USA, 2003.

[49] J. R. Brown, *Recommended Chemical Soil Test Procedures for the North Central Region. No. 1001. Missouri Agricultural Experiment Station*, University of Missouri, Columbia, MS, USA, 1998.

[50] S. Hofer, *Determination of Ammonia (Salicylate) in 2M KCl Soil Extracts by Flow Injection Analysis. QuikChem Method 12-107-06-2-A*, Lachat Instruments, Loveland, CO, USA, 2003.

[51] W. McGill and C. Figueiredo, "Total nitrogen," in *Soil Sampling and Methods of Analysis*, pp. 201–211, CRC Press, Boca Raton, FL, USA, 1993.

[52] D. V. Guebel, B. C. Nudel, and A. M. Giulietti, "A simple and rapid micro-Kjeldahl method for total nitrogen analysis," *Biotechnology Techniques*, vol. 5, no. 6, pp. 427–430, 1991.

[53] C. P. Jantalia, A. D. Halvorson, R. F. Follett, B. J. Rodrigues Alves, J. C. Polidoro, and S. Urquiaga, "Nitrogen source effects on ammonia volatilization as measured with semi-static chambers," *Agronomy Journal*, vol. 104, no. 6, pp. 1595–1603, 2012.

[54] T. B. Parkin and R. T. Venterea, "USDA-ARS GRACEnet project protocols," in *Chapter 3. Chamber-Based Trace Gas Flux Measurements*, pp. 1–39, Sampling Protocols, Beltsville, MD, USA, 2010.

[55] R. T. Venterea, "Theoretical comparison of advanced methods for calculating nitrous oxide fluxes using non-steady state chambers," *Soil Science Society of America Journal*, vol. 77, no. 3, pp. 709–720, 2013.

[56] SAS Institute, *Base SAS® 9.3 Procedures Guide: Statistical Procedures*, SAS Institute Inc., Cary, NC, USA, 2011.

[57] M. Mehata, "*Measuring the influence of bedding on soil nitrogen losss and corn crop nitrogen characteristics for fall applied solid beef cattle manure in Eastern South Dakota*," M.S. thesis, South Dakota State University, Brookings, SD, USA, 2018.

[58] M. Mehata, E. Cortus, and J. Darrington, *Comparing the Soil Nitrogen Losses for Fall Applied Manure and Inorganic Fertilizer in the Northern Great Plains. ASABE Paper 1701037*, ASABE, St. Joseph, MI, USA, 2017.

[59] S. E. Allaire-Leung, L. Wu, J. P. Mitchell, and B. L. Sanden, "Nitrate leaching and soil nitrate content as affected by irrigation uniformity in a carrot field," *Agricultural Water Management*, vol. 48, no. 1, pp. 37–50, 2001.

[60] P. G. Aronsson and L. F. Bergström, "Nitrate leaching from lysimeter-grown short-rotation willow coppice in relation to N-application, irrigation and soil type," *Biomass and Bioenergy*, vol. 21, no. 3, pp. 155–164, 2001.

[61] J. L. Havlin, J. D. Beaton, W. L. Nelson, and S. L. Tisdale, *Soil Fertility and Fertilizers: An Introduction to Nutrient Management*, Pearson Prentice Hall, Upper Saddle River, NJ, 2005.

[62] L. Wyland, L. E. Jackson, W. E. Chaney, K. Klonsky, S. T. Koike, and B. Kimple, "Winter cover crops in a vegetable cropping system: impacts on nitrate leaching, soil water, crop yield, pests and management costs," *Agriculture, Ecosystems & Environment*, vol. 59, no. 1-2, pp. 1–17, 1996.

[63] R. R. Bender, J. W. Haegele, M. L. Ruffo, and F. E. Below, "Modern corn hybrids' nutrient uptake patterns," *Better Crops*, vol. 97, no. 1, pp. 7–10, 2013.

[64] P. Scharf, J. Lory, and J. Grundler, *Best Management Practices for Nitrogen Fertilizer in Missouri, IPM1027*, University of Missouri-Columbia: M. Extension, Columbia, MO, USA, 2006.

[65] M. Asghari and R. G. Hanson, "Climate, management, and N effect on corn leaf N, yield, and grain N1," *Agronomy Journal*, vol. 76, no. 6, pp. 911–916, 1984.

[66] R. E. Voss, J. J. Hanway, and L. C. Dumenil, "Relationship Between Grain Yield and Leaf N, P, and K Concentrations for Corn (Zea mays L.) and the Factors that Influence this Relationship1," *Agronomy Journal*, vol. 62, no. 6, pp. 726–728, 1970.

[67] P. Kovács and T. J. Vyn, "Relationships between ear-leaf nutrient concentrations at silking and corn biomass and grain yields at maturity," *Agronomy Journal*, vol. 109, no. 6, pp. 2898–2906, 2017.

[68] J. Huijsmans, J. Hol, and G. Vermeulen, "Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land," *Atmospheric Environment*, vol. 37, no. 26, pp. 3669–3680, 2003.

[69] F. Y. Ayadi, E. L. Cortus, M. J. Spiehs, D. N. Miller, and G. D. Djira, "Ammonia and greenhouse gas concentrations at surfaces of simulated beef cattle bedded manure packs," *Transactions of the ASABE*, vol. 58, no. 3, pp. 783–795, 2015.

[70] M. J. Spiehs, T. M. Brown-Brandl, D. B. Parker et al., "Use of wood-based materials in beef bedded manure packs: 1. Effect on ammonia, total reduced sulfide, and greenhouse gas concentrations," *Journal of Environment Quality*, vol. 43, no. 4, pp. 1187–1194, 2014.

[71] R. T. Venterea, "Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes," *Journal of Environment Quality*, vol. 39, no. 1, pp. 126–135, 2010.

[72] H. Akiyama and H. Tsuruta, "Nitrous oxide, nitric oxide, and nitrogen dioxide fluxes from soils after manure and urea application," *Journal of Environment Quality*, vol. 32, no. 2, pp. 423–431, 2003.

[73] R. Engel, D. L. Liang, R. Wallander, and A. Bembenek, "Influence of urea fertilizer placement on nitrous oxide production from a silt loam soil," *Journal of Environment Quality*, vol. 39, no. 1, pp. 115–125, 2010.

[74] C. A. M. De Klein and R. S. P. Van Logtestijn, "Denitrification in grassland soils in The Netherlands in relation to irrigation, N-application rate, soil water content and soil temperature," *Soil Biology and Biochemistry*, vol. 28, no. 2, pp. 231–237, 1996.

[75] C. Li, S. Frolking, and T. A. Frolking, "A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity," *Journal of Geophysical Research: Atmospheres*, vol. 97, no. D9, pp. 9759–9776, 1992.

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Research Article

Nitrogen Uptake Efficiency and Total Soil Nitrogen Accumulation in Long-Term Beef Manure and Inorganic Fertilizer Application

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Livestock manure is a common soil amendment for crop-livestock production systems. However, the efficiency of crop nitrogen (N) uptake from the manure-amended soil may not equate with that from inorganic N sources. The objective of this paper was to determine the efficiency of N uptake, grain yield, and total soil nitrogen (TSN) accumulation in beef manure-amended soil compared to the inorganic N fertilizer-amended soil. Data (1990–2015) from a long-term continuous winter wheat (*Triticum aestivum* L.) fertility experiment at Stillwater in Oklahoma, USA, were used in this report. Three of the six "Magruder Plot" treatments used in this study were manure, NPK plus lime (NPKL), and a check (no nutrients applied). Pre-plant N, P, and K were applied annually at 67, 14.6, and 27.8 $kg{\cdot}ha^{-1}$, respectively, while beef manure was applied every 4 years at 269 $kg\,N{\cdot}ha^{-1}$. The results indicated that grain N uptake in the manure treatment (48.1 $kg{\cdot}ha^{-1}$) was significantly ($p < 0.05$) lower than that in the NPKL treatment (60.2 $kg{\cdot}ha^{-1}$). This represents 20.1% efficiency of inorganic N uptake than the manure N uptake. The average grain yield (1990–2015) from the manure and NPKL treatments was 2265.7 and 2510.5 $kg{\cdot}ha^{-1}$, respectively, and was not significantly different. There was a trend of TSN increase over the study period for both manure and NPKL treatments. The average TSN from manure and NPKL treatments was 0.92 and 0.91 $g{\cdot}kg^{-1}$ soil, respectively, and was not significantly different. While no significant difference between manure and NPKL grain yield was observed, there was a significantly lower uptake efficiency of manure N compared to inorganic N. Furthermore, the low uptake efficiency of the manure N could suggest a potential for environmental pollution. Appropriate timing and application rate of manure N sources could optimize crop use efficiency and limit potential threat to the environment.

1. Introduction

Nitrogen (N) is an important plant nutrient and commonly the most deficient in many intensive cereal monocropping systems. Additions from both synthetic and animal manures help supplement the native N pool from organic matter mineralization and/or rainfall supply [1, 2]. However, applications in excess of plant requirements from both sources have been blamed for aboveground environmental pollution [3, 4]. Environmental pollution from synthetic N sources has been extensively investigated, and attempts have been made to compare it with that coming from manure. By virtue of its popular use especially under large-scale crop production, synthetic N sources are believed to cause the greatest threat to the environment. Inorganic sources are readily available and can be taken up by plants and/or lost within the soil system [5]. Manure N, on the contrary, has N mostly bound within organic fractions that require some kind of degradation so as to release available plant N [6, 7]. Accordingly, synthetic N could potentially cause more of an environmental threat relative to manure N. Some studies however note that animal manure N may comparatively lead to more environmental pollution depending on the source, rate, and timing of application [3, 8]. For instance, Chang and Entz [9] reported soil and groundwater contamination with increased leaching of NO_3-N in applied beef manure where annual losses of nitrogen ranged from 93 to 341 kg N·ha^{-1}. Losses were higher under irrigated treatments and when application exceeded annual recommended rates of 60 Mg·ha^{-1} wet weight. Therefore, the efficiency of plant N uptake and potential TSN accumulation strongly depend on the rate and frequency of application.

Total soil N is one of the indicators of soil fertility in an agricultural ecosystem [10]. Earlier studies indicate that TSN in the surface layers of most cultivated soils varies between 0.6 g·kg^{-1} and 5 g·kg^{-1} although it could reach up to 25 g·kg^{-1} in peat [11]. Xu et al. [12] noted that this figure fluctuates depending on the land use and management system. Indisputably, agriculture takes a greater portion of the liability for the fluctuation. Several research reports present contrasting views on whether agriculture, particularly crop production, leads to a buildup or depletion of soil organic N [10, 12, 13]. Generally, it appears that continuous crop production without replenishing soil nutrients would certainly deplete soil resources [14]. On the contrary, intensive or high input production systems may lead to buildup of certain soil nutrients. Much as continuous crop production can cause significant loss in the quantity of soil organic matter and total N [15], certain crop production practices may lead to buildup of carbon and N within the soil system. For instance, Aula et al. [13] demonstrated from long-term trials that application of inorganic N fertilizer at rates above 90 kg·ha^{-1} can increase and lead to buildup of TSN. The excess N in the soil system may pose an environmental threat if certain weather variables favor its loss. From an environmental perspective, total soil N, in addition to total soil phosphorus, is the cause of nonpoint source pollution for surface and groundwater [12]. This is true especially when inorganic N constitutes a higher proportion of the total soil N. Leaching and surface runoff through erosion of N applied in excess of plant needs are the main mechanisms for environmental pollution.

