Ph.D. in Agricultural Ecology
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Ammonia Emissions From Arable Lands
In Po Valley: Methodologies, Dynamics
And Quantification

Ph. D. Thesis
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Titolo in Italiano: “Emissioni Di Ammoniaca Da Terreni Agricoli In Pianura Padana: Metodologie, Dinamiche e Quantificazione”

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The aim of my Ph.D. work was to evaluate and to quantify the ammonia (NH₃) losses from arable lands in Lombardia plain (Po Valley), following the application of different fertilisers and considering different agronomic managements. Hence, to expand the lack of ammonia emissions data in Italy.

Different and innovative measurement techniques, together with estimation approaches, were assessed to determinate the most suitable method to evaluate the ammonia emission, aimed to the application at large-scale. The evaluation of NH₃ emissions was performed during eight field trials in Lombardia area. Ammonia emissions were directly measured by the use of the (i) eddy covariance system equipped with a fast sensor for NH₃ concentration, based on Tunable Infrared Laser Differential Absorption Spectrometry (TILDAS), estimated with the use of (ii) inverse dispersion models coupled with the use of long term exposure concentration samplers and (iii) with a mechanistic model. In the field trials, data of NH₃ concentration, atmospheric turbulence, weather conditions and soil temperature, were collected at hourly or sub-hourly scale, while physical and chemical characteristics of soil, daily. The management-related variables, the site geometry and the characteristics of fertilizers were also taken into account.

Finally all the collected data were used to evaluate the dynamics of the emission process on the basis of the amount of nitrogen applied, the characteristics of fertilisers, the application technique, the agronomic
management, the weather conditions at field scale, the NH₃ concentration measurements, and the atmospheric turbulence at high temporal detail.

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- XXXVIII Convegno Società Italiana di Agronomia. 21-22-23 settembre 2009, Firenze, Italy.
- XVI Nitrogen Workshop: Connecting different scales of nitrogen use in agriculture. 28-29-30 giugno – 1 luglio 2009, Torino, Italy.
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ABSTRACT

4.1 INTRODUCTION

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Chapter 1

INTRODUCTION
1.1 Alteration of nitrogen cycle

Nitrogen (N) is the main abundant element of atmosphere, hydrosphere and biosphere, its molecular form (N\textsubscript{2}) is the most plentiful form present in nature, but it is not directly usable by the majority of organisms, due to the large energy required for breaking its bonds (Galloway \textit{et al.}, 2003). N is also the most required element by crops, the global primary source of food. The agricultural soils are most often deficient in N content to supply the optimal nutrition levels of the crops (Godwin and Singh, 1998), even if the fixation of N\textsubscript{2} occurs in this medium. Since the N biological fixation is not sufficient to cover the N needs of crops, N fertilisers are widely employed in order to enhance the soil supply of such macroelement and to increase the food production.

The use of fertilisers in agriculture is exponentially increased from the 1960s (Galloway \textit{et al.}, 2003), as consequence of the discovery of the Haber-Bosh process. Moreover this growth has to continue due to demographic growth, changes in food preferences and agriculture intensification caused by the reduction of the production areas (Bouwman \textit{et al.}, 2011; FAO 2002). This increasing addition of N to expand agricultural production leads to large-scale alterations of the N cycle.

Anthropogenic flows of N result the mayor component of the earth’s nutrient cycles (Galloway, 2008), producing positive effects, as increase of yields, and negative effects as the release of reactive form of N (Nr) in the environment. In particular, significant fractions of the mobilized Nr are lost towards atmosphere by gaseous emissions of N compounds such as ammonia (NH\textsubscript{3}), nitrous oxide (N\textsubscript{2}O), oxidised nitrogen (NO\textsubscript{x}) and
nitric acid (HNO$_3$), and through leaching and runoff losses of nitrate (NO$_3^-$) to ground and surface waters (de Vries et al., 2001). Three N forms are mainly involved in the impact of the N excess on the environment: (i) NO$_x$ (NO and NO$_2$) mainly emitted by combustion processes; (ii) N$_2$O formed by nitrification and de-nitrification processes in the soil; (iii) reduced nitrogen, including NH$_3$ and ammonium (NH$_4^+$), mainly formed by agricultural practices.

1.2 Ammonia in the environment: ecological issues

Ambient NH$_3$ assumes an important role and growing interest among different atmospheric Nr species, as a key of the future negative impacts of N on terrestrial ecosystems (Sutton, 2006). In particular, the environmental issues due to NH$_3$ include mainly acidification of soils, eutrophication of water with loss of biodiversity, human health and the long-range transport of sulphur (S) and N (Sutton et al., 1993; Asman et al., 1998; Erisman et al., 2001; Harper, 2005). Moreover, by 2020 it is estimated that NH$_3$ will be the largest single contributor to acidification, eutrophication and formation of secondary particulate matter (Ammann et al., 2005).

Dry or wet deposition of ammonium particles to the ground contributes to soil acidification (van Breemen et al., 1982; Galloway, 2003), where NH$_4^+$ is nitrified in NO$_3^-$, with the realising of protons (H$^+$). Soil pH will decrease when the buffer capacity of the soil is exhausted, causing changing soil chemistry. In acidic soils indeed, elevate atmospheric deposition leads nutrient imbalances since the uptake of base nutrients (Ca$^{2+}$, Mg$^{2+}$, K$^+$, P) is reduced (Erisman and de Vries, 2000; Galloway,
This effect may be aggravated in natural systems where N is a limiting nutrient, causing increasing growth of the vegetal species and increased demand of these base cations (van der Eerden et al., 1998). The excess of N supply in natural or semi-natural ecosystems influences their structure, competitive processes, sensitivity to stresses and functionality of vegetal species. Furthermore, NH$_3$ by means of NH$_4^+$ aerosol depositions, if not absorbed by the vegetation, may lead to increased environmental loads, such as NO$_3^-$ in the groundwater, and producing indirect greenhouse gas (GHG) emissions as nitrous oxide and ozone (O$_3$) (Galloway et al., 2008; Sutton et al., 2011).

Direct deposition of NH$_4^+$ aerosols to water contribute significantly to the eutrophication phenomenon, with consequent negative effects on aquatic life and biodiversity. Surface freshwater ecosystems (wetlands, streams, lakes and rivers) receive most of their N from atmospheric deposition and from biological nitrogen fixation (Galloway, 2003), where an increase in N deposition leads to degradation of the resource. Marine ecosystems, receiving N from freshwater, groundwater and from atmospheric depositions, result frequently in excessive algae growth with consequences on biota due to hypoxic status of water.

Atmospheric particles formed by the reactions of NH$_3$ in the troposphere, could interfere directly with radiation and energy balances through the increasing of earth albedo, or indirectly with clouds formation. Despite this effect cannot be quantified precisely, it contribute to a negative radiative forcing of about 1 W m$^{-2}$ (Schimel et al., 1996). Once released from the sources, NH$_3$ is rapidly dispersed in the turbulent atmosphere, going toward chemical reactions by forming ammonium
aerosols and incorporating in precipitation. Approximately 50% of the \(\text{NH}_3\) emitted does not react in atmosphere and returns as gas in dry deposition to natural surfaces, particularly wet surfaces and vegetation, within few kilometres (Asman, 1998; Ferm 1998). Estimates of the atmospheric lifetime of \(\text{NH}_3\) range from approximately 0.5 hours to 5 days (Fowler et al., 1997). This short lifetime is the result of rapid conversion of \(\text{NH}_3\) gaseous to \(\text{NH}_4^+\) ion on the liquid phase of atmosphere, causing wet deposition on surface. Once into the atmosphere, \(\text{NH}_4^+\) which is not deposited, is converted to \(\text{NH}_4^+\) aerosols in 5-10 days (Crutzen, 1983; Möller and Schieferdecker, 1985; Dlugi et al., 1997; Nemitz and Sutton, 2004). Depending on the rapidity of this conversion, emissions will primarily be deposited locally, afterwards \(\text{NH}_4^+\) will be made available for long-range transport, about from 100s to 1000s of kilometres (Irwin and Williams, 1988) because of the much lower deposition velocity of \(\text{NH}_4^+\) than \(\text{NH}_3\). The formation of aerosols is a function of the concentrations of strong acids and water vapour in atmosphere. Ammonia reacts irreversibly with sulphuric (\(\text{H}_2\text{SO}_4\)), and reversibly with nitric (\(\text{HNO}_3\)) and hydrochloric (\(\text{HCl}\)) acids, to form ammonium sulphate (\(\text{NH}_4\text{SO}_4\)), ammonium bisulphate (\(\text{NH}_4\text{HSO}_4\)), ammonium nitrate (\(\text{NH}_4\text{NO}_3\)) and ammonium chloride (\(\text{NH}_4\text{Cl}\)) in the form of aerosols. The formation of particulate inorganic will be in the form of solid (with diameter below 2.5 µg) or liquid in cloud or fog droplet depending on relative humidity.

Finally particulate matter (PM) is considered to be a major threat to human health through respiratory cardiovascular disorders, especially by long term exposure of PM smaller than 2.5 µg (PM\(_{2.5}\)); WHO (2005). At
the national level the incidence of agriculture in the formation of PM is about 4% of PM$_{2.5}$ (and 11% of PM$_{10}$) (ISPRA, 2011).

1.3 Ammonia emissions in agriculture

Ammonia concentration depends by the ecosystem (ECETOC, 1994), ranging from less than 1 µg m$^{-3}$ in remote regions to over 250 µg m$^{-3}$ near the sources (Krupa, 2003). Concentrations are affected by diurnal variations reaching their maxima during noon (Van der Molen et al., 1990), due to the temperature-driven of the NH$_3$ emission. In contrast, NH$_3$ accumulation occurs at night due to atmospheric inversions (Erisman et al., 1988). Differences of NH$_3$ concentrations are also observed during the year, typically trends are characterized by peaks in spring and summer (Allen et al., 1988) mainly caused by the application of manure and fertilizers, and by the increasing temperatures.

The sources of NH$_3$ are various, such animal waste, biomass burning, human excreta, fossil fuel combustion, synthetic fertilizers, soils with native vegetation and agricultural crops (Olivier et al., 1996; Bouwman et al., 1997). In particular, agriculture is known as the major source of atmospheric NH$_3$, contributing to 50% of NH$_3$ emissions in the world (Bouwman et al., 1997), over 90% in Europe (EEA, 2011) and 95% in Italy (ISPRA, 2011). Intensive animal production, housing and waste storage (Jarvis and Pain, 1990; Pain et al., 1998), and subsequent land application of manure (Génermont and Cellier, 1997; Asman et al., 2004) result the main NH$_3$ emitting activity. Other sources are crops which, depending on the above atmospheric NH$_3$ concentration, their phenology and N nutritional condition, can act either as sinks or sources of NH$_3$.
(Sutton et al., 1995; Hill et al., 2001). Regarding the sources in terms of size and duration, the NH$_3$ emissions originate typically from small areas, as animal housing and manure storage, and have short and intense activity as volatilization after manure application (Loubet et al., 2009b).

NH$_3$ is mainly produced by the conversion of N present in urea and acid uric, and excreted by livestock or supplied by mineral fertilizers, to ammoniacal nitrogen (NH$_4^+$). This transformation occurs rapidly (often within few days) and requires a key enzyme, urease, which is present in feces and soil. Moreover, NH$_3$ can be produced by the conversion of complex organic N forms contained in the soil or faces, but this process is more slow than the previous and could occur within months. The major sources of ammoniacal nitrogen into the soil are the aerobic degradation of organic matter, atmospheric depositions and the application of fertilizers. Into the soil, the NH$_4^+$ cation is dissolved and adsorbed on positively charged clay particles and is relatively immobile.

The ammonia emission is based on its transfer from the air in contact with the ammoniacal solution to the above free air. Removal ammonia from surface-atmosphere interface is function of atmospheric stability and atmospheric turbulence. As NH$_3$ is lost by volatilization, NH$_4^+$ ions dissociate to NH$_3$ and H$^+$ to maintain the equilibrium: the net result is that volatilization tends to decrease pH and reduce the volatilization rate (Harper, 2005).

### 1.4 Techniques for quantifying NH$_3$ fluxes

Reliable NH$_3$ quantification is important to control abatement strategies, to derive emission factors used in national and international
emission inventories, to validate models and to evaluate the ammonia exchange over natural surfaces in the continuum soil-plants-atmosphere.

The nature of the NH$_3$ molecule is “sticky”, its hydrophilic nature gives it the ability to bind and unbind from solid surfaces used in air sampling systems, as well as to absorb and disassociate in water, influencing greatly the measurements (Brodeur et al., 2009). Furthermore, NH$_3$ is emitted by human sources increasing the potential for sample contamination (Sutton et al., 2000).

The measurement of ammonia emission is critical and many techniques were developed, even if there is not a standardized method. Each technique varies in its sensitivity, selectivity, speed and cost; furthermore, measuring NH$_3$ is often expensive, extensive and time consuming (Aneja 1997; Harper and Sharpe, 1998). Together with the improvement of measurement methods and the development of new techniques, empirical or semi-empirical models able to estimate the NH$_3$ emission from fertilizer application have been developed (Génermont and Cellier, 1997; Søgaard et al, 2002). Among techniques available nowadays to measure or estimate NH$_3$ the most known and here described are: (i) fluxes measurement approaches, (ii) concentration-based dispersion modelling and (iii) ammonia emission models.

(i) Fluxes measurement approaches

Among the techniques developed to measure directly the flux, there are enclosure methods (Moisier, 1989) and micrometeorological methods (Denmead and Raupach, 1993; Kaimal and Finnigan, 1994). The enclosure methods are the chambers (Hutchinson and Livingston, 1993) and wind tunnels (Lockyer, 1984). These two techniques have the
advantage of simplicity in measure, possibility of many replicates in field experiments and limited costs. The disadvantages are the limited spatial representativeness of the measurements, the forcing of the natural emission and the potential memory effect due to the stickiness of the NH$_3$ molecule.

Several micrometeorological methods are currently used to measure NH$_3$ and other trace gases. These approaches are based on the measure of gas above the ground without disturbing the natural exchange between soil or crop surface and atmosphere. They could be applicable from small plot to field size scale, over short and long time scales. The theory imposes requirements as the stationary of the scalar concentration, the homogeneity of surface in horizontal directions and the flatness of the soil (Stull, 1988). These conditions are needed to be sure that the vertical fluxes are not affected by horizontal advective components (Meyers and Baldocchi, 2005). Micrometeorological methods include the integrated horizontal flux (IHF; Schjoerring et al., 1992), the aerodynamic gradient (AEG; Flechard and Fowler, 1998) and the eddy covariance (EC; Whitehead et al., 2008; Brodeur et al., 2009). IHF method is used in small plots (Sintermann et al., 2011) and, despite it was the most used technique during the past 20 years, it has the disadvantage of long time response, time consuming and big uncertainty in measure (Misselbrook et al., 2005). The AEG is the most commonly used techniques nowadays, it is a technique sensitive to advection of NH$_3$ affecting the flux measurement, but it requires sensors with high resolution (Loubet et al., 2010) and it is affected by large uncertainties (Milford et al., 2009). The EC is been recently extended to the NH$_3$ measurements with the recent
progress on fast response sensors to detect this gas. This method is considered as the most direct and least error-prone approach for measuring fluxes at field scale (Ammann, 1999; Sutton et al., 2007; Sintermann et al., 2011) and is described in Chapter 2 of this thesis. The advantage of this technique is to perform continuous measurement of NH$_3$ fluxes at hourly scale over large areas. The disadvantages are the complexity and high cost of the equipment.

(ii) Concentration-based dispersion modelling

NH$_3$ emissions in field can be estimated using dispersion models that relate concentration measurements performed at field scale to the atmospheric turbulent conditions and to the emission rate of the corresponding source. The underlying hypotheses are that the studied tracer should be conservative and that the volatilisation flux should be spatially homogeneous. Models employed here will be “Lagrangians-type” i.e. Windtrax described by Flesch et al. (2004) and “Eulerians-type” i.e. FIDES described by Loubet et al. (2001, 2010) as accurately described in the Chapter 2 of this thesis. The advantages of these models are that they could be applied using long term cheap concentration samplers (Loubet et al., 2011). The disadvantages are related to the sensibility of the outputs to the turbulent parameters (Flesch et al., 2004; Loubet et al., 2010) as specified in chapter 3 of this thesis.

(iii) Ammonia emission models

Deterministic and empirical models, more or less complex, can be used to estimate the emission of NH$_3$, modelling the aspects associated to the volatilisation, such as the influence of climate, the agricultural technique and the soil and fertilizer properties. Among the deterministic models
here we used Volt’Air developed by Gènermont and Cellier., (1997) as described in Chapter 2. Moreover, the meta-model ALFAM (Søgaard et al., 2002) has been applied in Chapter 4. The employment of a model of ammonia fluxes has the advantage of permitting the comparison of different nitrogen application techniques at field level with a workload for just measuring input variables, although a test on the performances of a model is needed through a direct measurement. The disadvantage in several cases is application in different environment and the up-scaling of the estimation, since the calibration procedure is most often site-specific.

1.5 Factors affecting ammonia volatilization by arable lands

Ammonia losses occur predominantly from the surface of ammoniacal solutions in water. These losses are mainly associated with animal slurries, manure, urine, and secondly by the use of inorganic fertilizers (Asman, 1992). Ammonia and ammonium in equilibrium in the solution constitutes the total ammoniacal N (TAN = NH₃ + NH₄⁺). The dissociation and the successive loss of NH₃ from the solution is the complex physical and chemical process known as volatilization (Sommer et al., 2003): it is governed mainly by NH₄⁺ concentration, temperature and pH of the medium, evaporation rates, dew formation and turbulent transport of NH₃.

In storage and application of livestock manure is essential to know the ammonia losses in order to efficiently improve the use of N for crop production. Distortions in the estimation of emissions could leads to a
reduction in the crops production (if overestimated), or in above mentioned environmental risks as N runoff or nitrate leaching (if underestimate).

The main factors influencing the total amount of NH$_3$ lost from organic and inorganic fertilizers are: the concentration of NH$_3$ at liquid surface and the transfer of NH$_3$ from surface to atmosphere, function of the meteorological conditions, i.e. air temperature, wind speed, solar radiation and field surface roughness (Sommer et al., 1991; Moal et al., 1995; Genermont and Cellier, 1997; Sommer and Hutchings, 2001; Søgaard et al., 2002; Webb et al., 2010). Among these, the solar radiation has a great direct and indirect effects on the phenomenon. Solar radiation increases the turbulence in the atmosphere by means of the action on wind and temperature, producing increasing of the transport of NH$_3$ up to the surface (Sommer and Hutchings, 2001). High temperature increases in turn evaporation, concentrating TAN in the ammoniacal solutions that encouraging emission because of the lower concentration of NH$_3$ in the above air. The effect of wind speed is strongly related to the emission, since the wind transports NH$_3$ upwards by turbulent transfer and sideways by advection (Sommer et al. 1991). Volatilised ammonia is removed by the wind taking low ammonia concentration in the air above the solution, stimulating further volatilization. However, high wind speed dries the upper layer of the soil and of the manure, facilitating the infiltration of solution and the crust formation, resulting in decreased ammonia volatilization (Huijsmans, 2003). Finally, rainfall and irrigation at the time of spreading dilute TAN and allow its soil infiltration, resulting in an overall reduction of the NH$_3$ emission rate.
Infiltration into the soil could be reduced also by the interception of the slurry by the canopy.

The surface and the timing in the application of fertilisers assumes also fundamental importance influencing the NH$_3$ emission, i.e. field application methods, presence or absence of incorporation and infiltration rate into the soil. However, these factors are combined with the proper characteristics of the fertiliser, as pH, TAN concentration and dry matter of the manure.

The manure composition, and thus the content of N, varies widely depending on animal species, diet and from housing management (Sommer and Hutchings, 2001). For example, manures from animal houses contains high levels of dry matter since they are a mixture of corporeal excreta, bedding, feed and water, while manures collected from slatted floors contain more water and less bedding materials. Furthermore, poultry manure varies widely in function of the housing type. About the infiltration, high dry matter content of slurries can act as soil colloid to further restrict or foster the infiltration the liquid part of manure, due to its high water retention capacity (Peterson and Andersen, 1996; Gènermont and Cellier, 1997; Miselbrook et al., 2000; Sommer et al., 2001).

Chemical and physical characteristics of the soil such as texture and structure, soil water content, chemical cation exchange capacity (CEC) and pH, contribute to affect the volatilization of ammonia. In dry soils ammonia emissions are reduced because of the ammoniacal solutions may be adsorbed and infiltrate through the pores, reducing its contacts with air (Van der Molen et al., 1989). On the contrary, wet or very dry
soils reduce infiltration, facilitating ammonia emission. The increasing of porosity can be obtained by tillage before slurry application and by incorporation of organic material (Sommer et al., 2003). However, few studies have quantified the effect of soil type on NH\textsubscript{3} emission rates, even if results showed that sandy soils have an emission rate higher than peat and clay soils (Sommer and Hutchings, 2001).

NH\textsubscript{3} emissions were reported to be very sensitive to slurry and soil pH conditions, where the losses increase by increasing of pH values (Genermont and Cellier, 1997; Sommer and Hutchings, 2001; Sommer et al., 2003; Misselbrook et al., 2005), for example lowering the value of slurry pH of 1 units from 7 reduces the emission over 20\% (Bussink et al., 1994; Génermont and Cellier, 1997). Soil pH lower than 6 reduce significantly the emissions, whereas values of 9 increase the emission up to 50\% (Jarvis and Pain, 1990).

Surface application of fertilizers, specially manure using splash plate, resulted the commonly method employed in Europe (Burton et al., 1996) and in Italy (CRPA, 2006). Once the ammoniacal solution is on the field surface, meteorological factors and soil conditions affecting the NH\textsubscript{3} volatilization, acting in increasing or reducing the emission.

In order to reduce the emissions of ammonia after fertilization, numerous methods are developed to apply and incorporate fertilisers into the field since the loss of NH\textsubscript{3} varies widely in function of the employed method (Sommer and Hutchings, 2001; Søgaard et al., 2002; Huijsmans et al., 2003; Rotz, 2004). In general, the reduction of the surface exchanging area between fertiliser and air causes a net reduction of atmospheric emissions. On arable land, incorporation of broadcast-
applied manure or its direct injection into the soil is an effective solution to reduce ammonia volatilization (Van Der Molen et al., 1990; Huijsmans, 1991; Ismail et al., 1991; Søgaard et al., 2002; Huijsmans et al., 2003). In particular, injection of manure using shallow slot injection is an effective method of reducing NH$_3$: the use of small volume of distributed slurry and the depth of injection increase the effectiveness in emission reduction (Smith et al., 2000). On grasslands, the use of surface-banding manure with trailing-hose or trailing-shoe applicators is a compromise between injection and surface spreading. Band spreading permits a more uniform application with respect to the splash plate, placing the manure under crop canopies without contaminating foliage.

