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**Ammonia Emissions From Arable Lands
In Po Valley: Methodologies, Dynamics
And Quantification**

Ph. D. Thesis

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The aim of my Ph.D. work was to evaluate and to quantify the ammonia (NH_3) 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 NH_3 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 NH_3 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 NH_3 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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- Bernardoni E., **Carozzi M.**, Fumagalli M., Acutis M., 2011. “Tecnica di misura dei fenomeni di ruscellamento superficiale”. Atti XIV Convegno Nazionale di Agrometeorologia AIAM - L'agrometeorologia per l'azienda agraria. Bologna, 7-9 giugno 2011, pp 99-100
- Perego A., Acutis M., **Carozzi M.**, Bernardoni E., Brenna S., 2010. Model forecast of N dynamics in Po Plain under different cropping systems provided for EU Nitrates Directive derogation. Proceedings of the 12th Congress of the European Society for Agronomy, Montpellier (Italy), August 29th-September 3rd, p. 379-380.
- **Carozzi M.**, Ferrara R. M., Bernardoni E., Bassi L., Brenna S., Acutis M., 2010. “Emissioni Di Ammoniaca Da Suoli Agricoli: Approccio A Diffusione Passiva”. Atti del XIII Convegno Nazionale di Agrometeorologia - Agrometeorologia nella gestione integrata dei sistemi agro-forestali e dell'ambiente; Bari, 8-10 giugno 2010. Italian Journal of Agrometeorology. Patron Ed. Bologna, p. 93-94.
- Ferrara R.M., Loubet B., Betrolini T., **Carozzi M.**, Acutis M., Di Tommasi P., Magliulo V., Martinelli N., Rana G., 2010. “Ammonia volatilization after slurry spreading in North Italy: comparison between eddy covariance measurements and inverse dispersion modeling”. Proceedings of 5th Nitro Europe, Open Science Conference. Reactive Nitrogen and the European Greenhouse Gas Balance, 3-4 February 2010, Solothurn, Switzerland, p. 75-76.
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- Acutis, M., Bechini, L., Fumagalli, M., Perego, A., **Carozzi, M.**, Bernardoni, E., Brenna, S., Pastori, M., Mazzetto, F., Sali, G., Vidotto, F., 2008. “Gestione dell’azoto sostenibile a scala aziendale, Itinerari tecnici – Progetto GAZOSA” - Regione Lombardia, Quaderno della Ricerca n. 94, 52 pp.
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INTRODUCTION

1.1 Alteration of nitrogen cycle

Nitrogen (N) is the main abundant element of atmosphere, hydrosphere and biosphere, its molecular form (N_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 *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_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 *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 *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_3), nitrous oxide (N_2O), oxidised nitrogen (NO_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_2O 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 N 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, elevated 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,

2003). 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 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 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 NH_3 gaseous to NH_4^+ ion on the liquid phase of atmosphere, causing wet deposition on surface. Once into the atmosphere, NH_4^+ which is not deposited, is converted to 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 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 NH_4^+ than 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 (H_2SO_4), and reversibly with nitric (HNO_3) and hydrochloric (HCl) acids, to form ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), ammonium bisulphate (NH_4HSO_4), ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl) 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 ($\text{PM}_{2.5}$); 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 PM₁₀) (ISPRA, 2011).

1.3 Ammonia emissions in agriculture

Ammonia concentration depends by the ecosystem (ECETOC, 1994), ranging from less than 1 $\mu\text{g m}^{-3}$ in remote regions to over 250 $\mu\text{g m}^{-3}$ 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 NH₃ emission. In contrast, NH₃ accumulation occurs at night due to atmospheric inversions (Erisman *et al.*, 1988). Differences of NH₃ 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 NH₃ 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 NH₃, contributing to 50% of NH₃ 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 (G nermont and Cellier, 1997; Asman *et al.*, 2004) result the main NH₃ emitting activity. Other sources are crops which, depending on the above atmospheric NH₃ concentration, their phenology and N nutritional condition, can act either as sinks or sources of NH₃

(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 NH₃ fluxes at hourly scale over large areas. The disadvantages are the complexity and high cost of the equipment.