Some research reports that continuous application of N fertilizer can increase the likelihood of TSN accumulation with time [16]. However, N from fertilizers in excess of plant requirements is not the only factor in the equation. Biological processes such as symbiotic and nonsymbiotic N_2 fixation in addition to atmospheric N in rainfall contribute a substantial amount of TSN [17, 18]. These biological or natural processes, which significantly influence soil N availability and subsequently crop yield, are independent of N fertilizer application rates and largely controlled by the environment [19]. In addition to atmospheric N_2 fixation, microorganisms contribute to the availability of mineral N under favorable soil temperature, moisture, and aeration. Free-living decomposer microbes convert organic matter into nutrients for plants and other microorganisms, while rhizosphere organisms are symbiotically associated with plant roots and free-living N fixers [20]. These microorganisms are capable of extracting N from organic matter and other soil substances and subsequently releasing available plant N to the soil pool. Knops and Tilman [15] studied N and carbon dynamics in an abandoned field and reported that the rate of N accumulation depended on atmospheric deposition and symbiotic fixation by legumes. Jurgensen [21] reported that N fixation by autotrophic microorganisms can reach 70 kg·ha^{-1}·yr^{-1}. Therefore, N from the soil pool is subject to either plant uptake or various loss pathways. If N supply from fertilizer, symbiotic or nonsymbiotic fixation, and/or straw mineralization exceeds plant requirements, significant quantities can be either lost or immobilized. Immobilization, which is a biological process, is in turn dictated by environmental conditions. This is the reason for TSN accumulation under continuous fertilizer N application.

2. Materials and Methods

The Magruder Plots located at Stillwater in Oklahoma, USA, is a long-term continuous winter wheat (*Triticum aestivum* L.) fertility experiment situated on a Kirkland silt loam (fine, mixed, thermic Udertic Paleustolls). The experiment was started by Alexander C. Magruder and included a manure treatment that was started in 1892, while inorganic fertilizer treatments were initiated in 1929 [22]. The six treatments included in this long-term experiment are manure, P, NP, NPK, NPK plus lime (NPKL), and an unfertilized check plot, where no nutrients have been applied. However, only three treatments (manure, NPKL, and check) were used for this report. Plot sizes are 30 m by 5 m. Inorganic chemical fertilizer treatments were applied every year prior to planting. Nitrogen was applied as urea (46-0-0) at a rate of 67 kg N·ha^{-1}, P was applied at 14.6 kg P·ha^{-1}, and K was applied at 27.8 kg K·ha^{-1}, while beef manure was applied every 4 years at 269 kg N·ha^{-1} (Table 1). Therefore, similar quantities of N (269 kg) were provided both in the manure-treated and inorganic N-treated plots during a four-year period in which manure was applied once. Lime was applied when soil pH dropped below 5.5.

It is important to note that, at the time of establishment of this long-term experiment, modern statistics did not exist. Consequently, replications were not included in the experimental design. However, a long-term study of this nature can be used as a basis for understanding the effect of manure application and general agronomic management including yield potentials as well as losses of crop nutrient elements. For this work, only data from 1990 to 2015 were used due to availability of data on total soil N. Wheat grain was harvested with a Massey Ferguson 8XP combine and yield data recorded for each year reported in this study. Wheat subsamples were taken and oven-dried at 105°C for 24 hours. These samples were then ground to pass a 1 mm mesh size. Total elemental grain N for each sample, expressed as a percent, was determined using dry combustion analysis (LECO TruSpec) [23]. Each year, post-harvest soil samples were also taken, oven-dried, and ground for TSN analysis. Grain N uptake was determined by multiplying yield times grain N content and expressed in kg·ha^{-1} (Table 2). Analysis of variance was performed using the GLM procedure in SAS 9.4 [24], and means were separated using Tukey's HSD. Due to lack of replications, the study period (years) was used to estimate experimental error during analysis of variance. Comparisons were made between average grain yield, N uptake, and TSN for the

Table 1: Treatment structure, composition, and description for Magruder Plots located at Stillwater in Oklahoma, USA.

Treatment	Composition	Description	Input sources	Form and quantity applied
1	Manure	Cattle manure applied every 4 years	Cattle manure	Cattle manure 269 kg N·ha^{-1}
2	—	Check, no nutrient applied	—	—
3	P	P applied each year	TSP	P_2O_5 (0-34-0)
4	NP	N and P applied each year	Urea, TSP	N, P_2O_5 (67-34-0)
5	NPK	N, P, and K applied each year	Urea, TSP, KCl	N, P_2O_5, K_2O (67-34-34)
6	NPKL	N, P, and K applied each year + lime applied when soil pH < 5.5	Urea, TSP, KCl + Aglime	N, P_2O_5, K_2O + lime (67-34-34)

Table 2: Wheat grain yield (kg·ha^{-1}), grain N content (%), N uptake (kg·ha^{-1}), and total soil N (g·kg^{-1} soil) of Magruder Plots (1990–2015) located at Stillwater in Oklahoma, USA.

Year	Grain yield (kg·ha^{-1})			Grain N (%)			N uptake (kg·ha^{-1})			Total soil N (g·kg^{-1} soil)		
	Manure	Check	NPKL	Manure	Check	NPKL	Manure	Check	NPKL	Manure	NPKL	Check
1990	2325.1	1451.5	2184.0	2.04	2.00	2.28	47.4	29.0	49.8	0.70	0.76	0.59
1991	1753.9	1115.5	2963.5	2.33	2.04	2.44	40.8	22.8	72.2	0.70	0.76	0.59
1992	1429.2	903.2	1973.7	2.17	1.96	2.35	31.0	17.7	46.4	0.74	0.77	0.60
1993	2499.5	1259.6	2754.3	2.22	1.91	2.26	55.5	24.1	62.2	0.74	0.77	0.60
1994	1510.1	628.4	1865.4	2.23	2.34	2.39	33.6	14.7	44.7	0.95	0.99	0.62
1996	1669.2	967.7	1884.3	2.28	2.18	2.28	38.1	21.1	43.0	1.07	0.93	0.69
1997	3454.1	1397.8	4186.6	2.28	2.18	2.28	78.8	30.5	95.5	1.17	1.07	0.69
1998	2071.8	974.4	2591.9	2.31	2.03	2.43	47.9	19.8	63.0	—	—	—
1999	2744.6	1767.5	2527.9	2.31	2.50	2.32	63.3	44.2	58.7	—	—	—
2000	2473.4	1511.6	2377.7	2.25	1.80	2.12	55.7	27.3	50.3	—	—	—
2001	2563.0	795.1	2663.8	2.32	2.24	2.30	59.5	17.8	61.1	0.59	0.68	0.52
2002	2369.4	1212.0	2790.4	1.96	1.85	2.52	46.4	22.4	70.3	0.68	0.68	0.49
2005	2956.8	1209.6	2956.8	2.43	1.96	3.02	72.0	23.7	89.2	—	—	—
2006	2225.1	1414.8	3112.7	2.14	2.02	2.65	47.6	28.5	82.4	1.09	0.98	0.74
2008	3473.6	1823.5	3281.4	1.74	1.91	2.21	60.5	34.9	72.5	—	—	—
2009	166.7	330.0	357.5	2.12	1.92	2.08	3.5	6.3	7.4	1.05	0.95	0.79
2010	2313.4	1244.4	2669.3	2.51	2.60	2.81	58.1	32.3	75.1	1.05	0.95	0.79
2011	1286.8	431.9	1675.5	2.25	2.17	2.83	29.0	9.4	47.4	0.84	0.76	0.72
2012	2655.7	1022.8	3007.9	1.94	1.79	1.96	51.6	18.3	58.9	0.81	0.77	0.53
2013	2860.0	1029.5	3571.7	1.58	1.69	1.60	45.1	17.4	57.3	0.96	1.01	0.63
2014	2243.5	1161.6	2365.9	1.69	1.78	1.85	38.0	20.6	43.8	1.46	1.65	1.23
2015	3117.4	1816.1	4048.2	1.77	1.73	1.80	55.2	31.3	72.9	1.04	1.04	0.81

NPKL = nitrogen, phosphorus, potassium, and lime; check = no fertilizer applied; manure = beef manure applied every four years.

manure-treated plots and the inorganic N-treated plots. Correlation analysis was performed to determine the degree of linear relationship between TSN content in the manure and NPKL treatments (Table 3).

3. Results and Discussion

The results indicate that wheat grain yield was higher in the NPKL plot but not significantly different from that in the manure plot. Over the period reported in this study, the average grain yields recorded were 2510 and 2265 kg·ha^{-1} in NPKL and manure treatments, respectively (Table 3).

As was expected, grain yields from both treatments were significantly higher than those obtained in the control plot recorded at 1165 kg·ha^{-1}. Lentz and Lehrsch [25] made similar observations where the contribution of manure to sugarbeet yield was either equal to or more than that of mineral N fertilizer depending on the application rate and timing. According to Eghball and Power [26], the observation that manure can produce grain yields equal to or greater than those of synthetic fertilizer application is true when the application rate is based on the correct N or P requirement. The manure application rate used in this study was based on the N requirement that was purposely matched with the N rate from the inorganic source (NPKL). Abdulmaliq et al. [27] recommended curing livestock manure for up to 6 weeks in order to obtain corresponding yield levels or even more than those of chemical fertilizer N application. This work shows that the manure soil amendment can sustainably support an intensive cereal-based cropping system when compared to inorganic sources. If the impact of manure and mineral N on crop yield is identical, it is possible to imagine that any environmental concerns associated with mineral N application could equally be experienced through manure soil amendment. Accordingly, the potential for environmental contamination needs to be assessed alongside increasing biomass or grain yield as the usefulness of manure application in crop production is considered. Therefore, the quality can be assessed by determining efficiency of N uptake and TSN accumulation over time.

Table 3: Analysis of variance for wheat grain yield, grain N uptake, and TSN including summary of relationships between these variables in manure, check, and NPKL treatments (1990–2015) of Magruder Plots located at Stillwater in Oklahoma, USA.

Treatment	Grain yield ($kg{\cdot}ha^{-1}$)		Grain N uptake ($kg{\cdot}ha^{-1}$)		TSN ($g{\cdot}kg^{-1}$ soil)	
Treatment means						
Manure ($n = 22$)	2265.7^{A}		48.11^{B}		0.920^{A}	
Check ($n = 22$)	1165.6^{B}		22.82^{C}		0.684^{B}	
NPKL ($n = 22$)	2510.5^{A}		60.19^{A}		0.913^{A}	
Correlation coefficient						
	$P > F$	R	$P > F$	R	$P > F$	R
Manure vs NPKL	<0.0001	0.89	<0.0001	0.84	<0.0001	0.93
Manure vs check	<0.0001	0.79	<0.0001	0.73	<0.0001	0.87
NPKL vs check	<0.001	0.67	<0.01	0.58	<0.0001	0.92

NPKL = nitrogen, phosphorus, potassium, and lime-treated plot; check = no fertilizer applied; manure = beef manure applied every four years; TSN = total soil nitrogen; treatment means within the same column with the same letter superscript are not significantly different (Tukey's HSD test).

