

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/292617137>

NH₃ emissions from land application of manures and N-fertilisers: A review of the Italian literature

Article in *Italian Journal of Agrometeorology* · December 2015

CITATIONS

20

READS

1,304

3 authors:



Sara Minoli

Climate Focus

30 PUBLICATIONS 1,525 CITATIONS

SEE PROFILE



Marco Acutis

University of Milan

263 PUBLICATIONS 4,909 CITATIONS

SEE PROFILE



Marco Carozzi

French National Institute for Agriculture, Food, and Environment (INRAE)

70 PUBLICATIONS 1,119 CITATIONS

SEE PROFILE

NH₃ emissions from land application of manures and N-fertilisers: a review of the Italian literature

Sara Minoli,^{a,c,*} Marco Acutis^a, Marco Carozzi^b

Abstract: *One of the major pathways of nitrogen (N) loss from agricultural systems is represented by ammonia (NH₃) volatilisation. At the global scale, soil application of livestock manures and N-fertilisers represents one of the main sources of this atmospheric pollutant. A literature review was carried out over 78 field trials in order to collect and summarise the research on NH₃ emission from land application of manure and N-fertiliser in Italy. Data availability proved to be still limited in terms of coverage of the national territory, representativeness of the measurement method used, type of fertiliser and application strategies explored. Coherently with their importance as NH₃ emission sources, livestock manures and urea have been the most assessed materials. From a methodological perspective, the measurements were mostly performed on non-representative scales and the collected data present large weaknesses due to lacking information on the variables that regulate losses of this gas to the atmosphere. The measured emission factors (EFs) have proved to be consistent with the ranges reported by international literature, showing appreciable differences in magnitude among manures and synthetic N-fertilisers and among different field management practices. This is supported by the ALFAM model estimation, which has also shown a strong dependency upon the simulated measurement methods. The reviewed EFs for the different type of fertilisers were compared with the values used by the European and Italian emission inventories. Despite the agreement between these values, our analysis emphasized that the reviewed EFs cannot be regarded as representative for the national territory, mainly because of inconsistencies in the measurement methods.*

Keywords: *ammonia, emission factors, fertilisers management, measurement methods, mitigation strategies, emission inventories.*

Riassunto: *Una delle principali vie di perdita di azoto dai sistemi agricoli è rappresentata dalla volatilizzazione dell'ammoniaca (NH₃). A scala globale, l'applicazione di effluenti di allevamento e di fertilizzanti azotati, rappresenta una delle maggiori sorgenti di questo inquinante atmosferico. In questo studio è condotta una revisione di 78 esperimenti in pieno campo, con l'obiettivo di raccogliere e riassumere la ricerca sui fattori di emissione (EFs) di NH₃ da suoli agricoli, in Italia. La disponibilità di dati si è dimostrata essere limitata, in termini di copertura del territorio nazionale, rappresentatività dei metodi di misura utilizzati, tipologie di fertilizzanti e strategie di applicazione indagate. Coerentemente con la loro importanza come sorgenti di emissione di NH₃, gli effluenti di allevamento e l'urea sono stati i materiali maggiormente indagati. Da un punto di vista metodologico, le misure sono state per lo più effettuate su scale non rappresentative e i dati raccolti presentano ampi punti di debolezza, a causa di informazioni carenti sulle variabili che regolano le perdite di questo gas verso l'atmosfera. I fattori di emissione misurati sono risultati coerenti con gli intervalli di valori riportati dalla letteratura internazionale, mostrando differenze quantitativamente apprezzabili tra effluenti zootecnici e fertilizzanti azotati di sintesi e tra differenti pratiche gestionali. Ciò è supportato dalle stime del modello ALFAM, che ha inoltre mostrato avere una forte dipendenza dai metodi di misura simulati. Gli EFs revisionati per i diversi tipi di fertilizzanti sono stati confrontati con i valori utilizzati dagli inventari di emissione europei ed italiani. Nonostante l'accordo tra questi valori, la nostra analisi ha messo in rilievo che gli EFs revisionati non possano essere considerati rappresentativi per il territorio nazionale, principalmente a causa di incongruenze nei metodi di misura.*

Parole chiave: *ammoniaca, fattori di emissione, gestione dei fertilizzanti, metodi di misura, strategie di mitigazione, inventari delle emissioni.*

* Corresponding author's e-mail: sara.minoli@pik-potsdam.de

^a DiSAA, Department of Agricultural and Environmental Sciences, University of Milan, Milan, Italy.

^b INRA, INRA-AgroParisTech, UMR 1402 ECOSYS, Ecologie fonctionnelle et écotoxicologie des agroécosystèmes, Thiverval-Grignon, France.

^c now at: PIK, Potsdam Institute for Climate Impact Research, Research Domain Climate Impacts & Vulnerabilities, Potsdam, Germany.

Received 20 December 2014, accepted 27 July 2015

1. INTRODUCTION

Nitrogen (N) is an essential compound for the growth of most living organisms and it is a limiting factor in addressing the increasing food production demand. In the second half of the XIX century this has led to the discovery of how to synthesise reactive N forms (Nr: organic bound N and inorganic N compounds, except N₂), in order to produce agricultural fertilisers. Since the production of Nr

has been increasing rapidly, outgrowing the rate of Nr conversion back to unreactive N₂, Nr started accumulating in natural systems (Galloway *et al.*, 2003; Erisman *et al.*, 2007; Zavattaro *et al.*, 2012). Nowadays, the amount of Nr used for food production is estimated to be 10 times higher than the real needs, due to inefficiencies in different processes which cause environmental negative externalities (Erisman *et al.*, 2013). Nr is widely dispersed by hydrologic and atmospheric transport processes, subsequently transformed and accumulated in the environment. This results in detrimental effects on human health (WHO, 2005) and ecosystems degradation (Galloway *et al.*, 2003).

One of the major pathways of Nr losses from agricultural systems is ammonia (NH₃) volatilisation (Beusen *et al.*, 2008; Sutton *et al.*, 2011; Amann *et al.*, 2013). Globally, the areas with the highest emission rates per square meter are located in Europe, in the Indian subcontinent and in eastern China (Clarisse *et al.*, 2009). The source densities are strictly related to the livestock distribution and to the intensity of synthetic N-fertilisers use. This is due to the volatilisation that evolves from the microbial breakdown of N-organic compounds to ammonium (NH₄⁺) in animal excreta, soil and litter, as well as directly from synthetic N-fertilisers application to crops, or indirectly through the plant canopy (Bouwman *et al.*, 1997; Massad *et al.*, 2008; Sutton *et al.*, 2013). According to Beusen *et al.* (2008) most of the global emissions from livestock production come from animal housing and manure storage systems (31-55%), from the spreading of animal manures (23-38%) and from grazing (17-37%). Manure and N-fertilisers cover the major part (approximately 56%) of the total NH₃ global emissions from the planetary surface, estimated to be 65.4 Tg N yr⁻¹ for 2008 (Sutton *et al.*, 2013). These sources produce so called "hot spots" of NH₃ emissions, since the volatilisation process usually concerns small emitting surfaces or extinguishes rapidly especially during field manure application. Within the Italian context, the Northern Regions (Lombardy; Veneto; Emilia-Romagna; Piedmont) are characterised by the presence of intensively managed agriculture and high livestock densities (2.8; 1.7; 1.2; 1.0 LSU·haUAA⁻¹, respectively) usually above the European average of 1.0 LSU·haUAA⁻¹ (EUROSTAT, 2007). These activities are mostly localised in the Po Plain, which makes this land one of the most relevant NH₃ emitting sources in Europe (Clarisse *et al.*, 2009).

Once emitted from the earth's surface, NH₃ is absorbed by plants' leaves, dry deposited near the

source of emission, dissolved in atmospheric water forming NH₄⁺, or readily reacts with atmospheric acids such as H₂SO₄, HCl and HNO₃ (Mosier, 2001; Krupa, 2003; Renard, 2004). These reactions affect human health, the earth's radiation budget (Schimel *et al.*, 1996) and precipitation, serving as cloud condensation nuclei (Renard, 2004). In the soil, NH₃ becomes a nutrient input for the ecosystems, playing an important role in N-induced species diversity alteration processes and contributes to soil acidification (Krupa, 2003). Finally, from an agronomic perspective, volatilisation of NH₃ from fertilisers is one of the main causes of the low crop N use efficiency, as referred to the ratio between N uptake by plants and the N applied to the field by the fertilisation (Bouwman *et al.*, 2002).

1.1. Emission inventories

Due to its negative effects on health and environment, NH₃ has become object of scientific research and regulatory policies in order to reduce and prevent air pollution at country level and cross-borders. The Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (Gothenburg Protocol, 1999), amended in 2012, introduced emission reduction commitments by 2020 for multiple pollutants including NH₃. EU Member States have to reduce their total NH₃ emissions by 6% (Italy 5%) with respect to 2005 levels, and are obliged to report annual inventories on the pollutant emissions.

The most acknowledged inventories on air pollutants are the data reported by the Member States under the United Nations Economic Commission for Europe (UNECE; 2012) Convention on Long-range Transboundary Air Pollution (CLRTAP) and the EU National Emission Ceilings Directive (NECD). These inventories are based on the EMEP/EEA (European Monitoring and Evaluation Programme of the European Environment Agency, 2013) guidebook.

The guidebook defines the guidelines to calculate the NH₃ emission factors (EF) from different agricultural sources on the base of the available data and the characteristics of the emission sources themselves. These include livestock manure management (including field application), synthetic fertilisers application, soil and crop foliage. The EF is then defined as the cumulative N-NH₃ loss expressed as the percentage of applied total ammoniacal nitrogen (TAN) content for the manures or of applied total nitrogen (TN) for the fertilisers.

As a party of the UNECE/CLRTAP, Italy has to submit annually data on air pollutant emissions in order to fulfil the expected obligations. The national

emission inventory is compiled by the Institute for Environmental Protection and Research (ISPRA) following the EMEP/EEA guidelines. In the last informative inventory report by ISPRA (Romano *et al.*, 2014), NH₃ emissions from the agriculture sector were estimated to be 386 Gg (95% of national emissions). The key categories identified for NH₃ emissions are manure management, accounting for emissions from spreading, and agricultural soils, in which emissions from synthetic fertilisers are included. These two categories represent 73% and 22% of total national emissions respectively; the remaining 5% mainly originates from road transport, waste treatment and industries (Romano *et al.*, 2014). According to Córdor *et al.* (2008) four regions (Lombardy; Emilia-Romagna; Veneto; Piedmont) contribute to most of the NH₃ emissions from cattle, pig and poultry manure field application, while the largest emissions from pastures come from grazing sheep, most of which are present in the Sardinia, Lazio, Campania and Sicily regions. Essentially the estimation procedure to determine the NH₃ releases from manure management derives from the quantification of the N excreted annually for different livestock categories. This quantity is divided in two different fluxes depending on whether animals are bred indoors (housing, storage and manure application) or outdoors (grazing). Emissions from synthetic N-fertilisers are obtained by the specific EFs for different types of fertiliser. A detailed description of the methodology can be found in Córdor *et al.* (2008), Córdor (2011) and Romano *et al.* (2014).

Agricultural NH₃ emissions inventories have been mainly used in order to identify the major sources, but a detailed and accurate quantification of NH₃ emissions from hot spot sources, assumes a key role in defining environmental priorities and providing recommendations for implementing effective policies. Indeed it is important to get better knowledge of the factors driving NH₃ volatilisation, to be able to predict the emissions and the chemical transformations of NH₃ in the environment, to produce detailed emission factors for inventories, as well as to assess agricultural production processes' impact (e.g. by Life Cycle Analysis; Meier *et al.*, 2014) and to promote abatement strategies. Furthermore, emissions quantification should be as accurate as possible in order to reduce uncertainties in the global scale estimation. To achieve accurate estimates the effect of fertiliser characteristics, of different agrotechniques, as well as of different meteorological variables, should be assessed starting from direct measurement approaches (Ellis *et al.*, 2010; Sintermann *et al.*, 2011a; Velthof *et al.*, 2012).