(ii) Concentration-based dispersion modelling

NH₃ 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 NH₃, 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 ($TAN = NH_3 + NH_4^+$). The dissociation and the successive loss of NH_3 from the solution is the complex physical and chemical process known as volatilization (Sommer *et al.*, 2003): it is governed mainly by NH_4^+ concentration, temperature and pH of the medium, evaporation rates, dew formation and turbulent transport of NH_3 .

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; Søggaard *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_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_3 emissions were reported to be very sensitive to slurry and soil pH conditions, where the losses increase by increasing of pH values (Génermont 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_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_3 varies widely in function of the employed method (Sommer and Hutchings, 2001; Søggaard *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; Sogaard *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

- Allen, A.G., Harrison, R.M., Wake, M.T., 1988. A mesoscale study of the behavior of atmospheric ammonia and ammonium. *Atmospheric Environment* 22, 1347–1354.
- Ammann, C., Bertok, I., Cofala, J., Gyarmas, F., Heyes, C., Klimont, Z., Schöpp, W., and Winiwarter, W., 2005. Baseline Scenarios for the Clean Air for Europe (CAFE) Programme. Final Report, IIASA, Laxenburg, Austria.
- Ammann, C.: On the Applicability of Relaxed Eddy Accumulation and Common Methods for Measuring Trace Gas Fluxes, *Zürcher Geographische Schriften*, 73, Geographisches Institut ETH, Zürich, Switzerland, 229 pp., 1999.
- Aneja, V.P., 1997. Summary of discussion and research recommendations. In: *Proceedings of the Workshop on Atmospheric Nitrogen Compounds: Emissions, Transport, Transformation, Deposition and Assessment*. Raleigh, NC, USA, North Carolina State University, pp. i-ix.
- Asman W. A. H., Sutton M. A., Schjørring J. K., 1998. Ammonia: emission, atmospheric transport and deposition, *New Phytologist*, 139, 27–48.
- Asman, W. A. H. 1992. Ammonia emission in Europe: Update emission and emission variations. Report 228471008. National Institute of Public health and Environmental protection, Bilthoven, The Netherlands.
- Asman, W.A.H., Hutchings, N.J., Sommer, S.G., Andersen, J., Münier, B., Gènermont, S. et al. 2004. Emissions of ammonia. In: *Emissions of Air Pollutants* (eds R. Friedrich & S. Reis), pp. 111–143. Springer, Berlin.
- Bouwman L, Goldewijk KK, Van Der Hoek KW, Beusen AH, Van Vuuren DP, Willems J, Rufino MC, Stehfest E., 2011. Livestock and Global Change Special Feature: Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900-2050 period. *Proceedings of the National Academy of Sciences of the United States of America* U S A. 2011 May 16,
- Bouwman, A.F., Lee, D.S., Asman, W.A.H., Dentener, F.J., Van Der Hoek, K.W., Olivier, J.G.J., 1997. A global high-resolution emission inventory for ammonia. *Global Biogeochem. Cycl.* 11, 561–587.
- Brodeur, J.J., Warland, J.S., Staebler, R.M. & Wagner-Riddle, C. 2009. Technical note: laboratory evaluation of a tunable diode laser system for eddy covariance measurements of ammonia flux. *Agricultural & Forest Meteorology*, 149, 385–391.