There was a significant difference in grain N uptake among treatments. Grain N uptake varied from 3.5 to 78 $kg{\cdot}ha^{-1}$ in the manure treatment and 7.4 to 95 $kg{\cdot}ha^{-1}$ in the NPKL treatment (Table 2). The average grain N uptake of 60.2 $kg{\cdot}ha^{-1}$ in the NPKL treatment was significantly higher ($p < 0.05$) than that of 48.1 $kg{\cdot}ha^{-1}$ in the manure treatment. Grain N uptake in both the NPKL and manure treatments was significantly higher ($p < 0.05$) than that in the control treatment recorded at 22.8 $kg{\cdot}ha^{-1}$ (Table 3). The pattern of change in average grain N uptake over the study period for the two inputs was similar, as illustrated in Figure 1.

The high inconsistency in grain N uptake could be attributed to changes in the environmental variables especially rainfall and temperature over the study period. In some years, grain N uptake exceeded the amount of N in manure or inorganic fertilizer applied. For instance, in 1997, grain N uptake was 78 and 95 $kg{\cdot}ha^{-1}$ in the manure and NPKL treatments, respectively (Table 2). These values were higher than 67 $kg\,N{\cdot}ha^{-1}$ applied in the fertilizer. The same observation was made in 2005 where grain N uptake was 72 and 89 $kg{\cdot}ha^{-1}$ in the manure and NPKL treatments, respectively. This phenomenon is not unusual and can be explained by the random abiotic and/or biological events that favor the availability of N from sources other than fertilizer. The additional grain N comes from rainfall, symbiotic and non-symbiotic fixation of atmospheric N_2, and mineralization of soil organic matter. In an analysis that included data from 213 site-years, Dhital and Raun [19] reported that maize grain yield and the optimum fertilizer N rate varied from year to year. This suggested that the influence of the environment was reflected in resultant N uptake from soil amendment sources. In the current study, no significant grain yield differences were observed between the manure and NPKL treatments. Likewise, grain N uptake was expected to follow the same trend. Nonetheless, this was not observed. Increased grain yield in the manure treatment that was statistically equivalent with grain yield in the NPKL treatment could be due to increased NH_4-N supply that is known to be more efficient [28]. Improved soil physical and/or biological properties in the manure treatment could also explain the matching yield levels with the NPKL treatment. Shirani et al. [29] attributed the increased biomass yield with manure amendments to improved soil physical properties. Similarly, Haynes and Naidu [30] noted that crop grain yield increases due to manure were likely a result of increased water-holding capacity, porosity, infiltration capacity, and hydraulic conductivity. Therefore, it is possible to have an identical wheat grain yield under manure and inorganic N treatments despite the low N uptake efficiency in the manure treatment.

At a constant N application rate of 67 $kg{\cdot}ha^{-1}$ for both manure and NPKL treatments, TSN content in these treatments recorded at 0.92 and 0.91 $g{\cdot}kg^{-1}$ of soil, respectively, was not significantly different ($p > 0.05$). The small difference in average TSN content (0.01 $g{\cdot}kg^{-1}$ of soil) between the manure and NPKL treatments demonstrates a comparable level of TSN content in these treatments (Table 3). However, significant differences were observed ($p < 0.05$) when compared to the check treatment (0.68 $g{\cdot}kg^{-1}$ of soil). Much as no significant differences were observed in TSN content between manure and NPKL treatments, linear regression over the study period showed a difference in the slope components of the regression equations (Figure 2). The slope for NPKL ($r^2 = 0.20$) was not significant ($p > 0.05$), while that for manure ($r^2 = 0.24$) was significant ($p < 0.05$). The significance in the rate of accumulation of TSN under manure treatment is due to comparatively low uptake efficiency of the manure N. Although there is a difference in significance of the slope components, a similar trend of TSN with time for the two inputs was observed (Figure 2). Additionally, the correlation coefficient ($r = 0.93$) showed a positive linear relationship and suggests comparable levels of TSN content in the manure- and NPKL-treated plots (Table 3). Similar observations were made in a long-term study by Aula et al. [13] where an average increase in TSN of 0.64 $g{\cdot}kg^{-1}$ was noted at three locations comparing two sets of samples (1993 and 2014) for treatments where high inorganic N was applied. Evidence that recovery of the applied N fertilizer was far below the quantity applied was present. In 2009, for instance, only 3.5 and 7.4 $kg\,N{\cdot}ha^{-1}$ were recovered in the grain in manure and NPKL treatments, respectively. This in part is a result of unfavorable environmental conditions for optimum plant uptake and that could also have been a result of a near total crop failure circumstance. Substantial quantities of the

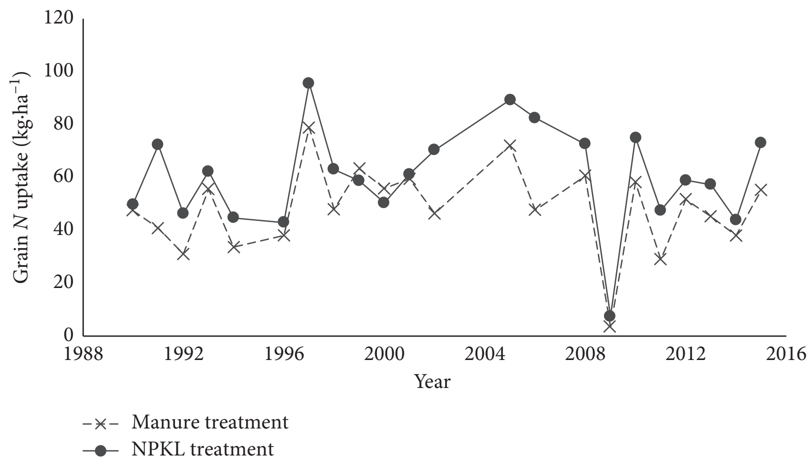

Figure 1: Changes in grain N uptake in manure and NPKL treatments, 1990–2015.

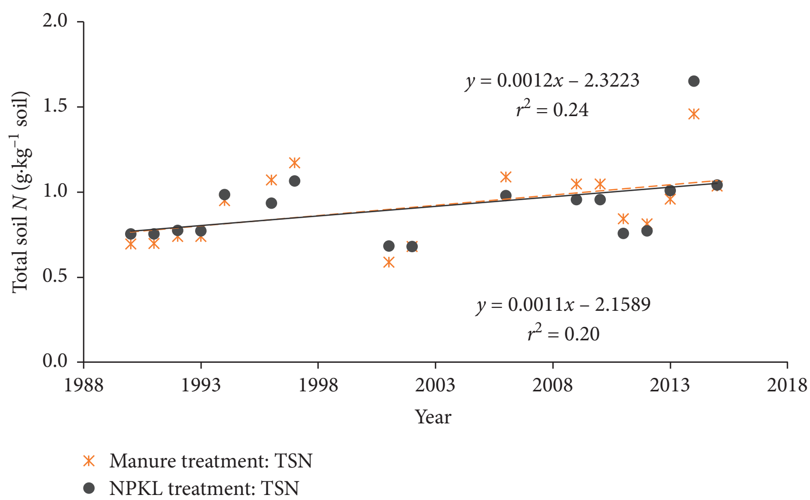

Figure 2: Total soil N accumulation in manure and NPKL treatments, 1990–2015.

applied N could be lost or immobilized within the soil system. If changes in the soil environment favor N immobilization, formation of soil organic N reduces crop uptake but favors TSN accumulation. Sarr et al. [18] reported a loss of N fertilizer between 55 and 60% and soil immobilization between 36 and 40% in a tracer N study. In the same study, N fixation from the inoculated plants increased N recovery by 81%. This implies that atmospheric fixation may counter the effect of seasonal dynamics which dictates the availability of N for plant uptake and further explains the cause for the TSN accumulation despite low grain N recovery.

4. Conclusion

From 1990 to 2015, N uptake was 20% greater in the NPKL treatment than manure treatment, while grain yield from the two sources (manure and NPKL) was not significantly different. Manure N uptake was notably lower compared to the uptake from inorganic N sources as it is, in most cases, not readily available for immediate crop uptake. This observation is similar to that by Ma et al. [31] who reported a significantly lower manure N uptake efficiency compared to inorganic N uptake efficiency even when grain yield levels were comparable for the two input sources. It is also important to note that the observation made in this study indicates a strong influence of the environment on the uptake of N from both manure and inorganic sources evidenced by high variation in this parameter. A positive trend of TSN accumulation in soil over time was similar for organic and inorganic sources. Animal manure can produce similar yield levels to inorganic N fertilizer despite the low N uptake efficiency. The fact that identical quantities of N were supplied from the two input sources, low N uptake from the manure N source could suggest a potential for environmental pollution. Appropriate timing and application rate of manure N sources could optimize crop use efficiency and limit potential threat to the environment.

Data Availability

The dataset used for this study was obtained from a long-term winter wheat fertility experiment “Magruder Plots” located at Stillwater and are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

[1] J. M. Powell, S. Fernández-Rivera, P. Hiernaux, and M. D. Turner, "Nutrient cycling in integrated rangeland/cropland systems of the Sahel," *Agricultural Systems*, vol. 52-, no. 2-3, pp. 143–170, 1996.

[2] B. Singh and Y. Singh, "Reactive nitrogen in Indian agriculture: inputs, use efficiency and leakages," *Current Science*, article 00113891, vol. 94, no. 11, pp. 1382–1393, 2008.

[3] S. R. Carpenter, N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith, "Nonpoint pollution of surface waters with phosphorus and nitrogen," *Ecological Applications*, vol. 8, no. 3, pp. 559–568, 1998.

[4] G. P. Robertson and S. M. Swinton, "Reconciling agricultural productivity and environmental integrity: a grand challenge for agriculture," *Frontiers in Ecology and the Environment*, vol. 3, no. 1, pp. 38–46, 2005.

[5] J. A. Camargo and Á Alonso, "Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment," *Environment International*, vol. 32, no. 6, pp. 831–849, 2006.

[6] K. Mengel, "Turnover of organic nitrogen in soils and its availability to crops," *Plant and Soil*, vol. 181, no. 1, pp. 83–93, 1996.

[7] G. P. Robertson and P. M. Groffman, "Nitrogen transformations," in *Soil Microbiology, Ecology and Biochemistry*, pp. 341–364, 3rd edition, 2007.

[8] G. Torstensson, H. Aronsson, and L. Bergström, "Nutrient use efficiencies and leaching of organic and conventional cropping systems in Sweden," *Agronomy Journal*, vol. 98, no. 3, pp. 603–615, 2006.

[9] C. Chang and T. Entz, "Nitrate leaching losses under repeated cattle feedlot manure applications in southern Alberta," *Journal of Environment Quality*, vol. 25, no. 1, pp. 145–153, 1996.

[10] Y. Wang, X. Zhang, and C. Huang, "Spatial variability of soil total nitrogen and soil total phosphorus under different land uses in a small watershed on the Loess Plateau, China," *Geoderma*, vol. 150, no. 1-2, pp. 141–149, 2009.