Tillage operations, as ploughing or harrowing, after the application of fertilisers, contribute to reducing the emission by burying the material into the soil. As well are the best efficient methods to reduce emission from surface spreading. The timing of tillage is also a crucial aspect in the reduction practices, the abatement efficiency can range from 12% to over 90% if the incorporation of slurry occurs within 24 or 4 hours, respectively (Sommer and Hutchings., 2001; Huijsmans et al., 2003).

The timing of application assumes a relevant aspect since the weather conditions affect the emission. Avoiding the application of organic fertilisers during the warmer part of the day, result in reducing emissions (Sommer et al. 1991; Sommer and Jacobsen 1999). However, manure application on frozen soils is not recommended because of the possibility of runoff contamination in spring. Moreover, the emission of NH$_3$ resulted to be sensible to the manure application rate, where in increasing of volumes applied, the emission are, in proportion, reduced (Sommer
and Hutchings, 2001). This is due firstly to the drying of the first layer of slurry, that allows to the below liquid to penetrate into the soil.

1.6 Framework and objectives

Although the Po Valley (north Italy) is considered one of the most important ammonia emitting regions in Europe (Clarisse et al., 2009; Skjøth et al., 2011), few data are available for an evaluation of the ammonia budget at field level in arable lands (Valli et al., 2001; ISPRA, 2011). Therefore, the main purpose of this thesis is to evaluate the dynamics and to quantify the ammonia volatilization from arable lands, following the use of fertilisers with different agronomic techniques in this region, and to expand the database of ammonia emissions in Italy.

The work is divided in three parts:

1. In the first part, the outputs of the three above cited models (Volt’air, WinTrax and FIDES) are compared with the measurements of ammonia fluxes by eddy covariance, at hourly, daily and seasonal scales for two surface slurry spreading events followed by incorporation into the soil. A discussion on advantages, disadvantages and performances of each model is given in order to determine the most suitable method able to evaluate the ammonia emission in Po Valley at field scale.

2. In the second chapter, the models selected in the first part were used. Ammonia concentration measurements following cattle slurry spreading, with two different
application techniques (surface spreading with incorporation and injection) in the Po Valley, is reported. The evaluation of the two above mentioned inverse dispersion models to quantify ammonia emissions was carried out. The estimated NH$_3$ emission rates and their significance with regards to the Italian context were also discussed.

3. In the final part, the emissions of NH$_3$ estimated from slurry and urea application in seven field trials performed in three different locations of Po Valley were compared, in order to evaluate the best practices in reducing NH$_3$ loss from arable land. The emission factors relative to different agronomical practices (slurry injection, slurry surface spreading with and without incorporation, urea surface spreading) are given, taking into account the main factors affecting the NH$_3$ volatilization phenomenon and describing its dynamics.
References


GENERAL INTRODUCTION


Chapter 1


Chapter 2

Dynamics of ammonia volatilisation and evaluation of three models to quantify emissions from slurry spreading

*Keywords.* Eddy covariance, inverse dispersion model, mechanistic model, slurry spreading, incorporation technique, ammonia volatilization, arable land
Abstract

The performance of three models to estimate ammonia (NH$_3$) fluxes have been evaluated, comparing the simulated fluxes with the direct eddy covariance (EC) flux measurements performed during the application of dairy slurry in two intensively managed agricultural fields in northern Italy. The EC system was equipped with a fast sensor for NH$_3$ concentration measurements based on Tunable Infrared Laser Differential Absorption Spectrometry. The three employed models were: two concentration-based inverse dispersion models ("Lagrangian"-type, WindTrax, and "Eulerians"-type, FIDES), coupled with the use of long term exposure concentration samplers, and one deterministic model, Volt'Air. The comparison showed good agreements especially between the two inverse dispersion models ($R^2 = 1$) and between them and the EC ($R^2$ from 0.55 to 0.79, modelling efficiency from 0.45 to 0.78). The inverse dispersion models turn out to be of great utility and gave different, but comparable results with respect to the reference technique (slopes of regression 0.8, cumulated emissions 30-40% lower) and have shown to be sensible to the turbulence parameters, especially friction velocity and roughness length. The deterministic model Volt’Air was able to reproduce the trend of the volatilization process, but provided very high emission values compared to the EC measured fluxes (65-70% higher), due to its sensibility to the soil surface and slurry pH.
2.1 Introduction

Ammonia (NH₃) plays an important role in atmospheric chemistry. It is the most abundant alkaline gas and is involved in the formation of particular matter by neutralization of acidic gases in atmosphere (Duyzer et al., 1994; Asman et al., 1998). Therefore, the determination of NH₃ emissions and depositions is of fundamental importance for studying the atmosphere evolution at different space and time scales. Moreover, agricultural activities are the major source of NH₃ emissions to the atmosphere, contributing about 90% of the total in Western Europe according to recent estimates; the field application of slurry was found to have the most important role in the atmospheric NH₃ dynamics (Jarvis and Pain, 1990; Sommer et al., 1991, Erisman et al., 2008). From the agricultural perspective the estimation of the NH₃ volatilisation after fertilisation is important to evaluate the nitrogen (N) budget and the correct technique for increasing the nitrogen efficiency at field and farm scale.

The various agricultural techniques used for nitrogen application differ in their impact on the amount of NH₃ released, thus the exact evaluation of the ammonia fluxes at field level is necessary to have the whole control of its impact on the environment. In general, ammonia volatilisation starts after an application of fertiliser and results in four steps: an increase in the ammoniacal nitrogen stock in the field, transfers between soil layers, equilibrium between different forms of ammoniacal nitrogen and transfer in the atmosphere. The strongest emissions are observed during the first day after the application. This process lasts between several days and several weeks after application: it depends on fertiliser type, soil type, cultivation techniques (dose, incorporation,
ploughing, etc.) and climatic conditions (temperature, wind speed, rainfall, etc.) (Sommer et al., 1991; Moal et al., 1995; Genermont and Cellier, 1997; Sommer and Hutchings 2001; Søgaard et al., 2002; Misselbrook et al., 2005).

However, large uncertainty exists on NH$_3$ dynamics in the soil-plant-atmosphere continuum due to the scarcity of direct reliable flux measurements. This can mainly be attributed to difficulties in measuring fluxes of such a reactive compound (Harper, 2005). Measurement of NH$_3$ concentrations at field scale are affected by the wide ambient variability, from less than 0.035 µg m$^{-3}$ in remote regions to over 250 µg m$^{-3}$ near sources (Krupa, 2003). One major difficulty for the development of measuring techniques for atmospheric NH$_3$ is its simultaneous presence in the gaseous, the particulate (e.g., ammonium nitrate) and the liquid phases (NH$_4^+$ fog) (Normann, 2009). The measurement technique should be specific to the gas-phase and not modify the gas-aerosol equilibrium which depends on environmental conditions (Mozurkewich, 1993). Furthermore the ‘sticky’ nature of the ammonia molecule greatly influences the measurements, for its hydrophilic nature that gives it the ability to bind and unbind from solid surfaces used in air sampling systems, as well as to absorb and disassociate in water (Brodeur et al., 2009). Finally, NH$_3$ is emitted by other non-agricultural sources (i.e. transport, pets and wild animals, biomass burning and humans) increasing the potential for sample contamination (Sutton et al., 2000; Dragosits et al., 2010). Moreover, the sources and sinks of NH$_3$ are spatially highly heterogeneous (Sutton et al., 1998; Dragosits et al. 2002) and further considering its reactive nature and the dependence of NH$_3$
exchanges by environmental factors, two are the techniques suitable to its determination at field scale: (i) the micrometeorological measurement methods, due their non-intrusive feature (Denmead, 1983; Kaimal and Finnigan, 1994) and (ii) the modelling starting from easily measurable variables as inputs. A model of ammonia fluxes has the advantage of permitting the comparison of different nitrogen application techniques at field level with a workload for just measurable input variables, although a test on the performances of a model is needed through a direct measurement.

The nature of flow measurements has been highlighted by several recent studies comparing different approaches (i.e. Hensen et al., 2009b, Milford et al., 2009, von Bobrutzki et al., 2009), where strong differences were found among them. Eddy Covariance (EC) is considered the most direct and least error-prone approach for measuring fluxes at field scale (Ammann, 1999; Sutton et al., 2007; Denmead, 2008, Fowler et al., 2009; Sintermann et al., 2011), but it requires fast trace gas analyzer to resolve the major part of the turbulent spectrum, ranging from frequencies of about 10 to 0.001 Hz (Businger and Delany, 1990). Only recently, several sensitive and fast responding instruments for NH$_3$ became available that theoretically opened the possibility to perform EC flux measurements. Ferrara et al. (2012) demonstrated that EC technique where a Quantum Cascade - Tunable Infrared Laser Differential Absorption Spectrometry (QC-TILDAS) coupled with a sonic anemometer can be used as “reference method” to measure ammonia fluxes in the field, if a correction function is applied.

The most suitable models to estimate ammonia fluxes are based on two approaches: (1) the dispersion theory and (2) the soil-atmosphere
continuum description. The purpose of the first approach is to define the gas concentrations downwind of a known source, starting from the pollutant emission rate and the meteorological conditions. The second approach is based on the deterministic modelling of all the aspects of the ammonia volatilisation, such as the influence of climatic data, the agricultural technique and the soil and slurry properties on NH$_3$ fluxes. In this work three well known models are tested: two versions of the dispersion theory, (1a) FIDES-2D (Loubet et al., 2001) and (1b) WindTrax (Flesch et al., 1995) and (2) Volt’Air, a deterministic model developed by Générmont and Cellier (1997).

Although the Po Valley (north Italy) is considered one of the most important ammonia emitting regions in Europe (Clarisse et al., 2009; Skjøth et al., 2011), few data are available for an evaluation of the ammonia budget at field level in arable lands. The only information available are reported in Valli et al. (2001) and ISPRA (2011), where the national NH$_3$ emission factors (EF) are calculated by taking into account the climatic conditions, the animal productivity and the manure management systems, by using the EMEP/CORINAIR guidebook (EMEP/CORINAIR, 2007; EMEP/EEA, 2009).

Here, the outputs of the three above cited models are compared with the measurements of ammonia fluxes by EC, at hourly, daily and seasonal scales, in a site of Po Valley for two surface slurry spreading events followed by incorporation into the soil. A discussion on advantages, disadvantages and performances of each model is given in order to determine the most suitable method able to evaluate the ammonia emission in Po valley at field scale.
2.2 Material and methods

2.2.1 Site description

The field trials were performed during the springs 2009 (SI-09) and 2011 (SI-11), in a farm located in Landriano (Po Valley, Northern Italy, Lat. 45°19′ N, Long. 9°16′ E, Alt. 88 m a.s.l.). The two experimental fields were situated close to each other and had a similar agronomic management (Figure 2.1).

SI-09 was carried out from 26th March to 3rd April 2009 on a loam texture soil in a field of 3.9 ha, covered by maize stubbles. Soil, at the beginning of the experiment, on 0-20 cm layer, had a water content of 0.17 m$^3$ m$^-3$ and pH of 7.1. The field surface was spread with 87 m$^3$ ha$^-1$ of dairy slurry on 27th March, using splash plate technique associated to umbilical spreading system. The application started at 8:30 a.m., from the left side of the field to the opposite, and lasted in total 5 hours. After 24 hours from the spreading start, the slurry was incorporated by means of a disc harrower working at 25 cm depth; the duration of harrowing was 1.5 hours. The applied total ammoniacal nitrogen (TAN) was 95 kg N-NH$_3$ ha$^-1$.

The SI-11 was performed from 6th to 13th April 2011 in a 4.3 ha loam texture soil covered by sparse 10 cm tall Lolium multiflorum Lam. The initial soil water content and pH in the 0-10 cm layer were 0.21 m$^3$ m$^-3$ and 6.4, respectively. Dairy slurry was applied on 7th April, at a rate of 75 m$^3$ ha$^-1$, corresponding to a TAN of 109 kg N-NH$_3$ ha$^-1$. The spreading technique was the same used in SI-09. The distribution started from the right side of the field to the opposite and lasted about 5 hours. Slurry was
incorporated through a 25 cm depth disc harrowing, started about 30 hours after the day of application, and lasted 2 hours.

Representative slurry samples (2 dm³) were collected during the spreading’s day to analyze physics and chemicals properties as pH, percentage of dry matter (DM), TAN and total Kjeldahl nitrogen (TKN). In the same day soil bulk density (BD), cation-exchange capacity (CEC) and calcium carbonate (CaCO₃) samples were collected (Table 2.1). Furthermore, soil was sampled daily at 0-10 cm and 10-20 cm depths to

Figure 2.1. Site map of experimental fields during the trials in Landriano in 2009 (SI-09) and 2011 (SI-11).
characterize pH, water content, organic matter, nitrous and ammoniacal nitrogen. All samples were collected and analyzed in triplicates.

Furthermore, meteorological variables were measured by a standard station (Lastem, Milano, IT) working at hourly time step, and at 180 and 250 m away from the center of the SI-09 and SI-11 fields, respectively. Air temperature $T_a$, ($^\circ$C), relative humidity $RH$ (%), global solar radiation $R_g$ (W m$^{-2}$) and precipitation $P$ (mm) were measured at 1.8 m above ground.

**Table 2.1. Main characteristics of the slurries applied during the trials Landriano 2009 (SI-09) and 2011 (SI-11).**

<table>
<thead>
<tr>
<th></th>
<th>Dry matter g kg$^{-1}$</th>
<th>pH</th>
<th>TAN kg N-NH$_4^+$ ha$^{-1}$</th>
<th>TKN kg N ha$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI-09</td>
<td>44</td>
<td>8.0</td>
<td>95</td>
<td>188</td>
</tr>
<tr>
<td>SI-11</td>
<td>55</td>
<td>7.8</td>
<td>109</td>
<td>223</td>
</tr>
</tbody>
</table>

**2.2.2 Description of the methods**

2.2.2.1 *Direct NH$_3$ flux measurements: the Eddy Covariance technique*

The eddy covariance is a micrometeorological method to measure the vertical turbulent flux within atmospheric boundary layers (Kaimal and Finnigan, 1994). The transport of a scalar, like NH$_3$ gas, is due to the eddying motion of the atmosphere and the relative flux is obtained by correlating the instantaneous vertical wind speed ($w$) with the instantaneous concentration of the gas ($\chi$), both measured at the same height and location at a frequency of eddies in natural environments, that means at least 10 Hz (Denmead, 1983; Baldocchi *et al.*, 1988).

The vertical flux of the scalar ($F\chi$) is given by
where the over-bar indicates average on a time interval and the Reynolds decomposition has been applied, i.e. the instantaneous value of the entity is equal to the sum of its mean state and its fluctuation from the mean, $\chi = \bar{\chi} + \chi'$. The vertical turbulent flux is the covariance of a time series of the fluctuations in vertical velocity and concentration of a scalar entity over the time interval often chosen equal to half an hour or one hour. This turbulent flux can be measured directly by EC method, but the main vertical velocity ($\bar{w}$) can be considerate zero only if dry air is sampled, that means without heat and/or water vapour fluxes between the surface and the atmosphere, otherwise the Webb et al. (1980) corrections have to be applied. However, the relative importance of these corrections depends on the background concentration of the gas and the magnitude of the typical flux (Denmead, 1983). For trace gas with small background concentration and large fluxes, such as ammonia, these corrections are not important and can be neglected.

Flux loss is inevitable with any EC system, especially employing closed-path analysers to which the air sample is transported into the measuring cell by means of a tube. Nowadays, a variety of methods can be chosen to correct these underestimated measured fluxes by means of frequency response correction factors (e.g. Ammann et al., 2006; Shimizu, 2007; Aubinet et al., 2000; Massman 2000; Eugster and Senn, 1995). The entities of these losses can be also of the order of 40% of the actual fluxes as reported by Ferrara et al. (2012). Here, the theoretical transfer-function approach (i.e. Moore, 1986) and the inductance method
(Eugster and Senn, 1995) were used to correct the EC data of SI-09 and SI-11, respectively, considering the availability of information needed for the two above-mentioned spectral correction approaches. A sonic anemometer is used for fast measurements of $w$, while fast response sensor for gas concentration is often based on infrared spectroscopy. Micrometeorological measurement were performed using a three-dimensional sonic anemometer (Gill-R2, Gill Instruments Ltd, UK) located in the center of each field at 1.45 m and 1.25 m above ground for SI-09 and SI-11, respectively.

**Fast analyser for NH$_3$ concentration measurements: the QC-TILDAS**

A QC-TILDAS (Aerodyne Research Inc., ARI, Billarica, Massachusetts, USA) was used to measure NH$_3$ concentration at high frequency (10Hz) (Zahniser et al., 2005). The spectrometer combines a pulsed QC laser (Alpes Lasers, Neuchâtel, Switzerland), an optical system and a computer-controlled system that incorporates the electronics for driving the QC laser along with signal generation and data acquisition. The QC laser used in the NH$_3$ instrument operates near 10.31 µm (967 cm$^{-1}$) where NH$_3$ has strong absorption line. The optical system collects light from the QC laser and directs it through a multi-pass absorption cell (optical absorption path length 76 m, volume 0.5 l, pressure about 40 torr) onto a Thermo Electrically cooled photovoltaic detectors (Vigo Systems). Concentrations are real-time determined from the spectra through a non-linear least-squares fitting algorithm (Levenberg-Marquardt) that uses spectral parameters from the HITRAN
NH$_3$ samples were acquired by a heated inlet tube, 2.5 m long with 3/8” outer diameter and made in inert paraformaldehyde (PFA), placed near the transducers pairs of the sonic anemometer. The setup of the inlet was done to remove more than 50% of particles larger than 300 nm in the air sample relying on inertia; in particular, the flow was split into two branches: 90% of the flow makes a sharp turn and is pulled into the optical cell by a pump (VARIAN TriScroll 600 Series), the other 10% is pulled by a second air pump (VARIAN, mod SH110). This inlet design is optimized to eliminate the need of filters and any interference they may cause.

Standard calibrations were performed every 6 hours with a 1 ppm ammonia tank through a metal valve plugged before the PFA T-shape: a calibration factor of about 3 was detected.

To ensure a proper functioning of whole system, the laser box was conditioned to 20°C by means of an air-conditioning system in order to avoid instrumental drifts due to temperature fluctuations.

2.2.2.2 **Modelling NH$_3$ fluxes**

NH$_3$ emissions from field can be determined using dispersion models (Flesch et al., 2004; Sommer et al., 2005; McBain and Desjardins, 2005; Loubet et al., 2001, 2009, 2010; Todd et al., 2008; Sintermann et al., 2011). Their purpose is to define the gas concentrations downwind of a known source, starting from the pollutant emission rate and the meteorological conditions. In this study dispersion models were used in
inversion mode, therefore the estimation of the source is obtained relating the measure of gas concentration within an emission plume (one or more spatialized points), with the emission rate of a known and spatially-limited source area.

2.2.2.2.1 Inversion models

The inversion technique is based on the general superposition principle (Raupach, 1989; Thomson, 1987), which relates the measured concentration at a location \((x, y, z)\), to the source strength \((S)\) strength at another location \((x_s, y_s, z_s)\), with the use of a dispersion function \(D(x, y, z / x_s, y_s, z_s)\) (in s m\(^{-1}\)):

\[
\chi(x, y, z) = \chi_{bgd} + \int S(x_s, y_s, z_s) D(x, y, z) \, dx_s \quad \text{(eq. 2.2)}
\]

where \(\chi_{bgd}\) is the background concentration, assumed to be constant with height. The basic hypothesis in this approach are:

(i) the NH\(_3\) source is considered homogeneous and at constant concentration at the canopy height (Loubet and Cellier, 2001);

(ii) no atmospheric chemical reactions are supposed (conservation of mass), indeed the effect on the NH\(_3\) concentration in a small scale approach is not expected to be large (Nemitz et al., 2009);

and

(iii) the soil surface characteristics are considered to be homogeneous, i.e. the roughness length \((z_0)\) and the zero-plane displacement \((d)\) are constant.
Two inverse methods are profitably employed to characterize the atmospheric turbulent transport and derive the dispersion function $D$: Lagrangian-type, like “Windtrax” model described by Flesch et al. (2004), and Eulerian-type, like “FIDES-2D” (“FIDES”) model described by Loubet et al. (2001).

The selected backward Langrangian stochastic model (bLS) WindTrax combine the Monin-Obukhov similarity theory (MOST) (Stull, 1988) to characterise the turbulent transport with an interface where source area and concentration sensors can be mapped. The MOST theory states that over short time intervals (e.g. 30 min) the atmospheric turbulence properties, in the low atmosphere, are known from four variables: wind direction $WD$ (degree to north), friction velocity $u_*$ (m s$^{-1}$), Monin-Obukhov length $L$ (m) and $z_0$ (m). To obtain $D$, the model calculates thousands of trajectories upwind of the sensors, to determine the number of the resulting particle-ground intersections within or outside a given source area ($N_{source}$ “touchdowns”). At the same time is recorded the vertical velocity of the wind ($w_0$) of those trajectories that intersect the source area:

$$D = \frac{1}{N} \sum_{N_{source}} \left| \frac{2}{w_0} \right|$$  \hspace{1cm} (eq. 2.3)

The estimation of the flux ($S$) is simply obtained from the above described equations:

$$S = (\chi - \chi_{bgd}) \times D^{-1}$$  \hspace{1cm} (eq 2.4)
Using the Eulerian approach, in the FIDES model the source is subdivided into grid cells, each contributing to the observed concentration at a certain measurement height. A marked difference with respect to the bLS model is the possibility to consider the surface as a “concentration driven source” as opposed to a “flux driven source” (Loubet et al., 2001, 2009, 2010). In fact, FIDES is employed to infer the emission strength from the source \( S \), using \( \chi \) and \( \chi_{\text{bgd}} \), while bLS simulates the transport of tracer from a source to a measurement location. The local-scale dispersion-exchange model is a steady state, two-dimensional model, along-wind direction \( x \) and vertical ascendancy \( z \) (where \( z \) is the height above \( d \)). In this model the transfer coefficient \( D(x, z/x_s, z_s) \) was estimated using the Huang (1979) semi-analytical dispersion model:

\[
D(x - x_s, z) = \frac{A}{(x - x_s)^\beta} \exp \left[ -\frac{(z - d - z_0)^\alpha + (z_s - d - z_0)^\alpha}{B \cdot (x - x_s)} \right]
\]

(eq 2.5)

Where \( \Delta x \) is the grid size, \( A, B, \alpha, \) and \( \beta \) are defined as:

\[
A = \frac{\alpha}{a^v \cdot (b\alpha^2)^\beta \cdot \Gamma(\beta)}
\]

(eq 2.6)

\[
\alpha = 2 + p - n
\]

(eq 2.7)

\[
v = (1 - n)/\alpha
\]

(eq 2.8)

\[
\beta = (1 + p)/\alpha
\]

(eq 2.9)

\[
B = b/(a \alpha^2)
\]

(eq 2.10)
Where $\Gamma$ is the molar ratio between $[\text{NH}_4^+] / [\text{H}^+]$ (Nemitz et al., 2000), while $a$, $b$, $p$ and $n$ are defined as function of wind speed ($U$), vertical diffusivity ($K$), $d$ and $z_0$:

$$U(z) = a(z - d - z_0)^p$$  
(eq. 2.11)

$$K(z) = b(z - d - z_0)^n$$  
(eq 2.12)

In this approach the source $S$ is modelled as:

$$S(x) = -\frac{\chi(x, d + z_0) - \chi_c}{R_b}$$  
(eq 2.13)

Where $\chi(d + z_0)$ is the concentration at the top of the canopy, $\chi_c$ is the canopy compensation point (Sutton et al., 1998), $x$ is the downwind distance and $R_b$ the pseudo-laminar layer resistance, accounting for nonsimilarity between momentum and NH$_3$ transfer in roughness sublayer, derived by Garland (1977).

