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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)).

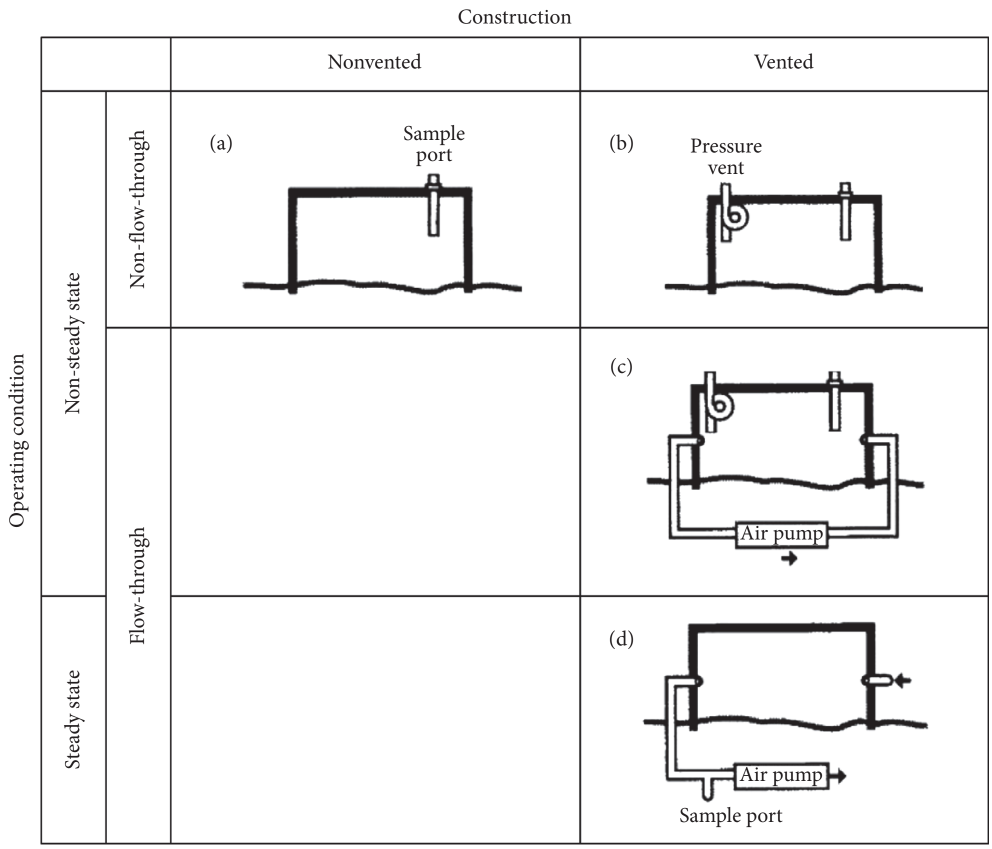


Figure 1: Chambers classification by Matson and Harriss [34].