1.2. Measurement methods

To date several techniques have been employed to quantify the exchange of trace gases like NH₃, between land surfaces and the atmosphere (McGinn and Janzen, 1997; Misselbrook *et al.*, 2005; van Bobruzki *et al.*, 2010). Each of these has a specific scale of application and working principle. The most applied approaches could be classified into three different methods: enclosure methods, micrometeorological methods and concentration based inverse-dispersion modelling.

Enclosure methods are based on the principle of measuring the changes in the concentration of a trace gas within a chamber that isolates an air volume above the soil surface. Chambers could be classified as static or dynamic depending on the absence or the presence of air exchange over time inside the volume. A particular type of dynamic chamber often used for NH₃ measurement is the wind tunnel (Lockyer, 1984; Sommer *et al.*, 1991). It consists of an upside-down U-shaped plastic shield facing the emission source and the flow of incoming air perpendicular to the NH₃ flux. Fluxes are computed by measuring concentration of NH₃ in the air entering and leaving the tunnels. The funnel system is another type of dynamic chamber developed by Balsari *et al.*, (1994), consisting of a reverse funnel covering a surface of approximately 0.1 m². As in the wind tunnel system, a controlled air flow passes through the system and to an acid solution able to trap NH₃. The concentration is later determined by titration. The principal advantages of the enclosure methods are their general low cost, easy application and the opportunity to afford simultaneous comparative studies with many treatments. On the other hand, chambers are not well-suited to take into account the complexity and the spatial variability of the emitting sources. This is due to the limited surface area on which the measurement occurs, the alteration of the surrounding microclimatic variables and the reactivity of the NH₃ molecule (Whitehead *et al.*, 2007) that interferes with the structures and devices (Denmead, 2008; Sintermann *et al.*, 2012).

Micrometeorological methods rely on physical principles that govern the exchange of mass and energy across land and atmosphere, which are driven by the turbulent movements in the boundary layer. These methods are mainly represented by the eddy covariance and the aerodynamic gradient, in which the flux of gas is vertically measured over an emitting surface. Eddy covariance is based on the direct measurement of the turbulent motions (eddies) responsible for vertical transport of scalars

(Stull, 1988). In order to account for all the sizes of these motions a fast-response sensor is required (Ferrara *et al.*, 2012). The aerodynamic gradient is an alternative method used to determine the flux where fast response sensors are unavailable. In this method the flux is calculated by measuring the vertical concentration gradient of the gas and the coefficient of turbulent diffusion. Therefore, it requires measures of concentration at different heights above the upwind emitting area, as well as the knowledge of turbulent parameters (Denmead *et al.*, 1977; Sutton *et al.*, 1993). The micrometeorological mass-balance integrated horizontal flux (Denmead *et al.*, 1977) is a technique often used to measure NH₃ emission from an emitting source. This technique equates the vertical flux of the gas from the source area of limited upwind extent with the net integrated horizontal flux at a known downwind distance from the source. Compared to the other two, this method requires smaller experimental plots, wind dominancy and regular shaped sources. For a detailed overview of these methods refer to Baldocchi (1988), Moncrieff *et al.* (1997), McGinn and Janzen (1997). Micrometeorological techniques are more expensive and complex than enclosure methods and require homogeneous source strength. They do not disturb the micro-environment above the emitting source, can integrate big surfaces and allow continuous measurements.

Finally, concentration based inverse-dispersion models are acknowledged as useful tools to estimate gaseous fluxes from one or multiple emitting sources. The principle is to measure the gas concentration downwind from a source in order to infer the source strength itself on the basis of high frequency wind measurements and the shape of the source (Flesch *et al.*, 2004). The main advantages are the low cost, the opportunity to estimate fluxes at different scales and with multiple sources and not perturbing the environment in which emissions occur (Flesch *et al.*, 1995; Loubet *et al.*, 2010; Loubet and Carozzi, 2015). The disadvantages are the low temporal resolution in the flux description and the high uncertainties associated to long integration periods.

The purpose of this paper is to evaluate the current state of knowledge of NH₃ emissions from manure and N-fertiliser application in the Italian agricultural lands by reviewing the available literature. The target is to present and summarise measured emission factors obtained by field experimental trials, the explored fertiliser types, the management

practices, the field conditions and the applied measurement methods. An evaluation of the extent and quality of the reported data, a comparison between Italian and European experiences based on measures, estimates and inventory indications are also provided.

2. METHODOLOGY

A literature review was carried out with the aim to collect and summarise the research on NH₃ emissions from fertilised agricultural soils in Italy. Data were collected from different sources: peer reviewed journals, international conference proceedings and technical reports. Only the studies reporting data about direct measurement from organic or synthetic N-based fertilisers, and for which EF were available or computable, were accounted for in the current survey. Moreover, we considered only studies carried out in open field trials, excluding those experiments conducted in the laboratory. This is because lab-trials take into account only a limited number of factors affecting NH₃ emission and the artificial conditions often created in confined environment can seriously influence the validity of the results. Conversely, even if field trials are often characterised by uncontrollable forces, they have the advantage of quantifying the emissions to the atmosphere more realistically.

A summary of the literature reporting the results of the trials carried out in Italy and published since 1994 is reported in the Appendix 1. We found 11 papers for a total of 78 trials reported in peer reviewed journals (63 trials), scientific technical reports (10 trials) and conference proceedings (5 trials), which met our minimum information requirements. Some papers have not been accounted for in the survey since they did not report all the necessary information, for example fertiliser characteristics (Gioelli *et al.*, 2004; Balsari *et al.*, 2006), or because they reported a different data analysis on the same datasets of other papers (Carozzi *et al.*, 2012b, 2013c; Ferrara *et al.*, 2010; 2012) or reported results of laboratory trials (Pedrazzini and Tarsitano, 1986; Rossi and Rossi, 1987; Miele *et al.*, 1990; Dinuccio *et al.*, 2011). Information about experiment location, time period and experimental conditions have been collected. Particularly we focused on the relevant factors influencing the NH₃ volatilisation process from fertiliser application:

- Soil conditions: water content, pH, surface coverage, texture;
- Meteorological conditions: air temperature, wind speed;

- Fertiliser characteristics: nature (animal, vegetal or synthetic), form, chemical characteristics (TN, TAN, pH, dry matter (DM) content);
- Fertiliser application technique: spreading technique, incorporation;
- Application rate (volume and N amount).

Measurement units and nomenclature were harmonised in order to enable direct comparison between different studies. Note that some features, where available, are referred to manures only (TAN, pH, DM, volume) and not reported for synthetic fertilisers which are considered of standard composition. In addition, we recorded the various techniques used to measure the NH_3 emissions and the associated trial scale (i.e. small plot, field-scale). When not directly provided by the authors the EFs in term of %TAN were computed on the base of the available data about fertiliser features and applied amount.

Furthermore, the EFs obtained from cattle and pig slurry were compared to the estimates produced by the ALFAM regression model (Søgaard *et al.*, 2002), accordingly to the characteristics of each field trial. The agreement between measured and estimated values was then assessed and used to describe the dataset features and to critically examine the consistency of the Italian trials results. The following indexes were used to assess the measured and modelled data: the relative root mean square error (RRMSE; Jørgensen *et al.*, 1986) (min. 0, max. $+\infty$, best 0), the model efficiency (E; Nash and Sutcliffe, 1970) (min. $-\infty$, max. 1, best 1), the coefficient of residual mass (CMR; Loague and Green, 1991) (min. $-\infty$, max. $+\infty$, best 0), the coefficient of determination of the linear regression (R^2 ; min. 0, max. 1, best 1) and the slope of the linear regression (b; min. $-\infty$, max. $+\infty$, best 1). This analysis was not performed for other organic fertiliser, nor for synthetic N-based fertilisers, because regression models for these materials are not yet available. Finally, to complete our survey, we also looked at the EFs reported by the reference inventories.

2.1. The ALFAM model

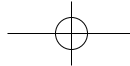
This model derives from multiple non-linear regression on over 800 experiment datasets provided by 13 institutes and 7 European countries (Denmark, Italy, the Netherlands, Norway, Sweden, Switzerland and UK; www.alfam.dk). The kinetic that underlies the volatilisation phenomenon is described by means of a Michaelis–Menten equilateral hyperbole, where the quantity of cumulative NH_3 loss is affected by most of the factors reported above (soil moisture, air tem-

perature, wind speed, slurry nature, TAN and DM, application technique and measurement method). The strength of this model is that it is based on a large dataset, it considers many variables affecting the volatilisation phenomena and can be used by means of a simple collection of experimental data. The selected literature dataset for cattle and pig slurries were used to set up and run the ALFAM model. Since the available information was not always consistent with the variables requested by the model, we filled missing values with assumptions. Particularly, the settings for the initial soil moisture conditions are limited to two available options (“dry” or “wet”), but the model documentation (Søgaard *et al.*, 2002) does not provide reference values or thresholds to define the soil moisture state. Thus, the initial soil moisture was arbitrarily assumed to be “dry” instead of “wet”. The reason behind this choice is that all the field operations, like fertilisation, are commonly carried out with soil water content under the field capacity. Wind speed is usually reported since all type of measurement methods need to determine this information; consequently, for enclosure methods, we used null value or the air velocity within the chamber or wind tunnel. ALFAM also requires specifying the application techniques and measurement methods. Manual application of slurry was classified into the group of surface spreading techniques. For the measurement method we classified inverse-dispersion modelling into the micrometeorological methods group, since it is based on high frequency wind statistics for the so called surface layer of the atmosphere. The funnel system was grouped with the dynamic chambers because of the functioning system principle.

3. RESULTS

3.1. Characteristics of the literature dataset

Our survey reveals that the experiments were carried out only in four administrative Regions (Piedmont, Lombardy and Emilia-Romagna, in Northern Italy, and Apulia in Southern Italy), although the information about the location of the experiments was not always reported in the papers (i.e. Balsari *et al.*, 2008; 2009). Autumn and spring are the periods in which most of the experiments were performed, corresponding to the usual periods where tillage bedding operations occur for autumn-winter and spring-summer growing crops. Reported data have been collected over a quite large array of soil conditions, with regard to soil texture and pH, and soil surface coverage. Regarding all the



Fertiliser	Type	Meas. Method		
		Enclosure methods	Inverse-dispersion models	Micrometeorological methods
Cattle	slurry	12	6	-
	solid manure	8	-	-
Pig	slurry	21	-	-
	solid manure	8	-	-
Poultry	solid manure	4	-	-
Green manure		-	-	2
Urea		15	2	-
Total		68	8	2

Tab. 1 - Number of trials sorted on the base of the fertiliser type and the measurement method used to quantify NH_3 losses.
Tab. 1 - Numero di prove ordinate sulla base del tipo di fertilizzante e del metodo di misura utilizzato per quantificare le perdite di NH_3 .

measurements, 12% were performed on bare soil or crop residues, while 82% were carried out during the cropping season; the remaining 6% was unspecified by the authors.

An overview of the measurement methods used to quantify NH_3 losses is reported in Tab. 1. In the database collected, micrometeorological methods (e.g. aerodynamic gradient) and inverse-dispersion modelling are less often used than enclosure methods (wind tunnel, static chambers, dynamic chambers and funnel system). Correspondingly, most of the experiments have been carried out on small plots, which represent 87% of the total, while only a few datasets were collected under real operational field-scale conditions. This is notable for instance, looking also at the applied N load. In fact there is a clear difference in the N amounts between field-scale and small plot experiments, that are on

average equal to $186.4 \text{ kg N ha}^{-1}$ (range $103.4\text{-}274.3 \text{ kg N ha}^{-1}$) for field-scale and $70.5 \text{ kg N ha}^{-1}$ (range $10.4\text{-}120.0 \text{ kg N ha}^{-1}$) for the small plots (see Appendix 1).

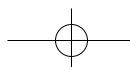
The most scrutinised materials were organic fertilisers, particularly pig and cattle manures, in both solid and slurry forms. These two organic materials represent 71% of the reviewed trials and have only been studied in the three northern regions. Other investigated materials were poultry manure, green manure and urea. Average characteristics of animal manures reported in the reviewed papers are summarised in Tab. 2.