Both models use the same data inputs that are the mentioned turbulence parameters $WD$, $u^*$, $L$, $z_0$, obtained by the sonic anemometer, combined with the ammonia concentration measurements at the same height. To ensure an homogeneous surface layer where the principles of the MOST theory could be applied in the models, a prevailing value of $z_0$ was calculated as the median of the values of $z_0$ derived from sonic anemometer, excluding data with $|L| < 5$ m and $u^* < 0.2$ m s$^{-1}$ (Flesch et al., 2004; McBain et al., 2005; Todd et al., 2008; Hensen et al., 2009a; Loubet et al., 2009). Values of $z_0$ used here were 0.02 and 0.04 m for SI-09 and SI-11, respectively.
Passive diffusion samplers for long term concentration measurements

The field NH$_3$ concentration was measured using a passive and time averaged approach, based on ALPHA samplers (Adapted Low-cost Passive High Absorption) (Tang et al., 2001, Sutton et al., 2001). The applicability of a long term concentration measurement to estimate NH$_3$ emissions was discussed by Loubet et al., (2011). The operating principle of ALPHA samplers is based on the capture of gaseous NH$_3$ on acid support. These tools are designed to measure NH$_3$ air concentration less than 1 µg m$^{-3}$ (Leith et al., 2004); in the present study was reached 4 mg m$^{-3}$. The samplers have the advantage of being suitable for use at field scale, requiring relatively inexpensive budget and simple exposure equipment. Structurally, it consists of one open end 6 mm long, 21 mm inner diameter polyethylene cylinder. One end contains a 5 µm PTFE membrane, through which NH$_3$ gas diffuses and is adsorbed onto a circle filter paper (Whatman 3MM Chr) coated with a solution of citric acid (13%) and methanol located at the other end of the diffusion path. The PTFE membrane prohibits particle collection and has the role to form a quasi-laminar layer of air adjacent to its outer surface which serves to establish a turbulence-free diffusion path between the membrane and the collection filter (Pinder, 2011). Three set of samplers were put in the field center to measure NH$_3$ concentration following slurry spreading, and three set were placed about 1200 m far from the fertilised area and at least 600 m from each known ammonia source to measure background concentration. Samplers were exposed at the same height of the sonic anemometer for a time never longer than 12 hours, and reduced to about 2 hours on the day of the slurry application. After the exposure the filters were extracted in 3 ml of deionized water and the N-NH$_4^+$ content
determined by the indophenol blue colorimetric method and spectrometer (FOSS, FIAstar 5000 system, Denmark).

2.2.2.2 Deterministic model: Volt’Air

The deterministic model Volt’Air (Génermont and Cellier, 1997) was developed to describe ammonia volatilisation after slurry application under field conditions. This model, unlike other deterministic ones (Rachhpahl-Singh, Nye, P.H., 1986; Van der Molen et al., 1990), considers the influence of all parameters affecting the volatilisation phenomena such as climatic data, agricultural technique, soil and slurry properties. Furthermore, the process is simulated with short time intervals over several days or several weeks following fertilisation. The main components of the model, together with their interrelation are shown in Figure 2.2. In particular, the architecture of Volt'Air is organized around a series of six sub-models, three of them focused on ammoniacal N transfers and equilibria between ammoniacal N species:

(i) physical and chemical equilibria in the soil
(ii) aqueous and gaseous ammoniacal N transfers through the soil
(iii) gaseous ammonia transfer from the soil to the atmosphere.

The other three simulate heat and water transfers in the soil:

(iv) water
(v) heat
(vi) energy budget, water and heat exchange between the soil and the atmosphere.
These latter three models are necessary to simulate transport and to manage the equilibria governed by the heat and ammoniacal nitrogen concentration. The assumptions of the model are that soil physical and chemicals properties do not change spatially within a definite soil layer and that soil physical properties remain unchanged during whole simulation period. Moreover, N transformation by soil organic matter mineralization, ammoniacal N organization or uptake by plants, oxidation or nitrification and mineralization of organic N by slurry are not accounted for, due to the rapid evolution of the NH$_3$ emission phenomenon. Volt’Air idealizes soil profile into a series of sub-layers, definite by the user for numbers and thickness. Each soil layer is assumed to be a homogeneous, incompressible and isotropic porous medium.
(i) The physicochemical equilibria module is calculated on the base of the assumptions of the aqueous phase is supposed to be ideal (solute concentration close to zero, solute activities equal to their molar concentration), and equilibria occurs instantaneously (Bouwmeester and Vlek, 1981). The solubility of ammonia results from two equilibria, ionization (eq 2.14) and liquid-gas equilibria (eq 2.15):

\[
\begin{align*}
NH_4^+ (aq) + H_2O & \rightleftharpoons NH_3(aq) + H_3O^+ (aq) \quad \text{(eq 2.14)} \\
NH_3 (aq) & \rightleftharpoons NH_3(g) \quad \text{(eq 2.15)}
\end{align*}
\]

where \( NH_4^+ \) (aq) is aqueous ammonium ion, \( NH_3 \) (aq) is aqueous ammonia and \( NH_3 \) (g) is gaseous ammonia. The partitioning between \( NH_4^+ \) (aq) and \( NH_3 \) (aq) is determinate by the pH of solution and by the reaction equilibrium constant, instead the partitioning between \( NH_3 \) (aq) and \( NH_3 \) (g) is regulated by the Henry's law constant. Moreover, for each layer of the soil profile, Volt’Air takes into account the adsorption of \( NH_4^+ \) (aq) ions on clay minerals and soil organic compounds (\( NH_4^+ \) (s)) using the Freundlich's isotherm (eq 2.16) (Bolt, 1976):

\[
NH_4^+ (aq) \rightleftharpoons NH_4^+ (s) \quad \text{(eq 2.16)}
\]

(ii) The \( NH_4^+ \) (aq) and \( NH_3 \) (g) transfer between the soil layers is simulate on the basis of Fick’s law and depends on the \( NH_4^+ \) and \( NH_3 \) ion concentrations in the aqueous phase, their water diffusion coefficient (equal for the two molecules), temperature, soil water content and medium porosity. The diffusion of \( NH_3 \) (g) in the soil macroporosity is
also simulated using the air diffusion coefficient (Van der Molen et al., 1990).

(iii) The NH$_3$ (g) transfer from the soil surface to the atmosphere is calculated on the basis of the local advection analytical solution proposed by Itier and Perrier (1976). This analytical solution demonstrate that surface flux depends only by NH$_3$ (g) surface concentration, roughness length, field’s length in the main wind direction and on the local meteorological conditions.

(iv) The Darcy’s law generalized to vadose zone is instead employed to calculate the water transfer between soil layers. Water retention and hydraulic conductivity models of Clapp and Hornberger (1978) and van Genuchten–Mualem (van Genuchten, 1980) are implemented to the purpose: input parameters for the latter mentioned models can be obtained from direct measurements, or rather estimated from pedotransfer functions. Water as well as heat transfer are considered one-dimensional vertical and calculated in the centre of each soil layers, whereas interactions between heat and water flow are not taken into account.

(v) The heat transfer between soil layers is simulated using Fourier’s law.

(vi) The energy budget uses the energy balance equation of the bare soil surface (eq 2.17) to calculate surface temperature and evaporation:

$$R_n - G = H + \lambda E$$  \hspace{1cm} (eq 2.17)

where $R_n$ is the net radiation of the surface, $G$ the soil heat flux, $H$ the sensible heat flux and $\lambda E$ the latent heat flux or evaporation; all the fluxes
being expressed in W m\(^{-2}\). These parameter can be calculated from standard meteorological data and readily available soil parameters. The input data employed to parameterize the Volt’Air model during the two trials are presented in Appendixes A, B and C.

### 2.2.3 Statistics

The statistics used to evaluate the performances of the modelling approaches with respect to the EC measurements were the relative root mean square error (\(RRMSE\); Jørgensen et al., 1986), the modelling efficiency (\(E\); Nash and Sutcliffe, 1970) and the coefficient of residual mass (\(CRM\); Loague and Green, 1991). Moreover were calculated the slope of the regression line between the EC and each approach and the coefficient of determination (\(R^2\)) that allows to know how the variance of the measured data is explained by the simulation approaches.

The \(RRMSE\) is a relative measure of the accuracy of the simulated data from measured, and is defined as follow

\[
RRMSE = \sqrt{\frac{\sum_{i=1}^{n} (O_i - P_i)^2}{\bar{O}}} \cdot 100
\]

(eq. 2.18)

were \(n\) is the number of observations, \(O_i\) and \(P_i\) represent the observed and predicted data. In our case, the predicted data are the values obtained from the inverse dispersion models and Volt’Air model. The \(E\) allows to evaluate the efficiency of the modelling. The optimal value of \(E\) is 1, furthermore values greater than 0 indicate that the estimations is better
than the average of observations; negative values of $E$ indicate that the average of the observations is a better predictor of the model. $E$ is defined as:

$$E = 1 - \frac{\sum_{i=1}^{n} (O_i - P_i)^2}{\sum_{i=1}^{n} (P_i - \bar{P}_i)^2}$$  \hspace{1cm} \text{(eq 2.19)}$$

The $CRM$ provides information on the tendency to overestimate (if $<0$) or underestimate (if $>0$) the observed data. The optimal value of $CRM$ is 0, and has been calculated as follows:

$$CRM = \frac{\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} P_i}{\sum_{i=1}^{n} O_i}$$  \hspace{1cm} \text{(eq 2.20)}$$
2.3 Results

2.3.1 Micrometeorological conditions

Table 2.2 presents the statistics of hourly data of precipitation, temperature, wind, relative humidity and global solar radiation recorded during the two trials. During SI-09, the mean wind speed was 1.5 m s\(^{-1}\) with main direction S (Figure 2.3). In addition, an important rain event of 55 mm occurred from the day following the spreading, after incorporation. During SI-11, the average wind speed was 1.3 m s\(^{-1}\) with prevailing direction O (see Figure 2.3); in 2011 the temperature was higher than during 2009, however the meteorological conditions during the two trials were within the seasonal averages (period 1988-2011).

Table 2.2. Meteorological variables in SI-09 and SI-11 during the respective trials.

<table>
<thead>
<tr>
<th></th>
<th>Rain mm</th>
<th>Temperature °C</th>
<th>Relative humidity %</th>
<th>Wind speed m s(^{-1})</th>
<th>Global solar radiation W m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI-09</td>
<td>mean</td>
<td>11.2</td>
<td>94.5</td>
<td>1.5</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>19.4</td>
<td>100</td>
<td>5.6</td>
<td>630</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>3.1</td>
<td>71.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>cumulated</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SI-11</td>
<td>mean</td>
<td>18.5</td>
<td>86</td>
<td>1.3</td>
<td>222</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>32</td>
<td>97</td>
<td>3.4</td>
<td>823</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>7.4</td>
<td>16</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>cumulated</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.4 and 2.5 show the trends of the atmospheric stability (1/L), friction velocity (\(u^*\)) and wind speed (\(U\)) in both the field trials. The 1/L parameter displayed general nocturnal stability peaks (positive) and negative values during daily instability, especially in SI-11. The \(u^*\) shows
a typical daily maximum with minimum at night, following the course of the wind speed. However, during the rain event occurred in SI-09 the values of \( u^* \) was almost constant and low. Furthermore, Table 2.3 reported the statistics on the \( u^* \) and \( L \) trends measured during the experimental campaigns.

Figure 2.3. Main and day-night wind direction (WD) during the trials in Landriano in 2009 (SI-09) and 2011 (SI-11).
Figure 2.4. Trail in Landriano 2009 (SI-09): friction velocity ($u^*$) and wind speed (red dotted line) on upper panel; inverse Monin-Obukhov length (1/L) during day (gray line) and nighttime (black line) on lower panel.

Figure 2.5. Trail in Landriano 2011 (SI-11): friction velocity ($u^*$) and wind speed (red dotted line) on upper panel; inverse Monin-Obukhov length (1/L) during day (gray line) and nighttime (black line) on lower panel.
Table 2.3. Main statistics of atmospheric turbulence (friction velocity, $u^*$ and Monin-Oboukhov length, $L$), together with NH$_3$ concentration measured by the QC-TILDAS and measured in the fertilised field ($C_{field}$) and at background level ($C_{bgd}$) by the Alpha samples, during SI-09 and SI-11.

<table>
<thead>
<tr>
<th></th>
<th>$u^*$ m s$^{-1}$</th>
<th>$L$ m</th>
<th>$C_{field}$ µg m$^{-3}$</th>
<th>$C_{bgd}$ µg m$^{-3}$</th>
<th>QC-TILDAS µg m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SI-09</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>0.00</td>
<td>-1816</td>
<td>8</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>max</td>
<td>0.41</td>
<td>8216</td>
<td>886</td>
<td>84</td>
<td>1526</td>
</tr>
<tr>
<td>mean</td>
<td>0.14</td>
<td>135</td>
<td>197</td>
<td>39</td>
<td>181</td>
</tr>
<tr>
<td>median</td>
<td>0.12</td>
<td>6</td>
<td>53</td>
<td>26</td>
<td>20</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.10</td>
<td>629</td>
<td>271</td>
<td>33</td>
<td>343</td>
</tr>
<tr>
<td><strong>SI-11</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>0.01</td>
<td>-259</td>
<td>12</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>max</td>
<td>0.41</td>
<td>7269</td>
<td>973</td>
<td>29</td>
<td>1928</td>
</tr>
<tr>
<td>mean</td>
<td>0.15</td>
<td>50</td>
<td>191</td>
<td>16</td>
<td>154</td>
</tr>
<tr>
<td>median</td>
<td>0.14</td>
<td>0</td>
<td>48</td>
<td>15</td>
<td>59</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.09</td>
<td>514</td>
<td>268</td>
<td>7</td>
<td>260</td>
</tr>
</tbody>
</table>

2.3.2 Ammonia concentrations

Figures 2.6 and 2.7 show the time-series of measured NH$_3$ concentration during SI-09 and SI-11, respectively, at different temporal resolution, 30 min for the QC-TILDAS instrument and variable between 2 and 10 hours for the Alpha samplers. The QC-TILDAS data have been corrected, by using a calibration factor equal to 3; it was found during the calibration procedure carried out periodically during the trials (Ferrara et al., 2012). Both the methods reproduce similar time courses of ammonia concentration, although Alpha samplers have detected lower levels than the QC-TILDAS device, especially in SI-09. The mean initial values of concentration, measured before the spreading, were: 26.7 and 1.2 µg m$^{-3}$ in 2009 and 67.6 and 39 µg m$^{-3}$ in 2011 by Alpha and QC-TILDAS, respectively. In order to overcome the different time resolution of the two devices, the QC-TILDAS measurements were averaged in the sampling interval of Alpha device.
Figure 2.6. \( \text{NH}_3 \) concentration measured during the trial in Landriano in 2009 (SI-09) by the QC-TILDAS (black line), by the Alpha samplers (red lines) and rainfall. For the Alpha samplers the standard deviations are reported too.

Figure 2.7. \( \text{NH}_3 \) concentration measured during the trial in Landriano in 2011 (SI-11) by QC-TILDAS (black line), by the Alpha samplers (red lines) and rainfall. For the Alpha samplers the standard deviations are reported too.
As indicated by the QC-TILDAS, the peak value of ammonia concentration in SI-09 (1,525 μg m\(^{-3}\)) was reached 1.5 hours after the slurry spreading corresponding to a mean value of 1,330 μg m\(^{-3}\) on the accumulation time of the Alpha samplers exposed in the same period. The same peak as measured by Alpha was, instead, 817 μg m\(^{-3}\) (see Figure 2.6). The concentration path measured with the QC-TILDAS allows to observe in detail the time course of the NH\(_3\), that begins to increase 2 hours after the start of the spreading. After the peak in the morning, the NH\(_3\) concentration detected by the Alpha approach rose down, while the QC-TILDAS showed other peaks achieved during the night. The soil tillage, combined with the rain event, dropped the presence of NH\(_3\) in atmosphere, as detected by both devices.

The trends observed in SI-11 (see Figure 2.7), considering the QC-TILDAS data, showed two peaks, because of a short break during the spreading. The first of 1566 μg m\(^{-3}\) was reached 2.5 hours after the beginning, followed by a largest second peak of 1,928 μg m\(^{-3}\) reached just before the end of the application. The Alpha samplers detected the same peaks, the first of 774 μg m\(^{-3}\) and the second of 1,181 μg m\(^{-3}\), corresponding to the time-averaged values of 1,003 μg m\(^{-3}\) and 1,102 μg m\(^{-3}\) obtained by the QC-TILDAS device. Afterwards, the concentration values showed a reduction, with a further decreasing after the incorporation. After the tillage, the ammonia concentration remained low and near to the reference background value, even if the concentration of the QC-TILDAS displayed series of small peaks.

Figure 2.8 shows the relationship between the NH\(_3\) concentrations measured through the Alpha and the time averaged QC-TILDAS values, in both trials. The graph shows a general underestimation of the values...
obtained using the Alpha samplers, although with a general good coherency ($R^2 = 0.86$ and $0.90$ for SI-09 and SI-11, respectively). The bias (in %) between the two instruments, defined as the percentage of the difference between the angular coefficient of the linear regression forced to the origin of the axis and the unit, indicates values of -44% for SI-09 and -14% for SI-11. In Table 2.3 the statistics relative to the measurements of the NH$_3$ concentrations by the Alpha and the QC-TILDAS are reported.

![Figure 2.8. Scatter plot between the concentration measured by the Alpha and the QC-TILDAS, during the trails in Landriano 2009 (SI-09) and 2011 (SI-11). Dotted line represents 1:1 line.](image)
2.3.3 Ammonia fluxes: dynamics description

The NH$_3$ fluxes measured by EC and simulated by the above-described models are presented in Figures 2.9 and 2.10. Different vertical scales were used to present the time series before (upper panels) and after (lower panels) the fertilisation on 27$^{\text{th}}$ March for SI-09 and on 7$^{\text{th}}$ April for SI-11. The maximum value of flux reached by each approach is reported, as kg N ha$^{-1}$ h$^{-1}$, in Table 2.4 for SI-09 and Table 2.5 for SI-11.

2009 (SI-09)

The fluxes measured by EC showed a maximum just after the end of slurry distribution (141,640 ng m$^{-2}$ s$^{-1}$). In the following, the NH$_3$ fluxes rose down close to zero around 8:00 pm. During the night and the first hours of the day after the spreading a small ammonia emission was detected, with a suddenly decreasing just after the slurry incorporation. During the following days, until the end of the trial, no ammonia fluxes were measured. Both the inverse dispersion models described the same emission trend. Nevertheless, the WindTrax model flux values resulted to be always higher than FIDES estimations (on average 40%). The fluxes estimated by the two inverse dispersion models started to show the ammonia emission even before the spreading, probably due to higher concentration levels measured by the Alpha samples with respect to the background levels; the QC-TILDAS did not recorded a such increase of the NH$_3$ concentration (see Figure 2.9). Furthermore, both inverse models showed a maximum value of ammonia fluxes (for example, 113,876 ng m$^{-2}$ s$^{-1}$ for WindTrax) half hour early with respect to EC measurement. The peak of
the flux was reached simultaneously with the end of the spreading, for both inverse models.

Figure 2.9. SI-09: NH$_3$ fluxes measured by eddy covariance technique and simulated by two inverse dispersion models (WindTrax and FIDES) and a deterministic model, Volt’Air. The vertical colour bars represent the duration of slurry spreading and incorporation. Upper panel is referred to the spreading day, lower panel represent the days after fertilisation.
Volt’Air model simulated ammonia emissions starting from the beginning of the spreading. In this case, the main first peak was achieved just before the end of the spreading (163,350 ng m\(^{-2}\) s\(^{-1}\)), followed by a second one. Volt’Air reached the minimum values 2 hours after the other two models and the EC technique.

For all the models the ammonia emission values were reduced by the slurry incorporation, occurred at the beginning of the following day, even if these approaches detected a small but gradual increase until the late afternoon. However, the inverse dispersion models marked a sudden decrease at 6:00 pm whereas Volt’Air showed a reduction to levels close to zero around midnight. The levels remain substantially unchanged until the end of the experimental trial.

### Table 2.4. Emission factors expressed as total nitrogen (TKN; Total Kjeldahl Nitrogen) and ammoniacal nitrogen (TAN; Total Ammoniacal Nitrogen), cumulated and maximum value of the fluxes reached using Windtrax, FIDES, Volt’Air and measured by eddy covariance in Landriano 2009 (SI-09).

<table>
<thead>
<tr>
<th>Flux</th>
<th>Emission Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cumulated kg N ha(^{-1})</td>
</tr>
<tr>
<td>WindTrax</td>
<td>26</td>
</tr>
<tr>
<td>FIDES</td>
<td>18</td>
</tr>
<tr>
<td>Volt’Air</td>
<td>48</td>
</tr>
<tr>
<td>Eddy Covariance</td>
<td>12</td>
</tr>
</tbody>
</table>

**2011 (SI-11)**

All the NH\(_3\) fluxes in SI-11 as measured by EC showed values close to zero until the beginning of the spreading, while a first peak reached after 2 hours and half (169,482 ng m\(^{-2}\) s\(^{-1}\), see Figure 2.10). The emissions rose down after the application towards the evening hours, followed by an increasing at the beginning of the next day. The
incorporation, as described above, dropped the values of NH$_3$ emission. During the following days, until the end of the trial, no ammonia fluxes were measured.

Figure 2.10. SI-11: NH$_3$ fluxes measured by the eddy covariance technique and simulated by two inverse dispersion models (WindTrax and FIDES) and a deterministic model, Volt’Air. The vertical colour bars represent the duration of slurry spreading and incorporation. Upper panel is referred to the spreading day, lower panel represent the days after fertilisation.
The models described a similar trend. In particular, the inverse models described the peak (119,483 ng m\(^{-2}\) s\(^{-1}\) for FIDES and 115,830 ng m\(^{-2}\) s\(^{-1}\) for WindTrax) just before the end of the spreading (5 and half hours after the EC peak). Even during this trial, the levels of WindTrax were greater than the FIDES of about 30%. Volt’Air tracing the course of NH\(_3\) emission instantly from the fertilise application, reaching the value of 217,510 ng m\(^{-2}\) s\(^{-1}\) during the operation.