[11] J. M. Bremner and C. S. Mulvaney, "Nitrogen—total 1," in *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties Methodsofsoilan*, pp. 595–624, American Society of Agronomy, Madison, WI, USA, 1982.

[12] G. Xu, Z. Li, and P. Li, "Fractal features of soil particle-size distribution and total soil nitrogen distribution in a typical watershed in the source area of the middle Dan River, China," *Catena*, vol. 101, pp. 17–23, 2013.

[13] L. Aula, N. Macnack, P. Omara, J. Mullock, and W. Raun, "Effect of fertilizer nitrogen (N) on soil organic carbon, total N, and soil pH in long-term continuous winter wheat (*Triticum aestivum* L.)," *Communications in Soil Science and Plant Analysis*, vol. 47, no. 7, pp. 863–874, 2016.

[14] P. Omara, N. Macnack, L. Aula, and B. Raun, "Effect of long-term beef manure application on soil test phosphorus, organic carbon, and winter wheat yield," *Journal of Plant Nutrition*, vol. 40, no. 8, pp. 1143–1151, 2017.

[15] J. M. H. Knops and D. Tilman, "Dynamics of soil nitrogen and carbon accumulation for 61 years after agricultural abandonment," *Ecology*, vol. 81, no. 1, pp. 88–98, 2000.

[16] R. L. Westerman, R. K. Boman, W. R. Raun, and G. V. Johnson, "Ammonium and nitrate nitrogen in soil profiles of long-term winter wheat fertilization experiments," *Agronomy Journal*, vol. 86, no. 1, pp. 94–99, 1994.

[17] W. R. Raun and G. V. Johnson, "Improving nitrogen use efficiency for cereal production," *Agronomy Journal*, vol. 91, no. 3, pp. 357–363, 1999.

[18] P. S. Sarr, J. W. Okon, D. A. B. Begoude et al., "Symbiotic N2-fixation estimated by the ^{15}N tracer technique and growth of *Pueraria phaseoloides* (Roxb.) Benth. inoculated with *Bradyrhizobium* strain in field conditions," *Scientifica*, vol. 2016, Article ID 7026859, 10 pages, 2016.

[19] S. Dhital and W. R. Raun, "Variability in optimum nitrogen rates for maize," *Agronomy Journal*, vol. 108, no. 6, pp. 2165–2173, 2016.

[20] H. M. El-Sharkawi, "Effect of nitrogen sources on microbial biomass nitrogen under different soil types," *ISRN Soil Science*, vol. 2012, Article ID 310727, 7 pages, 2012.

[21] M. F. Jurgensen, "Relationship between nonsymbiotic nitrogen fixation and soil nutrient status-a review," *Journal of Soil Science*, vol. 24, no. 4, pp. 512–522, 1973.

[22] K. Girma, S. L. Holtz, D. B. Arnall, B. S. Tubaña, and W. R. Raun, "The Magruder plots: untangling the puzzle," *Agronomy Journal*, vol. 100, no. 3, pp. S–11, 2008.

[23] J. S. Schepers, D. D. Francis, and M. T. Thompson, "Simultaneous determination of total C, total N, and ^{15}N on soil and plant material," *Communications in Soil Science and Plant Analysis*, vol. 20, no. 9-10, pp. 949–959, 1989.

[24] SAS Institute Inc, *Base SAS 9.4 Procedures Guide: Statistical Procedures*, SAS Institute Inc, Cary, NC, USA, IInd edition, 2013.

[25] R. D. Lentz and G. A. Lehrsch, "Nitrogen availability and uptake by sugarbeet in years following a manure application," *International Journal of Agronomy*, vol. 2012, Article ID 120429, 12 pages, 2012.

[26] B. Eghball and J. F. Power, "Phosphorus- and nitrogen-based manure and compost applications," *Soil Science Society of America Journal*, vol. 63, no. 4, pp. 895–901, 1999.

[27] S. Y. Abdulmaliq, Y. A. Abayomi, M. O. Aduloju, and O. Olugbemi, "Effects of curing period of livestock droppings on the growth and yield of okra (*Abelmoschus esculentus* L.) varieties," *International Journal of Agronomy*, vol. 2016, Article ID 3513954, 7 pages, 2016.

[28] S. R. Olsen, "The role of organic matter and ammonium in producing high corn yields," in *The Role of Organic Matter in Modern Agriculture*, pp. 29–54, Springer, Dordrecht, Netherlands, 1986.

[29] H. Shirani, M. A. Hajabbasi, M. Afyuni, and A. Hemmat, "Effects of farmyard manure and tillage systems on soil physical properties and corn yield in central Iran," *Soil and Tillage Research*, vol. 68, no. 2, pp. 101–108, 2002.

[30] R. J. Haynes and R. Naidu, "Influence of lime, fertilizer and manure applications on soil organic matter content and soil physical conditions: a review," *Nutrient Cycling in Agroecosystems*, vol. 51, no. 2, pp. 123–137, 1998.

[31] B. L. Ma, L. M. Dwyer, and E. G. Gregorich, "Soil nitrogen amendment effects on nitrogen uptake and grain yield of maize," *Agronomy Journal*, vol. 91, no. 4, pp. 650–656, 1999.

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Research Article

Nitrogen Use Efficiency and Gaseous Nitrogen Losses from the Concentrated Liquid Fraction of Pig Slurries

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Processed manure can be an alternative source of nutrients for untreated manure and mineral fertilizers. Mineral concentrates (MCs) are derived from reversed osmosis of the liquid fraction of separated pig slurries. The emissions of ammonia (NH_3) and nitrous oxide (N_2O) from different (processed) manures and fertilizers were tested in an incubation experiment and a greenhouse experiment with grass as a test crop. Dry matter yields and nitrogen (N) uptake were also determined in the greenhouse experiment. Incorporation into the soil decreased on NH_3 emission but increased N_2O emission for all nitrogen products (mineral fertilizer, untreated slurry, MC, and solid fraction of separated slurry). Incorporation of both MC, slurries, and mineral fertilizers increased N_2O emission in the incubation experiment. The lowest apparent N recovery (ANR) in the pot experiment with grass was obtained for incorporated pig slurry (30–39%) and surface-applied MC (33–38%), while the highest ANRs were obtained for liquid ammonium nitrate (45–53%) and acidified MC (43–55%). It is concluded that MCs have a similar N fertilizer value as mineral N fertilizers if NH_3 emission is reduced by incorporation or acidification.

1. Introduction

Livestock manure is a valuable source of nutrients for crops and organic matter for soil. However, high losses of nitrogen (N) and phosphorus (P) have caused environmental problems related to soil, water, and air quality in many regions with intensive livestock farming systems [1]. In the European Union, a series of environmental policies has been implemented to decrease N emissions [2]. Lower inputs by fertilizers and manures have decreased both nitrate (NO_3^-) leaching to ground and surface waters and gaseous emissions to the atmosphere as ammonia (NH_3) and nitrous oxide (N_2O) in the EU in 2000–2008 [3]. However, further improvements in manure management are needed to meet the environmental targets. Improved manure management based on high-technology manure processing and transport of processed manures from intensive livestock regions to regions with arable cropping systems is seen as an important measure to decrease nutrient losses to the environment and increase nutrient use efficiency in intensive livestock systems [4, 5].

Separation of livestock slurries into a liquid and a solid fraction may increase both the N and P use efficiencies of manure and decrease losses to the environment [6]. The liquid fraction contains most of the N and potassium (K) and the solid fraction contains P and organic matter, so that application rates of both fractions can be tuned to the crop demand for nutrients. However, the volume of the liquid fraction is large, so that transport from the liquid fraction is costly. Reverse osmosis is a technique by which water can be removed from salt solutions [7, 8]. Application of reverse osmosis to the liquid fraction of separated slurry allowed a volumetric liquid manure reduction of 30 to 77% [9–12]. A lower volume of manure decreases the transport cost and may be a solution to transport excess of N from regions with a high livestock density to regions with arable cropping systems.

Field tests with the concentrated liquid fraction derived from reverse osmosis (mineral concentrate (MC)) showed that the nitrogen fertilizer replacement value (NFRV) is about 72–84% on maize and potato compared to calcium ammonium nitrate (CAN) fertilizer [13, 14]. Field experiments on grassland showed an N efficiency of 75% on sand and 58% on clay soil using CAN as a reference [15, 16]. Compared with liquid ammonium nitrate as a reference, the N efficiency of MC was 89% on sand and 92% on clay. The lower N efficiency of liquid fraction compared to the mineral fertilizer is likely related to gaseous N losses, mainly as NH_3 [17]. Several studies showed a lower NH_3 emission after application of liquid fraction than after application of untreated slurry [18–21]. This is attributed to the lower dry matter content of the liquid fraction than of slurry, by which the NH_4^+ rapidly infiltrates into the soil and NH_3 emission is reduced. However, studies in which manure is incorporated in the soil often show that incorporation of N in the soil increases N_2O emission because the higher N and lower oxygen concentrations in the soil after incorporation promote N_2O production during nitrification and denitrification [22]. However, the presence of organic matter in untreated slurry may increase N_2O emission because available organic matter is an energy source for denitrifying bacteria and promotes oxygen consumption in soils [23]. Clearly, there is a need to get more insights into the risk of NH_3 and N_2O emissions and N efficiency of liquid fractions of processed livestock slurries in order to increase the N use efficiency of slurries and to decrease the negative environmental effects of the use of slurries.

An incubation experiment was carried out to determine the risk of NH_3 and N_2O emissions from MC in comparison to untreated slurries, solid fractions of pig slurry, and mineral N fertilizers. It was hypothesized that the NH_3 emission from MC was smaller than that from untreated pig slurries because the N in MC infiltrates more rapidly into the soil than the N in slurries. It was also hypothesized that the difference in N_2O emission between MC and untreated pig slurry is difficult to predict because many factors (and interactions between factors) affect the production of N_2O during nitrification and denitrification in the soil, e.g., the pH and the concentrations of N, C, and oxygen of soils.

The apparent N recovery (ANR) of MC and untreated pig slurries were determined and compared with mineral N fertilizers in a pot experiment with grass as a test crop. It was hypothesized that abatement of NH_3 emission by incorporation or acidification of MC increased the ANR of MC.

2. Materials and Methods

2.1. Incubation Experiments

2.1.1. Mineral Concentrates. The experiments were carried out with pig slurries, MC (produced by reversed osmosis of the liquid fraction of separated slurries), and sold fractions of separated slurries derived from four manure processing plants (A, B, C, and D) [12]. There was one plant in which the digestate of codigested pig slurry and maize residues was treated: plant A. The other plants (B, C, and D) treated raw pig slurry, which was not digested or codigested. The separation techniques differed between the four plants. Plant A was used as a centrifuge, plants B and C a belt press, and plant D a screw press to separate digestate or slurries into liquid and solid fractions. Plant A used ultrafiltration and the other plants used air flotation for further cleaning of the liquid fraction. Plant B added both a coagulant (iron(III) sulphate) and flocculant (polyacrylamide), and the plants C and D added only polyacrylamide to promote the cleaning of the liquid fraction. The osmotic pressure was 60, 70, 60, and 40 bar for plants A, B, C, and D. The composition of the untreated slurries, MC, and solid fractions is presented in Table 1.