In most of the experiments (65%) the fertiliser has been manually distributed, while 26% report application by tractors, such as surface spreading (15 trials), trailing hose (4 trials), direct injection (1 trial). In the same way the soil cultivation after

Fertiliser	Type	n	TAN [g kg^{-1}]	TN [g kg^{-1}]	pH	DM [%]
			Mean	Mean	Mean	Mean
Cattle	slurry	18	1.7 (0.4)	3.1 (0.6)	7.6 (0.3)	5 (1)
	solid manure	8	1.6 (0.2)	4.9 (0.2)	8.5 (0.3)	22 (1)
Pig	slurry	21	2.3 (0.5)	3.3 (0.7)	7.8 (0.2)	3 (1)
	solid manure	8	2.6 (0.7)	6.7 (0.6)	8.3 (0.1)	25 (3)
Poultry	solid manure	4				31 (3)

Tab. 2 - Mean characteristics of animal manures reported in the reviewed papers. The standard deviation is reported in brackets, while n represents the number of the experiments. TAN is the Total Ammoniacal Nitrogen content, TN represents the Total Nitrogen content and DM is the dry matter content of the material. TAN and TN are expressed per kg of fresh matter.

Tab. 2 - Caratteristiche medie degli effluenti zootecnici riportati negli articoli revisionati. La deviazione standard è riportata tra parentesi, mentre n rappresenta il numero degli esperimenti. TAN è il tenore totale in azoto ammoniacale, TN rappresenta il tenore di azoto totale e DM è la sostanza secca del materiale. TAN e TN sono espressi per kg di sostanza tal quale.



distribution has not been practiced or not specified (68 trials), while in 5 trials, specific cultivation techniques (ploughing, harrowing) have been detailed (Carozzi *et al.*, 2013b).

3.2. Emission factors

The full dataset reveals large variability of the measured EFs. The average EF among all trials is approximately 25.1% of the applied TAN (median 19%; standard deviation 25.8%; range 1.8-127.6%; Q_1 5.5%; Q_3 29.7%). It is important to note that, when considering manures or slurries, NH_3 losses are usually referred to the TAN applied, since this represents the portion of N that is immediately susceptible to loss. This is not the case of urea, for which NH_3 losses are referred to the total N applied, since the entire N content of this fertiliser is in the form of an organic molecule ($CO(NH_2)_2$).

Fig. 1 shows the distributions of the EF per fertiliser type and the number of experiments. Pig and cattle slurries exhibit the largest EF variability with also some potential outliers, which represent extreme

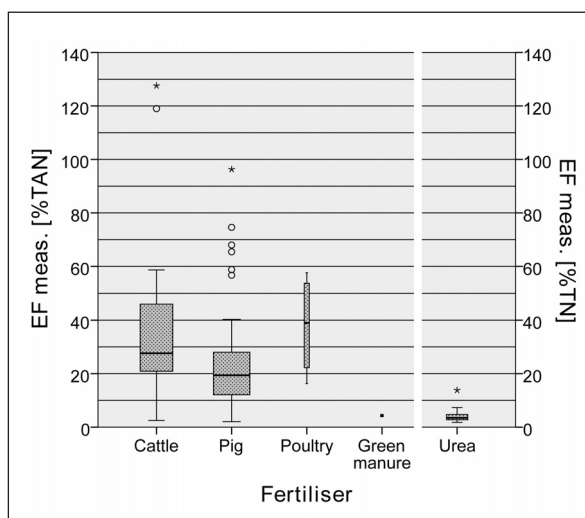


Fig. 1 - Distributions of the emission factor (EF) in function of the type of fertiliser. Dots and stars represent potential outliers, since their value is equal to more than 1.5 times the interquartile range away from the top or bottom of the box. The width of each boxplot is a function of the number of the experiments for each material. TAN is the total ammoniacal nitrogen of the organic fertilisers; TN is the total nitrogen of urea.

Fig. 1 - Distribuzione del fattore di emissione (EF) in funzione del tipo di fertilizzante. Punti e asterischi rappresentano potenziali outliers, distanziandosi dal limite superiore o inferiore del corpo della scatola, di un valore superiore a 1.5 volte la distanza interquartile. L'ampiezza di ogni boxplot è funzione del numero di prove per ciascun fertilizzante. TAN è l'azoto ammoniacale totale dei fertilizzanti organici; TN è l'azoto totale dell'urea.

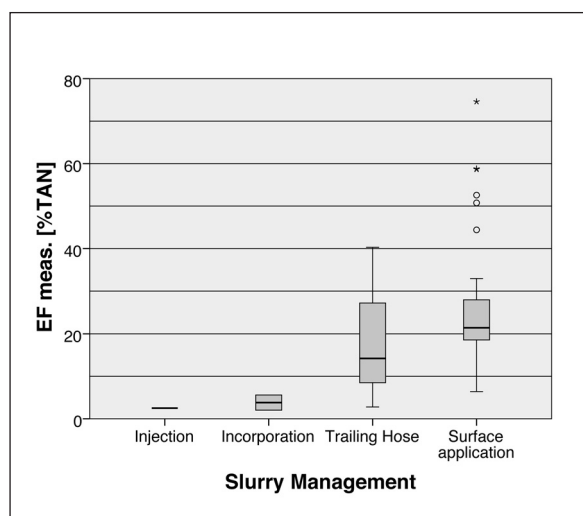


Fig. 2 - Overall effect of the fertiliser management on cattle and pig slurry emission factor (EF). The “incorporation” category involves only contextual incorporated fertilizer; surface application category comprehends mechanised, manual surface spreading and unspecified techniques. TAN is the total ammoniacal nitrogen.

Fig. 2 - Effetto generale della gestione dei liquami bovini e suini sul fattore di emissione (EF). La categoria “incorporation” tiene conto solo dell’incorporazione contestuale del fertilizzante; la categoria “surface application” comprende la distribuzione superficiale meccanizzata, manuale e le tecniche non specificate. TAN è l’azoto ammoniacale totale.

values in comparison with the series frequency distribution, e.g. obtained by Gioelli *et al.*, (2006) and Dinuccio *et al.*, (2012) from solid pig manures; by Valli *et al.*, (2003) from pig slurry; by Gioelli *et al.*, (2006) from cattle fertilisers. All of these values were measured on small plot scale, by means of enclosure methods and are characterised by the absence of soil cultivation after spreading and a moderately alkaline soil pH (unspecified in Valli *et al.*, 2003).

Cattle and pig slurry data were also classified in four categories following the soil application management (injection, incorporation, trailing hose and surface application) and analysed in order to identify the average effect on NH_3 cumulated emissions (Fig. 2). Although data were collected over unequal numbers of trials and there is high variability within each group, reduction management techniques, such as injection, incorporation and trailing hose, apparently have a reliable effect in lowering NH_3 emissions in comparison with surface application. In fact, we found reductions in EFs of 91%, 86% and 28% of the TAN, for injection, incorporation and trailing hose, respectively.

The EFs resulting from the application of the ALFAM model are reported in Appendix 1. These values are also plotted against the respective

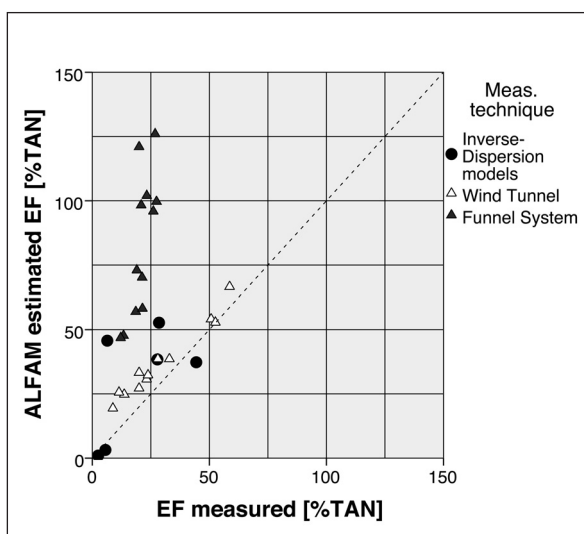


Fig. 3 - Cattle and pig slurry measured emission factor (EF) plotted against the ALFAM model results. Data are classified on the base of the measurement technique applied: inverse-dispersion models, wind tunnel, funnel system. TAN is the total ammoniacal nitrogen.

Fig. 3 - Fattori di emissione misurati da liquami bovini e suini, rappresentati contro i risultati del modello ALFAM. I dati sono classificati sulla base della tecnica di misurazione applicata: modelli di dispersione inversi, wind tunnel, funnel system. TAN è l'azoto ammoniacale totale.

measured values in Fig. 3, distinguishing them by the measurement technique used (inverse-dispersion model, wind tunnel, funnel system). Tab. 3 reports model performance indexes for the overall dataset, as well as sorted on the basis of the measurement technique.

To compare the values of the EFs reported by inventories (EMEP/EEA; ISPRA), a screening of the results obtained in the reviewed trials for different animal manures applied on field surface by tractors or by manual application, are summarised in Tab. 4. These values were computed taking into account all those EFs obtained from

trials where soil cultivation did not occur or occurred 24 hours after spreading, in order to match the values reported by the inventories. Indeed there is evidence that to be an effective abatement technique, cultivation should occur as soon as possible, within the first few hours after surface application, otherwise this operation is not able to mitigate the volatilisation phenomena that reach more than 90% of total losses in the first 24 hours (Sommer and Hutchings, 2001; Huijsmans *et al.*, 2003; Carozzi *et al.*, 2013a).

The only synthetic fertiliser tested in Italy for NH_3 emissions is urea. Two trials were carried out at field-scale both on a growing crop in Northern and in Southern Italy (Carozzi *et al.*, 2012a; Ferrara *et al.*, 2014). All the other trials (total $n=15$) were the object of comparative emission studies on small plots by static chamber technique, in order to test the effect of urea additive substances like urease and nitrification inhibitors (Nastri *et al.*, 2000). Statistics of EF obtained for all the trials testing urea, expressed in % of the applied N, are the following: mean 4.4%, minimum and maximum, 1.8% and 13.8%, standard deviation of 2.9%). It should be underlined that the maximum value of EF was obtained after three consecutive fertiliser applications during the same field trial in a dry environment, reported in Ferrara *et al.* (2014).

4. DISCUSSION

Our literature review revealed that data availability on NH_3 emissions from the application of livestock manures and N-fertilisers for Italian agriculture is still limited, in terms of coverage of the national territory, representativeness of the measurement method used, type of fertiliser explored and application strategies tested. Moreover, the information available or deducible from the conducted experiments is in some cases lacking in quality and in data reporting.

Dataset	RRMSE	E	CRM	R ²	b
Inverse dispersion modelling	102.0	-0.6	-0.5	0.4	0.8
Wind tunnel	32.1	0.7	-0.3	1.0	0.8
Funnel system	318.3	-206.6	-3.0	0.6	4.3
Overall	183.0	-9.6	-1.3	0.1	0.6

Tab. 3 - ALFAM model performance indexes, differentiated for the different measurement techniques simulated. RRMSE is the relative root mean square error, E is the model efficiency, CRM is the coefficient of residual mass, R² is the coefficient of determination of the liner regression, b is the slope of the linear regression.

Tab. 3 - Indici di performance del modello ALFAM differenziate per le diverse tecniche di misura simulate. RRMSE è l'errore quadratico medio relativo, E esprime l'efficienza di modellazione, CRM è il coefficiente di massa residua, R² è il coefficiente di determinazione della regressione lineare, b è la pendenza della regressione lineare.

Fertiliser	Type	EF meas. [%TAN]				
		Minimum	Maximum	Mean	EMEP	ISPRA
Cattle	slurry	6.4	58.7	30.4 (14.1)	55	37
	solid manure	18.5	127.6	55.4 (43.2)	79	65
Pig	slurry	7.7	74.6	23.1 (17.5)	40	24
	solid manure	5.4	96.3	42.2 (33.7)	81	-
Poultry	solid manure	49.8	57.6	53.7 (5.5)	66-69	63-67

Tab. 4 - Statistics of the emission factors (EFs) obtained for cattle, pig and poultry manures applied by surface spreading or manually distributed to the field and the corresponding EF reported by EMEP/EEA (Cooperative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) guidebook (2013) and ISPRA (Italian Institute for Environmental Protection and Research) inventory (2014). Standard deviation is reported in brackets.