Moreover, with respect to SI-09, during SI-11 there was not decreasing of ammonia fluxes after the slurry incorporation, probably because it occurred during the afternoon, instead of the morning and the emission were already in decreasing phase. Furthermore, the models considered showed emissions during the hotter hours of the days after the incorporation, while EC did not detect them. This phenomenon gradually exhausted during the time course.

Table 2.5. Emission factors expressed as total nitrogen (TKN; Total Kjeldahl Nitrogen) and ammoniacal nitrogen (TAN; Total Ammoniacal Nitrogen), cumulated and maximum value of the fluxes reached using Windtrax, FIDES, Volt’Air and measured by eddy covariance in Landriano 2011 (SI-11).

<table>
<thead>
<tr>
<th>Flux</th>
<th>Emission Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%TKN</td>
</tr>
<tr>
<td>cumulated</td>
<td>maximum</td>
</tr>
<tr>
<td>kg N ha(^{-1})</td>
<td>kg NH(_3) ha(^{-1}) h(^{-1})</td>
</tr>
<tr>
<td>WindTrax</td>
<td>31</td>
</tr>
<tr>
<td>FIDES</td>
<td>29</td>
</tr>
<tr>
<td>Volt'Air</td>
<td>72</td>
</tr>
<tr>
<td>Eddy Covariance</td>
<td>20</td>
</tr>
</tbody>
</table>
2.3.4 Method inter-comparison

The comparison between simulated and measured NH$_3$ fluxes is reported in Figure 2.11 and in Table 2.6. The high values of R$^2$, especially in SI-11, are indicative of a good agreement either between the measured and the simulated fluxes or among the different modeling approaches. For the two trials, the relationships between each inverse dispersion model and EC (Figure 2.11a and 2.11b) are the same, since the relationship between FIDES and WindTrax (Figure 2.11d) is close to 1:1, especially during SI-11, with R$^2$ close to 1 (see Table 2.6); for these two methods the error bars (average value of ±14% and ±30% of the flux in SI-09 and SI-11, respectively) were not reported.

Table 2.6. Summary of statistics and linear regression results of the eddy covariance (EC) against WindTrax, FIDES and Volt’Air models, during the two trials.

<table>
<thead>
<tr>
<th></th>
<th>RRMSE</th>
<th>E</th>
<th>CRM</th>
<th>Slope</th>
<th>Intercept</th>
<th>R$^2$</th>
<th>Mean measured (EC)</th>
<th>Mean simulated</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI-09</td>
<td>Fides</td>
<td>189</td>
<td>0.78</td>
<td>0.1</td>
<td>0.9</td>
<td>0.79</td>
<td>3.7</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>Windtrax</td>
<td>307</td>
<td>0.45</td>
<td>-1.0</td>
<td>0.7</td>
<td>4.9</td>
<td>0.55</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>Volt’air</td>
<td>694</td>
<td>-1.91</td>
<td>-2.3</td>
<td>1.6</td>
<td>6.0</td>
<td>0.55</td>
<td>3.7</td>
</tr>
<tr>
<td>SI-11</td>
<td>Fides</td>
<td>270</td>
<td>0.59</td>
<td>-0.7</td>
<td>0.8</td>
<td>2.9</td>
<td>0.64</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>Windtrax</td>
<td>280</td>
<td>0.55</td>
<td>-0.7</td>
<td>0.7</td>
<td>3.4</td>
<td>0.60</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>Volt’air</td>
<td>618</td>
<td>-1.40</td>
<td>-3.0</td>
<td>2.0</td>
<td>3.9</td>
<td>0.78</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Also the Volt’Air model compared to the other approaches showed good R2, especially in SI-11. In particular, to compare Volt’Air data with the EC data, these latter were block-averaged to hourly values in order to match the time resolution of the model, parameterized with hourly data inputs. Moreover, the slopes of the linear regression (Figure 2.11c, e, and
Figure 2.11. Scatter plot between eddy covariance (EC) and the models reported in the text: (a) FIDES, (b) WindTrax and (c) Volt’Air, during the trials in Landriano 2009 (SI-09) and 2011 (SI-11). (d) is the scatter plot between WindTrax and FIDES; (e) is the scatter plot between Volt’Air and WindTrax; (f) is the scatter plot between Volt’Air and FIDES. Dotted line represents 1:1 line.
f) indicated that Vol’Air widely overestimate the fluxes both in SI-09 and in SI-11, whereas the inverse dispersion models simulated values close to EC measurements (see Figure 2.11a and b). All the models overestimated the ammonia fluxes with respect to measurement, as indicated by the negative values of the CRM index. In particular, FIDES is the simulation model which gives values of NH3 fluxes more close to the EC measurements. The values of $E$ index indicate that the inverse dispersion models made an overall good prediction of EC measurements, whereas the FIDES model presents values of the index slightly higher than WindTrax, especially in SI-09. The same index $E$ evaluated Volt’Air as a bad predictor of the measurement, since it assumed negative values. Finally, values assumed by the $RRMSE$ indicates that the inverse dispersion models produce a more accurate estimation than the deterministic model Volt’Air.

2.4 **Discussion and conclusion**

The evident relationship between the values of turbulence parameters and the concentrations indicates that when there was no turbulence, the NH$_3$ remained at soil surface and did not reach the instruments. The dependence of the flux estimated by inverse dispersion models from the values of $u^*$ is evident especially after the main emission peak in both the experiments. The rain event occurred in SI-09 reduced sharply the concentration of NH$_3$ in the air (see Figure 2.6), and therefore the emitted flux simulated by the inverse dispersion models. The Volt’Air model was affected by the rainfall with a reduction in the flux. For inverse models, according to Loubet *et al.* (2011), the fluxes are systematically
underestimated with the height and when integrated concentrations are used; this is linked to surface temperature and wind speed, the main drivers of the emission.

The NH$_3$ volatilisation detected by EC measurements during the two trials carried out in north Italy followed the typical trend as described by Sommer and Hutchings (2001), where the loss rate is usually highest immediately after slurry application and normally falls rapidly as the concentration of TAN in soil surface decreases due to emission, infiltration, absorption in the soil matrix, or converted to nitrate (van der Molen et al. 1990; Sommer et al. 2004).

After 24 h from spreading, before the starting of the incorporation the cumulated NH$_3$ emission measured by EC was 95% of the total lose in SI-09 and 94% during SI-11. The actual emission factor calculated with EC data is equal to 12.7 %TAN in 2009 and 18.6 %TAN in 2011 (see Tables 2.4 and 2.5); these values are similar to the ones found in literature (Sintermann et al., 2011a), although in our case the slurry was incorporated in the soil just one day after the spreading. On the other hand, Sanz et al. (2010) found 20% using WindTrax, Loubet et al. (2010) 37.5% using the aerodynamic gradient method.

About the outputs of the presented models, in 2009 after 24 h from spreading before the starting of the incorporation, the cumulated NH$_3$ emission was 90% of the total value for Volt’Air, while were 70% for FIDES and 65% for WindTrax. In SI-11, these estimations were 92%, 76% and 73% for Volt’Air, FIDES and WindTrax, respectively. Therefore, in terms of time evolution of ammonia volatilisation, Volt’Air presented values very close to the measured one, while inverse models underestimated the cumulated percentage in the first 24 hours.
Before the incorporation in SI-11 the emission increased by 13%, 15% for FIDES and Windtrax, while for Volt’Air and EC approaches the emissions exhausted already at 24 h from spreading. The maximum cumulated emission is reached at the end of the trials; the only exception is reported by Volt'Air that simulated the plateau at 48 hours from spreading in SI-09. Finally, the inverse dispersion models still have 25-35% of emissions to release during the subsequent days of measurement.

The Volt’Air model, according to Gènermont and Cellier (1997), Le Cadre (2004), Smith et al. (2009) and Garcia (2010), is very sensible to the soil surface and slurry pH. In fact, results indicate that increase in slurry pH of 1.0 point in SI-09 and SI-11 increases the emission factor of 22% and 50% respectively. Changes in soil pH due to a supply of slurry were not taking into account by the model because the diversity of chemical species in the composition of the slurry makes a mechanistic modelling difficult.
References


DYNAMICS OF AMMONIA VOLATILIZATION


DYNAMICS OF AMMONIA VOLATILIZATION


Chapter 3

Estimation of ammonia volatilisation following slurry spreading: comparison of two inverse dispersion models

Keywords. Inverse dispersion models, uncertainty analysis, slurry injection, slurry spreading, incorporation technique, ammonia volatilization, arable land.
Abstract

The performance of two inverse dispersion models to quantify ammonia fluxes has been evaluated. In particular, NH$_3$ volatilization following cattle slurry spreading has been estimated for two different application techniques, surface spreading with incorporation and injection into the soil, applied during two trials carried out in northern Italy. Passive diffusion samplers, for measuring air NH$_3$ concentrations, and a sonic anemometer, for characterizing atmospheric turbulence, were employed to parameterize the inverse models FIDES and WindTrax. The latter was employed in two versions: the differences were about the origin of the turbulence statistics (similarity theory or sonic anemometer). The analysis showed that the uncertainty of the two employed method ranged from 3 to 11%, resulting comparable to other explored measurement techniques. The sensibility of the models to the roughness length parameter and friction velocity highlighted the importance of the measurement of atmospheric turbulence, to avoid overestimation or underestimation of the fluxes. Finally, the direct injection of slurry into the soil resulted the most effective method for reducing N loss during and following slurry application, showing emission of 2% of the total ammoniacal nitrogen applied.
3.1 Introduction

Ammonia (NH$_3$) is the most abundant alkaline trace gas in the atmosphere, which deposition leads to various environmental issues for ecosystems, such as acidification of soils, eutrophication of aquatic ecosystems, forest decline and decrease in biodiversity (Galloway et al., 2003). Moreover, NH$_3$ plays a key role in the neutralization of the atmospheric acids and the formation of particulate matter that causes human health, visibility problems and radiative forcing (Asman et al., 1998; Battye et al., 2003). From an agronomic perspective, ammonia losses from applied mineral and organic fertilisers is a loss of nitrogen (N) which cannot be used by plants for increasing their productivity.

In Europe more than 90% of the NH$_3$ emissions come from agriculture (EEA, 2011), livestock manure and fertilisers being the main emitters. Even if in developed countries in Europe, NH$_3$ emissions have been reduced by about 24% between 1990 and 2008 (EEA, 2010), mainly due to the reduction of farm animals (especially cattle), by 2050 the global NH$_3$ emissions are expected to double, due to demographic growth, changes in food preferences and agriculture intensification (Bouwman et al., 2011). Italian NH$_3$ emission inventories, elaborated by ISPRA (2011), report that 95% of NH$_3$ emissions originate from agriculture and about 82% from livestock. Moreover, ammonia emissions in Italy are concentrated in the Po Valley (Skjøth et al., 2011), where 36%, 64% and 30% of the national cattle, pigs and poultry are bred, respectively (ISTAT, 2011). This is combined to an increasing demand, from the society and the institutions (states, EC) for improving farm management to increase nitrogen (N) use efficiency in animal production and to
reduce N escape into the environment. Good agronomical practices for reducing the NH$_3$ losses in atmosphere regard the management of organic fertiliser such as the slurry spreading. In particular, the incorporation of slurry and/or its direct injection are efficient ways to reduce NH$_3$ emissions to the atmosphere (Sommer and Hutchings, 2001; Søgaard et al., 2002; Huijsmans et al., 2003; Rotz, 2004).

Even if NH$_3$ volatilisation following application of organic fertilisers has been widely investigated (i.e. Génermont and Cellier, 1997; Génermont et al., 1998; Sommer and Olesen, 2000; Sommer et al. 2003), most of the published studies have been carried out in northern European countries where the climate is cooler than in Italy and the agricultural practices adopted are different. At the Italian national level, the NH$_3$ emission factors (EF) based on field measurements are very limited and EF from the literature are often used. Even if these EF are calibrated on national conditions, by taking into account the climatic conditions, the animal productivity and the manure management systems (Valli et al., 2001), this lack of experimental evidences is critical.

Since two decades, several measurement techniques have been developed and improved to measure NH$_3$ fluxes. While at the beginning, enclosure methods (Svensson and Ferm, 1993) and mass balance techniques using denuders (Schørring et al., 1992) were preferred, afterwards the development of online analysers have promoted the development of the aerodynamic gradient method (Wyers et al. 1993; Kruit et al. 2007; Milford et al. 2009) and more recently the eddy covariance and relaxed eddy accumulation methods (Famulari et al. 2005; Whitehead et al., 2008; Brouder et al., 2009; von Bobrutzki et al.,
2010; Twigg et al., 2011; Sintermann et al., 2011b). However, enclosure methods have significant disadvantages such as the alteration of the environmental conditions and small sampling surface (Denmead and Raupach, 1993). These limitations are overcome by micrometeorological methods that, therefore, have to be preferred for NH$_3$ flux measurements.

The inverse dispersion modelling has also been long used (Wilson et al. 1982, 1983) for estimating the NH$_3$ emission using NH$_3$ concentrations measured downwind from the source (e.g., Flesch et al., 2004). It has especially been used with small circular plots (from 20 to 50 m radius; Sintermann et al., 2011a) with the sampling mast located in the centre. However, more recently, this method has been generalised to estimate the NH$_3$ for different source geometry with an Eulerian approach (the FIDES model; Loubet et al., 2001) or a Lagrangian Stochastic approach (the WindTrax model; Flesch et al., 2004; Sommer et al., 2005). Loubet et al. (2010) have further shown that this method can be applied using passive diffusion samplers like ALPHA samplers (Sutton et al., 2001a; Tang et al., 2001), making it a quite simple and inexpensive method for long monitoring of NH$_3$ exchanges.

In this study we report ammonia concentration measurements following cattle slurry spreading with two different application techniques in the Po Valley, using passive diffusion samplers. Therefore, we evaluate two inverse dispersion models to quantify ammonia emissions, using the measured concentrations, and to evaluate the uncertainty associated with this methodology. The estimated NH$_3$ emission rates and their significance with regards to the Italian context are then discussed.
3.2 Materials and Method

3.2.1 Field trials

The experiments were performed in two farms in the Po Valley (Northern Italy), using two different application techniques: direct slurry injection into the soil (INJ-09) in Bigarello (Lat. 45°11' N, Long. 10°54' E, Alt. 23 a.s.l.) and surface spreading followed by incorporation (SI-10) in Cornaredo (Lat. 45°29' N, Long. 09°1' E, Alt. 140 a.s.l.) (Figure 3.1).

INJ-09 was conducted in a 2.8 ha field, on silty-clay bare soil. At the beginning of the trial the soil water content in the 0-10 cm layer was 0.36 m$^3$ m$^{-3}$ and the soil pH was 7.5. The field was spread with 68.5 m$^3$ ha$^{-1}$ of fresh cattle manure the 24$^{th}$ September. Slurry was injected directly into the soil by means of two 1.40 m spaced anchors, working at 25 cm depth. The injection lasted 4.5 hours and was performed with 2 tanks of 20 m$^3$, with distance of 9.5 m between each transit. After 24 hours the slurry was incorporated in 8 hours with a 0.40 m ploughing. The applied total ammoniacal nitrogen (TAN) was 139 kg N-NH$_3$ ha$^{-1}$, while the total Kjeldahl nitrogen (TKN), as the sum of organic nitrogen, NH$_3$ and ammonium (NH$_4^+$), was 192 kg N ha$^{-1}$ (Table 3.1).

<table>
<thead>
<tr>
<th></th>
<th>Dry matter $\text{g kg}^{-1}$</th>
<th>pH</th>
<th>TAN $\text{kg N-NH}_4^+ \text{ ha}^{-1}$</th>
<th>TKN $\text{kg N ha}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>INJ-09</td>
<td>34</td>
<td>8.0</td>
<td>139</td>
<td>192</td>
</tr>
<tr>
<td>SI-10</td>
<td>55</td>
<td>6.5</td>
<td>92</td>
<td>204</td>
</tr>
</tbody>
</table>

Table 3.1. Main characteristics of the slurries applied during Bigarello 2009 (INJ-09) and Cornaredo 2010 (SI-10) field trials.
SI-10 was performed in a 2.7 ha sandy-loam soil with 5 cm high wheat stubbles. The initial soil water content in the 0 to 10 cm layer was 0.25 m$^3$ m$^{-3}$ while the pH was 5.5. The field was spread with 54 m$^3$ ha$^{-1}$ of fresh dairy slurry the 17$^{th}$ March 2010, with surface spreading. The spreading was carried out with an alternate passage of two tanks of 19 and 16 m$^3$. The slurry was then incorporated 24 hours later by a 0.3 m depth ploughing. Both spreading and tillage went on for 7 hours, starting at 08:00 a.m.. The TAN applied was 91.5 kg N-NH$_3$ ha$^{-1}$, while the TKN was 203 kg N ha$^{-1}$ (see Table 3.1).

Figure 3.1. Site map of experimental fields during the trials in Bigarello in 2009 (INJ-09; top) and Cornaredo 2010 (SI-10; bottom).
Representative slurry samples (3 dm$^3$) were collected during the day of the application in different times from the tanks of slurries, to determine pH, percentage of dry matter (DM), TAN and TKN. Samples were analysed in triplicates. During the experiment, the soil pH, water content, organic matter, nitrous and ammoniacal nitrogen were daily measured at 0-10 cm, 10-20 cm and 20-40 cm depths. The field measurements began two days before the spreading and went on for 7 and 12 days after for INJ-09 and SI-10, respectively.

### 3.2.2 Micrometeorological measurements

A three-dimensional ultrasonic anemometer (USA-1, METEK GmbH, Elmshorn, Germany) was placed in the centre of each field at 1.50 and 1.40 m above ground for INJ-09 and SI-10, respectively, sampling at 10 Hz. The wind speed ($U$), wind direction ($WD$), friction velocity ($u^*$), Monin-Obukhov length ($L$) and the surface roughness length ($z_0$) were calculated from the sonic anemometer. In particular, the friction velocity (m s$^{-1}$) is derived from the formula of Weber (1999):

$$u_* = \sqrt{-\frac{\overline{u'w'}}{}}$$  \hspace{1cm} (eq. 3.1)

where the prime indicates the fluctuations of the wind components $u$ and $w$ along the three directions $x$ (alongwind), $y$ (crosswind), and $z$ (vertical), respectively. $L$ (m) was calculated from the similarity theory (Stull, 1988) under horizontally homogeneous and steady state conditions:
\[ L = - \frac{u^3 T}{k g \overline{wT'}} \]  

(eq. 3.2)

where \( T (°K) \) is the mean air temperature within the surface boundary layer, \( k \) is the von Kármán’s constant (0.41), \( g \) is the acceleration due to gravity (9.8 m s\(^{-2}\)), and \( \overline{w'T'} \) is the covariance between \( w \) and \( T \).

To avoid estimation problems due to extreme atmospheric stability conditions (Sommer et al., 2005) in the modelling approach, \( u^* \) and \( L \) were filtered in order to screen out condition when Monin-Obukhov Similarity Theory was most likely to be violated (Flesch et al., 2004; Todd et al., 2008; Hensen et al., 2009; Loubet et al., 2009). The imposed thresholds were \(|L| < 5 \text{ m} \) and \( u^* < 0.2 \text{ m s}^{-1} \).

The roughness length \( z_0 \) was derived from the wind speed profile relationship:

\[ z_0 = \frac{z}{\exp \left( \frac{U k}{u^* - \Psi} \right)} \]  

(eq. 3.3)

where \( z \) (m) is the height of sonic anemometer above the ground surface, \( U \) is the horizontal component of wind speed (m s\(^{-1}\)) and \( \Psi \) is a Monin–Obukhov universal function calculated from the approach described by Flesch et al. (2004). A constant value of \( z_0 \), obtained by the median value of each experiment, was used. The values were 0.030 and 0.006 m for INJ-09 and SI-10, respectively.
In both experiments a standard weather station (HOBO, Onset Computer Corporation, USA) was employed to measure air temperature $T_a$ ($^\circ$C), relative humidity $RH$ (%), global solar radiation $R_g$ (W m$^{-2}$) and precipitations $P$ (mm) (Table 3.2). The first two quantities were measured at the same height of the sonic anemometer, while precipitations and solar radiation were measured at 1.8 m. In INJ-09 the station was placed in the field, while in SI-10 it was 350 m far from the field centre.

Table 3.2. Meteorological variables in Bigarello 2009 (INJ-09) and Cornaredo 2010 (SI-10) trials. Standard deviation of the mean is in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Rain mm</th>
<th>Temperature °C</th>
<th>Relative humidity %</th>
<th>Wind speed m s$^{-1}$</th>
<th>Global Radiation W m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>INJ-09 mean</td>
<td>19.2 (0.3)</td>
<td>77.6 (1.3)</td>
<td>0.94 (0.28)</td>
<td>177 (26)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>27.4</td>
<td>96.6</td>
<td>4.21</td>
<td>619</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>11.6</td>
<td>46.1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>cumulate</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SI-10 mean</td>
<td>12.2 (3.6)</td>
<td>79.9 (14.5)</td>
<td>0.20 (0.53)</td>
<td>110 (178)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>19.8</td>
<td>97.0</td>
<td>2.78</td>
<td>698</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>3.9</td>
<td>37.2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>cumulate</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.3 Ammonia concentration measurements using passive diffusion samplers

The NH$_3$ air concentration was measured using ALPHA samplers (Adapted Low-cost Passive High Absorption), a time averaged approach developed by Tang et al. (2001) and Sutton et al. (2001a), based on the capture of the trace gas on acid paper filter.
The ALPHA samplers were positioned in the centre of each field at the same height as the sonic anemometer to measure NH$_3$ concentration ($C$) from slurry application. Samplers were changed two times per day, after dawn and just before sunset in order to follow the change of atmospheric turbulence, which affects the dispersion of pollutants. To measure the background concentration of NH$_3$ ($C_{bgd}$), a sample point was located more than 600 m away from the fields and away from any known sources of NH$_3$ (in a grassland in INJ-09 and on the top roof of a five-floors building in SI-10). The positions of the ALPHA samplers and the shape of the fields were mapped by GPS coordinates (see Figure 3.1). For each sampling point a series of three replicates were employed.

The NH$_3$ concentration was obtained by the extraction of each filter in distilled water solution and by the analysis of the solutions through colorimetry (FIAstar 5000 system, FOSS, Denmark), obtaining first the concentration of N-NH$_4^+$ from which is achieved the NH$_3$ one. The air NH$_3$ concentration was calculated on the basis of the volume of air $V_a$ sampled by ALPHA ($V_a = 0.003241315$ m$^3$) multiplied for the time exposure $t$ (hours) (Sutton et al., 2001b; Tang et al., 2008). The mean concentration and relative standard deviation ($\sigma$) of the three replicates were calculated for background ($\sigma_{C_{bgd}}$) and field measurements ($\sigma_C$).