2.1.2. Experiment with Arable Soil. An incubation experiment was carried out to quantify the NH_3 and N_2O emissions from surface-applied and incorporated fertilizers, slurries, and processed slurries. This experiment was carried out using a sandy soil from an experimental farm with an arable crop rotation (Rolde, The Netherlands, 52°57′N, 6°39′E). The organic matter content of the soil was 4.4%, pH-KCl 5.1, and total N 1.22 g·kg^{-1}. The soil was air-dried and sieved with a 10 mm sieve. The treatments included an unfertilized control, three mineral fertilizers with different types of N (calcium ammonium nitrate, urea, and urean, i.e., a liquid fertilizer containing urea and ammonium nitrate), four untreated pig slurries (A, B, C, and D), four solid fractions (derived from separation of slurries A, B, C, and D), and four MC (produced by reversed osmosis of the liquid fraction of separated slurries A, B, C, and D). The experiment was carried out for 2 application methods (surface application and incorporation), 16 treatments, and in 3 replicates. The incubation was conducted using bottles of 1 litre to which 600 g dry soil was added. The surface area of the soil in the bottles was 69.4 cm^2. After filling the bottles with dry soil, water was added to achieve moisture content below field capacity. Thereafter, the bottles with moist soil were preincubated for 1 week at 20°C to activate microorganisms in soil. Thereafter, fertilizers and manures were applied to the soils. The incubation experiment was carried out at 20°C. The soil was brought at gravimetric moisture contents similar to field capacity by adding water, taking the amount of water added with (treated) slurries into account. Field capacity is the moisture content of the soil after excess water has drained (generally, a few days after rainfall). The moisture content of the soil was kept stable until day 7 by weighing the bottles and adding water after each measurement. At day 7, water was added to simulate rainfall (7 mm). Rainfall is an important factor controlling N_2O emission because it enhances denitrification and the N_2O production during nitrification.

All fertilizers and slurries were both surface applied and incorporated and were applied at a rate equivalent to 170 kg·N per ha (the maximum amount for livestock manure of the Nitrates Directive of the European Union). The fluxes of NH_3 and N_2O were measured 12 times: ½, 1, 2, 4, 7, 8, 11, 14, 21, 22, 23, and 28 days after N application. The concentration of NH_3 and N_2O was measured using an

Table 1: Composition of the tested products (expressed on basis of fresh weight).

Experiment	Product[1]	Dry matter ($g\cdot kg^{-1}$)	N ($g\cdot N\cdot kg^{-1}$)	NH_4-N ($g\cdot N\cdot kg^{-1}$)	NH_4-N/total N	P ($g\cdot P\cdot kg^{-1}$)	pH
Incubation	Pig slurry A	92	7.7	4.8	0.62	1.8	8.2
	Pig slurry B	89	6.9	4.5	0.65	1.8	7.7
	Pig slurry C	84	6.8	4.5	0.66	1.7	7.3
	Pig slurry D1	92	5.3	2.9	0.54	2.7	7.5
	Average	89	6.7	4.2	0.62	2.0	7.7
	MC A	18	6.6	4.1	0.62	0.6	8.6
	MC B	46	7.7	7.4	0.96	0.0	7.7
	MC C	46	9.1	7.7	0.85	0.4	7.9
	MC D1	24	5.5	5.1	0.92	0.1	7.9
	Average	34	7.2	6.1	0.84	0.3	8.0
	Solid fraction A	272	11.1	6.2	0.56	6.7	n.a.[2]
	Solid fraction B	290	12.4	5.2	0.42	6.3	n.a.
	Solid fraction C	313	12.9	5.1	0.40	7.3	n.a.
	Solid fraction D1	259	11.1	4.4	0.39	7.5	8.2
	Average	284	11.9	5.2	0.44	7.0	8.2
Pot	Slurry D2	71	6.3	4.1	0.65	1.5	7.7
	MC D2	58	8.0	7.1	0.89	0.3	7.9

[1]The different manure treatment plants are indicated with A, B, C, and D. D1 (used in the incubation experiment) and D2 (used in the pot experiment) represent different sampling times at plant D. [2]n.a.: not analysed.

Innova 1312 photoacoustic gas analyser. At each measurement time, the bottles were closed with a stopper and the concentrations of NH_3 and N_2O were measured in the headspace directly after closing the bottle and after about 1 hour. Values were corrected for ambient N_2O concentration and for mixing of the sample with the gas of the previous measurement which was present in the analyser. The emission was calculated assuming a linear increase, as described in more detail in various studies [24, 25, 26]. However, the increase of NH_3 concentration in closed systems generally decreases in time because of the accumulation of NH_3 in the air in the headspace. Therefore, the results of one experiment can only be used to compare the risk of NH_3 emissions between the fertilizers and slurries, but the NH_3 emission measured using closed systems will largely underestimate the real emissions. The total emission of NH_3 and N_2O in the experimental period was calculated by linear interpolation of the fluxes determined at different times.

2.2. Pot Experiment

2.2.1. Set Up. A greenhouse pot experiment with ryegrass (*Lolium perenne* L., Barnhem) was designed as a simple two-factor treatment. The aim of the experiment was to quantify ANR, and NH_3, and N_2O emissions at different soil water contents (50, 60, and 80% of water holding capacity), as soil water contents may affect the N losses by NH_3 and N_2O emission and by that ANR of fertilizers. The experiment included an unfertilized control, two fertilizers (calcium ammonium nitrate applied as solid fertilizer and liquid ammonium nitrate), an untreated pig slurry, surface-applied MC, incorporated MC, incorporated mixture of MC and pig slurry, and an acidified MC. A mixture of pig slurry and MC was used as an N source because this is often used in practice. Application of MC required specific application techniques, but the application of mixtures of MC and slurries does not require specific application equipment. Incorporation and acidification of MC were tested as measures to abate NH_3 emission. The mixture of pig slurry and MC and the acidified MC were prepared three days before application to the pots. The MC was acidified by slow addition of 175 ml 2 M H_2SO_4 to 1 L MC in a beaker (0.7 $mol\cdot H\cdot L^{-1}$ MC). The pH of the acidified MC was 5.08 after 12 hours. All N treatments were carried out at three soil water contents and four replicates per treatment (in total 96 pots).

The tested pig slurry and MC were obtained from plant D but collected at a different time than the sample used in the incubation experiment. The experiment was conducted using 5.5-L plastic pots with a height of 22 cm and a diameter of 20 cm. The pots were filled with a loamy sand soil (3.0% organic matter and 4.1% clay) with only low amounts of available nitrogen (1 M KCl extract: <0.6 mg NH_4-N/kg dry matter and 7.3 mg NO_3-N kg dry matter) collected at the Droevendaal experimental farm (Wageningen 51°59′N, 5°39′E, The Netherlands). Each pot was filled with 6 kg of fresh soil. A watering tube with a diameter of 5 cm was placed in the middle of the pot to attain an even spread of moisture throughout the soil after watering. Seven weeks before the start of the experiment, grass was sown. To each pot, an additional amount of 0.8 kg of fresh soil was added together with 3 grams of grass seeds (*Lolium perenne* L., Barnhem: 3 g of seeds per pot). After six weeks, the grass sod developed in the pots was cut to a height of approximately 5 cm. In the week that followed, different soil water contents were established by daily giving different amounts of water resulting in 50%, 60%, and 80% of the water holding capacity. These water contents were maintained gravimetrically during the whole experiment. The water was added via the watering tube in each pot.

Incorporation of slurry into the soil by injection was simulated by creating a slit in the middle of the of the pot in the grass sod with a knife to a depth of approximately 5 cm.

Surface application of slurry was simulated by applying the slurry between the grass in the middle of the pot. The application rates of slurry and MC were based on results of analyses of the composition of these products just after collection of 1 to 2 weeks before experiments started. As the N content may change during storage and varies between batches, the N content of the actual batches used in the pot experiment was analysed after at the time of application. For some of the products, the N content was different that the N content which was used to derive the N application rates in the experiment. As the N content alters during storage and varies between batches, the N content of the actual batches used in the pot experiment was analysed after the start of the experiment, resulting in different N additions between the treatments. The N application rates were 10.5 g N m^{-2} for fertilizers and pig slurry, 6.6 g N m^{-2} for (acidified) MC, and 8.3 g·N·m^{-2} for the mixture of pig slurry and MC. During the experimental period, the temperature in the greenhouse generally varied between 18 at night and 20°C during day time. The treatments were applied after a warm period.

2.2.2. Measurements. Emissions of N_2O and NH_3 were measured using flux chambers (height 10 cm) connected with tubes to an Innova 1312 photoacoustic gas analyser. The tube to the gas analyser was heated to prevent water condensation in the tube. The NH_3 concentration in the headspace of the flux chamber was measured at 0 and 4 minutes after closing the flux chamber. NH_3 measurements were performed during the first three days after the N application. After this period, NH_3 emissions were negligible. Emission of N_2O was calculated from the change in concentration between 0 and 30 minutes after closing the flux chamber. The emissions were calculated using the volume of the flux chamber and tubing (4.26 L) and area of the soil surface (314 cm^2). The measured N_2O concentrations in the headspace were corrected for the amount of N_2O which was pumped from one flux chamber into the next flux chamber. This amount was calculated by multiplying the internal volume of the gas analyser and connecting tubes (about 2.5% of the headspace volume) with the N_2O concentration in the analyser and tubes (which is equal to the N_2O concentration of the previous measurement). Grass was cut at approximately 5 cm above the soil after 27 days and after regrowth, at 56 days. The dry matter content of the grass was determined after drying for 48 h at 70°C. Total N contents were determined spectrophotometrically by means of segment flow analysis [27].

2.2.3. Calculations and Data Analysis. The apparent nitrogen recovery (ANR) was calculated as the ratio of the N uptake in the shoot and the applied N, corrected for the average shoot N from the unfertilized control treatment at the same soil moisture content. The relative N fertilizer value (NFRV) of an organic fertilizer is the percentage of the applied N, which has the same effect on crop N yield as mineral fertilizer. The NFRV is calculated as the ANR of the tested product compared to the ANR of the CAN treatment at the highest soil moisture content.

2.3. Data Analysis. Data were statistically analysed using ANOVA with Genstat 16th Edition (VSN Int. Ltd.). For the incubation experiments, the between-treatment differences in log-transformed NH_3 and N_2O emissions were tested using Fisher's protected LSD analysis. The data were log-transformed to stabilize variance. For the pot experiment, a two-way ANOVA was performed for treatment and soil moisture content as factors and their interactions. A three-way ANOVA was performed for the N_2O and NH_3 emissions in the pot experiment including the factor time of analysis. Between-treatment differences were tested using Fisher's protected LSD analysis. Except the NH_3 emission, all tested parameters of the pot experiment did have a normal distribution. The NH_3 emissions were not normally distributed, also after log transformation, and were analysed using the one-way nonparametric Kruskal–Wallis test.