-
- Burton, C.H., Martinez, J. (Eds.), 1996. Animal manure and Environment. Eau-Agriculture-Territoires. Special Issue 1996.
- Bussink, D.W., J.F.M. Huijsmans & J.J.M.H. Ketelaars, 1994. Ammonia volatilization from nitric-acid-treated cattle slurry surface applied to grassland. *Netherlands Journal of Agricultural Science* 42: 293-309.
- Clarisse, L., C. Clerbaux, F. Dentener, D. Hurtmans and P.F. Coheur (2009), Global ammonia distribution derived from infrared satellite observations, *Nat. Geosci.*, 2(7), 479–483.
- CRPA, 2006. Progetto MeditAIRaneo: settore Agricoltura. Relazione finale. Technical report on the framework of the MeditAIRaneo project for the Agriculture sector, Reggio Emilia - Italia
- Crutzen, P.J., 1983. Atmospheric interactions – homogeneous gas reactions of C, N and S containing compounds. In: Bolin, B., Cook, R.B. (Eds.), *SCOPE 21: The Major Biogeochemical Cycles and their Interactions*. J. Wiley and Sons, Chichester, pp. 67–111.
- Denmead, O.T., Raupach, M.R., 1993. Methods for measuring atmospheric gas transport in agricultural and forest systems. In: *Agricultural Ecosystem Effect on Trace Gases and Global Climatic Change*. ASA Special Publication no. 55, pp. 19-43.
- Dlugi, R., Kins, L., Seiler, T., Seidl, W., Seifert, P., Kasper, A., Sievering, H., Zelger, M., Kohler, E. and Reusswig, K., 1997. The chemical behavior and deposition of ammonium nitrate, nitric acid and ammonia. In: P.D.S. Slanina (Editor), *Biosphere-atmosphere exchange of pollutants and trace substances: experimental and theoretical studies of biogenic emissions and of pollutant deposition*. Springer-Verlag Berlin, pp. 426-432.
- ECETOC, 1994. Ammonia emissions to air in Western Europe. In: ECETOC Technical Report No. 62, Belgium.
- EEA, 2011. NEC Directive status report 2010. Technical report No 3/2011. <http://www.eea.europa.eu/publications/nec-directive-status-report-2010>
- Erisman JW, de Vries W., 2000. Nitrogen deposition and effects in European forests. *Environmental Reviews* 8: 65–93.
- Erisman, J.W., Otjes, R., Hensen, A., Jongejan, P., van den Bulk, P., Khlystov, A., Möls, H., and Slanina, S., 2001. Instrument development and application in studies and monitoring of ambient ammonia, *Atmos. Environ.*, 35, 1913–1922.
- Erisman, J.W., Vermetten, A., Asman, W.A.H., Waijers-Yjpelaan, A., Slanina, J., 1988. Vertical distribution of gases and aerosols: the behavior of ammonia and

- related components in the lower atmosphere. *Atmospheric Environment* 22, 1153–1160.
- FAO, 1992. *FAO production yearbook 1991*, vol 45. FAO, Rome.
- Ferm, M., 1998. Atmospheric ammonia and ammonium transport in Europe and critical loads: a review. *Nutrient Cycling in Agroecosystems* 51, 5–17.
- Flechar, C. R. and Fowler, D., 1998. Atmospheric ammonia at a moorland site. II: Long term surface/atmosphere micrometeorological flux measurements, *Q. J. Roy. Meteor. Soc.*, 124, 759–791.
- Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P. and Sharpe, R.R., 2004. Deducing ground-to-air emissions from observed trace gas concentrations: A field trial. *Journal of Applied Meteorology*, 43(3): 487-502.
- Fowler D, Skiba U, Hargreaves KJ. 1997. Emissions of nitrous oxide from grasslands. Pages 147–164 in Jarvis SC, Pain BF, eds. *Gaseous Nitrogen Emissions from Grasslands*. North Wyke (United Kingdom): Institute of Grassland and Environmental Research.
- Galloway JN, Townsend AR, Erismann JW, Bekunda M, Cai ZC, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA. 2008. Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* 320: 889–892.
- Galloway, J.N., Aber, J.D., Erismann, J.W., Seitzinger, S.P., Howarth, R.W., Cowling E.B., Cosby B.J., 2003. The Nitrogen Cascade. *BioScience*, 53 (4): 341-356.
- G nermont, S., and P. Cellier, 1997: A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. *Agricultural and Forest Meteorology*, 88:145-167.
- Godwin, D.C., Singh, U., 1998. Nitrogen balance and crop response to nitrogen in upland and lowland cropping systems. *Systems approaches for sustainable agricultural development. Understanding options for agricultural production (volume 7)*. Tsuji, G.Y., Hoogenboom, G., Thornton P.K. editors. Kluwer Academic Publisher, Great Britain, 55-76.
- Harper, L.A., 2005. Ammonia: measurement issues. In J.L. Hatfield, J.M. Baker and M.K. Viney (Eds): *Micrometeorology in Agricultural systems*. Agronomy Monograph, 47. ASA, CSSA and SSSA, Madison, Wisconsin, USA, 345-379.
- Harper, L.A., Sharpe, R.R., 1998. Atmospheric ammonia: issues on transport and nitrogen isotope measurement. *Atmos. Environ.* 32, 273–277.