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

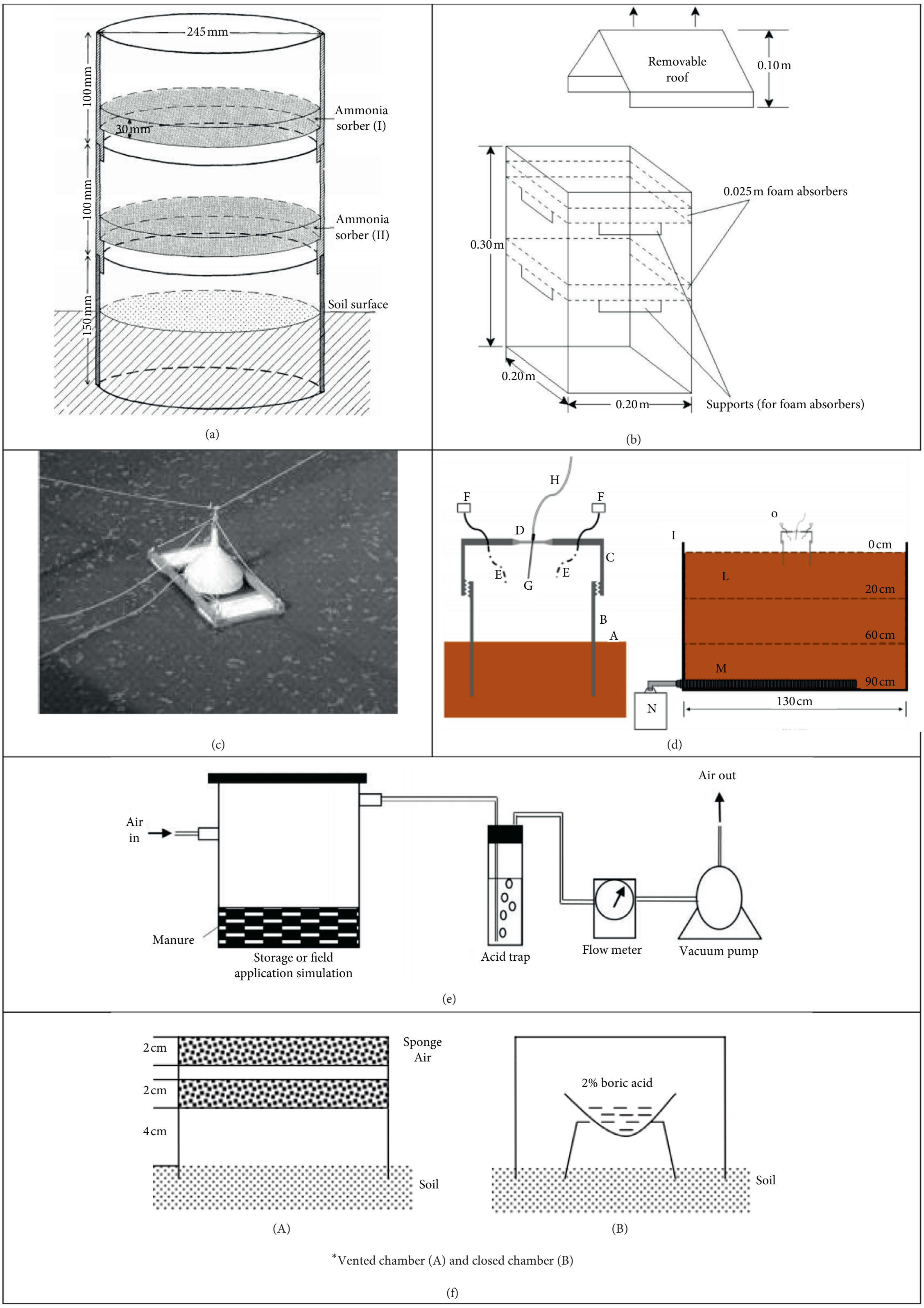


FIGURE 2: Some of the different chamber methods found in the literature. (a) Nômmik [36]. (b) Smith et al. [37]. (c) Balsari et al. [38]. (d) Verdi et al. [39]. (e) Ndegwa et al. [40]. (f) Wang et al. [41].

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

$$F = \overline{w'c'}, \quad (3)$$

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:

$$F = -K\frac{dc}{dz}, \quad (4)$$

Table 2: Main dynamic chambers characteristics and reference studies.

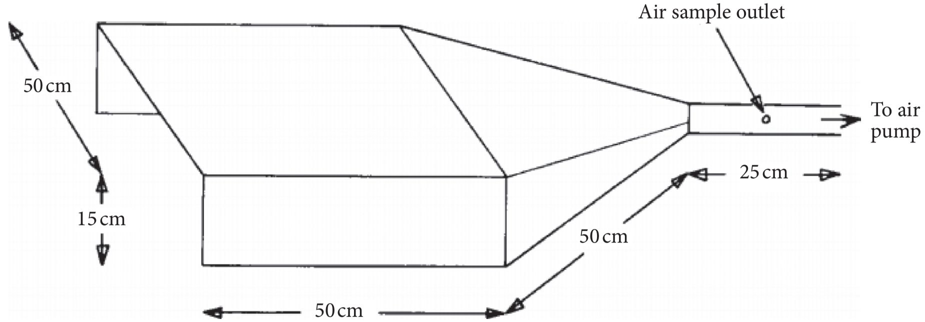
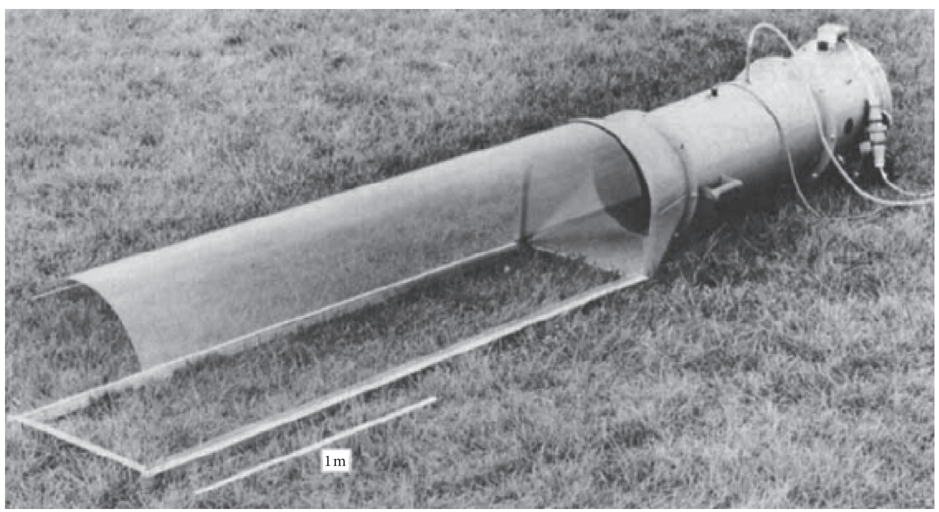
Chamber method	Measurement surface area (m)	Airspeed (m s^{-1})	Chamber characteristics	Pros and cons	Reference
	0.25^2	Variable (0.07 max)	It consisted of a polycarbonate chamber (50 cm by 50 cm) open to one side and the bottom.	(i) Minimizes the temperature and wind speed differences with outside. (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.