3. Results

3.1. Composition of the Products. Table 1 shows the composition of the tested products. The dry matter contents were lowest in the MC (on average 34 g·kg^{-1}), intermediate in the pig slurries (89 g·kg^{-1}), and highest in the solid fractions (284 g·kg^{-1}). The N contents in the fresh product were highest in the solid fraction and that of NH_4^+-N was highest in the MC. The P content of MC was on average 0.3 g·kg^{-1} and much lower than those of pig slurries (2.0 g·kg^{-1}) and solid fraction (7.0 g·kg^{-1}). The ratio of NH_4^+-N to total N was higher for MC (0.84) than slurries (0.62) and solid fraction (0.44). The average pH of MC was 8.0 and was higher than the average pH of pig slurries of 7.7.

3.2. NH_3 and N_2O Emissions from Arable Soil. Ammonia emission from MC, pig slurry, and the solid fraction surface applied to arable soils was highest directly after application and decreased within a week to levels similar to the control (Figure 1). The NH_3 emission from surface-applied urea followed a different pattern and peaked at day 2 (Figure 1). The emission from surface-applied CAN was negligible. Incorporation decreased NH_3 emission, and emission was negligible for most fertilizers and manures after incorporation (Table 2). Emission of NH_3 after surface application was on average statistically higher for MC, followed by pig slurry, and solid fraction (Table 2). This was not shown for plant B; NH_3 emission from untreated slurry B was significantly higher than that from MC B. The total NH_3 emission from surface-applied urea was similar to that from surface-applied MC A and B but lower than that from MC C and D.

Emission of N_2O from fertilizers and manures gradually increased after application to soil (Figure 2). Application of water at day 7 increased N_2O emissions of all treatments. Total emission N_2O was on average significantly higher after incorporation than after surface application (Table 2). For products of plants A, B, and C, the N_2O emission at incorporation in the arable soil was highest for MC, followed by untreated slurry and the solid fraction (Table 2). However, the differences were in most cases not statistically

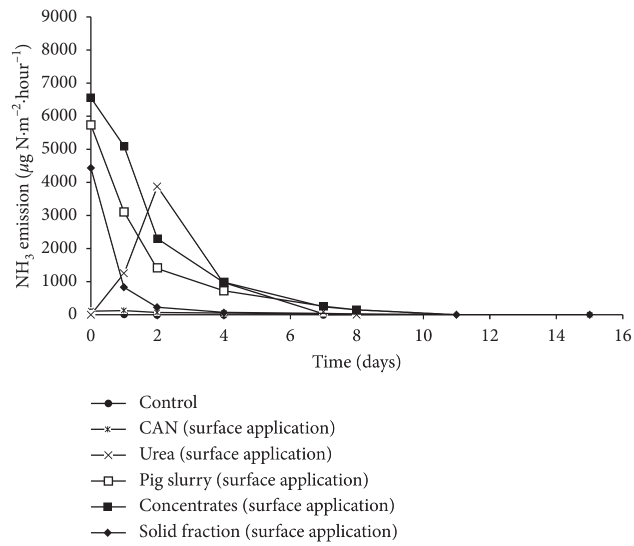

Figure 1: Ammonia emission from surface-applied manure products (average of four plants) and fertilizers applied to an arable sandy soil. After 7 days, 7 mm water was added to simulate rainfall. See Table 2 for the total emissions of all treatments of this experiment.

Table 2: Total ammonia and nitrous oxide emissions from different fertilizers and application techniques.

Fertilizer	Ammonia emission (mg N m^{-2})			Nitrous oxide emission (mg N m^{-2})			
	Surface applied		Incorporated	Surface applied		Incorporated	
Control	−1	aa	−1	0	ab	0	a
Calcium ammonium nitrate	12	ab	4	5	bc	30	bc
Urea	229	ghij	8	156	gh	248	gh
Urean	15	bc	2	76	fg	47	bcde
Slurry A	285	hijk	12	53	def	97	def
MC A	360	ijk	−1	18	cd	179	fgh
Solid fraction A	173	fghi	0	12	bc	15	ab
Slurry B	316	ijk	13	78	efg	124	efg
MC B	125	fg	0	11	bc	129	fg
Solid fraction B	84	ff	−4	0	a	86	def
Slurry C	284	hijk	9	31	cdef	82	def
MC C	493	k	6	27	cde	167	fg
Solid fraction C	45	de	6	8	bc	43	bcd
Slurry D	155	fgh	10	193	h	297	hi
MC D	470	jk	−2	63	ef	111	cdef
Solid fraction D	32	cd	−1	431	i	646	i
One-way ANOVA							
Fertilizer	$P < 0.001$		$P = 0.537$	$P < 0.001$		$P < 0.001$	
Two-way ANOVA							
Fertilizer	$P < 0.001$; l.s.d.[1] = 0.66			$P < 0.001$; l.s.d.[1] = 0.25			
Application method	$P < 0.001$; l.s.d.[1] = 0.23			$P < 0.001$; l.s.d.[1] = 0.09			
Fertilizer × method	$P < 0.001$; l.s.d.[1] = 0.93			$P < 0.001$; l.s.d.[1] = 0.36			

[1]l.s.d. of log-transformed values. Results of an incubation experiment with samples from an arable sand soil. The statistics and least significant difference (l.s.d.) values are based on log-transformed values. Different letters indicate statistical significant differences between fertilizers.

significant. By contrast, for plant D, the N_2O emission from incorporated MC was statistically significant smaller than that from untreated slurry and solid fraction.

3.3. Greenhouse Pot Experiment. The highest N uptake by grass was obtained at the highest soil moisture content (80% water holding capacity) and using CAN and liquid NH_4NO_3 as the N fertilizer (Table 3). The nitrogen use efficiency (ANR) varied from 30 to 55% (Table 3). ANR and NFRV were significantly higher at 80% than at 50% water holding capacity (Table 3). The lowest ANRs were obtained for incorporated pig slurry (30–39%) and surface-applied MC (33–38%), while the highest ANRs were obtained for liquid NH_4NO_3 (45–53%) and acidified MC (43–55%). At the highest moisture content, the NFRV of incorporated (93%) and acidified MC (106%) was significantly higher than that of surface-applied MC (72%; Table 3). Averaged over all moisture contents, there was no statistically significant difference between incorporated and acidified MC, liquid

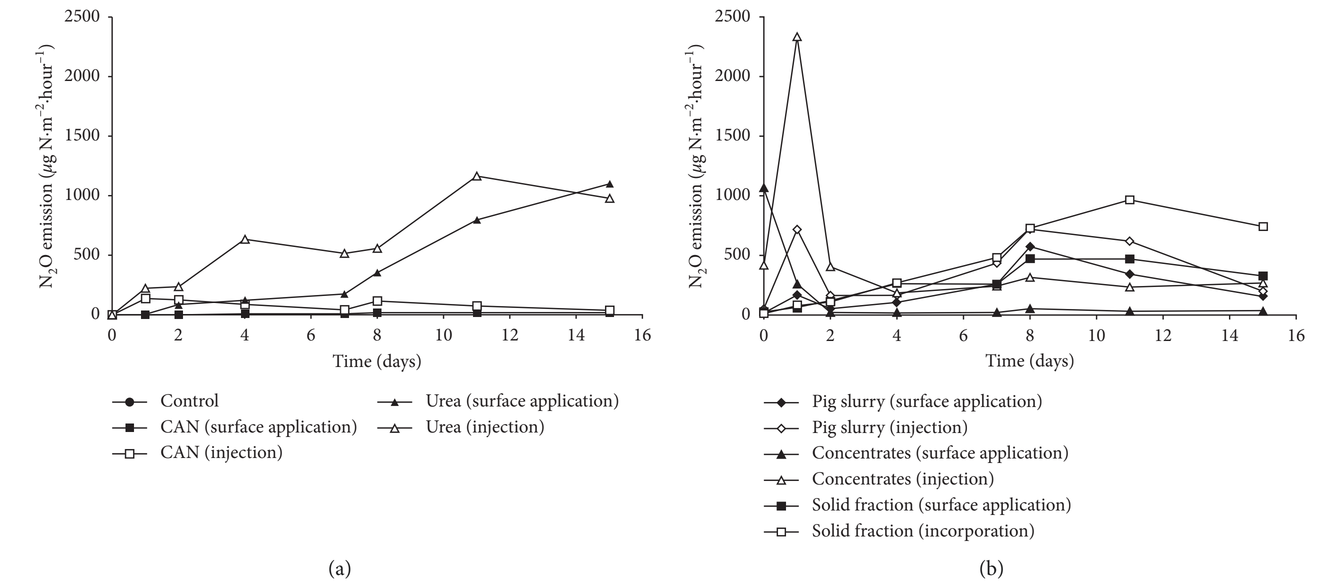

Figure 2: Nitrous oxide emission from incorporated and surface-applied fertilizers (a) and manures (average of four plants in (b)) applied to an arable sandy soil. Results of an incubation experiment with samples from an arable sand soil. After 7 days, 7 mm water was added to simulate rainfall. See Table 2 for the total emissions of all treatments of this experiment.

NH_4NO_3, and CAN (Table 3). The NFRV of the incorporated mixture of pig slurry and MC was 74–82% and between those of incorporated pig slurry (58–76%) and incorporated MC (83–106%).

Emission of NH_3 emission could only be detected at the day of the treatment, and emissions were negligible in the days thereafter (results not shown). The highest NH_3 emission was measured for surface application of MC at the lowest moisture content. No NH_3 emission could be determined for CAN, liquid NH_4NO_3, and acidified MC. The N_2O emissions in the pot experiment were significantly affected by the N source, the soil moisture content, and its interaction (Table 3). The highest N_2O emission was found for pig slurry and the mixture of pig slurry and MC (Table 3). The N_2O emission of acidified MC was lower than of incorporated MC.

4. Discussion

4.1. Emission of NH_3. It was hypothesized that the NH_3 emission from MC was smaller than that from untreated pig slurries because the N in MC infiltrates more rapidly into the soil than the N in slurries. However, the results of the incubation experiment showed that NH_3 emission at surface application was on average higher for MC than for untreated pig slurry, solid fraction, and mineral N fertilizer. Obviously, the positive effect on ammonia emission of the higher fraction of NH_4 in total N and the higher pH of MC than of untreated slurry was larger than the negative effect of the low dry matter content. In various studies, mechanical separation decreased NH_3 emissions after manure application, which was attributed to the lower dry matter content of the liquid fraction, by which the ammonium rapidly infiltrates into soil [18–21]. Application of the liquid fraction of pig slurry reduced NH_3 emission by an average of 25% compared with untreated pig slurry in a study of Chantigny et al. [20]. By contrast, in an experiment of [28], NH_3 emissions of the liquid fraction of raw slurry increased by about 60% compared to raw cattle slurry. This was probably due to its higher pH and fraction of ammonium in total N.

There were considerable differences in NH_3 emission between MC of the plants A, B, C, and D. These differences could not be explained by differences in composition (not shown), which is most likely due to the fact that were differences between the plants in composition of the treated slurry and in the method of separation and treatment of manure.