-
- Hill, P. W., J. A. Raven, B. Loubet, D. Fowler, and M. A. Sutton., 2001: Comparison of gas exchange and bioassay determinations of the ammonia compensation point in *Luzula sylvatica* (Huds.) Gaud. *Plant Physiology*, 125:476-487.
- Huijsmans, J.F.M., Hol, J.M.G., Hendriks, M.M.W.B., 2001. Effect of application technique, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to grassland. *Netherlands Journal of Agricultural Science* 49, 323–342.
- Huijsmans, J.F.M., Hol, J.M.G., Vermeulen, G.D., 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. *Atmos. Environ.* 37, 3669–3680.
- Hutchinson, G.L., Livingston, G. P., 1993. Use of chamber systems to measure trace gas fluxes. In L.A. Harper, A.R.Mosier, J.M. Duxbury and D.E. Roston (Eds): *Agricultural ecosystem effects on trace gases and global climate change*. American Society of Agronomy Spec. Publ. 55, Madison, Wisconsin, 63 – 78.
- Irwin, J.G., Williams, M.L., 1988. Acid rain: chemistry and transport. *Environmental Pollution* 50, 29–59.
- Ismail, K.M., Wheaton, F.W., Douglass, L.W., Potts, W., 1991. Modelling ammonia volatilization from loamy sand soil treated with liquid urea. *Transactions of the ASAE* 34, 756–763.
- ISPRA, 2011. Italian emission inventory 1990-2009. Information inventory report 2011. *Rapporti* 138/2011. Available at: <http://www.eea.europa.eu/publications/european-union-emission-inventory-report>.
- Jarvis, S.C. and B.F. Pain. 1990. Ammonia volatilisation from agricultural land. *The fertiliser society proceedings*. No. 298. pp.1-35. The Fertiliser Soc., London.
- Kaimal, J. C., Finnigan J. J., 1994: *Atmospheric Boundary Layer Flows: Their Structure and Measurement*. Oxford University Press, 289 pp.
- Krupa, S.V. 2003. Effects of atmospheric ammonia (NH₃) on terrestrial vegetation: a review. *Environmental Pollution*, 124, 179–221.
- Lockyer, D.R. 1984. “A system for the measurement in the field of losses of ammonia through volatilization”. *J. Sci. Food Agric.* 35:837-848.