In SI-10, in order to get a better time resolution during the day of the spreading and the day after, the field sampler’s time exposure was organized in a different way than described above. Starting from 8:00 a.m. in the morning, one new series of ALPHA was introduced in field every 2 hours and was exposed for 6 hours. To complete the sequence, two other series were exposed only for 2 hours, one from 8:00 a.m. and
one from 6:00 p.m.. This superposition, covering the day from 08:00 a.m. to 8:00 p.m., allowed to obtain the concentration every 2 hours by means of a subsequent subtraction of the mean NH$_3$ concentration of each three replicate of ALPHA, but with a large enough concentration of NH$_4^+$ in the sampler.

### 3.2.4 Estimation of NH$_3$ volatilisation using inverse dispersion modelling

The inverse dispersion modelling is based upon the superimposition principle (Thomson, 1987), which relates the concentration in the middle of the field, $C$, to the volatilisation flux $S$ and the background concentration $C_{bgd}$ with the transfer coefficient $D$ (e.g. Loubet et al., 2010):

$$C = D \times S + C_{bgd} \quad \text{(eq. 3.4)}$$

The underlying hypotheses are that the studied tracer is conservative and that the volatilisation flux is spatially homogeneous. The first hypothesis is reasonable for NH$_3$ as its reaction time with acids in the atmosphere is below the transport time at the spatial scale studied here (Nemitz et al., 2009). The spatial homogeneity of the volatilisation flux has to be verified for NH$_3$ as the volatilisation flux itself depends on the concentration at the surface. However, Loubet et al. (2010) have shown that the heterogeneity of the volatilisation flux can be neglected as long as the fetch is larger than 20 m such as during the trials described in this
work. The inversion modelling simply consists in estimating $S$ from equation (eq. 3.4) as:

$$S = \left( C - C_{bgd} \right) \times D^{-1} \quad \text{(eq. 3.5)}$$

A dispersion model is required to estimate $D$ (s m$^{-1}$). Two models were used to compute $D$, the FIDES model (Loubet et al., 2010) and the WindTrax model (Flesch et al., 2004).

The FIDES model is based on Philip (1959) solution of the advection-diffusion equation, which assumes power law profiles for the wind speed $U(z)$ and the vertical diffusivity $K_z(z)$. This approach also assumes no chemical reactions in the atmosphere and a homogeneous surface in terms of dynamics (roughness, $U$, $K_z$). The dispersion model is detailed in Loubet et al. (2010). The transfer coefficient $D$ was estimated as:

$$U(z) = az^p$$
$$K_z(z) = bz^n$$

$$D = \frac{Q(t)}{\sigma_y \sqrt{2\pi}} \exp \left( -\frac{(Y)^2}{2\sigma_y^2} \right) \times \frac{(zz_s)^{(1-n)/2}}{b\alpha X} \times \exp \left( -\frac{a(z^\alpha + z_s^\alpha)}{b\alpha^2 X} \right) \times I_{-\nu} \left( \frac{2a(zz_s)^{\alpha/2}}{b\alpha^2 X} \right)$$

$$\sigma_y = \frac{1}{\sqrt{2}} C_y x^{-\frac{2-m}{2}}$$

$$\quad \text{(eq. 3.6)}$$

where $\alpha = 2 + p + n$, $\nu = (1 - n) / \alpha$, and $I_{-\nu}$ is the modified Bessel function of the first kind of order $-\nu$, and $C_y$ and $m$ were taken from Sutton (1932). Here, $X = [(x - x_s) \sin(WD) - (y - y_s) \cos(WD)]$ and $Y = [(x - x_s) \cos(WD) - (y - y_s) \sin(WD)]$. The values of $a$, $b$, $p$ and $n$ were
inferred by linear regression between ln($U$), ln($K_z$) and ln($z$), over the height between $2 \times z_0$ to 20 m, using $U(z)$ and $K_z(z)$ estimated from the Monin-Obukhov similarity theory (see e.g., Stull, 1988 and Kaimal & Finnigan, 1994). Following Loubet et al. (2001), to solve equation (3.6), the height of the emitting surface is taken as $z_s = 1.01 z_0 + d$, where $d$ is the displacement height.

The WindTrax model combines the backward Lagrangian stochastic (bLS) dispersion model described by Flesch et al. (2004) with an interface where sources and sensors can be mapped. The transfer coefficient $D$ is calculated by releasing 50,000 trajectories from the concentration sensor location for each time step and recording the vertical velocity ($w_0$) of those that intersects the ground in the field area ($N$). The transfer coefficient is computed as:

$$D = \frac{1}{N} \sum \left| \frac{2}{w_0} \right|$$

(eq. 3.7)

In a bLS model (WindTrax), the model input are the turbulence parameters statistics. Two versions of Windtrax were used: (1) WT-I in which the turbulence parameters were determined from the similarity theory. The input data of WT-I were $u_*$, $L$, $z_0$ and wind direction. In the second version (2) WT-II, the turbulence statistics were directly taken by the sonic anemometer: averages $U$, $V$, $W$; standard deviations $\sigma_u$, $\sigma_v$, $\sigma_w$ and cross correlations $\overline{u'w'}$, $\overline{u'v'}$, $\overline{v'w'}$ of the components of the wind speed along the three axes ($x$, $y$, $z$).
The transfer coefficient $D$ assumes a central position on the study of the emissions, estimated from the NH$_3$ concentrations. To understand the effects of $D$ using long term exposure samplers, a further estimation using a time-averaged value of the coefficient, $\bar{D}$, on the basis of the exposure time of the samplers, was done.

### 3.2.5 Uncertainty analysis

The uncertainty in the flux estimation $S (\sigma_S)$, due to the uncertainty on NH$_3$ concentration measurements was estimated using equation (3.8) (Bevington and Robinson, 2002):

$$
\sigma_S = D^{-1} \times \sqrt{\sigma_c^2 + \sigma_{bgd}^2} \quad \text{(eq. 3.8)}
$$

The uncertainty due to the determination of the transfer coefficient $D$ was not included in this uncertainty analysis, but the difference among the models and approaches used here (WT-I, WT-II and FIDES) was considerate as an estimation of the variability of $D$.

Moreover, to understand the overall uncertainty related to the concentration measurements, a Bootstrap procedure (Efron and Tibshirani, 1998) was employed. The purpose of this inferential scheme was to achieve an assessment of the degree of generalizability of flux estimation starting from a restricted set of data. The first step was to generate a big number (10,000) of possible averaged concentration (bootstrap samples). Each bootstrap sample was obtained by random sampling, with replacement, all the replicated measure of concentration...
obtained at each exposure time. To obtain the flux, the values of each sample were first subtracted from the average value of $C_{bgd}$, in relation to their exposure period, then the equation 3.5 was applied using averaged $D$ in according to the exposure time (i.e. $\bar{D}$). The probable values of $S$ obtained from each combination, allowed to derive a probability distribution:

$$(C_{1.1}, C_{1.2}, C_{1.3}; C_{2.1}, C_{2.2} ... C_{n.3})$$

$$\begin{align*}
(C_1^* \times \bar{D}_1; C_2^* \times \bar{D}_2; ... C_n^* \times \bar{D}_n) & \rightarrow S_1^* \\
(C_1^* \times \bar{D}_1; C_2^* \times \bar{D}_2; ... C_n^* \times \bar{D}_n) & \rightarrow S_2^* \\
& \vdots \\
(C_1^* \times \bar{D}_1; C_2^* \times \bar{D}_2; ... C_n^* \times \bar{D}_n) & \rightarrow S_n^* \\
\end{align*}$$

(eq 3.9)

where $C_{n*3}$ are all the field NH$_3$ concentrations including replications, and $C_n^*$ is a bootstrap sample for each exposure time. The expected value of this distribution provides, according to the theory of the Bootstrap (Efron and Tibshirani, 1997), a statistically reliable indication of the probable outcome of the employed models. The knowledge of the standard deviation of the distribution obtained delivers important information on the uncertainty of the measure.
Chapter 3

3.3 Results

3.3.1 Micrometeorological conditions

During the trials, the weather conditions did not deviate substantially from the monthly mean values measured from 1988 to 2007 for INJ-09 and from 1988 to 2009 for SI-10.

The atmospheric stability parameter \(1/L\) in INJ-09 showed nocturnal stability peaks (positive) and negative values during daily instability, with larger peaks in the first part of the experimentation. The daily trend of friction velocity showed a typical maximum during the day and a minimum at night, following the wind speed (Figure 3.2; Table 3.3); the mean wind direction was North during the whole experiment.

Table 3.3. Main statistics of atmospheric turbulence parameters \(u^*\) and \(L\), and \(\text{NH}_3\) concentration measured in the fertilised field \(C\) and its background level \(C_{\text{bgd}}\), during Bigarello 2009 (INJ-09) and Cornaredo 2010 (SI-10).

<table>
<thead>
<tr>
<th></th>
<th>(u^*) (m\ s^{-1})</th>
<th>(L) (m)</th>
<th>(C) (\mu g\ m^{-3})</th>
<th>(C_{\text{bgd}}) (\mu g\ m^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>INJ-09</td>
<td>min</td>
<td>0.01</td>
<td>-586</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>0.38</td>
<td>1,144</td>
<td>95.2</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>0.10</td>
<td>-1.42</td>
<td>35.1</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>0.07</td>
<td>0.18</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>(\sigma)</td>
<td>0.09</td>
<td>106</td>
<td>21.3</td>
</tr>
<tr>
<td>SI-10</td>
<td>min</td>
<td>0.001</td>
<td>-4,083</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>0.33</td>
<td>75,724</td>
<td>315.2</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>0.08</td>
<td>198</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>0.06</td>
<td>-0.01</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>(\sigma)</td>
<td>0.07</td>
<td>105</td>
<td>74.9</td>
</tr>
</tbody>
</table>
Figure 3.2. Inverse Monin-Obukhov length (1/L) during day and nighttime (upper panel); friction velocity (u*) and wind speed (lower panel) in Bigarello 2009 (INJ-09) trial.

Figure 3.3. Inverse Monin-Obukhov length (1/L) during day and nighttime (upper panel); friction velocity (u*) and wind speed (lower panel) in Cornaredo 2010 (SI-10) trial.
Small precipitations were observed during SI-10 from the 20th to 23rd of March (0.4 mm) and on the 26th of March (5.2 mm). The stability parameter $I/L$ showed substantial condition of stability both during night and day, without high negative values. The $u_*$ parameter showed smaller values during the rain events (see Figure 3.3, Table 3.3), while the prevalent wind direction was South West during the day and West during the night-time.

### 3.3.2 Ammonia concentrations

The NH$_3$ concentration observed in the field before the fertilisation events was equal to its background value in both the case studies (13 and 5 µg m$^{-3}$ at INJ-09 and SI-10, respectively).

In INJ-09, NH$_3$ concentration in the field rose after the beginning of the slurry injection to reach a maximum value of 95.2 µg m$^{-3}$ (14 hours average) during the night, 10 hours after the slurry application (Figure 3.4 and Table 3.3). The soil tillage led NH$_3$ field concentration to drop below background values, before to increase slightly above background values the following days.

In SI-10, NH$_3$ concentration in the field peaked at 315.2 µg m$^{-3}$ (2 hours averaged) after a rapid increase after the start of the slurry spreading, and fell at night to 46 µg m$^{-3}$ (Figure 3.5 and Table 3.3). At the beginning of the following day, NH$_3$ concentration in the field reached a second peak of 99 µg m$^{-3}$ and then decreased after ploughing. There were no further peaks, and NH$_3$ concentration in the field followed the background concentration except the 23rd of March.
Figure 3.4: NH$_3$ concentrations measured in the centre of the fertilised field and in its background values in Bigarello 2009 (INJ-09). The vertical colour bars show the duration of slurry spreading and ploughing. The error bars show standard deviations.

Figure 3.5: NH$_3$ concentrations measured in the centre of the fertilised field and in its background in Cornaredo 2010 (SI-10). The vertical colour bars show the duration of slurry spreading and ploughing. The error bars show standard deviations.
3.3.3 Uncertainties in ammonia concentrations

The measure of variability (\(\sigma\)), relative to the mean each three ALPHA exposed, ranged from 0.4 to 8.1 \(\mu\)g m\(^{-3}\) in INJ-09, with an averaged value of 2.5 \(\mu\)g m\(^{-3}\). For SI-10, the mean variation of \(\sigma\) was 6.7 \(\mu\)g m\(^{-3}\) with values between 0.07 and 41.8 \(\mu\)g m\(^{-3}\). Figure 3.6 a) and 3.6 b) shows the relations existing between the \(\sigma\) and the mean values of concentration, \(C\), measured for each sampling period during the trials. An absence of a robust relation between background concentration and \(\sigma\) (values of \(R^2\) equal to 0.15 and 0.10 for INJ-09 and SI-10, respectively) was found. Conversely the relation between the concentration and the \(\sigma\) of the measurement performed in the field resulted significant for SI-10 (\(R^2\) equal to 0.41), while INJ-09 resulted not related (\(R^2\) equal to 0.10. Furthermore the regression analysis performed on these data showed that there was no significant relation (\(P > 0.05\)), except for the values collected in the field during SI-10 (\(P < 0.01\)).

Instead, a significant score of the regression analysis (\(P < 0.01\)) is obtained between the mean values of N-NH\(_4^+\) obtained from the analysis of each filter and their related \(\sigma\). As shown in Figure 3.6 c) and d) at INJ-09 \(R^2\) is equal to 0.73 while resulted 0.23 at SI-10. No relations have been found between the CV calculated for air NH\(_3\) concentration and the time of exposure.
Figure 3.6. Scatter plots reporting the average of NH$_3$ concentration and relative standard deviation ($\sigma$) for measurements in the field (▲) and at the background (△) in (a) Bigarello 2009 (INJ-09) and (b) Cornaredo 2010 (SI-10). Regression between the mean of N-NH$_4^+$ concentration from all the samples analysed (♦) and the standard deviation in (c) Bigarello 2009 (INJ-09) and (d) Cornaredo 2010 (SI-10).
3.3.4 Ammonia emissions following slurry spreading

In both trials there was a rapid increase of the flux following slurry application which followed the concentration pattern, with a first high peak followed by a nocturnal minimum and a second high peak after the sunrise. In both the trials the slurry incorporation the day after its application caused a sudden drop of the NH$_3$ emission (Figure 3.7 and 3.8).

In INJ-09, the fluxes peaks showed large differences and peaked at different times depending on the model used: 4 hours for WT-I, 7 hours for WT-II and 6 hours for FIDES. With the start, and for the entire duration of the incorporation, all the models simulated NH$_3$ deposition due to the lower level of concentration measured in the field, compared to the background value. Afterwards, 16 hours following the end of the incorporation (i.e. 48 hours after the slurry injection), the fluxes showed a series of lower peaks until the end of the experimentation. The NH$_3$ fluxes estimated by the three approaches were similar in trends but not in absolute values; the FIDES estimations had absolute values always higher than the others.

Overall, on average taking into account all the three models (WT-I, WT-II and FIDES), the NH$_3$ volatilisation peaks in INJ-09 were 7,745 ± 4,106 ng NH$_3$ m$^{-2}$ s$^{-1}$ using $D$ and 5,039 ± 1,466 ng NH$_3$ m$^{-2}$ s$^{-1}$ using $\overline{D}$; (Table 3.4). In SI-10, the fluxes peaks were almost equal for the employed models and appeared at the same time 5 or 6 hours after spreading. On average the peaks were 33,021 ± 186 ng NH$_3$ m$^{-2}$ s$^{-1}$ using $D$ and 29,760 ± 688 ng NH$_3$ m$^{-2}$ s$^{-1}$ using $\overline{D}$; (Table 3.5). INSERT table 3.4 and 3.5 and FIGURE 7, 8.
Figure 3.7: Upper panel: NH$_3$ flux during Bigarello 2009 (INJ-09) simulated by the inverse dispersion models: WindTrax using the turbulence parameters (WT-I); WindTrax using the three components of wind speed (WT-II); and FIDES. Lower panel: uncertainty in the modelling approaches employed due to the uncertainty in the concentrations measurements. The vertical colour bars represent the duration of slurry distribution and ploughing.
Figure 3.8: Upper panel: NH$_3$ fluxes during Cornaredo 2010 (SI-10) simulated by the inverse dispersion models: WindTrax using the turbulence parameters (WT-I); WindTrax using the three components of the wind (WT-II); and FIDES. Lower panel: uncertainty in the modelling approaches employed due to the uncertainty in the concentrations measurements. The vertical colour bars represent the duration of slurry spreading and ploughing.
### Table 3.4. Cumulated and maximum NH$_3$ fluxes obtained for Bigarello 2009 (INJ-09) using the models: WindTrax with the turbulence parameters (WT-I); WindTrax with the three components of the wind speed (WT-II); and FIDES. Moreover, the emission factor (EF) accompanied by error (±err%) is reported as percentage of TAN and TKN. The results are relative to simulations using the transfer coefficient, and its time averaged on exposition time ($\bar{D}$).

<table>
<thead>
<tr>
<th>INJ-09</th>
<th>Flux</th>
<th>Emission Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cumulated</td>
<td>maximum</td>
</tr>
<tr>
<td></td>
<td>kg N-NH$_3$ ha$^{-1}$</td>
<td>kg N-NH$_3$ ha$^{-1}$ h$^{-1}$</td>
</tr>
<tr>
<td>WT-I</td>
<td>3.4</td>
<td>0.36 ± 0.02</td>
</tr>
<tr>
<td>WT-II</td>
<td>2.1</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>FIDES</td>
<td>3.5</td>
<td>0.21 ± 0.01</td>
</tr>
<tr>
<td>WT-I $\bar{D}$</td>
<td>2.9</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>WT-II $\bar{D}$</td>
<td>1.6</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>FIDES $\bar{D}$</td>
<td>2.5</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>mean ± σ</td>
<td>0.28 ± 0.07</td>
<td>[0.19 ± 0.01$^b$] ± 0.01</td>
</tr>
</tbody>
</table>

# the σ is calculated as the σ of the lines above including two other values per line (mean + σ and mean – σ)

### Table 3.5 Cumulated and maximum NH$_3$ fluxes obtained for Cornaredo 2010 (SI-10) using the models: WindTrax with the turbulence parameters (WT-I); WindTrax with the three components of the wind speed (WT-II); and FIDES. Moreover, the emission factor (EF) accompanied by error (±err%) is reported as percentage of TAN and TKN. The results are relative to simulations using the transfer coefficient, and its time averaged on exposition time ($\bar{D}$).

<table>
<thead>
<tr>
<th>SI-10</th>
<th>Flux</th>
<th>Emission Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cumulated</td>
<td>maximum</td>
</tr>
<tr>
<td></td>
<td>kg N-NH$_3$ ha$^{-1}$</td>
<td>kg N-NH$_3$ ha$^{-1}$ h$^{-1}$</td>
</tr>
<tr>
<td>WT-I</td>
<td>5.9</td>
<td>0.97 ± 0.04</td>
</tr>
<tr>
<td>WT-II</td>
<td>4.3</td>
<td>0.99 ± 0.04</td>
</tr>
<tr>
<td>FIDES</td>
<td>4.7</td>
<td>0.98 ± 0.08</td>
</tr>
<tr>
<td>WT-I $\bar{D}$</td>
<td>5.7</td>
<td>0.86 ± 0.03</td>
</tr>
<tr>
<td>WT-II $\bar{D}$</td>
<td>4.7</td>
<td>0.89 ± 0.03</td>
</tr>
<tr>
<td>FIDES $\bar{D}$</td>
<td>4.3</td>
<td>0.90 ± 0.08</td>
</tr>
<tr>
<td>mean ± σ</td>
<td>0.49 ± 0.07</td>
<td>0.93 ± 0.05</td>
</tr>
</tbody>
</table>

# the σ is calculated as the σ of the lines above including two other values per line (mean + σ and mean – σ)
The cumulative NH$_3$ fluxes showed a rapid increase in both the trials (Figure 3.9 and 3.10). For INJ-09, the volatilisation process continued slowly also after the slurry incorporation into the soil (see Figure 3.7), while during SI-10 the ploughing causes the end of the NH$_3$ losses (see Figure 3.8) and even deposition (see Figure 3.10). In INJ-09, FIDES and WT-I gave the highest cumulative volatilisation, while WT-II gave 40% smaller values (see Table 3.4). In SI-10 the cumulative volatilization estimated by WT-I was 20% and 27% higher than FIDES and WT-II, respectively. On average the cumulated flux was 0.28 ± 0.07 and 0.49 ± 0.07 g N-NH$_3$ m$^{-2}$ in INJ-09 and SI-10, respectively.

In both the experiments, the cumulative fluxes calculated using time-averaged transfer coefficient ($\bar{D}$) were lower compared to those obtained from hourly $D$ values, except for WT-II in SI-10 (see Table 3.4 and 3.5). The emission factors (as %TAN) for the two experiments using $D$ were on average 2.0 ± 0.7% and 5.4 ± 1.3%, for INJ-09 and SI-10, respectively; the standard deviation being calculated over the range of models and including the uncertainty in the concentration measurements (see Table 3.4).

The cumulative flux obtained using $\bar{D}$ in INJ-09 was 77%, 87% and 86% of the cumulative flux derived using $D$, for FIDES, WT-I, WT-II, respectively. These gaps were lower during the SI-10, where the cumulative flux estimated using $\bar{D}$ was 95%, 98% and 110% of cumulative flux estimated using $D$ for FIDES, WT-I and WT-II, respectively (see Table 3.5).
Figure 3.9: Cumulated NH$_3$ volatilisation (g m$^{-2}$) for Bigarello 2009 (INJ-09) obtained by the three inverse dispersion models: WindTrax using the three components of the wind (WT-II), WindTrax using the turbulence parameters (WT-I) and FIDES. The solid lines are relative to hourly output of the models, while dotted lines are relative to output obtained using the mean of the mass transfer coefficient ($\bar{D}$; dotte line). In the graph are indicated the cumulated uncertainties (vertical bars).
Figure 3.10: Cumulated NH$_3$ fluxes (g m$^{-2}$) in Cornaredo 2010 (SI-10) obtained from WindTrax using the three components of the wind (WT-II), WindTrax using the turbulence parameters (WT-I) and FIDES. The solid lines are relative to hourly output of the models, while dotted lines are relative to output obtained using the mean of the mass transfer coefficient ($\bar{D}$; dotte line). In the graph are indicated the cumulated uncertainties (vertical bars).
3.4 Discussion

3.4.1 Uncertainties in estimating NH\textsubscript{3} volatilisation

Passive samplers employed in this study are appropriate tool for determining long term NH\textsubscript{3} concentration (Leith et al. 2004; Bleeker et al., 2009; Pinder et al., 2011). During INJ-09, for all the measuring period, the concentration’s CV had a mean value of 10% (ranging from 1.5 to 24%). About the SI-10, the ALPHA superposition technique employed during the first two days allowed to investigate with more time detail the dynamic of the NH\textsubscript{3} volatilisation, nevertheless the CV resulted in values greater than the typical reference ones, that means 15% reported by Tang et al. (2004). In particular, during the SI-10 trial, the CV reached even mean of 60% during the superposition periods, with a minimum and maximum ranging from 7 to 220%, while during the other days, without superposition, the mean value was 19%, ranging from 1 to 80%. The larger CV obtained at SI-10 is due to singular lower values of concentration retrieved by subsequent subtraction implemented in the superimposed samplers. The $\sigma$ indeed, resulted in the same order of magnitude each other, and the Hartley test indicates the homogeneity of the Considering these results, it seems that the superposition strategy is a non-virtuous strategy in presence of high NH\textsubscript{3} concentrations, and where could be more suitable to expose samplers alone for two hours or less. In all the experiments the greater variation in CV was found in the background samples than the field ones, probably due to the ALPHA sensitivity.
The bootstrap analysis revealed the magnitude of uncertainty related to the application of long term passive samplers (ALPHA) to the inverse dispersion models, which resulted normally distributed (Figure 3.11). The uncertainty ranging from 3 to 11%: INJ-09 scored 7% using WT-I, 11% using WT-II and 5% using FIDES, while in SI-10 Windtrax obtain 3% in both configuration and FIDES 5%. These values of uncertainty resulted lower and within of the overall uncertainty from the sensitivity analysis from of each model, about 30-40% for FIDES, detailed in Loubet et al. (2010) and about 10-20% for WindTrax (Flesch et al., 2004). These results highlight the applicability of the inverse models to low costs monitoring.