Tab. 4 - Statistiche dei fattori di emissione (EFs) ottenuti per gli effluenti bovini, suini e avicoli applicati superficialmente o manualmente distribuiti sul campo e l'EF corrispondente riportato dalle linee guida EMEP/EEA (programma di monitoraggio e valutazione del trasporto a lunga distanza degli inquinanti atmosferici in Europa; 2013) e dall'inventario ISPRA (Istituto Italiano per la Protezione e la Ricerca Ambientale; 2014). La deviazione standard è riportata fra parentesi.

Most of the published trials occurred in three North Italian regions, which represent the areas where most of the national livestock load is reared (51% of bovines, 76% of pigs and 39% of poultry; ISTAT, 2010) and which are characterised by intensive agriculture. Given the importance of the Po basin as one of the most relevant emitting sources in Europe (Clarisse *et al.*, 2009), it is then consistent to have the greatest number of experiments carried out in these regions, especially those that are directed to measure emissions for manure field management. Nevertheless, synthetic N-fertilisers are also largely applied to soils here (Bouroufi *et al.*, 2009), but only a few studies have tested NH_3 losses from these materials (Nastri *et al.*, 2000; Carozzi *et al.*, 2012a). Except for the Apulia region, which is the only Italian monitored area representative of the Mediterranean climate, no other data is available for the rest of the national territory. For instance, NH_3 volatilisation from manure field application in Italian Mediterranean regions has never been studied despite the presence of considerable livestock loads, i.e. in Campania and Sardinia.

A recurring aspect is the lack of data on the location and the period in which the experiments were performed: in some cases neither geographical coordinates nor even the region of the experimental site were reported, nor the year or the month of the trial periods.

In our survey, we have noticed a broad lack of information regarding some of the driving factors and the surrounding conditions affecting NH_3 volatilisation processes. The small number of collected values and the nature of these factors preclude the possibility of conducting an overall analysis of their direct influence on the emission

process. Nevertheless, when available we consider it of importance to report this information, not only to facilitate the interpretation of the results, but also to help other researchers in compiling and analysing emission databases in future works. For this reason in Appendix 1 we decided to annotate for each of trials the available information on soil conditions (i.e. texture, pH, moisture), soil surface properties (i.e. coverage) and meteorological variables (i.e. air temperature, wind speed), even if they have not been deeply discussed in the text. NH_3 volatilisation from fertilised soil is indeed a complex phenomenon, in which many variables take part and control loss of volatilised NH_3 . These variables can have a key role in driving the equilibrium between NH_3 and ammonium (NH_4^+) forms in their liquid or gas phases in the soil, in influencing the interaction of the fertiliser with the soil matrix, or in governing the gas exchange between the soil surface and the atmosphere. Soil pH is a critical variable controlling the loss of volatilised NH_3 ; emissions take place even when soil is acidic, and increase with increasing soil pH (Court *et al.*, 1964; Générmont and Cellier, 1997; Lægheid *et al.*, 1999), even though predicting when and where soil pH affects the fluxes is still an open question (Flechard *et al.*, 2013). Ammonia losses can also depend on the soil texture (Krupa, 2003), information specified by most authors in this review, which is an indicator of the soil cation-exchange capacity (Martel *et al.*, 1978), that can modulate NH_3 loss by restricting the pH changes or by increasing the soil buffering capacity and by increasing the adsorption of NH_4^+ (Havlin *et al.*, 1998). Texture is also involved in the determination of the soil porosity, and therefore the infiltration of the liquid fraction of slurries or the

dissolved N-based fertilisers (Sommer *et al.*, 2003). Together with porosity, the soil water content is recognised as a determining aspect influencing fertiliser infiltration and consequently NH_3 volatilisation rates (Sommer and Hutchings, 2001). Moreover, the presence of crops has the general effect of reducing emissions when the leaf area covers the soil surface (Walker *et al.*, 2013) except in the case of a fertiliser distributed over the crop. In this situation, the presence of the canopy (i.e. in grasslands), as well as of crop residues on the soil surface, restricts the contact between the distributed fertiliser and the soil, thus increasing NH_3 releases (Moal *et al.* 1995; Pisante *et al.*, 2014). In the papers we reviewed, the soil coverage is usually qualitatively described, but frequently without reporting details on the crop height, the crop growth stage, or the soil surface fraction covered by the canopy. Finally, meteorological variables play a central role in governing emission processes from the soil after fertilisation, since the transfer of gaseous NH_3 to the free atmosphere takes place by both diffusion and convection (Sommer *et al.*, 2003). The incident solar radiation has both direct and indirect effects on the phenomenon, by increasing soil surface temperature and then the atmospheric turbulence responsible for the gas transport (Sommer and Hutchings, 2001). This variable however has been reported only by three reviewed articles (Rana and Mastrorilli, 1998; Carozzi *et al.*, 2013b; Ferrara *et al.*, 2014). Conversely, two other important meteorological variables that can be used to estimate NH_3 emission, air temperature and wind speed (Huijsmans *et al.*, 2003), have been reported in most of the experiments (86% and 56% respectively).

With regard to the measurement methods used to quantify NH_3 losses, our review highlights that most of the experiments have been performed in small plots and by means of enclosure methods, while only a few data were collected under real operational field-scale conditions, by applying micrometeorological methods or inverse-dispersion modelling. To date, field-scale experiments for trace gas emission quantification are encouraged and supported by the literature (e.g. Baldocchi, 1988; Flesch *et al.*, 2004; Famulari *et al.*, 2004; Denmead, 2008; Hensen *et al.*, 2015) and the use of the associated measurement methods is increasing in research (Whitehead *et al.*, 2008; Norman *et al.*, 2009; von Bobruzki *et al.*, 2010; Sintermann *et al.*, 2011b; Ferrara *et al.*, 2012; 2014; Loubet and Carozzi, 2015). Apart from the limits associated with

the enclosure methods explained in the introductory chapter, operating on a small plot instead of field-scale hampers the possibility to collect data under real operational conditions. In this review we found also that the distribution practices are strictly associated to the measurement methods and scale. Manual application is always coupled with enclosure methods and small plots, while surface spreading is used with micrometeorological methods or dispersion modelling, both at field-scale. Similarly, the measurements performed by enclosure methods, thus on small plots, have lower N loads than those performed by micrometeorological methods or dispersion models (larger scale) and result in higher EF (i.e. 22% higher for the slurries, the most studied matrixes). Furthermore, the N applied to soils by manual application (average of 32.4 kg TAN ha⁻¹) is always considerably lower than the N amounts in surface spreading by tractors (average of 72.9 kg TAN ha⁻¹). The last aspect and the heterogeneity in the techniques used to measure NH_3 emissions limit the possibility of comparing absolute amounts of NH_3 losses, for example between two fertiliser application procedures. This also contributes to increase the variability among the EFs and leads to difficulties in the statistical analysis within different fertilisers or application methods.

Despite the heterogeneity of the collected data, some clear patterns in the measured NH_3 emission factors have emerged. In fact, the high variability of the EFs for the types of fertiliser accounted for is in agreement with the variability observed and reviewed by other authors in Europe or on other continents.

With regard to the organic fertilisers for instance, Menzi *et al.* (1998) found a range of emissions from 27 to 94% on grasslands by using pig and cattle slurries; Huijsmans *et al.* (2001) using the similar soil cover and fertiliser types, measured emissions from 8.5 to 97.7% of the TAN, while Huijsmans *et al.* (2003) measured from 33 to 100% of TAN in arable lands by using pig slurry. For details, see the review of Sintermann *et al.* (2012).

In our survey we found unexpected EFs over 100% of the TAN for farmyard manures, values that were also encountered by Misselbrook *et al.* (2005) in experiments conducted using wind tunnels. The authors state that this fact raises the question as to whether rapid mineralisation occurred or whether the TAN content of solid manures was systematically under-estimated. However, according to Sommer *et al.* (2003) the contribution of the mineralisation process to NH_3 emission is negligible, since it is a

relatively slow process, and only small amounts of organic N are mineralised during the first few weeks after application.

The TAN, pH and DM content of manures are main factors driving NH_3 volatilisation along with the soil and meteorological conditions (Sommer and Hutchings, 2001; Sogaard *et al.*, 2002; Huijsmans *et al.*, 2003; Misselbrook *et al.*, 2005). As it is well known, the volatilisation rate increases with an increase in manure application rate (Huijsmans *et al.*, 2003; Ni *et al.*, 2012) therefore the more nitrogen applied, the greater the emissions in quantitative terms. However, NH_3 emission from surface-applied slurry, expressed as a proportion of the TAN applied, decreases with increasing application rate as a greater proportion of the slurry is likely to infiltrate into the soil, even if the relation may not be linear (Sommer and Hutchings, 2001). Manure physical and chemical properties, as well as the application rate in term of TN or TAN, were in most cases described or derivable in the collected literature and have been used to interpret the results obtained. In agreement also with the mean values reported by other authors (e.g. Sommer and Hutchings, 2001), the manures used in the reviewed trials are characterised by a higher DM content (+17%, cattle; +22%, pig) and by a moderately more alkaline pH than the slurries (+0.9, cattle; +0.5, pig). As reported in Tab. 4, the average values of the EFs are apparently higher for solid manure than for slurry, both for cattle (+25.0%) and pig (+19.1%) fertilisers. Furthermore, compared with cattle slurry, pig slurry is characterised by a higher concentration of mineral N (both TN and TAN forms) and by a lower level of DM, which might have determined a mean lower EF value for the latter. DM is indeed known as a factor limiting slurry soil infiltrability (Sommer and Hutchings, 2001; Sommer *et al.*, 2003). Otherwise, analysis based on larger datasets, such as the one published by Sintermann *et al.* (2012), did not find a significant difference between cattle and pig slurry EFs. Too few data about poultry manures have been collected to allow a discussion on their behaviour in term of NH_3 losses. The only data available show EF of the same order of magnitude as solid manure from other animal categories.

The comparison between the averaged EF values for surface application of livestock manures and the values indicated in the official inventories (Tab. 4) showed that they are closer to the values used by ISPRA for computing the national annual emission inventory, than to the default ones included in the EMEP/EEA guidebook. Sintermann *et al.* (2012)

suggest that the reference EMEP/EEA values could be indeed overestimated, probably because of measurements carried out at a medium-plot scale (by means of mass-balance integrated horizontal flux), which yielded higher emissions than the field-scale based ones. In the same publication, the authors discuss the limits of using EFs derived by small scale approaches, such as enclosure methods. These should be used in order to compare the relative effect of different management options only, but should be avoided when the aim is to obtain absolute EFs, such as those needed by the inventories. On the other hand, ISPRA's EFs are mainly based on small scale measurements (Valli *et al.*, 2006; Romano *et al.*, 2014), as well as are most of the trials accounted for in our analysis. On this basis, it is not possible to conclude that the EFs used in the national inventory, nor the average value of our analysis, can be considered more accurate than the default one indicated in the EMEP/EEA guidebook.

Another important factor affecting NH_3 volatilisation from field applied manure is the magnitude of its surface that remains exposed to air over time (Génermont and Cellier, 1997). Injection or broadcasting and subsequent incorporation of manure, are able to reduce manure exposure to the air, and have been recognised to be one of the most effective mitigation strategies used to abate the amount of NH_3 released into the atmosphere (Sommer and Hutchings, 2001; Huijsmans *et al.*, 2003; Webb *et al.*, 2010; Carozzi *et al.*, 2013b,c). The results of our survey show that the most accounted for spreading technique was the broadcast spreading, while other spreading techniques or agronomical abatement strategies are scarcely considered, preventing a direct comparison among different methods. Although few data are available, different reduction methods have shown to be effective in lowering NH_3 volatilisation in cattle and pig slurries. As expected, direct injection and the rapid incorporation of the manure by soil cultivation during the spreading, gave the best results in terms of NH_3 reduction, while trailing hose technique lead to a wider range of values, lower but partially comparable with the surface application. The differences found in the EFs agreed to some extent with the values indicated by EMEP/EEA (2013) guidelines and in other international literature reviews (i.e. Huijsmans *et al.*, 2003; Webb *et al.*, 2010), with ranges from 70 to 80% for injection, from 35 to 95% for incorporation, as a function of the timing of its execution, and 30% TAN for trailing hose.