- Loubet B., Générmont S., Ferrara R., Bedos C., Decuq C., Personne E., Fanucci O., Durand B., Rana G., Cellier P., 2010 - An inverse model to estimate ammonia emissions from fields. *European Journal of Soil Science*, 61, 5, 793–805.
- Loubet B., Générmont S., Personne E., Massad R.S., 2011. Can we estimate ammonia emissions by inverse modelling with time averaged concentrations? *Proceedings of Nitrogen & Global Change Key findings – future challenges*, Edinburgh April 11 – 15, 2011 [Unpublished].
- Loubet, B., Asman, W.A.H., Theobald, M.R., Hertel, O., Tang, Y.S., Robin, P., Hassouna, M., Dammgen, U., Genermont, S., Cellier, P. and Sutton, M.A., 2009b. Ammonia Deposition Near Hot Spots: Processes, Models and Monitoring Methods. *Atmospheric Ammonia*. Springer Netherland, 205-267 pp.
- Loubet, B., Milford, C., Sutton, M.A. & Cellier, P. 2001. Investigation of the interaction between sources and sinks of atmospheric ammonia in an upland landscape using a simplified dispersion-exchange model. *Journal of Geophysical Research*, 106, 24183–24195.
- Meyers, T.P., Baldocchi, D.D., 2005. Current micrometeorological flux methodologies with applications in agriculture. In J.L. Hatfield, J.M. Baker and M.K. Viney (Eds): *Micrometeorology in Agricultural systems*. Agronomy Monograph, 47. ASA, CSSA and SSSA, Madison, Wisconsin, Usa, 381-396.
- Milford, C., Theobald, M. R., Nemitz, E., Hargreaves, K. J., Horvath, L., Raso, J., Dämmgen, U., Neftel, A., Jones, S. K., Hensen, A., Loubet, B., Cellier, P., and Sutton, M. A., 2009. Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived from an inter-comparison of gradient measurements, *Biogeosciences*, 6, 819–834.
- Misselbrook, T.H., F.A. Nicholson, B.J. Chambers, and R.A. Johnson. 2005. Measuring ammonia emissions from land applied manure: An intercomparison of commonly used samplers and techniques. *Environ. Pollut.* 135:389–397.
- Misselbrook, T.H., Van Der Weerden, T.J., Pain, B.F., Jarvis, S.C., Chambers, B.J., 2000. Ammonia emission factors for UK agriculture. *Atmos. Environ.* 34, 871-880.
- Moal, J.F., Martinez, J., Guiziou, F., Coste, C.M., 1995. Ammonia volatilization following surface-applied pig and cattle slurry in France. *J. Agric. Sci.* 125, 245-252.

- Möller, D., Schieferdecker, H., 1985. A relationship between agricultural NH₃ emissions and the atmospheric SO₂ content over industrial areas. *Atmospheric Environment* 19, 695–700.
- Mosier, A.R. Chamber and isotopic techniques. 1989. In *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*. Dahlem Konferenzen. Andreae, M.O. and Schimel, D.S. (eds.). Chichester: John Wiley & Sons Ltd. pp. 175-187.
- Nemitz, E. and Sutton, M.A., 2004. Gas-particle interactions above a Dutch heathland: III. Modelling the influence of the NH₃-HNO₃-NH₄NO₃ equilibrium on size-segregated particle fluxes. *Atmospheric Chemistry and Physics*, 4: 1025- 1045.
- Olivier, J.G.J., Bouwman, A.F., Van der Maas, C.W.M., Berdowski, J.J.M., Veldt, C., Bloos, J.P.J., Visschedijk, A.J.H., Zandveld, P.Y.J., Haverlag, J.L., 1996. Description of EDGAR Version 2.0: A set of global emission inventories of greenhouse gases and ozone depleting substances for all anthropogenic and most natural sources on a per country basis and on 1° x 1° grid. RIVM Techn. Report 771060 002; TNO-MEP Report R96/119. National Institute of Public Health and the Environment/Netherlands Organization for Applied Scientific Research, Bilthoven.
- Pain, B. F., van der Weerden, T. J., Chambers, B. J., Phillips, V. R., and Jarvis, S. C., 1998: A new inventory for ammonia emissions from UK agriculture, *Atmos. Environ.*, 32, 309–313.
- Petersen, S.O., Andersen, M.N., 1996. Influence of soil water potential and slurry type on denitrification activity. *Soil Biol. Biochem.* 28, 977-980.
- Rotz, C. A. 2004. Management to reduce nitrogen losses in animal production. *J. Anim. Sci.* 82 (E. Suppl.): E119-E137.
- Schimel, D., D. Alves, I. Enting, M. Heimann, F. Joos, D. Raynaud, T. Wigley, et al., 1996: Chapter 2, Radiative Forcing of Climate Change. In: *Climate Change 1995: The Science of Climate Change*. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change [Houghton, J.T., L.G. Meira Filho, B.A. Callander, N. Harris, A. Kattenberg, and K. Maskell (eds.)]. Cambridge University Press, pp 65-131.
- Schjoerring J. K., Sommer S. G. & Ferm M. 1992. A simple passive sampler for measuring ammonia emission in the field. *Water, Air and Soil Pollution* 62, 13-24.