Figure 3.11. Frequency distribution of cumulated NH₃ loss as kg N ha⁻¹ calculated in Cornaredo 2010 (SI-10) with a bootstrap analysis, using WindTrax approach with the turbulence parameters.
To assess the difference between the prediction of the two models (WindTrax, in the configuration WT-I and WT-II, and FIDES), it could be useful to use indices able to measure the average magnitude of the error, which means the RMSE (root mean squared error; Fox, 1981) and/or the MAE (mean absolute error; Schaeffer, 1980). Despite these indexes are indicated to evaluate observed and simulated data, here they could be used to perform a simple interpretation of the difference between the results of the two models in terms of hourly flux. In particular, considering the MAE, both the values obtained in the two experiments denoted a low coherence between the flux estimations, with an average gap of $670 \pm 183 \text{ ng m}^{-2} \text{s}^{-1}$ in INJ-09 and $1,317 \pm 221 \text{ ng m}^{-2} \text{s}^{-1}$ in SI-10. Moreover, the RMSE were $1,157 \pm 369 \text{ ng m}^{-2} \text{s}^{-1}$ and $3,299 \pm 230 \text{ ng m}^{-2} \text{s}^{-1}$ for INJ-09 and SI-10, respectively, denoting large differences between the estimated fluxes.

The largest flux estimation is obtained using the approach with prescribed $u^*$, $L$, and $z_0$ (WT-I and FIDES). In fact, in both experiments the WT-II based on the three wind components gave the lower values of cumulated flux. These differences may be attributed to the fact that when $u^*$, $L$ and $z_0$ are given, the reconstructed wind speed is very sensitive to $z_0$ and also to the stability correction functions which are uncertain (Flesch et al, 2004). Using the turbulence parameters as input, both models, WT-I and FIDES, appeared sensible to the values of $z_0$ as found by Loubet et al. (2009). Moreover, estimating fluxes trough the $\bar{D}$ parameter, derived from the average of $D$ by the exposure time of the samplers would tend to underestimate the flux, as found by Loubet et al. (2011).
3.4.2 Dynamics of NH$_3$ volatilisation following slurry spreading

In INJ-09, the main peak in NH$_3$ volatilisation occurred at the end of the slurry spreading because the spreading started in the side of the field upwind with respect to the location of the samplers. Therefore, the ALPHA samplers could not capture all the NH$_3$ emitted in the first half of the fertilisation period. In SI-10 this problem did not occur since the application started at the same time from the centre to the both sides of the field.

Bearing in mind the previous issue, the NH$_3$ volatilisation detected during the trials followed the typical trend as described by Sommer and Hutchings (2001), where losses occur rapidly following slurry application, with 30 to 70% of the total loss occurring within the first 6 to 12 hours (Sommer and Hutchings, 1995; Meisinger and Jokelo, 2000). In this study, during INJ-09, 50% of the emission occurred in 12 hours according to the results described by Pain et al. (1989) and Moal et al. (1995) in similar experimental conditions. Moreover, after 24 hours from the slurry spreading, 60% of NH$_3$ was volatilised and volatilisation stopped 7 days later. The emission in INJ-09 was smaller than in SI-10 with an emission of 15.8 mg m$^{-2}$ h$^{-1}$ during the hours of daylight in the spreading day. After the soil tillage, the emission continued producing nocturnal peaks. This may be due to an unefficient incorporation, which could have led to slurry being brought back at the surface. In SI-10, most of the volatilisation occurred within 26 hours: at the end of the spreading operation, the cumulate loss was already 85%. During the day after, there was still small NH$_3$ volatilisation, which stopped just after incorporation.
3.4.3 Ammonia emission factors

The NH$_3$ emission and, then, the relative EF depend by parameters linked to weather, soil, manure application method and manure characteristics (Huijsmans et al., 2003). In order to reduce NH$_3$ losses following the application of manure, abatement strategies have been investigated, considering all the factors involved in NH$_3$ volatilisation. In particular, manure application methods have been shown to be among the most cost-effective practice available to farmers to reduce NH$_3$ emissions. For example, NH$_3$ volatilisation may be reduced by minimizing exposure of the manure surface to air and by increased contact with the soil: both these conditions could be reached by the direct injection of slurry into the soil (see Webb et al., 2010 for a review). Moreover, field studies have shown that NH$_3$ volatilisation tends to be linearly or sigmoidally related to the DM content (Sommer and Olesen, 1991): slurries with lower DM content, tend to have great fluidity and, therefore, to infiltrate more readily into the soil where ammonium is protected from volatilisation by adsorption onto soil colloids. Moreover the solid particles in slurry have a high water-retention capacity, which can act to further restrict or foster the infiltration (Sommer et al., 2003). These two conditions, reduced surface of exchange due to direct slurry injection and slurry with low DM content (3.4%), have been satisfied during the INJ-09 of this study. The EF estimated was $2.0 \pm 0.7\%$ TAN in perfect accordance with results reported by Huijsmans et al. (2003) which resume available NH$_3$ volatilisation measurements performed under actual different conditions, finding that the mean total volatilisation, expressed as % of the TAN applied was 2% for deep placement.
Where applicable, low emission techniques such as injection can give about 70% reduction in NH$_3$ emission, compared to surface spreading, even if there still is some debate over the effectiveness of manure injection to decrease emissions and the effect of pollutant swapping due to increasing in nitrate leaching (Erisman et al., 2008). An alternative could be the fast incorporation of the slurry after the spreading: as reported by Sommer and Hutchings (2001), NH$_3$ emissions by slurries can be reduced by more than 80% if incorporation by ploughing or other cultivation is achieved soon after application (see and chapter 4 of this thesis). However, the reduction efficiency of incorporation falls off very quickly the longer the delay between manure application and ploughing: high reduction in NH$_3$ emission could be achievable when the slurry are harrowed or ploughed in within 4-6 hours after application to the soil (see a review by Webb et al, 2010). In our case, during SI-10 the ploughed happened only 24 hours after the surface spreading, when the most important NH$_3$ emission have been already occurred, however our estimated EF was 5.4 ± 1.27% TAN, lower than the data reported in literature. In particular, Huijsmans et al. (2003) report a weighted mean of 17% TAN loss after surface incorporation. A possible explanation of our low EF could be found in the meteorological and soil conditions. About our meteorological conditions, during the day of spreading in the SI-10, the wind speed ranged between 0.10 and 2.7 m s$^{-1}$, with low values during the spreading time in the morning (see Figure 3.3). In particular, the wind speed decreased after 9:00 a.m. to 0.7 m s$^{-1}$, the turbulence broke down and NH$_3$ field emission was inhibited; successively, the wind speed increased slowly until the end of the spreading at 3:00 p.m., rising
to 2.7 m s\(^{-1}\) and increasing NH\(_3\) emission, followed by a decreasing of wind speed during the second part of the day. Probably, in the first phase of the slurry spreading and after the end of the spreading, the wind speed was not enough for the gas phase resistance to be negligible and NH\(_3\) emission was abated, resulting in a total low EF. The wind speed effect on volatilisation process have been investigated by several authors; for example Sommer et al. (1991) showed that NH\(_3\) losses increased when wind speed increased from 1.5 to 2.5 m s\(^{-1}\); Huijsmans et al. (2003) found that an increase in wind speed from 2 to 5 m s\(^{-1}\) resulted on average in an 74% increase in total volatilisation for surface incorporation. Moreover, NH\(_3\) emissions were reported lower in experiment in which slurry was applied to a moist soil than dry one (Ferm et al., 1999) and NH\(_3\) volatilisation could be decreased by lowering the surface pH (Freney et al., 1983): during SI-10 the soil conditions, a moist soil with pH around 5.5, could be an inhibiting factor to NH\(_3\) volatilisation. At last, other two questions could be taken into account to explain our low EF during SI-10 with respect the relative values reported in literature (see review by Sintermann et al., 2011b): (i) in the last 30 years, the techniques for NH\(_3\) measurements have been improved and the EFs detected are decreasing with respect to old data; (ii) these latter are usually relative to medium size plot for which EFs are higher than the loss rates derived from field scale such as our trial; (iii) the data in literature are relative to splash plate spreading not followed by incorporation.

Considering the above discussion, in this study, the differences between the EF in both the experiments are due to the different
application manure technique, in accordance with results reported in literature where the injection considerably reduces emissions from 60 even up to 100% (Thompson and Meisinger, 2002; Søgaard et al., 2002; Huijsmans et al., 2003; Rotz, 2004; Webb et al., 2010) compared to traditional broadcast methods without successive incorporation. However, a national research of CRPA (Research Centre on Animal Production, 2011) revealed that the broadcast spreading with deflector dish is the prevailing method adopted in Italy and the use of low-emission techniques such as direct injection are still very limited.

Several experiments performed, especially in Northern Europe, are designed to examine the NH$_3$ volatilisation through different measurement techniques, wide range of weather, soil and agronomic situations, making difficult the comparison. For example, Søgaard et al. (2002), employing the ALFAM model, showed that, despite the dissimilar characteristics of Po Valley with respect to the experimental conditions in Northern Europe (i.e. low wind speed and high temperature), the emission could be comparable. Furthermore, parameterizing the ALFAM model on both the case studies, the EF obtained sounds like the EF calculated, making, however, a total incorporation when slurries has been applied (2.1% and 4.5% for INJ-09 and SI-10, respectively). The results obtained from the meta-model ALFAM, compared to more targeted analysis as that produced in this study, indicate that the meta-model could be used on the Po Valley, although the results obtained are the first on this area.
3.5 Conclusions

NH₃ emission rates for two case studies performed in Po Valley were quantified using one height passive samplers to determinate NH₃ concentration and by two different inverse dispersion models (WindTrax and FIDES). Optimized time of exposition of the samplers permitted to obtain less error propagated in the estimated flux.

Inverse dispersion models turn out to be of great utility and gave different, but comparable results. Parameterizing the model with the turbulence parameters permitted to obtain flux estimation greater than results by the same model WindTrax using the three wind components, mainly when volatilisation peaks occurred. The use of a mean of the transfer coefficient $D$, scaled on the basis of the samplers time exposure, gave results less but closer with the simple outputs of the models. The models sensibility to the $z_0$ parameter permits to highlight the importance of the measurement of atmospheric turbulence, performed with high frequency sonic anemometer, to avoid estimation or underestimation.

This research significantly expanded the database of ammonia emissions in Italy. NH₃ emissions tend to be lower in the case of slurry injection with respect to the surface spreading, due a reduction of contact surface between slurry and air. This result is in accordance with literature and the direct injection of slurry into the soil results the most effective method for reducing N loss during and following slurry application. Incorporation of surface-applied manure with a tillage operation stops NH₃ volatilisation, then rapid incorporation of slurry is important to reduce N loss, since a large portion of the ammonia emission occurs within a few hours of spreading (26 hours in this study when the surface
spreading is used). However, the injection technique bears significantly on the crop management costs, so it is a goal still difficult to achieve in Po Valley.

The uncertainty of the method here employed is comparable to other explored measurement techniques, which denotes its efficiency. The contextual comparison with other techniques could enhance the use of this method and, also, simplify the monitoring action of this pollutant.
COMPARISON OF TWO INVERSE DISPERSION MODELS

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Chapter 3


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Chapter 4

Mitigation strategies to reduce ammonia losses from fertilised arable soils

Keywords. application technique, incorporation technique, arable land, slurry application, urea spreading, inverse dispersion model, ammonia volatilization.
Abstract

To evaluate the best practices in reducing ammonia (NH$_3$) losses from fertilised arable land, seven field trials were performed in three different locations in northern Italy. Emission from cattle slurry and urea are assessed depending on the spreading techniques and the field incorporation procedures. The measurements were conducted by the use of long term exposure concentration samplers associated to the use of WindTrax inverse dispersion model. The results obtained indicate as the volatilization phenomena is exhausted in the first 24 hours after the spreading. The incorporation procedure of slurry resulted able to reduce the losses with respect to the surface spreading, where a contextual incorporation reaches reductions to the 87%. The best abetment strategy for NH$_3$ emissions from slurry has proved to be the direct injection into the soil, with a reduction of about 95% with respect to the surface spreading. The broadcasting application of urea reported that the volatilization phenomenon is slower over time, reaching the maximum loss of 3.8% of the total ammoniacal nitrogen in 4.5 days. The results obtained highlight the strong dependence of the volatilization by soil and weather conditions.
4.1 Introduction

Agriculture is known as a major source of atmospheric ammonia (NH₃), contributing 50% of global NH₃ emissions (Bouwman et al., 1997), over 90% in Europe (EEA, 2011). The reduction of atmospheric NH₃ emissions is an important issue in many countries to prevent environmental pollution by ammonia deposition (ECETOC, 1994; IPPC, 1996) and, furthermore, to reduce the loss of nutrients and energy from agricultural systems (Harper et al., 1983). In fact, NH₃, as the primary gaseous base in the atmosphere, influences the acidity of solid and aqueous phases, aerosol species, cloud water, and precipitation. Direct deposition of atmospheric nitrogen (N) compounds to land surfaces and water bodies is increasingly recognized as a significant contribution to ecosystem degradation via eutrophication and/or acidification (Fowler et al., 1998; Walker et al., 2000; Paerl et al., 2002).

The main agricultural sources of atmospheric NH₃ are the storage and application of livestock manure, followed by the application of synthetic fertilisers (Asman, 1992). Ammonia volatilization process may be responsible for the loss of 10–30% of the total N employed as fertiliser and excreted by animals (Bouwman et al., 2002). Particularly, the reduction of NH₃ emission from field-applied manure draws attention since it contributes largely to the overall NH₃ volatilization from livestock production. Knowledge of NH₃ emission from fertilising activities is also essential in the N balance for the efficient utilization of N for crop production, where distortions in the estimation of the phenomenon could lead to a reduction in the crops production
(overestimation), or in environmental risks as N runoff or nitrate leaching (underestimation).

The main factors influencing the total amount of NH$_3$ lost from manure are the concentration of NH$_3$ at liquid surface and the transfer of NH$_3$ from surface to atmosphere, function of the meteorological conditions, i.e. air temperature, wind speed, solar radiation and field surface roughness (Braschkat et al., 1997; Genermont and Cellier, 1997; Menzi et al., 1998; Misselbrook et al., 2005; Moal et al., 1995; Søgaard et al., 2002; Sommer and Olesen, 2000; Sommer and Hutchings, 2001; Sommer et al., 1991; Meisinger and Jokela, 2000; Webb et al., 2010). These factors are combined with the pH, the dry matter of the manure and the presence or absence of canopy, and its complexity. The area and the time of manure exposed are also key aspects influencing the NH$_3$ emission, i.e. field application methods, presence or absence of incorporation and infiltration rate into the soil.

Numerous methods are developed to apply and incorporate manure, consequently the loss of N varies widely depending on the method used (Rotz, 2004). On arable land, incorporation of broadcast-applied manure or its injection into the soil is effective solution to reduce ammonia volatilization (Hoff et al., 1981; Brunke et al., 1988; Van Der Molen et al., 1990; Amberger, 1991; Huijsmans, 1991; Ismail et al., 1991; Søgaard et al., 2002; Huijsmans et al., 2003). Knowledge of the effect of the above-mentioned factors with the application method can be decisive for an efficient strategy to reduce NH$_3$ volatilization.

Ammonia emissions in Italy are concentrated in the Po Valley, northern Italy, (Clarisse et al., 2009; Skjøth et al., 2011), where most of
the livestock productions are located (55%; ISTAT, 2011), corresponding to about 5% of the total number of cattle, pigs and ovine reared in EU-27 (EUROSTAT, 2011). The Italian NH₃ emission inventories, elaborated by using the EMEP/CORINAIR guidebook (EMEP/CORINAIR, 2007; EMEP/EEA, 2009) by ISPRA (2011), reported that over 95% of NH₃ emissions originates from agriculture and about 82% from livestock and 15% by synthetic N-fertilisers. Moreover, the most widely technique employed for the land application of slurries in Po Valley area is the broad spreading (78%), followed by band spreading (11%) and injection (11%) (CRPA, 2006). Land spreading of animal manure and the use of mineral fertilisers have a significant contribution in the national emission inventory, where reduction interventions be more effective (Valli and Còndor, 2011).

Nevertheless, measurements of NH₃ emissions from fertilisers at field-scale are still scarce in this area as reported by Valli et al. (2003) and Carozzi (chapter 2 and chapter 3, this thesis). Several measurement techniques have been developed and improved to measure NH₃ emissions without altering the environmental conditions (Svensson and Ferm, 1993; Schørring et al., 1992; Wyers et al. 1993; Businger and Oncley, 1990; Wienhold et al., 1994). Inverse dispersion methods are also been profitably used for estimating the emission using NH₃ concentrations measured downwind from the source (e.g., Flesch et al., 2004; Sommer, 2005; Loubet 2010). The results reported in chapter 2 of this thesis were found to be comparable with the eddy covariance technique, that could be considered as the reference measurement method for ammonia fluxes over agricultural soils. Here the inverse dispersion method, under the
version WindTrax, proposed by Flesch et al. (1995; 2004) was used to estimate the NH₃ fluxes. It uses a backward Lagrangian Stochastic approach (bLS), coupled with the use of passive diffusion samplers to measure NH₃ concentration (Tang et al., 2001). This bLS model is based on Monin–Obukhov similarity theory (MOST; Stull, 1988): it states that over short-time intervals (e.g., 30-60 min) the wind properties in the lower atmosphere are delineated from the atmospheric parameters of turbulence: friction velocity $u^*$, the Monin-Obukhov stability length $L$, the surface roughness length $z_0$ and wind direction $WD$.

This study compares the emissions of NH₃ estimated from slurry and urea application in seven field trials performed in three different locations of Po Valley, in order to evaluate the best practices in reducing NH₃ losses from arable land. The emission factors (EF) relative to different agronomical practices are given, taking into account main factors affecting the NH₃ volatilization phenomenon and describing its time dynamic.

### 4.2 Material and methods

#### 4.2.1 Experimental set-up

NH₃ volatilization was measured on six different experimental trials carried out using cattle slurry and one experiment using urea fertiliser. Two different application techniques with two incorporation procedures were used in the slurry experiments. These techniques could be suitably grouped into three application methods, based on their positioning of the slurry on or into the soil: (i) surface spreading; (ii) surface incorporation;
(iii) injection. Urea experiment is treated outside of this classification scheme due to the different type of fertiliser. The experiments were performed from 2009 to 2011 in three farms in PoValley located in: Landriano (Lat. 45°19’ N, Long. 9°16’ E, Alt. 88 m a.s.l), Bigarello (Lat. 45°11’ N, Long. 10°54’ E, Alt. 23 m a.s.l.) and Cornaredo (Lat. 45°29’ N, Long. 09°1’ E, Alt. 140 m a.s.l.). In Table 4.1 the characteristics of the trials are reported.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Site</th>
<th>Fertiliser</th>
<th>period</th>
<th>Fertilising technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-11</td>
<td>Bigarello</td>
<td>slurry</td>
<td>9 – 17 October 2011</td>
<td>surface spreading</td>
</tr>
<tr>
<td>SI-09</td>
<td>Landriano</td>
<td>slurry</td>
<td>26 March – 03 April 2009</td>
<td>surface, incorporation after 24 h</td>
</tr>
<tr>
<td>SI-10</td>
<td>Cornaredo</td>
<td>slurry</td>
<td>17 – 19 March 2010</td>
<td>surface, incorporation after 24 h</td>
</tr>
<tr>
<td>SI-11</td>
<td>Landriano</td>
<td>slurry</td>
<td>7 – 12 April 2011</td>
<td>surface, incorporation after 30 h</td>
</tr>
<tr>
<td>SIC-11</td>
<td>Bigarello</td>
<td>slurry</td>
<td>9 – 17 October 2011</td>
<td>surface, immediate incorporation</td>
</tr>
<tr>
<td>INJ-09</td>
<td>Bigarello</td>
<td>slurry</td>
<td>24 September – 1 October 2009</td>
<td>injection at 25 cm depth, incorporation after 24 h</td>
</tr>
<tr>
<td>UR-10</td>
<td>Landriano</td>
<td>urea</td>
<td>24 June – 17 July 2010</td>
<td>surface spreading</td>
</tr>
</tbody>
</table>
(i) **Surface spreading of cattle slurry:**

- The “SS-11” filed trial was performed in Bigarello from the 9th to 17th of October 2011 in a 4.3 ha silty-clay soil with corn stubble chopped on surface. At the beginning of the experiment, on 0-5 cm soil layer, the water content and pH were 0.22 m³ m⁻³ and 8.2, respectively. The field was spread on surface with 57 m³ ha⁻¹ of fresh dairy slurry on 10th of October, using a 20 m³ tank with splash plate technique and starting from one side to the other of the field. Spreading started at 8.00 a.m. and lasted 4 hours, providing a total ammoniacal nitrogen (TAN = NH₄⁺ + NH₃) content of 68 kg N ha⁻¹.

(ii) **Surface incorporation of cattle slurry**

- The “SI-09” was carried out from 26th March to 3rd April 2009 in Landriano on a loam texture soil, in a 3.9 ha field covered by maize stubbles. The 0-20 cm soil layer, at the beginning of the experiment had a water content of 0.17 m³ m⁻³ and pH of 7.1. The field surface was spread with 87 m³ ha⁻¹ of dairy slurry on 27th March, using splash plate technique associated to umbilical spreading system, starting from the edge of the field. After 24 hours from the spreading start, the slurry was incorporated by means of a disc harrower working at 25 cm depth for 1.5 hours. The applied TAN was 95 kg N ha⁻¹.

- “SI-10” was performed in Cornaredo in a 2.7 ha sandy-loam soil with 5 cm high wheat stubbles, from 15th to 29th March 2010. The initial soil water content from 0 to 10 cm was 0.25 m³ m⁻³.
while the pH was 5.5. On 17th of March 2010 fresh dairy slurry was applied (54 m$^3$ ha$^{-1}$) on soil surface using splash plate technique. The spreading was completed with an alternate passage of two tanks of 19 and 16 m$^3$ starting from the centre of the field. The slurry was incorporated 24 hours later by a 0.3 m depth ploughing. Both spreading and tillage went on for 7 hours, starting in the morning at 08:00 a.m. and the TAN applied was 92 kg N ha$^{-1}$.