The comparison of the collected data and those modelled by ALFAM helps to identify some interesting features of the analysed dataset and at the same time allows to examine the model behaviour under different conditions. Looking at measured and estimated EFs, our analysis highlights that the accuracy of ALFAM varies widely in relation with the measurement technique simulated. The best agreement for pig and cattle slurries is obtained for wind tunnel technique. Indeed, wind tunnels present the best values for all the calculated indexes (Tab. 4, $E = 0.7$; $R^2 = 1.0$; $b = 0.8$), while the funnel system ($E = -206.6$; $R^2 = 0.6$; $b = 4.3$) gives the worst performance. Inverse-dispersion model technique was well represented in four field experiment, while in two cases reported by Carozzi *et al.* (2013b) an overestimation by the model had occurred (trials carried out in March 2010 and in April 2011). Wind tunnel and the funnel system are both dynamic chambers (enclosure methods), based on completely different working principles and scales of measurement than inverse-dispersion models. Despite this fact, there is much more distance between results obtained for the first two techniques, than between wind tunnels and inverse-dispersion models. This raises doubts about the accuracy of the funnel system method, which is also the least documented method in literature. Contemporarily, the discrepancy of the model performances depending on the measurement method chosen, once again highlights the need for the collection of new datasets based on the use of the more accurate measurement methods. Furthermore, the disagreement of some measured and simulated EFs, such as the data recorded by Carozzi *et al.* (2013b), could be partially explained by factors or conditions not accountable for by the model, a typical limit of regressive models. In these trials for instance the soil pH was strongly acidic (pH 5.5) or slightly acidic (pH 6.4), and a late incorporation after spreading occurred (at least after 24 hours). Lastly, the results of the ALFAM model, especially those based on wind tunnels and inverse-dispersion models, show that the EFs measured in the Northern Italian regions are comparable and in agreement with those recorded in trials carried out in different European countries (located at Northern latitudes and thus in different climatic conditions), based on which the regressive model has been mainly developed.

The EFs reported from urea application, for all the trials reviewed, are substantially lower (fewer than 8% and one case reporting 13.8%) than organic fertilisers and are within the range found by other

authors which measured values ranging from 0.1 to 36% of the nitrogen applied (i.e. McInnes *et al.*, 1986; Sommer and Jensen, 1994; Rochette *et al.*, 2009; Turner *et al.*, 2010; Pacholski *et al.*, 2006). For a detailed review, see Ferrara *et al.* (2014). These are also low, on average, with respect to the percentage indicated by EMEP/EEA and ISPRA of 24.3% and 15% respectively. However, these values are not completely comparable since the EFs used in the inventories for urea refer to the total annual NH_3 lost from the crop, and do not distinguish between direct emission from the fertiliser and from the crop canopy leaves.

5. CONCLUSIONS

In this paper we reviewed the current literature concerning NH_3 emissions from manure and N-fertiliser application on Italian agricultural lands. Coherently with their importance as NH_3 emission sources, livestock manures and urea have been the most assessed matrixes in experimental trials, though some sources, like residual organic wastes or pastures, still remain unexplored. Considering fertiliser management, the most tested practice for both manures and urea is broadcast spreading, while fewer data are available on mitigation strategies, such as low emission spreading technique or soil cultivation after broad distribution.

The quality of the information derived from the conducted experiments resulted generally weak. This is mainly due to a lack of data collected during the trials, particularly for soil and meteorological variables. Moreover some issues arise from the measurement methods used. Few experiments have been performed at a field-scale, which would be preferable to minimise potential biases in flux quantification compared to small plots. Conducting experiments on a small scale has been recognised to increase the chances of testing far from real operational conditions (e.g. manual application, low N load), leading to less representative results. This considerations support the idea, in accordance with what was stated by Sintermann *et al.* (2012) for Europe, that in order to characterise NH_3 EFs for the Italian territory, in terms of influence of fertiliser characteristics, management, soil properties and meteorology, a new series of measurements would be strongly needed.

We found some relevant differences in the magnitude of the emissions between the type of fertiliser, especially between manures and synthetic N-fertilisers, while fewer differences can be found among different types of animal manures. On the contrary, our results highlight a clear effect of the fertiliser management practices which have been

compared for livestock slurries. For these matrixes, the application techniques affect the NH_3 emissions more than the fertiliser form itself, emphasizing the role of the field management to mitigate the emissions toward the atmosphere.

The agreement between the national data with the European literature is confirmed by the results obtained from the ALFAM model, especially with regard to data collected by means of the wind tunnel technique. The accuracy of the model has proven to be very dependent on the simulated measurement method and to be more accurate in estimating those measurement approaches whose use is currently discouraged.

The Italian NH_3 emission inventory compiled by ISPRA seems to propose EF values in line with those found in the reviewed literature for the fertiliser categories assessed. Our analysis has shown high variability of the EFs reported, as well as large weaknesses of the reviewed trials from a methodological perspective. This brings us to conclude that there is still much room for improvement, since these EFs are still far from being able to be considered as accurate. Since livestock wastes are one of the largest sources of atmospheric NH_3 , decreasing the uncertainty in measurements would have a major impact on the accuracy of the entire emission inventories. Finally, an interesting opportunity in enhancing emission spatial resolution at a national level is opened by the information collected in the last Italian agriculture census (2010), which contains the details of the manure field management practices with the relative land surface.

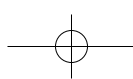
6. ACKNOWLEDGMENT

The authors gratefully acknowledge the project ARMOSA coordinated by the Department of Agricultural and Environmental Sciences of the University of Milan (DiSAA) and the Regional Agency for Agricultural and Forestry Development of Lombardy Region (ERSAF). We wish to express our gratitude to the members of the International Workshop of Ammonia Measurement (IWAM) initiative, to Dr. Christoph Müller (PIK) and Polina Voylokov (INRA EcoSys) for the deep reading of this paper. The authors wish to thank the anonymous reviewers for their comments and useful suggestions for improving the paper.

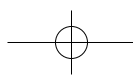
REFERENCES

Amann M., Klimont Z., Wagner F., 2013. Regional and Global Emissions of Air Pollutants: Recent Trends and Future Scenarios. *Annual Review of Environment and Resources*, 38: 31-55.

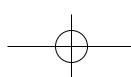
- Anderson N., Strader R., Davidson C., 2003. Airborne reduced nitrogen: ammonia emissions from agriculture and other sources. *Environment International*, 29(2): 277-286.
- Baldocchi D. D., Hicks B. B., Meyers T. P., 1988. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. *Ecology* 69: 1331-1340.
- Balsari P., Dinuccio E., Gioelli F., Santoro E., 2009. Ammonia losses from the land application of raw pig slurry and solid and liquid fractions generated from its mechanical separation. *Ecology and Future - Bulgarian Journal of Ecological Science*, 8(3): 28-31.
- Balsari P., Dinuccio E., Santoro E., Gioelli F., 2008. Ammonia emissions from rough cattle slurry and from derived solid and liquid fractions applied to alfalfa pasture. *Australian of Experimental Agriculture*, 48: 198-201.
- Balsari P., Gioelli F., Dinuccio E., 2006. Ammonia nitrogen emission from land spread farmyard manure. In *International Congress Series*, 1293: 327-330.
- Balsari P., Magrini G., Pons R., 1994. Ammonia losses from pig slurry storage: first results of field test. *Proceedings of the seventh technical consultation on the ESCORENA Network on animal waste management*, Bad Zwischenahn, Germany: 31-35.
- Beusen A. H. W., Bouwman A. F., Heuberger P. S. C., Van Drecht G., Van Der Hoek K. W., 2008. Bottom-up uncertainty estimates of global ammonia emissions from global agricultural production systems. *Atmospheric Environment*, 42(24): 6067-6077.
- Bouraoui F., Grizzetti B., Aloe A., 2009. Nutrient discharge from rivers to seas for year 2000. *JRC Scientific and Technical Reports*, EUR 24002 EN, 72 pp.
- Bouwman A. F., Boumans L. J. M., Batjes N. H., 2002. Estimation of global NH_3 volatilisation loss from synthetic fertilisers and animal manure applied to arable lands and grasslands. *Global Biogeochemical Cycles*, 16(2): 8-1.
- Bouwman A. F., Lee D. S., Asman W. A. H., Dentener F. J., Van Der Hoek K. W., Olivier J. G. J., 1997. A global high-resolution emission inventory for ammonia. *Global biogeochemical cycles*, 11(4): 561-587.
- Carozzi M., Ferrara R. M., Acutis M., Rana G., 2012a. Dynamic of ammonia emission from urea spreading in Po Valley (Italy): relationship with nitrogen compounds in the soil. *Proceedings of the 17th International Nitrogen Workshop*:



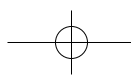
- Wexford Opera House, Wexford, Ireland. 26-29 June 2012: 66-67.
- Carozzi M., Ferrara R. M., Fumagalli M., Sanna M., Chiodini M., Chierichetti A., Brenna S., Rana G., Acutis M., 2012b. Field-scale ammonia emissions from surface spreading of dairy slurry in Po Valley. *Italian Journal of Agrometeorology*, 3: 25-34.
- Carozzi M., Ferrara R. M., Chiodini M., Giussani A., Minoli S., Perego A., Fumagalli M., Sanna M., Rocca A., Alfieri L., Rana G., Acutis M., 2013a. Mitigation of NH₃ emissions due to cattle slurry fertilisation. *Proceedings of XVI National Conference of Agrometeorology - Agrometeorology for environmental and food security*. Firenze, Italy. 4-6 June 2013: 39-40.
- Carozzi M., Ferrara R. M., Rana G., Acutis M., 2013b. Evaluation of mitigation strategies to reduce ammonia losses from slurry fertilisation on arable lands. *Science of the Total Environment*, 449: 126-133.
- Carozzi M., Loubet B., Acutis M., Rana G., Ferrara R. M., 2013c. Inverse dispersion modelling highlights the efficiency of slurry injection to reduce ammonia losses by agriculture in the Po Valley (Italy). *Agricultural and Forest Meteorology*, 171-172: 306-318.
- Clarisse L., Clerbaux C., Dentener F., Hurtmans D., Coheur P. F., 2009. Global ammonia distribution derived from infrared satellite observations. *Nature Geoscience*, 2(7): 479-483.
- Cóndor R. D., Di Cristofaro E., De Lauretis R., 2008. *Agricoltura: inventario nazionale delle emissioni e disaggregazione provinciale*. Istituto superiore per la protezione e la ricerca ambientale, ISPRA Rapporto tecnico 85/2008. Roma, Italia, 144 pp.
- Cóndor R. D., 2011. *Agricoltura: emissioni nazionali in atmosfera dal 1990 al 2009*. Istituto superiore per la protezione e la ricerca ambientale (ISPRA). Rapporto ISPRA 140/2011. Roma, Italia, 78 pp.
- Court M. N., Stephen R. C., Waid J. S., 1964. Toxicity as a cause of the inefficiency of urea as a fertilizer. *Journal of Soil Science*, 15: 42-48.
- Denmead O. T., Simpson J. R., Freney J. R., 1977. Direct field measurement of ammonia emission after injection of anhydrous ammonia. *Soil Science Society of America Journal*, 41: 1001-1004.
- Denmead O. T., 2008. Approaches to measuring fluxes of methane and nitrous oxide between landscapes and the atmosphere. *Plant and Soil*, 309(1-2): 5-24.
- Dinuccio E., Berg W., Balsari P., 2011. Effects of mechanical separation on GHG and ammonia emissions from cattle slurry under winter conditions. *Animal Feed Science and Technology*, 166: 532-538.
- Dinuccio E., Gioelli F., Balsari P., Dorno N., 2012. Ammonia losses from the storage and application of raw and chemo-mechanically separated slurry. *Agriculture, Ecosystems and Environment*, 153: 16-23.
- Ellis R. A., Murphy J. G., Pattey E., Haarlem R. V., O'Brien J. M., Herndon S. C., 2010. Characterizing a quantum cascade tunable infrared laser differential absorption spectrometer (QC-TILDAS) for measurements of atmospheric ammonia. *Atmospheric Measurement Techniques*, 3(2): 397-406.
- EMEP/EEA air pollutant emission inventory guidebook, 2013. Technical guidance to prepare national emission inventories. EEA Technical report No 12/2013. ISSN 1725-2237. (available at: <http://www.eea.europa.eu/publications/emep-eea-guidebook-2013>).
- Erismán J. W., Bleeker A., Galloway J., Sutton M. S., 2007. Reduced nitrogen in ecology and the environment. *Environmental Pollution*, 150(1): 140-149.
- Erismán J. W., Galloway J. N., Seitzinger S., Bleeker A., Dise N., Leach A. M., de Vries W., 2013. Consequences of human modification of the global nitrogen cycle. *Philosophical Transactions of The Royal Society B: Biological Sciences*, 368.1621: 20130116.
- EUROSTAT, Statistical Office of the European Communities, 2007. Database - Regional agriculture statistics - Structure of agricultural holdings - Overview - Farm livestock - Livestock: number of farms and heads of animals by livestock units (LSU) of farm and NUTS 2 regions. (<http://ec.europa.eu/eurostat/web/regions/data/database>)
- Famulari D., Fowler D., Hargreaves K., Milford C., Nemitz E., Sutton M. A., Weston K., 2004. Measuring eddy covariance fluxes of ammonia using tunable diode laser absorption spectroscopy. *Water, Air, and Soil Pollution: Focus* 4: 151-158.
- Ferrara R. M., 2010. Dinamica temporale della volatilizzazione dell'ammoniaca da terreni agricoli: misure micrometeorologiche su liquami e urea. *Italian Journal of Agrometeorology*, 2: 15-24.
- Ferrara R. M., Loubet B., Di Tommasi P., Bertolini T., Magliulo V., Cellier P., Eugster W., Rana G., 2012. Eddy covariance measurement of ammonia fluxes: Comparison of high frequency correction methodologies. *Agricultural and Forest Meteorology*, 158-159: 30-42.