- Sintermann J., Neftel A., Ammann C., Häni C., Hensen A., Loubet B. and Flechard C. R., 2011. Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories? *Biogeosciences Discuss.*, 8, 10069-10118.
- Skjøth C. A., Geels C., Berge H., Gyldenkerne S., Fagerli H., Ellermann T., Frohn L.M., Christensen J., Hansen K. M., Hansen K, Hertel O., 2011. Spatial and temporal variations in ammonia emissions – a freely accessible model code for Europe. *Atmos. Chem. Phys.*, 11, 5221–5236.
- Smith, R. I., Fowler, D., Sutton, M. A., Flechard, C., and Coyle, M., 2000. Regional estimation of pollutant gas deposition in the UK: model description, sensitivity analyses and outputs, *Atmos. Environ.*, 34, 3757–3777.
- Søgaard, H.T., Sommer S.G., Hutchings N.J., Huijsmans J.F.M., Bussink D.W., Nicholson F., 2002: Ammonia volatilization from field-applied animal slurry - the ALFAM model, *Atmospheric Environment*, 36, 3309–3319.
- Sommer, S. G. and Hutchings, N. J., 2001. Ammonia emission from field applied manure and its reduction – invited paper, *Eur. J. Agron.*, 15, 1–15.
- Sommer, S.G., Genemont, S., Cellier, P., Hutchings, N.J., Olesen, J.E. and Morvan, T., 2003. Processes controlling ammonia emission from livestock slurry in the field. *European Journal of Agronomy*, 19(4): 465-486.
- Sommer, S.G., Hutchings, N.J., Carton, O.T., 2001. Ammonia losses from field applied animal manure. Report No. 60, Plant Production, Danish Institute of Agricultural Sciences, Horsens, Denmark.
- Sommer, S.G., Jacobsen, O.H., 1999. Infiltration of slurry liquid and volatilization of ammonia from surface applied pig slurry as affected by soil water content. *J. Agric. Sci.* 132, 297-303.
- Stull, R.B., 1988. *An Introduction to Boundary Layer Meteorology*. Klumer Academic Publishers, Boston, Massachusetts, 666 pp.
- Sutton, M. A, Oenema, O., Erisman, J. W., Leip, A., van Grinsven, H., & Winiwarter, W., 2011. Too much of a good thing. *Nature*, 472(7342), 159-61.
- Sutton, M. A., Dragosits, U., Tang, Y. S., and Fowler, D., 2000. Ammonia emissions from non-agricultural sources in the UK, *Atmos. Environ.*, 34, 855–869.
- Sutton, M. A., E. Nemitz, J. W. Erisman, C. Beier, K. B. Bahl, P. Cellier, W. de Vries, F. Cotrufo, U. Skiba, C. et al., 2007. Challenges in quantifying biosphere-atmosphere exchange of nitrogen species. *Environmental Pollution*, 150:125-139.