- “SI-11” was carried out in Landriano from 6th to 13th April 2011, in a 4.3 ha loam texture soil, covered by sparse 10 cm tall *Lolium multiflorum Lam*. The initial soil water content and pH in the 0-10 cm layer were 0.21 m$^3$ m$^{-3}$ and 6.4, respectively. Dairy slurry was applied on 7th April at the rate of 75 m$^3$ ha$^{-1}$, corresponding to a TAN of 109 kg N ha$^{-1}$. The spreading was performed as in the SI-09 experiment, using splash plate associated to umbilical spreading system. The distribution started in the morning (8:30 a.m.) and lasted about 5 hours. Slurry was than incorporated in 2 hours through a 25 cm depth disc harrowing, started about 30 hours after the application.

- “SIC-11” filed trial was performed in Bigarello from the 9th to 17th of October 2011, simultaneously with SS-11 experiment, in a 2.9 ha silty-clay soil, covered by a regrowth of 5-10 cm tall *Sorghum Vulgsare L.*. The field was spread in 3.5 hours with 55 m$^3$ ha$^{-1}$ of fresh dairy slurry on 10th of October 2011, with surface spreading using a 19 m$^3$ tank with splash plate technique, providing a TAN of 66 kg N ha$^{-1}$. Slurry was
contextually incorporated during the same 3.5 hours, through a 15 cm depth disc harrowing. Spreading and incorporation started at 9.00 a.m.. The top soil (0-5 cm depth), at the beginning of the trial presented water content of 0.22 m$^3$ m$^{-3}$ and a pH of 8.

(iii) Injection of cattle slurry

- “INJ-09” was conducted from 22$^{\text{th}}$ September to 1$^{\text{st}}$ October 2009 in a 2.9 ha field in Bigarello, on silty-clay bare soil, the same field of SIC-11. At the beginning of the trial the soil water content between 0-10 cm was 0.36 m$^3$ m$^{-3}$ and the soil pH was 7.5. The filed was fertilised with 68.5 m$^3$ ha$^{-1}$ of fresh cattle slurry the 24$^{\text{th}}$ of September. The spreading started at 8:00 a.m., lasted 4.5 hours and was performed with 2 tanks of 20 m$^3$ which injected slurry into the soil by means of two anchors working at 25 cm depth, not covering the slot. TAN applied was 139 kg N ha$^{-1}$. Moreover, after 24 hours the slurry was incorporated in 8 hours with a 0.40 m depth ploughing.

Urea distribution

- “UR-10” field trial started from 14$^{\text{th}}$ June 2010 in Landriano on a 10 ha sandy-loam field cultivated with maize and ended the 17$^{\text{th}}$ of July 2010. Urea in granular form was surface spread the 18$^{\text{th}}$ of June for an amount of 106 kg N ha$^{-1}$ when the crop was at stage V8 (7.5 plant m$^{-2}$). Urea was not incorporated and there were not irrigation during the whole period. At the beginning of the trial the soil water content between 0-10 cm was 0.15 m$^3$ m$^{-3}$ and the soil pH was 6.2.
Representative slurry samples (2-3 dm³) were collected during the day of the fertiliser application at different times from the tanks of slurries, to determine pH, percentage of dry matter (DM) and TAN, summarized in Table 4.2. During the experiments, the soil pH, water content, organic matter, nitrous and ammoniacal nitrogen were daily measured at different soil depths.

Table 4.2. Main characteristics of the slurries and urea applied in the field trials: surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SIC-11); injection (INJ-09); and urea spreading (UR-10).

<table>
<thead>
<tr>
<th></th>
<th>Application rate m³ ha⁻¹</th>
<th>Dry matter g kg⁻¹</th>
<th>pH</th>
<th>TAN kg N-NH₄⁺ ha⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-11</td>
<td>57</td>
<td>30</td>
<td>7.5</td>
<td>68</td>
</tr>
<tr>
<td>SI-09</td>
<td>87</td>
<td>44</td>
<td>8.0</td>
<td>95</td>
</tr>
<tr>
<td>SI-10</td>
<td>54</td>
<td>55</td>
<td>6.5</td>
<td>92</td>
</tr>
<tr>
<td>SI-11</td>
<td>75</td>
<td>55</td>
<td>7.8</td>
<td>109</td>
</tr>
<tr>
<td>SIC-11</td>
<td>55</td>
<td>30</td>
<td>7.5</td>
<td>66</td>
</tr>
<tr>
<td>INJ-09</td>
<td>68.5</td>
<td>34</td>
<td>8.0</td>
<td>139</td>
</tr>
<tr>
<td>UR-10</td>
<td>230 a</td>
<td>-</td>
<td>-</td>
<td>106</td>
</tr>
</tbody>
</table>

*a* urea is reported as kg ha⁻¹

A three-dimensional ultrasonic anemometer was placed in the geometrical centre of each field at height between 1.25 to 1.50 m above ground during the trials with slurry, and kept 1 m above the canopy in UR-10. The anemometer was in any case in the equilibrium boundary layer, to provide the parameters of turbulence requested by the bLS. The friction velocity \( u_* \) (m s⁻¹), the Monin-Obukhov length \( L \) (m), the surface roughness length \( z_0 \) (m), the wind speed \( U \) (m s⁻¹) and wind direction \( WD \) (degree to north) were sampled at 10 Hz and averaged over 30 or 60 min (Table 4.3). Moreover, a standard weather station was placed close to each experimental field to measure air temperature (°C), relative
humidity (%), global solar radiation (W m\(^{-2}\)) and rainfall (mm) (Table 4.4).

Table 4.3. Averaged values of atmospheric turbulence (\(u^*\), L and \(z_0\)), \(\text{NH}_3\) concentration measured in the fertilised field (C) and ammonia background level (\(C_{\text{bgd}}\)) during the field trials: surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SI-11); injection (INJ-09); and urea spreading (UR-10).

<table>
<thead>
<tr>
<th></th>
<th>SS-11</th>
<th>SI-09</th>
<th>SI-10</th>
<th>SI-11</th>
<th>SIC-11</th>
<th>INJ-09</th>
<th>UR-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(u^*) m s(^{-1})</td>
<td>min</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>0.37</td>
<td>0.41</td>
<td>0.33</td>
<td>0.41</td>
<td>0.65</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>0.10</td>
<td>0.14</td>
<td>0.08</td>
<td>0.15</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>0.09</td>
<td>0.12</td>
<td>0.06</td>
<td>0.14</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>L m</td>
<td>min</td>
<td>-557</td>
<td>-1816</td>
<td>-4083</td>
<td>-259</td>
<td>-572</td>
<td>-586</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>735</td>
<td>8,216</td>
<td>75,724</td>
<td>7,269</td>
<td>735</td>
<td>1,144</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>3.8</td>
<td>135</td>
<td>198</td>
<td>50</td>
<td>2.2</td>
<td>-1.42</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>-0.05</td>
<td>6</td>
<td>-0.01</td>
<td>0</td>
<td>-0.05</td>
<td>0.18</td>
</tr>
<tr>
<td>C (\mu g) m(^{-3})</td>
<td>min</td>
<td>9</td>
<td>8</td>
<td>0.7</td>
<td>12</td>
<td>4.5</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>820</td>
<td>886</td>
<td>259.6</td>
<td>973</td>
<td>236</td>
<td>78.4</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>169</td>
<td>197</td>
<td>11</td>
<td>191</td>
<td>46</td>
<td>28.9</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>67</td>
<td>53</td>
<td>3.1</td>
<td>48</td>
<td>36</td>
<td>25.1</td>
</tr>
<tr>
<td>(C_{\text{bgd}}) (\mu g) m(^{-3})</td>
<td>min</td>
<td>7.7</td>
<td>2</td>
<td>3.1</td>
<td>8</td>
<td>7.7</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>34</td>
<td>84</td>
<td>12.6</td>
<td>29</td>
<td>34</td>
<td>35.2</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>19</td>
<td>39</td>
<td>6.3</td>
<td>16</td>
<td>19</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>16</td>
<td>26</td>
<td>5.5</td>
<td>15</td>
<td>16</td>
<td>18.5</td>
</tr>
<tr>
<td>(z_0) m</td>
<td>min</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>0.25</td>
<td>0.45</td>
<td>0.30</td>
<td>0.35</td>
<td>0.6</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>0.05</td>
<td>0.09</td>
<td>0.02</td>
<td>0.06</td>
<td>0.18</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>0.03(^a)</td>
<td>0.02(^a)</td>
<td>0.06(^a)</td>
<td>0.04(^a)</td>
<td>0.04(^a)</td>
<td>0.03(^a)</td>
</tr>
</tbody>
</table>

\(^a\) value obtained removing periods of potential MOST inaccuracy \(|L|<5m, u_<0.2\) m s\(^{-1}\) and \(z_0>1\) m.
Table 4.4. Average values of meteorological variables during the field trials: surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SIC-11); injection (INJ-09); and urea spreading (UR-10). The minimum and maximum values are indicated in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Rain mm</th>
<th>Temperature °C</th>
<th>Relative humidity %</th>
<th>Wind speed m s(^{-1})</th>
<th>Global Radiation W m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-11</td>
<td>0 (^a)</td>
<td>12.3 (0:25)</td>
<td>65.6 (29:98)</td>
<td>1.2 (0:4.7)</td>
<td>165 (0:702)</td>
</tr>
<tr>
<td>SI-09</td>
<td>55 (^a)</td>
<td>11.2 (3:19)</td>
<td>94.5 (71:100)</td>
<td>1.5 (0:5.6)</td>
<td>85 (0:630)</td>
</tr>
<tr>
<td>SI-10</td>
<td>5.2 (^a)</td>
<td>12.2 (4:20)</td>
<td>79.9 (37:97)</td>
<td>0.2 (0:2.8)</td>
<td>110 (0:698)</td>
</tr>
<tr>
<td>SI-11</td>
<td>0.8 (^a)</td>
<td>18.5 (7.5:32)</td>
<td>86 (16:97)</td>
<td>1.3 (0:3.4)</td>
<td>222 (0:823)</td>
</tr>
<tr>
<td>SIC-11</td>
<td>0 (^a)</td>
<td>12.3 (0:25)</td>
<td>65.6 (29:98)</td>
<td>1.2 (0:4.7)</td>
<td>165 (0:702)</td>
</tr>
<tr>
<td>INJ-09</td>
<td>0 (^a)</td>
<td>19.2 (11:27)</td>
<td>77.6 (46:96)</td>
<td>0.9 (0:4.2)</td>
<td>177 (0:619)</td>
</tr>
<tr>
<td>UR-10</td>
<td>44.8 (^a)</td>
<td>24.6 (13:34)</td>
<td>70 (36:100)</td>
<td>0.75 (0:4.6)</td>
<td>279 (0:955)</td>
</tr>
</tbody>
</table>

\(^a\)cumulative value

4.2.2 Measurement of ammonia concentration

The concentration of NH\(_3\) was measured using ALPHA samplers, a long term passive approach developed and discussed by Tang et al. (2001) and Sutton et al. (2001a). The operating principle of ALPHA samplers is based on the capture of gaseous NH\(_3\) on acid support (13% of citric acid), protected by a 5 µm PTFE membrane to avoid particle contamination and to establish a turbulence-free diffusion path between the membrane and the collection filter (Pinder, 2011). These tools are designed to measure NH\(_3\) air concentration from less than 1 µg m\(^{-3}\) (Leith et al., 2004) to over 1 mg m\(^{-3}\), as measured in this study. Samplers were exposed in three replicates, located on a mast in the centre of each field at the same height of the sonic anemometer to measure NH\(_3\) concentration (C) from the surface of the field. The heights were chosen in function of the fetch. The samplers were substituted between 2 hours, during the
strategies to reduce ammonia losses

spreading days, and two times per day, after dawn and just before sunset, in order to follow the change of atmospheric turbulence, and to reduce the uncertainty in the source estimation (Loubet et al., 2011). To measure the background concentration of NH$_3$ ($C_{bgd}$) a sample point was located more than 600 m away from the investigated fields and away from any possible NH$_3$ sources. The value of air NH$_3$ concentration was obtained through colorimetry (FIAstar 5000 system, FOSS, Denmark) and on the basis of the volume of air sampled by ALPHA, function of the time of exposure (Sutton et al., 2001b; Tang et al., 2008) (see Table 4.3).

4.2.3 The inverse dispersion modelling: WindTrax model

The inverse dispersion modelling is based on the superimposition principle (Thomson et al., 1987), which relates the concentration in the middle of the field, $C$, to the emitted flux from the surface, $S$, and the background concentration $C_{bgd}$, with the transfer coefficient $D$:

$$C = D \times S + C_{bgd}$$

(eq 4.1)

The inversion method simply consists in estimating $S$ from the above equation as:

$$S = (C - C_{bgd}) \times D^{-1}$$

(eq 4.2)

The hypotheses are: (i) no reaction of NH$_3$ with acids in the atmosphere occurs, which is reasonable at the spatial scale studied here
(Nemitz et al., 2009), (ii) the volatilisation flux is spatially homogeneous from surface, discussed in Loubet et Cellier (2001), and (iii) soil surface characteristics are not variables (i.e. $z_0$). For the latter sentence, the value of $z_0$ was taken as the median value of those values were the MOST theory was applicable, i.e. the values of $u_*$ less than 0.2 m s$^{-1}$, the values of $L$ larger and smaller than -5 and 5, and the values of $z_0$ over 1 m (UR-10 case), were excluded (Flesch et al., 2004, 2005; Todd et al., 2008; Hensen et al., 2009; Loubet et al., 2009).

The WindTrax model (Thunder Beach Scientific, Halifax, Canada) has been employed to estimate $D$. This model combines the backward Lagrangian stochastic dispersion theory described by Flesch et al., (1995; 2004) with an interface where sources and concentration sensors can be mapped. To obtain $D$, the model calculates thousands (50,000) of trajectories upwind of the sensors, to determine the number of the intersections within, or outside, the emitting source area ($N_{source}$). At the same time the vertical velocity of the wind ($w_0$) of those trajectories that intersect the source area are recorded in order to obtain $D$ as:

$$D = \frac{1}{N} \sum_{N_{source}} \left| \frac{2}{w_0} \right|$$

(eq 4.3)

The applicability of the bLS technique to long term passive samplers is possible only with short time intervals, since the energy fluxes typically change strongly over a timescale of a few hours. This variation leads to the change of atmospheric stability and turbulence, that increases during the day (unstable conditions) and decreases during the night (stable
conditions). Afterwards, the determination of \( S \) is possible only by periods of stationarity, reached by short integration time (typical less than 1 hour) of the turbulence parameters (\( u^* \), \( L \) and \( z_0 \)), as states the MOST theory.

![Cumulated NH\(_3\) fluxes (%TAN) obtained using WindTrax](image)

**Figure 4.1.** Cumulated \( NH_3 \) fluxes (%TAN) obtained using WindTrax (see text for explanation of the model) for different slurry spreading technique: surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SIC-11); injection (INJ-09).
4.3 Results and Discussions

4.3.1 Slurry spreading: ammonia emissions and abatement efficiency

The cumulate of the estimated NH$_3$ fluxes for the case studies performed using slurry as fertiliser, showed an overall rapid ammonia loss after the application (Figure 4.1 and Table 4.5). The surface spreading without incorporation (SS-11) scored the highest N loss, 44.4%, expressed as %TAN applied. The incorporation following surface application achieved lower levels of emitted ammonia; in particular, both incorporation after 30 hours (SI-11, 28.5%) and 24 hours (SI-09, 27.8%). If the incorporation was carried out immediately after the spreading of slurry, the loss was further abated (SIC-11, 5.6%). The best abatement strategy found was the injection one (INJ-09) where the total cumulated ammonia volatilization was only 2.5%TAN. The trial SI-10 showed an ammonia loss of 6.4%TAN, much lower with respect to the analogous managed trials SI-09 and SI-11. A possible explanation in this case could be the low value of pH of the employed slurry (6.5) and the soil type (sandy-loam) (see below). Furthermore, in this case the application rate was sensibly lower with respect the other applications (54 m$^3$ ha$^{-1}$). The comparison with the values of the EFs obtained, resulted possible by using the meta-model ALFAM (Søgaard et al., 2002) for the experiments of surface spreading (SS-11), surface spreading with incorporation (SIC-11) and slurry injection (INJ-09). The estimation provided values of EF very similar with the measurements obtained here, as 40%TAN for SS-11, about 3.5%TAN for SIC-11, and 2% for INJ-09.
### Table 4.5. Results of the maximum $\text{NH}_3$ peak, cumulated $\text{NH}_3$ fluxes and emission factor (EF) with error. Surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SIC-11); injection (INJ-09); and urea spreading (UR-10)

<table>
<thead>
<tr>
<th>Method</th>
<th>Flux cumulated kg N ha$^{-1}$</th>
<th>Flux maximum kg N ha$^{-1}$ h$^{-1}$</th>
<th>EF %TAN (±err%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-11</td>
<td>30.2</td>
<td>3.61</td>
<td>44.4 (±1.8%)</td>
</tr>
<tr>
<td>SI-09</td>
<td>26.4</td>
<td>3.38</td>
<td>27.8 (±6.1%)</td>
</tr>
<tr>
<td>SI-10</td>
<td>5.9</td>
<td>0.97</td>
<td>6.4 (±1.6%)</td>
</tr>
<tr>
<td>SI-11</td>
<td>31.1</td>
<td>3.43</td>
<td>28.5 (±1.1%)</td>
</tr>
<tr>
<td>SIC-11</td>
<td>3.7</td>
<td>0.25</td>
<td>5.6 (±8.7%)</td>
</tr>
<tr>
<td>INJ-09</td>
<td>3.4</td>
<td>0.36</td>
<td>2.5 (±0.6%)</td>
</tr>
<tr>
<td>UR-10</td>
<td>4.0</td>
<td>0.17</td>
<td>3.8 (±0.7%)</td>
</tr>
</tbody>
</table>

Figure 4.2. Cumulated $\text{NH}_3$ fluxes from WindTrax (see text for explanation of the model) reported as % of total emission during the first 48 hours from the beginning of the slurry spreading: surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SIC-11); injection (INJ-09).
The shape of the cumulate curve for the surface spreading without incorporation (SS-11) showed a rapid increase during the spreading operation (4 hours) and during the following 2 hours, reaching the 45% of the total NH$_3$ emitted in 6 hours. During the evening hours, the slope of the curve is reduced but the emission continued reaching 77% of the total emission in 24 hours (Figure 4.2). The plateau was reached after 168 hours from the spreading (see Figure 4.1). The field trials where the incorporation occurred 24 hours or 30 hours after the beginning of the spreading have lost, before the tillage event, respectively 64% of the total emission in SI-09 (at 24 h), 99% in SI-10 (at 24 h) and 85% in SI-11 (at 30 h) (see Figure 4.2).

A particular discussion has to be done for the SIC-11 where the emission factor (EF) obtained is the lower in comparison to the other incorporation experiments. Here, even if the incorporation followed step by step the spreading, the slope of the emission during the first 6 hours resulted similar to the slope of SS-11, highlighting the fact that the volatilization phenomenon occurs immediately after the spreading of slurry on the land. The resemblance with the SS-11 curve could be due to the parity of slurry and weather condition during the trials, and the similarity of the soils (see Figure 4.2). In this case, after 24 hours of the spreading the loss was over 50%, and from 6 to 84 hours the loss grew constantly about 0.6% h$^{-1}$; the ammonia volatilization ended after 170 hours. Moreover, during this trial a deposition of ammonia was detected as indicated by the trend of the cumulate ammonia fluxes which produced a decline from hours 84 to 108 (see Figure 4.1).
The course of the emission for the injection application technique (INJ-09) attained 51% of the total loss after 12 h, which rose to 71% after 24 hours (see Figure 4.2). Also in this case a slight ammonia deposition of 7% was detected from 24 to 48 hours after spreading.

The rates of ammonia emission resulted high in all the field trials during the first 8 hours, with average value of total loss of 6% h\(^{-1}\) in SS-11, 4% h\(^{-1}\) in SI-09 and SIC-11, 5% h\(^{-1}\) in SI-11 and INJ-09, while SI-10 reaching the highest values of 12% h\(^{-1}\). The maximum hourly loss in terms of N was 3.2 kg ha\(^{-1}\) h\(^{-1}\) in SS-11 and SI-11, 4 hours and 8 hours after the beginning of the spreading, respectively; about 2.7 kg ha\(^{-1}\) h\(^{-1}\) in SI-09 at 7 hours; 1.0 kg ha\(^{-1}\) h\(^{-1}\) in SI-10 at 4 hours; 0.23 kg ha\(^{-1}\) h\(^{-1}\) in SIC-11 at 2 hours; and 0.36 kg ha\(^{-1}\) h\(^{-1}\) in INJ-09 at 5 hours from the beginning of the spreading. During the noon hours, from c.a. 4:00 p.m. to 8:00 p.m. (8 to 12 hours after the spreading), the rate of emission decreased to 1 % h\(^{-1}\) in SS-10 and SIC-11, to 3% h\(^{-1}\) in SI-09 and INJ-09, 0.5% h\(^{-1}\) in SI-10, while remain constant for SI-11 (5% h\(^{-1}\)). During the first night of each trial, the rate of emissions reduced to values around 1.0 ± 0.5% h\(^{-1}\), rising again with the beginning of the day after. The only exceptions were observed in INJ-09, with a decreasing of the the rate of emission, and during SI-10, with the end of the emission in 24 hours. In any case starting from 24 hours after the slurry spreading, the rates gradually decreased.