- Ferrara R. M., Loubet B., Decuq C., Palumbo A. D., Di Tommasi P., Magliulo V., Masson S., Personne E., Cellier P., Rana G., 2014. Ammonia volatilisation following urea fertilisation in an irrigated sorghum crop in Italy. *Agricultural and Forest Meteorology*, 195-196: 179-191.
- Flecharde C. R., Massad R. S., Loubet B., Personne E., Simpson D., Bash J. O., Cooter E. J., Nemitz E., Sutton M. A., 2013. Advances in understanding, models and parameterisations of biosphere-atmosphere ammonia exchange. *Biogeosciences Discussions*, 10: 5385-5497.
- Flesch T. K., Wilson J. D., Yee E., 1995. Backward-time Lagrangian stochastic dispersion models and their application to estimate gaseous emissions. *Journal of Applied Meteorology*, 34(6): 1320-1332.
- Flesch T. K., Wilson J. D., Harper L. A., Crenna B. P., Sharpe R. R., 2004. Deducing ground-to-air emissions from observed trace gas concentrations: A field trial. *Journal of Applied Meteorology*, 43(3): 487-502.
- Galloway J. N., Aber J. D., Erisman J. W., Seitzinger S. P., Howarth R. W., Cowling E. B., Cosby B. J., 2003. The nitrogen cascade. *Bioscience*, 53(4): 341-356.
- Génermont S., Cellier P., 1997. A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. *Agriculture and Forest and Meteorology*, 88: 145-167.
- Génermont S., Cellier P., Flura D., Morvan T., Laville P., 1998. Measuring ammonia fluxes after slurry spreading under actual field conditions. *Atmospheric Environment*, 32(3): 279-284.
- Gioelli F., Airolidi G., Balsari P., Dinuccio E., 2004. Ammonia emission from land applied farm yard manure - First results. *Sustainable Organic Waste Management for Environmental Protection and Food Safety*, 1: 305-308.
- Gioelli F., Balsari P., Dinuccio E., Santoro E., 2006. Ammonia emission from the management of solid fraction derived from the mechanical separation of slurry. In: Soren, O., Peterson, E. (Eds.), *DIAS Report: 12th Ramiran International Conference. Technology for Recycling of Manure and Organic Residues in a Whole-Farm Perspective*, 2: 133-135.
- Gioelli F., Balsari P., Dinuccio E., Airolidi G., 2014. Band application of slurry in orchards using a prototype spreader with an automatic rate controller. *Biosystems Engineering*, 121: 130-138.
- Havlin J. L., Samuel T. L., Nelson W.L., Beaton J. D., 1998. Soil fertility and fertilizers: An Introduction to nutrient management. 6th ed. Prentice Hall, Upper Saddle River, NJ: 499 pp.
- Hensen A., Neftel A., Famulari D., Carozzi M., Janker H., Erisman J. W., Huijsmans J., Mosquera J., Latinga E., Berkhout A. J. C., de Haan B., 2015. International Workshop on Ammonia Measurements (IWAM). ECN Environment Engineering 13-4-2015.
- Huijsmans J. F. M., Hol J. M. G., Hendriks M. M. W. B., 2001. Effect of application technique, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to grassland. *Netherlands Journal of Agricultural Science* 49: 323-342.
- Huijsmans J. F. M., Hol J. M. G., Vermeulen G. D., 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilisation from manure applied to arable land. *Atmospheric Environment*, 37(26): 3669-3680.
- ISTAT, Istituto Nazionale di Statistica, 2010. VI Censimento generale dell'agricoltura, Rome, Italy. (<http://dati-censimentoagricoltura.istat.it/>)
- Jørgensen S., Kamp-Nielsen L., Chirstensen T., Windolf-Nielsen J., Westergaard B., 1986. Validation of a prognosis based upon a eutrophication model. *Ecological modelling*, 32 (1-3): 165-182.
- Krupa S. V., 2003. Effects of atmospheric ammonia (NH₃) on terrestrial vegetation: a review. *Environmental pollution*, 124(2): 179-221.
- Lægread M., Bøckman O. C., Kaarstad O., 1999. *Agriculture, fertilizers and the environment*. CABI Publishing, Wallingford, UK, 294 pp.
- Loague K., Green R. E., 1991. Statistical and graphical methods for evaluating solute transport models: overview and application. *Journal of contaminant hydrology*, 7(1): 51-73.
- Lockyer D. R., 1984. A system for the measurement in the field of losses of ammonia through volatilisation. *Journal of the Science of Food and Agriculture*, 35(8): 837-848.
- Loubet B., Génermont S., Ferrara R., Bedos C., Decuq C., Personne E., Fanucci O., Durand B., Rana G., Cellier P., 2010. An inverse model to estimate ammonia emissions from fields. *European journal of soil science*, 61(5): 793-805.
- Loubet B., Carozzi M., 2015. Evaluation of the inverse dispersion modelling method for estimating ammonia multi-source emissions using low-cost long time averaging sensor. EGU General Assembly 2015, 17, EGU2015: 15923.



- Martel Y. A., De Kimpe C.R., Laverdiere M.R., 1978. Cation-exchange capacity of clay-rich soils in relation to organic matter, mineral composition, and surface area. *Soil Science Society of America Journal*, 42: 764-767.
- Massad R.-S., Nemitz E., Sutton M. A., 2010. Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere. *Atmospheric Chemistry and Physics*. 10: 359-10 386.
- McGinn S. M., Janzen H. H., 1998. Ammonia sources in agriculture and their measurement. *Canadian Journal of Soil Science*, 78(1): 139-148.
- McInnes K. J., Ferguson R. B., Kissel D. E., Kanemasu, E. T., 1986. Field measurements of ammonia loss from surface application of urea solution to bare soil. *Agronomy Journal*, 78(1): 192-196.
- Meier M. S., Jungbluth N., Stoessel F., Schader C., Stolze M., 2014. Higher accuracy in N modeling makes a difference. In proceedings from: the 9th International Conference on Life Cycle Assessment in the Agri-Food Sector (LCA Food 2014), ACLCA, San Francisco, USA, 8-10 October 2014.
- Menzi H., Katz P. E., Fahrni M., Neftel A., Frick R., 1998. A simple empirical model based on regression analysis to estimate ammonia emissions after manure application. *Atmospheric Environment*, 32(3): 301-307.
- Miele S., Bianchi A., Mantellini G., 1990. Study of ammonia volatilisation losses from urea and urea-calcium nitrate adduct in laboratory trials. *Agricoltura Mediterranea*, 120(2): 190-195.
- Misselbrook T. H., Powell J. M., Broderick G. A., Grabber J. H., 2005. Dietary manipulation in dairy cattle: Laboratory experiments to assess the influence on ammonia emissions. *Journal of Dairy Science*, 88(5): 1765-1777.
- Moncrieff J., Valentini R., Greco S., Guenther S., Ciccioli P., 1997. Trace gas exchange over terrestrial ecosystems: methods and perspectives in micrometeorology. *Journal of experimental botany*, 48(5): 1133-1142.
- Mosier A. R., 2001. Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere. *Plant and Soil*, 228(1): 17-27.
- Nash J., Sutcliffe J. V., 1970. River flow forecasting through conceptual models part I-A discussion of principles. *Journal of hydrology*, 10(3): 282-290.
- Nastri A., Toderi G., Bernati E., Govi G., 2000. Ammonia volatilisation and yield response from urea applied to wheat with urease (NBPT) and nitrification (DCD) inhibitors. *Agrochimica*, 44: 231-239.
- NECD (National Emission Ceilings Directive) 2001/81/EC. Directive of the European Parliament and of the council of 23 October 2001 on national emission ceilings for certain atmospheric pollutants.
- Ni K., Pacholski A., Dirk Gericke D., Kage H., 2012. Analysis of ammonia losses after field application of biogas slurries by an empirical model, *Journal of Plant Nutrition and Soil Science*, 175(2): 253-264.
- Norman M., Spirig C., Wolff V., Trebs I., Flechard C., Wisthaler A., Schnitzhofer R., Hansel A., Neftel A., 2009. Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland). *Atmospheric Chemistry and Physics*, 9(8): 2635-2645.
- Pacholski A., Cai G., Nieder R., Richter J., Fan X., Zhu Z., Roelcke M., 2006. Calibration of a simple method for determining ammonia volatilization in the field – comparative measurements in Henan Province, China *Nutrient Cycling in Agroecosystems*, 74(3): 259-273.
- Pedrazzini F. R., Tarsitano R., 1986. Ammonia volatilisation from flooded soil following urea application, *Plant and Soil* 91: 101-107.
- Pisante M., Stagnari F., Acutis M., Bindi M., Brilli L., Di Stefano V., Carozzi M., 2014. Conservation Agriculture and Climate Change. In *Conservation Agriculture* (Farooq M., and Siddique K., Eds). Springer: 579-620.
- Rana G., Mastrorilli M., 1998. Ammonia emissions from fields treated with green manure in a Mediterranean climate. *Agricultural and Forest Meteorology*, 90(4): 265-274.
- Renard J. J., Calidonna S. E., Henley M. V., 2004. Fate of ammonia in the atmosphere - a review for applicability to hazardous releases. *Journal of hazardous materials*, 108(1): 29-60.
- Rochette P., MacDonald J. D., Angers D. A., Chantigny M. H., Gasser M. O., Bertrand N., 2009. Banding of urea increased ammonia volatilization in a dry acidic soil. *Journal of Environmental Quality* 38(4): 1383-1390.
- Romano D., Bernetti A., Córdor R. D., De Lauretis R., Di Cristofaro E., Lena F., Gagna A., Gonella B., Pantaleoni M., Peschi E., Taurino E., Vitullo M., 2014. Italian informative inventory report. Italian emission inventory 1990-2012, Institute for Environmental Protection and Research - ISPRA, Roma, Italy, 157 pp.