-
- Sutton, M. A., J. K. Schjorring, and G. P. Wyers, 1995: Plant-atmosphere exchange of ammonia. *Philosophical Transactions of the Royal Society London series A*, 351:261-278.
- Sutton, M., 2006. Scope and Overview of the UNECE Expert Workshop on Ammonia, Edinburgh, C. E. H.. *Clean Air*, (December), 1-8.
- Sutton, M.A., Fowler, D., Moncrieff, J.B., Storeton-West, R.L., 1993. The exchange of atmospheric ammonia with vegetated surfaces. II: fertilised vegetation. *Q. J. R. Meteorol. Soc.*, 119: 1047-1070.
- Sutton, M.A., Place, C.J., Eager, M., Fowler, D., Smith, R.I., 1995. Assessment of the magnitude of ammonia emissions in the United Kingdom. *Atmos. Environ.* 29, 1393–1411.
- Valli, L., Fabbri, C., and Bonazzi, G., 2001 A national inventory of ammonia and greenhouse gas emissions from agriculture in Italy, in: *Proceedings of the 9th Int. Conference on the FAO ESCORENA Network on recycling of agricultural, municipal and industrial residues in agriculture*, 153–159, Gargano, Italy.
- van Breemen, N., Burrough, P.A., Velthorst, E.J., Van Dobben, H.F., de Wilt, T., Ridder, T.B., Reijnders, H.F.R., 1982. Soil acidification from ammonium sulfate in forest canopy throughfall. *Nature*, 299, 548-550.
- van der Eerden L., de Vries W. and van Dobben H. 1998: Effects of ammonia deposition on forests in the Netherlands. *Atmospheric Environment* 32(3) Ammonia Special Issue, 525-532.
- Van Der Molen, J., D.W. Bussink, N. Vertregt, H.G. Van Faassen & D.J. Den Boer, 1989. Ammonia volatilization from arable and grassland soils. In: J.A. Hansen and K. Henriksen (Eds.), *Nitrogen in organic wastes applied on soils*. Academic Press, Londen, pp. 185-201.
- Van der Molen, J., Van Faassen, H.G., Leclerc, M.Y., Vriesema, R., Chardon, W.J., 1990. Ammonia volatilization from arable land after application of cattle slurry. I. Field estimates. *Netherlands Journal of Agricultural Science* 38, 145–158.
- Webb, J., Pain, B., Bittman, S., and Morgan, J., 2010. The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response-A review, *Agr. Ecosyst. Environ.*, 137, 39–46.
- Whitehead, J. D., Twigg, M., Famulari, D., Nemitz, E., Sutton, M. A., Gallagher, M. W., and Fowler, D., 2008. Evaluation of laser absorption spectroscopic

techniques for eddy covariance flux measurements of ammonia, *Environ. Sci. Technol.*, 42, 2041–2046.

WHO, 2005. World Health Organization. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide Global update 2005.

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 (NH₃) 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 NH₃ 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 (NH_3) 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 NH_3 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 NH_3 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 NH_3 dynamics (Jarvis and Pain, 1990; Sommer *et al.*, 1991, Erisman *et al.*, 2008). From the agricultural perspective the estimation of the NH_3 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 NH_3 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 NH₃ 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 NH₃ 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 NH₃ is its simultaneous presence in the gaseous, the particulate (e.g., ammonium nitrate) and the liquid phases (NH₄⁺ 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, NH₃ 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 NH₃ are spatially highly heterogeneous (Sutton *et al.*, 1998; Dragosits *et al.* 2002) and further considering its reactive nature and the dependence of NH₃

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 NH₃ 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 Générumont 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 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. 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-NH₃ 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 m³ m⁻³ and 6.4, respectively. Dairy slurry was applied on 7th April, at a rate of 75 m³ ha⁻¹, corresponding to a TAN of 109 kg N-NH₃ 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.