The incubation experiment (Table 2) and the pot experiment (Table 3) showed that incorporation of MC in the soil significantly reduced NH_3 emission. Incorporation of manure is considered a highly efficient technique to abate NH_3 emission [29]. The NH_3 emission after sod incorporation of MC to cereals was 3% of the applied NH_4-N in the MC and 12% when applied via a trailing hose dosing machine in a field study [30]. The NH_3 emission from MC applied with sod incorporation into grassland averaged 8% of the applied NH_4-N in this study. Decreasing the pH of slurry by acidification is another efficient option to reduce ammonia emission [31]. In the pot experiment, the NH_3 emission of the acidified MC was negligible, while the emission from surface-applied MC was highest. With a proper application technique or acidification, NH_3 emission from MC can be reduced strongly. Additional NH_3 abatement techniques may be applied to decrease NH_3 emission, including dilution with water and application during weather conditions with relatively low NH_3 emission, i.e., wet conditions and low wind speed [32]. Contrary to the expectations, soil moisture had no significant influence on the NH_3 emission in the pot experiment. On the

Table 3: N uptake of grass (sum 1st and 2nd cut), apparent N recovery (ANR), nitrogen fertilizer replacement value (NFRV)[2], total N_2O emission during the pot experiment, and average NH_3 emissions at the first day, at 50, 60, and 80% of the soil water holding capacity (WHC).

Treatment	N uptake (m^{-2})				ANR (%)				NFRV (%)				N_2O (mg N m^{-2})				NH_3 (g N m^{-2} day^{-1})		
	50%	60%	80%		50%	60%	80%		50%	60%	80%		50%	60%	80%		50%	60%	80%
Control	0.4	0.3	0.5	a									2	5	6	ab	0	0	0
CAN, surface-applied	4.9	5.3	6.0	d	43	47	52	bc	82	90	100	bc	17	11	19	c	0	0	0
Liquid NH_4NO_3, surface-applied	5.1	5.4	6.1	d	45	48	53	c	87	93	101	c	−2	2	10	a	0	0	0
Pig slurry, incorporated	3.4	3.9	4.5	c	30	36	39	a	58	69	76	a	12	21	34	d	0.2	0.1	0.1
MC, surface-applied	2.6	3.1	3.0	b	33	41	38	a	64	79	72	a	3	11	6	ab	0.9	0.3	0.3
MC, incorporated	3.3	3.5	3.8	c	44	48	49	bc	84	93	93	bc	9	3	16	b	0.1	0.2	0.4
Mixture pig slurry and MC, incorporated	3.6	3.8	4.1	c	39	42	43	ab	74	80	82	ab	17	11	37	d	0.4	0.2	0.2
Acidified MC, surface-applied	3.3	3.5	4.2	c	43	48	55	c	83	93	106	c	−1	−3	10	a	0	0	0
ANOVA[1]	a	a	b		a	ab	b		a	ab	b		a	a	b				
N source		<0.001				<0.001				<0.001				<0.001				$\chi^2 < 0.001$	
Moisture		<0.001				0.012				0.012				<0.001				$\chi^2 = 0.407$	
N source ∗ moisture		0.948				0.998				0.998				0.002					

[1]Values within columns with different treatments and different subscripts differ significantly ($P < 0.05$) and values in this row with different soil moisture contents and with different letters differ significantly ($P < 0.05$). [2]Values are calculated as the relative ANR compared to the ANR at CAN 80% WHC.

one hand, a lower soil moisture content might increase the infiltration of manures, but on the other hand, air-filled soil pores may promote gaseous emissions [33]. Possibly the variation in moisture conditions in the pot experiment was too small to detect effects.

4.2. Emission of N_2O. It was hypothesized that the difference in N_2O emission between MC and untreated pig slurry is difficult to predict because many factors (and interactions between factors) affect the production of N_2O during nitrification and denitrification in soil. In the incubation experiment, the N_2O emission from incorporated MC was on average higher than from incorporated untreated slurry although there were differences between the different plants (Table 2). The N_2O emission of MC of plant C was lower than that of untreated slurry C; this was found both in the incubation study and pot experiment (Tables 2 and 3). The N_2O emission from the solid fraction of plant C was also high. As also indicated for NH_3 emission, the difference between plants could not be explained by differences in composition (not shown). This is most likely due to the fact that there were differences between the plants in composition of the treated slurry and in the method of separation and treatment of manure. It is not clear which factor caused the high N_2O emission from the untreated slurry and solid fraction of plant D.

Bertora et al. [34] found that the N_2O emission of nontreated pig slurry (N_2O emission was 4.8% of applied N) was higher than that of the liquid fraction (2.6%) and solid fraction (1.8%) of separated pig slurry. Chantigny et al. [20] found no clear effects on pig slurry treatment on N_2O emission. Slurries contain organic C, including volatile fatty acids [35]. Volatile fatty acids are effective energy sources for denitrifiers [36]. When available C is applied to a NO_3-containing soil under wet conditions, denitrifying bacteria may use the C as energy source and the NO_3 can be transformed into gaseous N_2O and N_2. Despite the separation of liquid and solid fractions, MC also contains volatile fatty acids [37]. The presence of volatile fatty acids may have increased the N_2O emission from MC. The high N concentration in MC (about a factor 1.5–2 higher than in pig slurry) in combination with the high pH may have increased NH_3 concentration in the soil. This may have resulted in NH_3 toxification of nitrifier bacteria which in turn may increase N_2O emission [38, 39]. These effects are likely to be similar to those found in urine patches, in which N_2O emission is also relatively high [40].

Incorporation of slurries and MC are techniques to reduce NH_3 emission. However, incorporation of both MC, slurries, and mineral fertilizers increased N_2O emission in the incubation experiment. Also in other studies, it was shown that incorporation of manure increases N_2O emission [4]. The higher N_2O emission by incorporation than by surface application is most likely due to three factors: (i) the NH_3 emission with incorporation is lower by which mineral N content in soil is higher; (ii) the oxygen concentration is lower in the soil than on the top of the soil, increasing the chance on denitrification and N_2O production during nitrification, and (iii) in case of manure, the incorporation of organic C in the soil may increase biological oxygen consumption and, by that, the chance on denitrification and N_2O production during nitrification.

There was no statistical significant difference in N_2O emission between surface-applied MC and -acidified MC (Table 3). Also Fangueiro et al. [41] showed that acidification of slurry did not increase N_2O emission. Acidification instead of incorporation could be an option to decrease NH_3 emission with limited risk on increasing N_2O emission, but more tests are needed to confirm this because the fraction of N_2O in the total N loss by denitrification increases when the pH decreases [42].

Nitrification inhibitors can reduce the emission of N_2O from ammonium fertilizers with 30–50% [43, 44]. Adding nitrification inhibitors could be an option to decrease N_2O emission from MC. However, the effectiveness of nitrification inhibitors to decrease N_2O emission from MC has not been tested.

4.3. Nitrogen Use Efficiency. The efficiency of N in MC used as the fertilizer often depends on the NH_3 emission and the presence of organic N[14]. The NFRV of an organic fertilizer is the percentage of the applied N, which has the same effect on crop N yield as mineral fertilizer. In this study, the NFRV was determined by comparison with broadcast calcium ammonium nitrate (CAN), which is the most commonly used mineral N fertilizer in the Netherlands. The NFRV of incorporated MC in field experiments ranging from 54 to 84% [14, 16] were lower than in the pot experiment of this paper (93%) and 96% in the pot experiment of Klop et al. [17]. Probably, the difference in NFRV of MC between pot and field experiments is due to a lower NH_3 emission under the controlled conditions in the pot experiment. In the pot experiment (Table 3), the NFRV of MC was similar to that of liquid ammonium nitrate applied with the same incorporation technique. Similar results were found by Klop et al. [17]. The distribution of N in the soil differs between the broadcast applied CAN granules and of incorporated liquid fertilizers, and this could affect the N availability for crop roots and N transformation (mineralisation and denitrification) and be a factor that played a role in the differences in N use efficiency between CAN and the liquid fertilizers.

A long-term study demonstrated that higher grass yields can be achieved with separated liquid fraction of dairy slurry than with raw slurry at equivalent ammonium application rates [45]. This was attributed to more rapid soil infiltration of the liquid fraction, which reduces NH_3 emission. Removing solids from pig slurry by mechanical, chemical, and biological means reduced NH_3 losses from pig slurry applied to perennial grass [20]. MC should be incorporated or acidified to maximize ANR and to fulfil their potential as inorganic fertilizer replacement. Significant ANR differences between the four MC suggest the possibility for further optimization of the MC production process.

4.4. Use of Treated Manure. MC can be used as a liquid N-K fertilizer. The N in MC is mainly found in the NH_4 form (on average 84% of total N in the MC). The remaining N is organically bound. The pH of MC is high (about pH 8), so that MC should be incorporated to decrease NH_3 losses and increase ANR.

The solid fraction can be used in agriculture as a source of P and organic matter. The addition of iron flocculants to enhance separation of slurries in a liquid and solid fraction may reduce the short-time P efficiency of the solid fraction [46]. The solid fraction also contains N, from which 45% as NH_4-N (Table 1). This N should be considered in the fertilisation plan when farmers use solid fraction to decrease the risk of N leaching [47]. The NFRV of the solid fraction compared to CAN was 32 to 55% in field experiments with potatoes and 64% in an experiment with maize [48].

5. Conclusions

It is concluded that MC has a similar N fertilizer value as mineral N fertilizers if NH_3 emission is reduced by incorporation or acidification. Incorporation increased N_2O emission, and N_2O emission from incorporated MC was on average higher than from incorporated untreated pig slurry. Acidification instead of incorporation could be an option to decrease NH_3 emission with limited risk on increasing N_2O emission, but more tests are needed to confirm this. Adding nitrification inhibitors could be an option to decrease N_2O emission from MC, but the effectiveness of nitrification inhibitors to decrease N_2O emission from MC has not been tested.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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References

[1] W. Steffen, K. Richardson, J. Rockström et al., "Planetary boundaries: guiding human development on a changing planet," *Science*, vol. 347, no. 6223, article 1259855, 2015.

[2] O. Oenema, A. Bleeker, A. Braathen et al., "Nitrogen in current European policies," in *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives*, M. A. Sutton, C. M. Howard, J. W. Erisman et al., Eds., pp. 62–81, Cambridge University Press, Cambridge, UK, 2011.

[3] G. L. Velthof, J. P. Lesschen, J. Webb et al., "The impact of the nitrates directive on nitrogen emissions from agriculture in the EU-27 during 2000–2008," *Science of the Total Environment*, vol. 468-469, pp. 1225–1233, 2014.

[4] Y. Hou, G. L. Velthof, and O. Oenema, "Mitigation of ammonia, nitrous oxide and methane emissions from manure management chains: a meta-analysis and integrated assessment," *Global Change Biology*, vol. 21, no. 3, pp. 1293–1312, 2015.

[5] L. Ma, F. Wang, W. Zhang et al., "Environmental assessment of management options for nutrient flows in the food chain in China," *Environmental Science and Technology*, vol. 47, no. 13, pp. 7260–7268, 2013.

[6] C. H. Burton, "The potential contribution of separation technologies to the management of livestock manure," *Livestock Science*, vol. 112, no. 3, pp. 208–216, 2007.