- Rossi N., Rossi S. A. W., 1987. Volatilisation of ammonia after surface application of urea or ammonium fertilizers on calcareous soils. *Agrochimica* 31(1/2): 169-178.
- Schimel D., Alves D., Enting I., Heimann M., Joos F., Raynaud D., Wigley T., *et al.*, 1996. Chapter 2, Radiative Forcing of Climate Change. In: *Climate Change 1995: The Science of Climate Change. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change* [Houghton, J. T., L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg, and K. Maskell (eds.)]. Cambridge University Press: 65-131.
- Sintermann J., Ammann C., Kuhn U., Spirig C., Hirschberger R., Gärtner A., Neftel A., 2011a. Determination of field scale ammonia emissions for common slurry spreading practice with two independent methods. *Atmospheric Measurement Techniques*, 4(9): 1821-1840.
- Sintermann J., Spirig C., Jordan A., Kuhn U., Ammann C., Neftel A., 2011b. Eddy covariance flux measurements of ammonia by high temperature chemical ionisation mass spectrometry, *Atmos. Meas. Tech.*, 4: 599-616.
- Sintermann J., Neftel A., Ammann C., Häni C., Hensen A., Loubet B., Flechard C. R., 2012. Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories?. *Biogeosciences*, 9(5): 1611-1632.
- Søgaard H. T., Sommer S. G., Hutchings N. J., Huijsmans J. F. M., Bussink D. W., Nicholson F., 2002. Ammonia volatilisation from field-applied animal slurry-the ALFAM model. *Atmospheric Environment*, 36(20): 3309-3319.
- Sommer S. G., Olesen J. E., Christensen B. T., 1991. Effects of temperature, wind speed and air humidity on ammonia volatilization from surface applied cattle slurry. *The Journal of Agricultural Science*, 117: 91-100.
- Sommer S. G., Jensen C., 1994. Ammonia volatilisation from urea and ammoniacal fertilizers' surface applied to winter wheat. *Fertilizer Research*, 37: 85-92.
- Sommer S. G., Hutchings N. J., 2001. Ammonia emission from field applied manure and its reduction-invited paper. *European Journal of Agronomy*, 15(1): 1-15.
- Sommer S. G., Genermont S., Cellier P., Hutchings N. J., Olesen J. E., Morvan T., 2003. Processes controlling ammonia emission from livestock slurry in the field, *Eur. J. Agron.*, 19, 465-486.
- Stull, R.B., 1988. *An Introduction to Boundary Layer Meteorology*. Kluwer Academic Publishers, Dordrecht, The Netherlands, 666 pp.
- Sutton M. A., Pitcairn C. E. R., Fowler D., 1993. The exchange of ammonia between the atmosphere and plant communities. *Advances in Ecological Research*, 24: 301-389.
- Sutton M.A., Oenema O., Erisman J. W., Leip A., van Grinsven H., Winiwarter W., 2011. Too much of a good thing. *Nature*, 472(7342): 159-161.
- Sutton M. A., Reis S., Riddick S. N., Dragosits U., Nemitz E., Theobald M. R., Tang Y. S., Braban C.F., Vieno M., Dore A. J., Mitchell R. F., Wanless S., Daunt F., Fowler D., Blackall T. D., Milford C., Flechard C. R., Loubet B., Massad R., Cellier P., Personne E., Coheur P. F., Clarisse L., Van Damme M., Ngadi Y., Clerbaux C., Skjoth C. A., Geels C., Hertel O., Wichink Kruit R. J., Pinder R. W., Bash J. O., Walker J. T., Simpson D., Horvath L., Misselbrook T. H., Bleeker A., Dentener F., de Vries W., 2013. Towards a climate-dependent paradigm of ammonia emission and deposition. *Philosophical Transactions of the Royal Society B: Biological Sciences* 368: 20130166.
- Turner D. A., Edis R. B, Chen D., Freney J. R., Denmead O. T., Christie R., 2010. Determination and mitigation of ammonia loss from urea applied to winter wheat with n-(n-butyl) thiophosphorictriamide. *Agriculture Ecosystems & Environment* 137(3-4): 261-266.
- UNECE, 2012, 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone to the Convention on Long-range Transboundary Air Pollution, as amended on 4 May 2012 (http://www.unece.org/env/lrtap/multi_h1.html).
- Valli L., Fabbri C., Mazzotta V., Bonazzi G., 2003. *Clima, ambiente: tecniche di abbattimento per ammoniaca e gas serra da allevamenti suinicoli ed avicoli. Sessione tematica: meteo e clima. Atti VII conferenza delle agenzie ambientali. Milano, 24-26 Novembre 2003.* (<http://www.arpalombardia.it/7conferenza/index.htm>).
- Valli L., Bonazzi G., Fabbri C., Córdor R. D., 2006. Technical report on the framework of the MeditAIRaneo project for the Agriculture sector, Centro Ricerche Produzioni Animali - CRPA, Reggio Emilia, Italy, 136 pp.
- Velthof G. L., Van Bruggen C., Groenestein C. M., De Haan B. J., Hoogeveen M. W., Huijsmans J. F. M., 2012. A model for inventory of ammonia emissions from agriculture in the Netherlands. *Atmospheric environment*, 46: 248-255.

- von Bobruzki K., Braban C. F., Famulari D., Jones S. K., Blackall T., Smith T. E. L., Blom M., Coe H., Gallagher M., Ghalaieny M., McGillen M. R., Percival C. J., Whitehead J. D., Ellis R., Murphy J., Mohacsi A., Junninen H., Pogany A., Rantanen S., Sutton M. A., Nemitz E., 2010. Field inter-comparison of eleven atmospheric ammonia measurement Techniques. *Atmospheric Measurement Techniques* 3: 91-112.
- Walker J. T., Jones M. R., Bash J. O., Myles L., Meyers T., Schwede D., Herrick J., Nemitz E., Robarg W., 2013. Processes of ammonia air – surface exchange in a fertilized Zea mays canopy, *Biogeosciences*, 10: 981-998.
- Webb J., Pain B., Bittman S., Morgan J., 2010. The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response - A review. *Agriculture, Ecosystems and Environment*, 137(1): 39-46.
- Whitehead J. D., Longley I. D., Gallagher M. W., 2007. Seasonal and diurnal variation in atmospheric NH₃ in an urban environment measured using a quantum cascade laser absorption spectrometer. *Water Air Soil Pollution*, 183: 317-329.
- Whitehead J. D., Twigg M., Famulari D., Nemitz E., Sutton M. A., Gallagher M. W., Fowler D., 2008. Evaluation of laser absorption spectroscopic techniques for eddy covariance flux measurements of ammonia. *Environmental science and technology*, 42(6): 2041-2046.
- WHO-World Health Organization, 2005. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide Global update 2005, 20 pp.
- Zavattaro L., Grignani C., Acutis M., Rochette F., 2012. Mitigation of environmental impacts of nitrogen use in agriculture (preface to special issue). *Agriculture, Ecosystems and Environment*, 147: 1-3.

APPENDIX 1

Appendix 1 - Summary table of the reviewed papers. For each trial the following information are reported: the region, year and month (or season) in which occurred; the soil conditions, SWC is the soil water content ($m^3 m^{-3}$), soil texture classification (USDA), soil pH, soil coverage; T is the average air temperature ($^{\circ}C$) occurred during the trial, U is the average wind speed ($m s^{-1}$); the measurement technique; the trial scale; the fertiliser and its characteristics, type, TAN is the total ammoniacal nitrogen content ($g kg^{-1}$), TN is total nitrogen content ($g kg^{-1}$), pH, DM is the dry matter content (%); the fertiliser management, distribution technique, soil cultivation, volume applied ($m^3 ha^{-1}$), TN is the total nitrogen applied ($kg N ha^{-1}$), TAN is the total ammoniacal nitrogen applied ($kg N-NH_4^+ ha^{-1}$); the NH₃ emission, EF is the emission factor (%TAN), ALFAM EF is the emission factor estimated by the ALFAM model (%TAN). The columns signed by ^(A) are those necessary to estimate the EF by means of the ALFAM model.

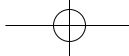
Appendice. 1 - Tabella riassuntiva degli articoli esaminati. Per ogni prova vengono indicate la regione, l'anno e il mese (o stagione) in cui si è svolta; le condizioni del terreno, SWC è il contenuto idrico del suolo ($m^3 m^{-3}$), tessitura del suolo (USDA), il pH del terreno, la copertura del suolo; T è la temperatura media dell'aria ($^{\circ}C$) durante l'esperimento, U è la velocità media del vento ($m s^{-1}$); la tecnica di misurazione; la scala di misura; il fertilizzante e le sue caratteristiche, il tipo, TAN è il contenuto totale di azoto ammoniacale ($g kg^{-1}$), TN è contenuto totale di azoto ($g kg^{-1}$), pH, DM è il contenuto di sostanza secca (%); la gestione del fertilizzante, la tecnica di distribuzione, la lavorazione del terreno, il volume applicato ($m^3 ha^{-1}$), TN è l'azoto totale applicato ($kg N ha^{-1}$), TAN è l'azoto ammoniacale totale applicata ($kg N-NH_4^+ ha^{-1}$); l'emissione di NH₃, EF è il fattore di emissione (% TAN), ALFAM EF è il fattore di emissione stimato dal modello ALFAM (% TAN). Le colonne contrassegnate da ^(A) sono quelle necessarie per valutare l'EF per mezzo del modello ALFAM.

Notes: S, A, W stand for summer, autumn, winter; LS stands for Loamy sand, SIC for Silty clay, SL for Sandy loam, L for Loam, S for sand, SIL for Silt loam, CL for Clay loam; st. is the growth stage, AGM is the aerodynamic gradient method, FS is the funnel system, I-DM is the inverse-dispersion model, OLDC is the open large dynamic chamber, SC is the static chamber, WT is the wind tunnel; NBPT is the urease inhibitors (N-(n-butyl) thiophosphoric triamide), DCD is the nitrification inhibitors (dicyandiamide); INJ is the injection, MN is the manual distribution, SS is the surface spreading, TH is the trailing hose; Gen. is a generic cultivation, Hrv is the harrowing, Mn is the manual cultivation, Plg is the ploughing, where available the time after spreading of the cultivation occurrence is reported in brackets, aft. stands for after, context. stands for contextual.