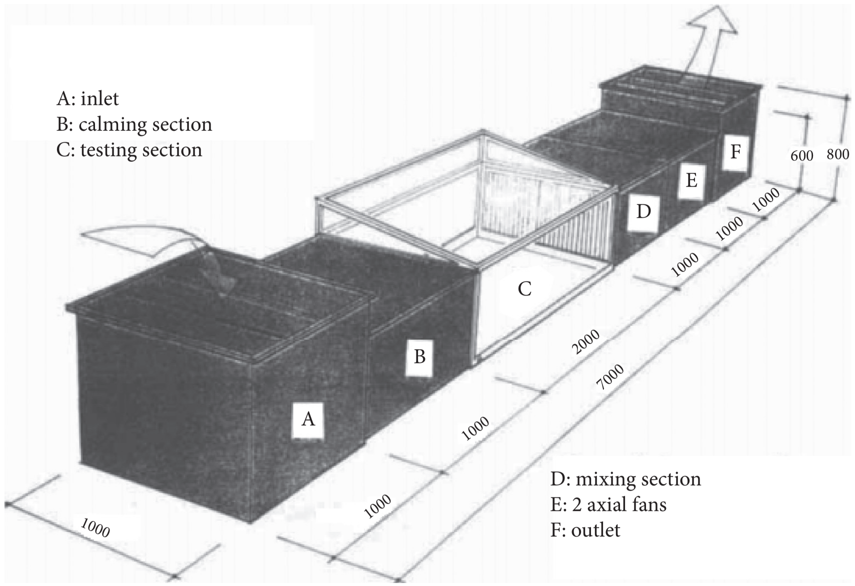
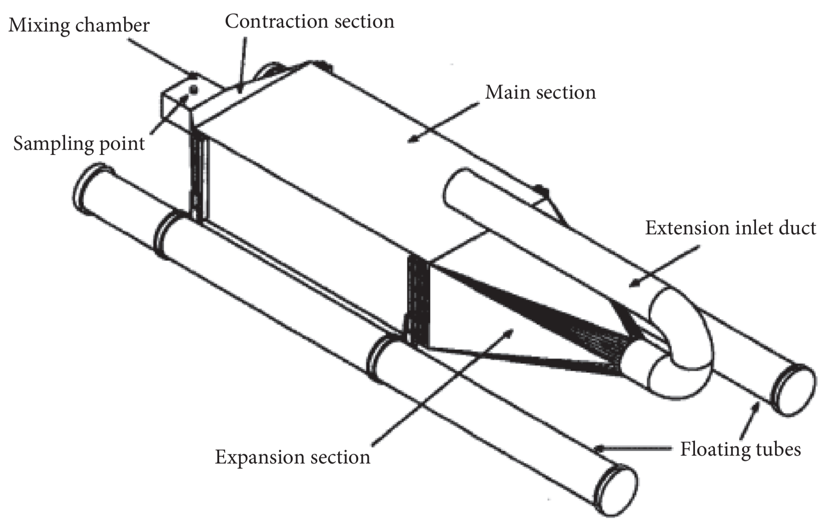
Chamber method	Measurement surface area (m)	Airspeed ($m\ s^{-1}$)	Chamber characteristics	Pros and cons	Reference
	2^2	0.3–3.5	Wind tunnel characterised by 6 following chambers: inlet, calming section, testing section, mixing section, 2 axial fans section, and outlet.	(i) Alteration of microclimatic 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.

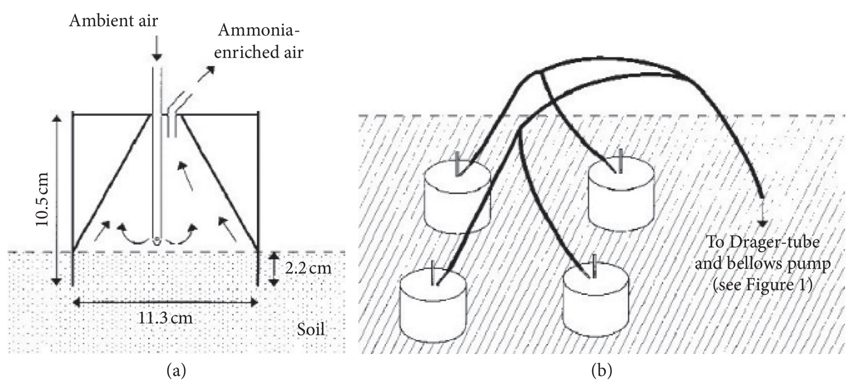
Chamber method	Measurement surface area (m)	Airspeed (m s^{-1})	Chamber characteristics	Pros and cons	Reference
	415^2	Variable	Dynamic chamber characterised by 4 chambers placed onto the emitting surface. Air is sucked from them simultaneously by a pump and the ammonia concentrations are measured by 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:

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

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

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

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	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.	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}		Wind tunnel efficiency could enhance with automatic control of airspeed inside the tunnel, according to ambient wind speed.	
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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