[7] L. Masse, D. I. Massé, and Y. Pellerin, "The use of membranes for the treatment of manure: a critical literature review," *Biosystems Engineering*, vol. 98, no. 4, pp. 371–380, 2007.

[8] A. Zarebska, D. Romero Nieto, K. V. Christensen, L. Fjerbæk Søtoft, and B. Norddahl, "Ammonium fertilizers production from manure: a critical review," *Critical Reviews in Environmental Science and Technology*, vol. 45, no. 14, pp. 1469–1521, 2015.

[9] J. G. Pieters, G. G. J. Neukermans, and M. B. A. Colanbeen, "Farm-scale membrane filtration of sow slurry," *Journal of Agricultural Engineering Research*, vol. 73, no. 4, pp. 403–409, 1999.

[10] L. Masse, G. Bellemare, and J. Dubreuil, "RO membrane filtration of pretreated swine manure with high levels of suspended solids," *Transactions of the ASABE*, vol. 55, no. 5, pp. 1815–1820, 2012.

[11] L. Thörneby, K. Persson, and G. Trägårdh, "Treatment of liquid effluents from dairy cattle and pigs using reverse osmosis," *Journal of Agricultural Engineering Research*, vol. 73, no. 2, pp. 159–170, 1999.

[12] P. Hoeksma and F. E. de Buisonjé, "Production of mineral concentrates from animal manure using reverse osmosis," in *Monitoring of Pilot Plants in 2012–2014*, Wageningen UR Livestock Research, Wageningen, Netherlands, 2015.

[13] J. J. Schröder, W. de Visser, F. B. T. Assinck, and G. L. Velthof, "Effects of short-term nitrogen supply from livestock manures and cover crops on silage maize production and nitrate leaching," *Soil Use and Management*, vol. 29, no. 2, pp. 151–160, 2013.

[14] J. J. Schröder, W. De Visser, F. B. T. Assinck, G. L. Velthof, W. Van Geel, and W. Van Dijk, "Nitrogen fertilizer replacement value of the liquid fraction of separated livestock slurries applied to potatoes and silage maize," *Communications in Soil Science and Plant Analysis*, vol. 45, no. 1, pp. 73–85, 2014.

[15] G. Holshof and J. C. van Middelkoop, *Stikstofwerking Van Mineralenconcentraten Op Grasland = N Fertilizer Replacement Value of Mineral Concentrates on Grassland*, Lelystad: Wageningen UR Livestock Research, Wageningen, Netherlands, 2014.

[16] J. C. van Middelkoop and G. Holshof, "Nitrogen fertilizer replacement value of concentrated liquid fraction of separated pig slurry applied to grassland," *Communications in Soil Science and Plant Analysis*, vol. 48, no. 10, pp. 1132–1144, 2017.

[17] G. Klop, G. L. Velthof, and J. W. Van Groenigen, "Application technique affects the potential of mineral concentrates from livestock manure to replace inorganic nitrogen fertilizer," *Soil Use and Management*, vol. 28, no. 4, pp. 468–477, 2012.

[18] P. Balsari, E. Dinuccio, E. Santoro, and F. Gioelli, "Ammonia emissions from rough cattle slurry and from derived solid and liquid fractions applied to alfalfa pasture," *Australian Journal of Experimental Agriculture*, vol. 48, no. 2, pp. 198–201, 2008.

[19] M. Hjorth, A. M. Nielsen, T. Nyord, M. N. Hansen, P. Nissen, and S. G. Sommer, "Nutrient value, odour emission and energy production of manure as influenced by anaerobic digestion and separation," *Agronomy for Sustainable Development*, vol. 29, no. 2, pp. 329–338, 2009.

[20] M. H. Chantigny, D. A. Angers, P. Rochette, G. Bélanger, D. Massé, and D. Côté, "Gaseous nitrogen emissions and forage nitrogen uptake on soils fertilized with raw and treated swine manure," *Journal of Environment Quality*, vol. 36, no. 6, pp. 1864–1872, 2007.

[21] B. Amon, V. Kryvoruchko, T. Amon, and S. Zechmeister-Boltenstern, "Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment," *Agriculture, Ecosystems and Environment*, vol. 112, no. 2-3, pp. 153–162, 2006.

[22] G. L. Velthof, P. J. Kuikman, and O. Oenema, "Nitrous oxide emission from soils amended with crop residues," *Nutrient Cycling in Agroecosystems*, vol. 62, no. 3, pp. 249–261, 2002.

[23] S. Qin, C. Hu, T. J. Clough, J. Luo, O. Oenema, and S. Zhou, "Irrigation of DOC-rich liquid promotes potential denitrification rate and decreases $N_2O/(N_2O+N_2)$ product ratio in a 0-2 m soil profile," *Soil Biology and Biochemistry*, vol. 106, pp. 1–8, 2017.

[24] D. Kool, E. Hoffland, E. Hummelink, and J. Vangroenigen, "Increased hippuric acid content of urine can reduce soil N_2O fluxes," *Soil Biology and Biochemistry*, vol. 38, no. 5, pp. 1021–1027, 2006.

[25] R. L. M. Schils, J. W. van Groenigen, G. L. Velthof, and P. J. Kuikman, "Nitrous oxide emissions from multiple combined applications of fertiliser and cattle slurry to grassland," *Plant and Soil*, vol. 310, no. 1-2, pp. 89–101, 2008.

[26] G. L. Velthof and O. Oenema, "Nitrous oxide fluxes from grassland in the Netherlands: I. Statistical analysis of flux-chamber measurements," *European Journal of Soil Science*, vol. 46, no. 4, pp. 533–540, 1995.

[27] I. Novozamsky, V. J. G. Houba, R. van Eck, and W. van Vark, "A novel digestion technique for multi-element plant analysis," *Communications in Soil Science and Plant Analysis*, vol. 14, no. 3, pp. 239–248, 1983.

[28] E. Dinuccio, W. Berg, and P. Balsari, "Effects of mechanical separation on GHG and ammonia emissions from cattle slurry under winter conditions," *Animal Feed Science and Technology*, vol. 166-167, pp. 532–538, 2011.

[29] S. Bittman, M. Dedina, C. Howard, O. Oenema, and M. Sutton, *Options for Ammonia Mitigation: Guidance from the Unece Task Force on Reactive Nitrogen*, NERC/Centre for Ecology & Hydrology, Edinburgh, UK, 2014.

[30] J. F. M. Huijsmans and J. M. G. Hol, *Ammonia Emission after Application of Mineral Concentrates on Arable Land and Grassland*, Plant Research International, Wageningen, Netherlands, 2011.

[31] S. Bittman, M. Dědina, C. Howard, O. Oenema, and M. Sutton, *Options for Ammonia Mitigation: Guidance from the UNECE Task Force on Reactive Nitrogen*, Centre for Ecology and Hydrology, Bailrigg, UK, 2014.

[32] S. G. Sommer and N. J. Hutchings, "Ammonia emission from field applied manure and its reduction-invited paper," *European Journal of Agronomy*, vol. 15, no. 1, pp. 1–15, 2001.

[33] P. A. Roelle and V. P. Aneja, "Characterization of ammonia emissions from soils in the upper coastal plain, North Carolina," *Atmospheric Environment*, vol. 36, no. 6, pp. 1087–1097, 2002.

[34] C. Bertora, F. Alluvione, L. Zavattaro, J. W. van Groenigen, G. Velthof, and C. Grignani, "Pig slurry treatment modifies slurry composition, N_2O, and CO_2 emissions after soil incorporation," *Soil Biology and Biochemistry*, vol. 40, no. 8, pp. 1999–2006, 2008.

[35] H. Kirchmann and A. Lundvall, "Relationship between N immobilization and volatile fatty acids in soil after application of pig and cattle slurry," *Biology and Fertility of Soils*, vol. 15, no. 3, pp. 161–164, 1993.

[36] J. W. Paul and E. G. Beauchamp, "Relationship between volatile fatty acids, total ammonia, and pH in manure slurries," *Biological Wastes*, vol. 29, no. 4, pp. 313–318, 1989.

[37] P. Ehlert, J. Nelemans, and G. Velthof, *Stikstofwerking Van Mineralenconcentraten: Stikstofwerkingscoëfficiënten En Verliezen Door Denitrificatie En Stikstofimmobilisatie Bepaald*

Onder Gecontroleerde Omstandigheden. Nitrogen Replacement by Mineral Concentrates, Alterra Wageningen UR, Wageningen, Netherlands, 2012.

[38] P. Chalk and C. Smith, *Chemodenitrification. Gaseous Loss of Nitrogen from Plant-Soil Systems*, pp. 65–89, Springer, Berlin, Germany, 1983.

[39] J. Heil, H. Vereecken, and N. Brüggemann, "A review of chemical reactions of nitrification intermediates and their role in nitrogen cycling and nitrogen trace gas formation in soil," *European Journal of Soil Science*, vol. 67, no. 1, pp. 23–39, 2016.

[40] O. Oenema, G. L. Velthof, S. Yamulki, and S. C. Jarvis, "Nitrous oxide emissions from grazed grassland," *Soil Use and Management*, vol. 13, no. 4, pp. 288–295, 1997.

[41] D. Fangueiro, J. L. S. Pereira, S. Macedo, H. Trindade, E. Vasconcelos, and J. Coutinho, "Surface application of acidified cattle slurry compared to slurry injection: impact on NH_3, N_2O, CO_2 and CH_4 emissions and crop uptake," *Geoderma*, vol. 306, pp. 160–166, 2017.

[42] M. Shaaban, Y. Wu, M. S. Khalid et al., "Reduction in soil N_2O emissions by pH manipulation and enhanced nosZ gene transcription under different water regimes," *Environmental Pollution*, vol. 235, pp. 625–631, 2018.

[43] H. Akiyama, X. Yan, and K. Yagi, "Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N_2O and NO emissions from agricultural soils: meta-analysis," *Global Change Biology*, vol. 16, no. 6, pp. 1837–1846, 2010.

[44] C. Gilsanz, D. Báez, T. H. Misselbrook, M. S. Dhanoa, and L. M. Cárdenas, "Development of emission factors and efficiency of two nitrification inhibitors, DCD and DMPP," *Agriculture, Ecosystems & Environment*, vol. 216, pp. 1–8, 2016.

[45] S. Bittman, D. E. Hunt, C. G. Kowalenko, M. Chantigny, K. Buckley, and F. Bounaix, "Removing solids improves response of grass to surface-banded dairy manure slurry: a multiyear study," *Journal of Environment Quality*, vol. 40, no. 2, pp. 393–401, 2011.

[46] J. J. Schröder, D. Uenk, and W. de Visser, *The Availability of Phosphate from Solid Fraction of Separated Liquid Manure*, Plant Research International, Wageningen, Netherlands, 2010.

[47] P. Sørensen and G. H. Rubæk, "Leaching of nitrate and phosphorus after autumn and spring application of separated solid animal manures to winter wheat," *Soil Use and Management*, vol. 28, no. 1, pp. 1–11, 2012.

[48] W. van Geel, W. van Dijk, and W. van den Berg, *Nitrogen Replacement Value of Mineral Concentrates in Potato: Report of Field Research in 2009 and 2010*, Praktijkonderzoek Plant & Omgeving, Lelystad, Netherlands, 2012.