Reference	Region	Year	Month	Soil conditions			Temp [°C]	Metro [m s ⁻¹]	Meas. tech. (A)	Trial scale	Fert. (A)	Fertiliser characteristics						Fertiliser application				NH3 emission	
				Texture	pH	Coverage						Type	TAN ^(A) [g kg ⁻¹]	TN [g kg ⁻¹]	pH	DM ^(A) [%]	Dist ^(A)	Cult ^(A)	Vol ^(A) [m ³ ha ⁻¹]	TN [kg N ha ⁻¹]	EF [kg N ha ⁻¹]	AlFAM ^(A) [% TAN]	
Balsani et al., 2009	A		S	LS	8.5	cut Alfalfa	18.4	0.6	WT	small plot	pig	slurry	3.0	4.3	7.8	3.5	MIN	none	9	40	28	200	33.3
	B		S	LS	8.5	cut Alfalfa	18.4	0.0	FS	small plot	pig	slurry	3.0	4.3	7.8	3.5	MIN	none	16	70	49	18.6	57.0
	C		S	LS	8.5	cut Alfalfa	18.4	0.6	WT	small plot	pig	slurry	3.0	4.0	8.0	2.4	MIN	none	10	40	30	200	27.2
	D		S	LS	8.5	cut Alfalfa	18.4	0.0	FS	small plot	pig	slurry	3.0	4.0	8.0	2.4	MIN	none	18	70	53	13.3	47.7
	E		S	LS	8.5	cut Alfalfa	18.4	0.6	WT	small plot	pig	solid manure	3.3	7.2	8.4	23.2	MIN	none		40	18	17.8	
	F		S	LS	8.5	cut Alfalfa	18.4	0.0	FS	small plot	pig	solid manure	3.3	7.2	8.4	23.2	MIN	none		70	32	200	
	G		A	LS	8.5	cut Alfalfa	11.4	0.6	WT	small plot	pig	slurry	2.0	3.6	7.8	3.5	MIN	none	11	40	22	23.2	30.7
	H		A	LS	8.5	cut Alfalfa	11.4	0.0	FS	small plot	pig	slurry	2.0	3.6	7.8	3.5	MIN	none	19	70	39	21.4	58.2
	I		A	LS	8.5	cut Alfalfa	11.4	0.6	WT	small plot	pig	slurry	2.1	3.2	7.8	2.1	MIN	none	13	40	26	13.6	24.8
	J		A	LS	8.5	cut Alfalfa	11.4	0.0	FS	small plot	pig	slurry	2.1	3.2	7.8	2.1	MIN	none	22	70	46	12.1	46.8
	K		A	LS	8.5	cut Alfalfa	11.4	0.6	WT	small plot	pig	solid manure	2.5	6.8	8.2	28.9	MIN	none		40	15	5.4	
	L		A	LS	8.5	cut Alfalfa	11.4	0.0	FS	small plot	pig	solid manure	2.5	6.8	8.2	28.9	MIN	none		70	26	8.1	
Balsani et al., 2008	A		S	LS	8.2	cut Alfalfa	27.8	0.0	FS	small plot	cattle	slurry	2.1	3.5	7.6	5.7	MIN	none	11	40	24	26.8	126.0
	B		S	LS	8.2	cut Alfalfa	27.8	0.0	FS	small plot	cattle	slurry	2.1	3.5	7.6	5.7	MIN	none	20	70	42	200	121.0
	C		S	LS	8.2	cut Alfalfa	27.8	0.6	WT	small plot	cattle	slurry	2.1	3.5	7.6	5.7	MIN	none	20	70	42	58.7	66.6
	E		S	LS	8.2	cut Alfalfa	27.8	0.0	FS	small plot	cattle	slurry	2.1	3.3	7.8	4.4	MIN	none	12	40	25	23.3	102.0
	F		S	LS	8.2	cut Alfalfa	27.8	0.0	FS	small plot	cattle	slurry	2.1	3.3	7.8	4.4	MIN	none	21	70	45	20.9	98.3
	G		S	LS	8.2	cut Alfalfa	27.8	0.6	WT	small plot	cattle	slurry	2.1	3.3	7.8	4.4	MIN	none	21	70	45	50.8	54.1
	H		S	LS	8.2	cut Alfalfa	27.8	0.0	FS	small plot	cattle	solid manure	1.8	5.1	8.7	22.8	MIN	none		40	14	34.3	
	I		S	LS	8.2	cut Alfalfa	27.8	0.0	FS	small plot	cattle	solid manure	1.8	5.1	8.7	22.8	MIN	none		70	25	28.6	
	J		S	LS	8.2	cut Alfalfa	27.8	0.6	WT	small plot	cattle	solid manure	1.8	5.1	8.7	22.8	MIN	none		70	25	47.9	
	K		A	LS	8.2	cut Alfalfa	12.5	0.0	FS	small plot	cattle	slurry	1.5	3.4	7.5	7.1	MIN	none	12	40	18	27.4	99.7
	L		A	LS	8.2	cut Alfalfa	12.5	0.0	FS	small plot	cattle	slurry	1.5	3.4	7.5	7.1	MIN	none	21	70	31	26.1	95.9
	M		A	LS	8.2	cut Alfalfa	12.5	0.6	WT	small plot	cattle	slurry	1.5	3.4	7.5	7.1	MIN	none	21	70	31	52.6	52.8
	N		A	LS	8.2	cut Alfalfa	12.5	0.0	FS	small plot	cattle	slurry	1.7	3.2	7.8	4.4	MIN	none	13	40	21	190	73.0
	O		A	LS	8.2	cut Alfalfa	12.5	0.0	FS	small plot	cattle	slurry	1.7	3.2	7.8	4.4	MIN	none	22	70	37	21.3	70.2
	P		A	LS	8.2	cut Alfalfa	12.5	0.6	WT	small plot	cattle	slurry	1.7	3.2	7.8	4.4	MIN	none	22	70	37	32.9	38.6
	Q		A	LS	8.2	cut Alfalfa	12.5	0.0	FS	small plot	cattle	solid manure	1.4	4.7	8.2	20.9	MIN	none		40	12	18.5	
	R		A	LS	8.2	cut Alfalfa	12.5	0.0	FS	small plot	cattle	solid manure	1.4	4.7	8.2	20.9	MIN	none		70	21	21.5	
	S		A	LS	8.2	cut Alfalfa	12.5	0.6	WT	small plot	cattle	solid manure	1.4	4.7	8.2	20.9	MIN	none		70	21	46.0	
Carozzi et al., 2012a	A	Lombardy	2010	June		Maize (st. V8)			FDM	field	Urea	Urea		460.0			SS		106			4.7	
Carozzi et al., 2013b	A	Lombardy	2011	Oct	0.22	Maize stubbles	12.3	1.2	FDM	field	cattle	slurry	1.2	1.9	7.5	3.0	SS	none	57	107	68	44.4	37.3
	B	Lombardy	2009	Mar	0.17	Maize stubbles	11.2	1.5	FDM	field	cattle	slurry	1.1	2.2	8.0	4.4	SS	Hrw (aft.24 h)	87	188	95	27.8	38.4
	C	Lombardy	2010	Mar	0.25	Wheat stubbles	12.2	0.2	FDM	field	cattle	slurry	1.7	3.8	6.5	5.5	SS	Plg (aft. 24 h)	54	204	92	6.4	45.7
	D	Lombardy	2011	Apr	0.21	Ryegrass	18.5	1.3	FDM	field	cattle	slurry	1.5	3.0	7.8	5.5	SS	Hrw (aft. 30 h)	75	223	109	28.5	52.7
	E	Lombardy	2011	Oct	0.22	re-growth Sorghum	12.3	1.2	FDM	field	cattle	slurry	1.2	1.9	7.5	3.0	SS	Hrw (context)	55	103	66	5.6	3.2
	F	Lombardy	2009	Sep	0.36		19.2	0.9	FDM	field	cattle	slurry	2.0	2.8	8.0	3.4	INI	Plg (aft. 24 h)	69	192	139	2.5	1.0

follow →





continues

Reference	Region	Year	Month	Soil conditions			Fert. (A)	Fertiliser characteristics						Fertiliser application				NH3 emission						
				SWC _v [m ³]	Texture	pH		Coverage	T _s [°C]	U _v [m ³]	Mech. tech. (A)	Trial scale	Type	TAN _v [g kg ⁻¹]	TN [g kg ⁻¹]	pH	DM _v [%]	Distrb. (A)	Cultiv. (A)	Vol _v [m ³ ha ⁻¹]	[kg N ha ⁻¹]	[kg N ha ⁻¹]	[% TAN]	[% TAN]
Dinuoco et al., 2012	A	Piedmont	S		LS	8.2	cut Alfalfa	27.6		WT	small plot	pig	slurry	2.6	3.6	7.8	4.0	MN	none	19	70	50	28.0	38.6
	B	Piedmont	S		LS	8.2	cut Alfalfa	27.6		WT	small plot	pig	slurry	1.9	2.1	8.1	1.3	MN	none	33	70	63	23.8	32.3
	C	Piedmont	S		LS	8.2	cut Alfalfa	27.6		WT	small plot	pig	solid manure	1.9	5.3	8.3	22.9	MN	none		70	25	96.3	
	D	Piedmont	W		LS	8.2	re-growth Alfalfa	5.8		WT	small plot	pig	slurry	2.3	3.0	7.9	3.0	MN	none	23	70	54	11.4	25.6
	E	Piedmont	W		LS	8.2	re-growth Alfalfa	5.8		WT	small plot	pig	slurry	1.5	1.8	8.1	1.1	MN	none	39	70	58	8.8	19.4
Ferrara et al., 2014	F	Piedmont	W		LS	8.2	re-growth Alfalfa	5.8		WT	small plot	pig	solid manure	1.5	6.6	8.3	23.1	MN	none		70	16	56.7	
	A	Apulia	2008	June		SIC	Sorghum	24.7	3.4	I-DM	field	Urea	Urea	460.0					240				13.8	
Gioelli et al., 2006	A	Piedmont				S		27.3	1.0	OLD	small plot	pig	solid manure	5.3	7.2	8.4	23.2			70	32	65.5		
	B	Piedmont				S		26.1	1.0	OLD	small plot	cattle	solid manure	1.8	5.1	8.7	22.8			70	25	119.0		
	C	Piedmont				S		13.1	1.0	OLD	small plot	pig	solid manure	2.5	6.8	8.2	28.9			70	26	68.0		
Gioelli et al., 2014	D	Piedmont				S		18.1	1.0	OLD	small plot	cattle	solid manure	1.4	4.7	8.2	20.9			70	21	127.6		
	A	Piedmont	June			SIL	orchard	22.4	0.6	WT	small plot	pig	slurry	2.1	2.9	7.5	3.1	TH	none	4	10	8	2.8	
	B	Piedmont	June			SIL	orchard	22.4	0.6	WT	small plot	pig	slurry	2.1	2.9	7.5	3.1	TH	Mn (context.)	4	10	8	2.0	
Nasri et al., 2000	C	Piedmont	June			SIL	orchard	22.4	0.6	WT	small plot	pig	slurry	2.2	3.0	7.3	3.1	SS	none	4	10	8	7.7	
	A	Emilia Romagna	1994	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			6.1	
	B	Emilia Romagna	1994	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea+NBPT	460.0				MN		120			2.7	
	C	Emilia Romagna	1994	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea+NBPT+DCD	460.0				MN		120			2.8	
	D	Emilia Romagna	1994	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			3.4	
	E	Emilia Romagna	1994	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea+NBPT	460.0				MN		120			1.9	
	F	Emilia Romagna	1994	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea+NBPT+DCD	460.0				MN		120			2.5	
	G	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		60			7.2	
	H	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		60			3.6	
	I	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		60			4.5	
	J	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			7.3	
	K	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			3.4	
	L	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			3.9	
M	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			3.5		
N	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			1.8		
O	Emilia Romagna	1995	Mar		L	Wheat	9.0		SC	small plot	Urea	Urea	460.0				MN		120			2.3		
Rana and Mastroianni, 1998	A	Apulia	1995	Mar		L	bare soil	9.6		AGM	field	green manure	bean					none	226			4.7		
	B	Apulia	1996	May		L	bare soil	18.4		AGM	field	green manure	bean					none	274			3.9		
Valli et al., 2003	A	Emilia Romagna	2001	June			grass			WT	small plot	pig	slurry					SS				19.4		
	B	Emilia Romagna	2001	June			grass			WT	small plot	pig	slurry					TH				14.2		
	C	Emilia Romagna	2001	June			grass			WT	small plot	pig	slurry					SS				17.6		
	E	Emilia Romagna	2002	Apr			grass			WT	small plot	pig	slurry					SS				74.6		
	F	Emilia Romagna	2002	Apr			grass			WT	small plot	pig	slurry					TH				40.3		
	G	Emilia Romagna	2002	Apr			grass			WT	small plot	pig	slurry					SS				58.8		
	H	Emilia Romagna	2001	Nov			bare soil			WT	small plot	poultry	solid manure					SS				28.0		
	I	Emilia Romagna	2001	Nov			bare soil			WT	small plot	poultry	solid manure					SS				28.0	Gen. (context.)	
	J	Emilia Romagna	2002	May			bare soil			WT	small plot	poultry	solid manure					SS				34.0		
	K	Emilia Romagna	2002	May			bare soil			WT	small plot	poultry	solid manure					SS				34.0	Gen. (context.)	