The trend of the slopes in Figure 4.1 and 4.2 highlighted the decline of ammonia emission in surface spreading (SS-11) already starting 24 hours after spreading. During SI-09 and SI-11, where the incorporation occurred respectively at 24 and 30 hours, harrowing dropped the
Chap

ter 4

emission rates which subsequently, however, continued slightly to grow. Conversely the immediate incorporation occurred in SIC-11 had an instantaneous effect in lowering the rate of the emission. These results are in agreement with studies on relationship between timing of incorporation and abatement efficiency: in particular, Huijsmans et al. (2003) reported an abatement in emission of 12% if incorporation in done after 24 hours from the spreading, rising over 90% if it occurs within 4 hours. However, considering that ammonia volatilization is a complex phenomenon affected by factors such as slurry characteristics, weather and soil conditions (Sommer et al., 2001), a comparisons, in absolute value, of ammonia losses due to different spreading techniques is not simple. An example of how large could be the differences in terms of NH\textsubscript{3} losses using the same fertilising technique, is given in trials SI-10, SI-09 and SI-11. In particular, the cumulated ammonia emission during SI-10 resulted four time less than the experiments SI-09 and SI-11. This difference could be explained considering all the other factors affecting ammonia volatilization, such as soil characteristics and weather condition. The low wind speed detected during the first hours of the spreading in SI-10 (0.7 m s\textsuperscript{-1}) could be responsible of an inhibition of NH\textsubscript{3} volatilization due to absence of mass transport Sommer et al. (1991). In this regard and Huijsmans et al. (2003) showed that NH\textsubscript{3} losses increased when wind speed increased from 2 to 5 m s\textsuperscript{-1} resulted on average in an 74% increase in total volatilisation for surface incorporation. Moreover, NH\textsubscript{3} emissions were reported to be very sensitive to slurry and soil pH condition, where the losses increases by increasing of pH values (Freney et al., 1983; Genermont and Cellier,
STRATEGIES TO REDUCE AMMONIA LOSSES

1997; Sommer and Hutchings, 2003; Sommer et al., 2003; Misselbrook et al., 2005). For instance lowering the value of pH of 1 units from 7 reduce the emission over 20% (Stevens et al., 1992; Bussink et al., 1994; Génermont and Cellier, 1997), whereas soil pH lower than 6 reduce significantly the emissions (Jarvis and Pain, 1990) and increasing to 9 gain the emission up to 50% (Court, et al., 1964). Among field trials where the incorporation occurred at or after 24 h, the effect of reduction on emission is more appreciable for SI-10 that present slurry pH of 6.5 and soil pH of 5.5, than SI-09 and SI-10. The effect of pH in SI-10 could be also due to the moisture content of the first soil layer, which contributes to lowering further the emission, due to a lower absorption of the liquid fraction into the wetter soils (Sommer & Christensen, 1991; Ferm et al., 1999).

On the other hand, a good evaluation of efficiency of abatement strategy is given by comparing the SS-11 and SIC-11 trials. These experimental campaigns were performed simultaneously in two close fields (1.2 km distant), having comparable characteristics in term of soil pH, moisture content and texture, using the same slurry (physical and chemical characteristics and amount), management and spreading technique. In this case, the simultaneous incorporation of the broad slurry by harrowing (15 cm depth), reduced the emissions of 87% with respect to the surface spreading, keeping in the soil about 41 kg N ha\(^{-1}\), corresponding to 39% of the N applied.
4.3.2 Ammonia emissions from urea

The NH\textsubscript{3} volatilization from urea is reported as cumulate in Figure 4.3, where the typical sigmoidal trend was observed (Meyers et al. 2006). The first stage of the volatilization process was governed by small NH\textsubscript{3} emissions after the surface application of urea that increased exponentially from 6 to 24 hours, reaching the maximum emission peak of 170 g N ha\textsuperscript{-1} h\textsuperscript{-1}. The behaviour indicated that the hydrolysis process has taking place, with a typical time lag for urea sources undergoing hydrolysis, according to results observed by several authors (Ferguson et al., 1987; Meyers et al., 2006; Ferrara, 2008).

![Figure 4.3. Cumulated NH\textsubscript{3} fluxes (%TAN) from WindTrax (see text for explanation of the model) for urea spreading (UR-10).](image-url)
During the first 24 hours, 35% of the total emission was recorded, with averaged NH$_3$ losses of 1.7 µg m$^{-2}$ s$^{-1}$. Starting from the day after, the NH$_3$ emission decreased, remaining always below 1 µg m$^{-2}$ s$^{-1}$ until the end of the trial. These values are in accordance with data reported by similar works carried out on maize field fertilised with urea. In particular, Zhu et al. (2000) found peaks of NH$_3$ close to 1 µg m$^{-2}$ s$^{-1}$ over a young maize field fertilised with broadcast application of urea at a rate of 138 kg N ha$^{-1}$; McInnes et al. (1986) reported an average ammonia flux from 1 to 4 µg m$^{-2}$ s$^{-1}$ following surface application of 120 kg N ha$^{-1}$, while Meyers et al. (2006) reported maximum fluxes of about 2.6 µg m$^{-2}$ s$^{-1}$ using urea-ammonium-nitrate. From 24 to 120 hours after the urea spreading, the slope of the emission curve was more or less constant around 0.4% h$^{-1}$, equivalent to a loss of 10 g N ha$^{-1}$ h$^{-1}$. At 120 hours the NH$_3$ loss was 83% of the total one. Starting from the 5$^{th}$ day, until the reaching of the maximum value of the accumulation (307 h), the emission rate was further reduced to values around 2.6 g N ha$^{-1}$ h$^{-1}$, indicating that the volatilization process was ending. At last, the cumulated loss decreased due to deposition events detected in the field and rose again slightly at the end of the trial.

The EF obtained from the trial was 3.8%, representing a total loss of 4 kg N ha$^{-1}$. Existing works performed on comparable experimental design, found values of EF higher than our, and ranging from 0.1 to 30% (McInnes et al., 1986; Sommer and Jensen, 1994; Rochette et al., 2009; Turner et al., 2010). The lower EF obtained could be due to the effect of the rainfall occurred from 16 to 52 hours after the fertiliser application, 32.7 mm whose 10 mm at 24 hours after urea spreading. The effect of
rainfall or irrigation resulted in an overall reduction of the volatilization process in accordance with results reported by Bowmann et al. (1987) that found a reduction between 30 and 90% in NH$_3$ volatilization when rain occurs in the first hours after application, within 3 to 24 hours.

### 4.4 Conclusions

The reduction of ammonia emissions from arable land following slurry application is significantly affected by the method of its application or incorporation, aimed to limiting the contact between ambient air and slurry, reducing the exchange surface. The operation of slurry incorporation into the soil after surface spreading results an efficient method to control the volatilization process and, therefore, to increase the availability of N for crop productions.

The results found show clearly that slurry incorporation procedure reduces the NH$_3$ loss with respect to the surface spreading. In particular, the faster is the incorporation after the slurry spreading, the higher are the benefits in terms of reduction in ammonia losses, with the best performance achieved when the incorporation takes place contextually with the spreading. In this case, a reduction of 87% in NH$_3$ loss with respect to surface spreading is recorded. However, the best abatement strategy for NH$_3$ emissions is reached with direct injection, with a loss of only 2.5%TAN (95%). Even if the application technique is fundamental, the NH$_3$ emission is also affected by the soil and weather condition at time of slurry application, as highlighted in the SI-10 trial during which the low values of wind speed and pH of soil and slurry inhibit NH$_3$
volatilization, resulting in a low NH₃ loss. Therefore, coupled to the management practices relative to the application techniques of the slurry, the soil and weather conditions have been taken into account in order to decrease N losses via NH₃ volatilization. The results of this study suggest to avoid the application of manure during the warmer part of the day, considering, however, the total amount of slurry to be applied and the length of the period available for application, in accordance with soil/weather conditions and legislation.
References


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Chapter 5

Conclusions
The plain area of Lombardia region (Po Valley) in north Italy is one of the most intensive agricultural areas and one of the most important ammonia emitting regions in Europe (Clarisse et al., 2009; Skjøth et al., 2011). Considering the environmental disease related to excess of reactive nitrogen compounds, the quantification of the NH$_3$ emissions after fertilisation practices is relevant to evaluate the correct management of the nitrogen at farm scale, in order to mitigate the contribution of the agriculture to environmental issues.

Since two decades, several measurement techniques have been developed and improved to measure NH$_3$ fluxes, even if the sticky nature of this compound complicates the NH$_3$ measurements under actual field conditions (Harper, 2005; Brodeur et al., 2009). The micrometeorological methods are considered a reliable approach since they avoid the alteration of the environmental conditions, which affect the ammonia exchange dynamic, and permit to investigate on large areas. Among the available micrometeorological techniques, the Eddy Covariance (EC) one is considered the most direct and least error-prone approach for measuring fluxes at field scale (Ammann, 1999; Sutton et al., 2007; Denmead, 2008, Fowler et al., 2009; Sintermann et al., 2011), therefore, it has been chosen as reference method for measuring ammonia fluxes.

The performance of three models to estimate ammonia fluxes have been tested in comparison with the direct EC NH$_3$ flux measurements during two trials with slurry spreading (see Chapter 2). The selected models have been: two versions of the dispersion theory, (1a) FIDES-2D (Loubet et al. 2001) and (1b) WindTrax (Flesh et al. 2004) and (2) Volt’Air, a deterministic model developed by Génermont and Cellier
The comparison has shown that the deterministic model Volt’Air reproduces the trend of the emission, but it is very sensible to the soil surface and slurry pH, providing very high emission values compared to the EC data. On the other hand, the inverse dispersion models, coupled with the use of long term exposure concentration samplers, turn out to be of great utility and gave different, but comparable results with the reference technique. The models have shown to be sensible to the turbulence parameters, especially friction velocity and roughness length, underlining the importance of accuracy in atmospheric turbulence measurements performed with high frequency sonic anemometer.

The use of inverse dispersion model results a simple and inexpensive method for long monitoring of NH₃ exchanges. Moreover, the uncertainty derived from their use is comparable to other explored measurement techniques, which denotes its efficiency (see Chapter 3). Therefore, the open access model WindTrax have been chosen for studying the difference in terms of NH₃ losses due to different agronomic practices (see Chapter 4). In particular, the reduction of ammonia emissions from arable land following application of fertilisers is significantly affected by the method employed and by the presence of incorporation into the soil. The results of this study have shown clearly that slurry incorporation procedure is effective to control and reduce the volatilization process and, therefore, to increase the availability of N for crop productions. The faster is the incorporation, the higher are the benefits in terms of reduction in ammonia losses, since a large portion of the ammonia emission occurs within few hours form the spreading: the best performance are achieved when the incorporation takes place
contextually with the spreading. In this case, a reduction of 87% in NH$_3$ loss with respect to surface spreading is recorded. However, the best abatement strategy for NH$_3$ emissions is reached with direct injection, with a loss of only 2.5%TAN, which means a reduction of about 95% with respect to the surface spreading. At last, the broadcasting application of urea is an efficient technique of fertilisation in terms of small N loss (NH$_3$ loss around 3.8%TAN). Moreover, the amount of NH$_3$ emission is also affected by the soil and weather conditions during the fertilizer application, especially temperature, wind speed and pH of soil and slurry, therefore the best practices for a correct management of nitrogen have to take into account also the timing of the application.

Finally this research significantly expanded the database of ammonia emissions in Italy. Reliable NH$_3$ quantification results a central aspect for decision makers, to promote abatement strategies and to derive emission factors used in national and international emission inventories. On the base of the results achieved, further research should be proposed with the main objective of define detailed management strategies to reduce NH$_3$ losses by land application of fertilisers. Furthermore, the investigation on gaseous losses of other form of nitrogen compounds, such as N$_2$O and NO$_3^-$, are needed on this topic.
Appendix
# Appendix A: General information required as input in Vol’Air model application for the two trials described in the text (SI-09 and SI-11).

<table>
<thead>
<tr>
<th>Input data</th>
<th>Units</th>
<th>Range</th>
<th>Information</th>
<th>SI-09</th>
<th>SI-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day of the beginning of the run</td>
<td>day of year</td>
<td>1 - 1000</td>
<td>must correspond to the time step of weather and optional variables input files</td>
<td>84.000</td>
<td>96.833</td>
</tr>
<tr>
<td>Day of the end of the run</td>
<td>day of year</td>
<td>1 - 1000</td>
<td></td>
<td>96.958</td>
<td>103.375</td>
</tr>
<tr>
<td>Time step of the model</td>
<td>minutes</td>
<td>1 - 180</td>
<td>P = field</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Type of experiment</td>
<td></td>
<td></td>
<td>T = wind tunnel</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>parcel length</td>
<td></td>
<td></td>
<td>&quot;yes&quot; or &quot;no&quot;</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>
| The available radiation with which the energy budget will be run | uppercase letter | G, N or X | G = global solar radiation  
N = net solar radiation  
X = disabled energy balance (wind tunnels) | G     | G     |
| Number of soil layers of the model             | dimensionless | 1 - 10    | user-defined in the soil input file                                         | 5     | 5     |
| Water retention model                          | dimensionless | CH or VG  | CH = Clapp & Hornberger model  
VG = van Genuchten-Mualem model | VG    | VG    |
| User choice for the origin of the parameters for the van Genuchten-Mualem model | dimensionless | 0 or 1    | 0 = calculations following Wösten et al. (1999) PTF  
1 = user defined parameters in the soil description file | 1     | 1     |
| Latitude                                       | ° N         | -90 : +90 |                                                                            | 45    | 45    |
| Albedo                                         | dimensionless | 0 - 1     | proposition of tabulated values (from Guyot, 1998)                          | 0.2   | 0.2   |
| Soil surface roughness length                  | m           | 0.001 - 1 |                                                                            | 0.02  | 0.04  |
| Reference height above soil surface for air temperature | m           | 0 - 10   | For wind-tunnel experiments, choose half the height of the canopy (often: 0.25 m) | 1.85  | 1.85  |
| Reference height above soil surface for water vapour pressure | m           | 0 - 10   | For wind-tunnel experiments, choose half the height of the canopy (often: 0.25 m) | 1.85  | 1.85  |
| Reference height above soil surface for wind speed | m           | 0 - 10   | For wind-tunnel experiments, choose half the height of the canopy (often: 0.25 m) | 10    | 10    |
### Appendix B: Cultural techniques required as input in Vol’Air model application for the two trials described in the text (SI-09 and SI-11).

<table>
<thead>
<tr>
<th>Input data</th>
<th>Units</th>
<th>Range</th>
<th>Information</th>
<th>SI-09</th>
<th>SI-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of application</td>
<td>dimensionless</td>
<td>0-3</td>
<td>0 = no application</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 = N fertiliser application organic or mineral</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 = pesticide application</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3 = N fertiliser and pesticide application</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of soil managements</td>
<td>dimensionless</td>
<td>0-5</td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Case of soil management, for each management**

<table>
<thead>
<tr>
<th>Day and hour of soil management</th>
<th>day of year</th>
<th>1 - 1000</th>
<th>87.334</th>
<th>98.375</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of cultivation technique</td>
<td>dimensionless</td>
<td>1</td>
<td>No choice for the moment: 1</td>
<td>1</td>
</tr>
<tr>
<td>Depth of cultivation</td>
<td>m</td>
<td></td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Proportion of incorporated soil</td>
<td>dimensionless</td>
<td>0-1</td>
<td>Eye appreciation: 0 no soil incorporation 1 only incorporation</td>
<td>0.8</td>
</tr>
<tr>
<td>Number of irrigations</td>
<td>dimensionless</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Case of irrigation, for each irrigation**

| Day and hour of irrigation        | day of year  | 1 - 1000 |         |        |
| Water volume applied              | mm = L m²    | 0 - 100  |         |        |

**Case of N fertiliser application**

| Type of fertiliser               | dimensionless| 10-40    | 10 = slurry surface applied                    | 10    | 10    |
|                                   |              |          | 20 = NH₄-NO₃ granules surface applied          |       |       |
|                                   |              |          | 30 = urea prills surface applied              |       |       |
|                                   |              |          | 35 = urea granules surface applied            |       |       |
|                                   |              |          | 40 = N solution surface applied               |       |       |

| Day and hour of N application     | day of year  | 1 - 1000 | 86.334 | 97.375 |

If “Type of fertiliser” ≠ 10 : Rate of N applied

<table>
<thead>
<tr>
<th>kg N ha⁻¹</th>
<th>m³ fresh slurry ha⁻¹</th>
<th>0 - 1000</th>
<th>density of slurry can be assumed to be 1000 kg m⁻³ if not available</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.18</td>
<td>75.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### APPENDIX

<table>
<thead>
<tr>
<th>Type of application technique</th>
<th>dimensionless</th>
<th>0-1</th>
<th>0 = surface</th>
<th>1 = bands</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
</table>

#### Case technique application bands

<table>
<thead>
<tr>
<th>Proportion covered by the product applied</th>
<th>dimensionless</th>
<th>0.01-0.99</th>
<th>0.33 for slurry; default is “NR”</th>
</tr>
</thead>
</table>

#### Case of slurry surface or incorporated = 10

<table>
<thead>
<tr>
<th>Type of modelling of the slurry layer</th>
<th>dimensionless</th>
<th>0-2</th>
<th>0 = slurry applied within the first layer of soil</th>
<th>1 = consideration of 1 individualized surface layer of slurry</th>
<th>2 = consideration of 2 individualized surface layers of slurry</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Dry mater content of the slurry</th>
<th>g kg⁻¹ fresh matter</th>
<th>0-1000</th>
<th>not directly used in the model</th>
<th>43.88</th>
<th>54.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen content of the slurry</td>
<td>g kg⁻¹ fresh matter</td>
<td>density of slurry, assumed to be 1000 kg m⁻³</td>
<td>2.160</td>
<td>2.970</td>
<td></td>
</tr>
<tr>
<td>Total Ammoniacal Nitrogen content of the slurry</td>
<td>g kg⁻¹ fresh matter</td>
<td>density of slurry, assumed to be 1000 kg m⁻³</td>
<td>1.095</td>
<td>1.450</td>
<td></td>
</tr>
<tr>
<td>Total Nitrate Nitrogen content of the slurry</td>
<td>g kg⁻¹ fresh matter</td>
<td>if available, otherwise NR</td>
<td>NR</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>Slurry pH</td>
<td>-</td>
<td>0.01-13.99</td>
<td>very important</td>
<td>8.00</td>
<td>7.76</td>
</tr>
<tr>
<td>Slurry CEC</td>
<td>cmol⁺ kg⁻¹ dry matter</td>
<td>if available, otherwise NR</td>
<td>NR</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>Slurry density</td>
<td>kg m⁻³</td>
<td>0-2000</td>
<td>if available, otherwise 1000 kg m⁻³</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Bulk density of the slurry dry matter</td>
<td>kg m⁻³</td>
<td>0-2000</td>
<td>if available, otherwise 1000 kg m⁻³</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Critical application rate for uniform application</td>
<td>m³ ha⁻¹</td>
<td>0 - 1000</td>
<td>60 m³ ha⁻¹ as a default value</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

#### Case water retention model = CH (general information)

Infiltration correction factor for the 1 layer of soil | dimensionless | 0 - 1 | 0.02 for liquid slurry spreading |

#### Case water retention model = VG (general information)

<table>
<thead>
<tr>
<th>VG parameters for the slurry:</th>
<th>teta_sat</th>
<th>m³ m⁻³</th>
<th>0 - 1</th>
<th>0.996</th>
<th>0.996</th>
</tr>
</thead>
<tbody>
<tr>
<td>VG parameters for the slurry:</td>
<td>teta_r</td>
<td>m³ m⁻³</td>
<td>0 - 1</td>
<td>0.373</td>
<td>0.373</td>
</tr>
<tr>
<td>VG parameters for the slurry:</td>
<td>alpha</td>
<td>m⁻¹</td>
<td>&gt; 0</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>VG parameters for the slurry:</td>
<td>n</td>
<td>-</td>
<td>&gt; 1</td>
<td>1.361</td>
<td>1.361</td>
</tr>
<tr>
<td>VG parameters for the slurry:</td>
<td>Ksat</td>
<td>m s⁻¹</td>
<td>&gt; 0</td>
<td>8.34E-08</td>
<td>8.34E-08</td>
</tr>
</tbody>
</table>

---

*Appendix C: Required soil inputs of Vol’Air model for the two trials described in the text (SI-09 and SI-11).*
<table>
<thead>
<tr>
<th>Input data</th>
<th>Units</th>
<th>Range</th>
<th>SI-09</th>
<th>SI-11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Layer 1</td>
<td>Layer 2</td>
</tr>
<tr>
<td>Layer depth</td>
<td>m</td>
<td>0 - 2</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Clay &lt; 2 µm</td>
<td>g kg⁻¹</td>
<td>0 - 1000</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>Silt 2-50 µm</td>
<td>g kg⁻¹</td>
<td>0 - 1000</td>
<td>454</td>
<td>454</td>
</tr>
<tr>
<td>Sand 50-2000 µm</td>
<td>g kg⁻¹</td>
<td>0 - 1000</td>
<td>373</td>
<td>373</td>
</tr>
<tr>
<td>Initial soil water content</td>
<td>g kg⁻¹</td>
<td>0 - 1000</td>
<td>138</td>
<td>138</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>0 - 14</td>
<td>7.14</td>
<td>7.14</td>
</tr>
<tr>
<td>Organic carbon</td>
<td>g kg⁻¹</td>
<td>0 - 1000</td>
<td>14.5</td>
<td>14.5</td>
</tr>
<tr>
<td>Initial N-NH₄ content</td>
<td>mg kg⁻¹</td>
<td>0 - 1000</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>Initial N-NO₃ content</td>
<td>mg kg⁻¹</td>
<td>0 - 1000</td>
<td>8.32</td>
<td>8.32</td>
</tr>
<tr>
<td>Cation exchange capacity</td>
<td>cmol kg⁻¹</td>
<td>0 - 200</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Bulk density</td>
<td>kg m⁻³</td>
<td>0 - 3</td>
<td>1423</td>
<td>1423</td>
</tr>
<tr>
<td>Water content at saturation</td>
<td>m³ m⁻³</td>
<td>0 - 1000</td>
<td>0.425</td>
<td>0.425</td>
</tr>
<tr>
<td>Residual water content</td>
<td>m³ m⁻³</td>
<td>0 - 1000</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>alpha</td>
<td>m⁻¹</td>
<td>&gt; 0</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>n</td>
<td>-</td>
<td>1 - 2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Saturation conductivity</td>
<td>m s⁻¹</td>
<td>10⁻⁶ - 10⁻⁴</td>
<td>2.59×10⁻⁰⁶</td>
<td>2.59×10⁻⁰⁶</td>
</tr>
</tbody>
</table>
Curriculum vitae

Marco Carozzi was born in Merate (LC) on November 5, 1980. He achieved a first level graduation in Agricultural Science and Technology (mark 103/110), from the University of the Study of Milan, on 11th November 2005. On 18th April 2008 he achieved a secondary graduation in Agro-environmental Science (mark 110/110 cum laude), from the same University. Since the graduation he collaborated continuously from the Department of Plant Production of the University of Milan, working on atmospheric gas emissions, agronomic modelling, soil conservation practices, hydraulic soil properties and soil water run-off. From December 2008 is admitted in a PhD in Agricultural Ecology from the University of the Study of Milan, obtaining a research grant (2011). During 2011 he spent a visiting period at INRA-UMR EGC of Thiverval-Grignon, France, working with ammonia emissions.
The research described in this thesis was carried out at the Department of Plant Production of Milan (Di.Pro.Ve.).

This study forms part of the regional project ARMOSA, where soil water and nitrogen dynamics in surface water, groundwater and atmosphere are measured and analysed under different cropping systems at real farm’s monitoring sites. Such project is currently on-going and coordinated by the Department of Plant Production of the University of Milan, the Regional Agency for Agricultural and Forestry Development of Lombardy Region (ERSAF), the Research Unit for Cropping Systems in Dry Environments (CRA-SCA) of Bari, and the Institute for Mediterranean Agricultural and Forestry Systems - National Research Council of Ercolano (CNR-ISAFOM), Naples, and financed by the Lombardy Region since 2002.

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