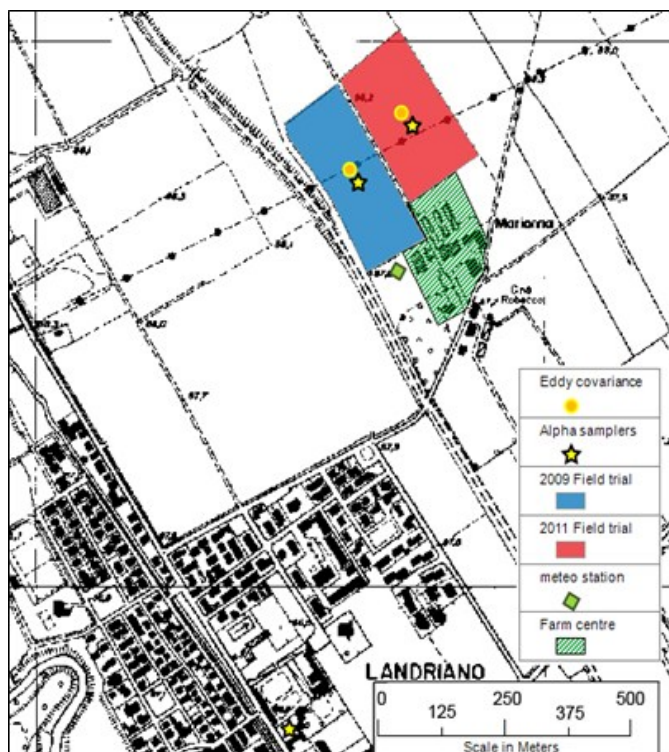


Figure 2.1. Site map of experimental fields during the trials in Landriano in 2009 (SI-09) and 2011 (SI-11).

Representative slurry samples (2 dm^3) 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 (CaCO_3) samples were collected (Table 2.1). Furthermore, soil was sampled daily at 0-10 cm and 10-20 cm depths to

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 , ($^{\circ}\text{C}$), 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).

	Dry matter g kg^{-1}	pH	TAN $\text{kg N-NH}_4^+ \text{ ha}^{-1}$	TKN kg N ha^{-1}
SI-09	44	8.0	95	188
SI-11	55	7.8	109	223

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 (χ), 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

$$F\chi = \overline{w\chi} = \bar{w} \cdot \bar{\chi} + \overline{w'\chi'} \quad (\text{eq. 2.1})$$

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 NH₃ concentration measurements: the QC-TILDAS

A QC-TILDAS (Aerodyne Research Inc., ARI, Billerica, Massachusetts, USA) was used to measure NH₃ 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 NH₃ instrument operates near 10.31 μm (967 cm^{-1}) where NH₃ 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

(High-resolution TRANsmission molecular absorption) database (Rothman *et al.*, 2003).

NH₃ 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 NH₃ fluxes*

NH₃ 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 χ_{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 Lagrangian 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:

$$D = \frac{1}{N_{\text{source}}} \sum \left| \frac{2}{w_0} \right| \quad (\text{eq. 2.3})$$

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

$$S = (\chi - \chi_{bgd}) \times D^{-1} \quad (\text{eq 2.4})$$

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 χ and χ_{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 ascendant 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:

$$D(x - x_s, z) = \frac{A}{(x - x_s)^\beta} \exp \left[-\frac{(z - d - z_0)^\alpha + (z_s - d - z_0)^\alpha}{B \cdot (x - x_s)} \right] \quad (\text{eq 2.5})$$

Where Δx is the grid size, A , B , α , and β are defined as:

$$A = \frac{\alpha}{a^v \cdot (b\alpha^2)^\beta \cdot \Gamma(\beta)} \quad (\text{eq. 2.6})$$

$$\alpha = 2 + p - n \quad (\text{eq 2.7})$$

$$v = (1 - n)/\alpha \quad (\text{eq 2.8})$$

$$\beta = (1 + p)/\alpha \quad (\text{eq 2.9})$$

$$B = b/(a \alpha^2) \quad (\text{eq 2.10})$$

Where Γ 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 :

$$U(z) = a(z - d - z_0)^p \quad (\text{eq. 2.11})$$

$$K(z) = b(z - d - z_0)^n \quad (\text{eq. 2.12})$$

In this approach the source S is modelled as:

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

Where $\chi(d + z_0)$ is the concentration at the top of the canopy, χ_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 $1 \mu\text{g m}^{-3}$ (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 $5 \mu\text{m}$ 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).

2.2.2.2.2 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.

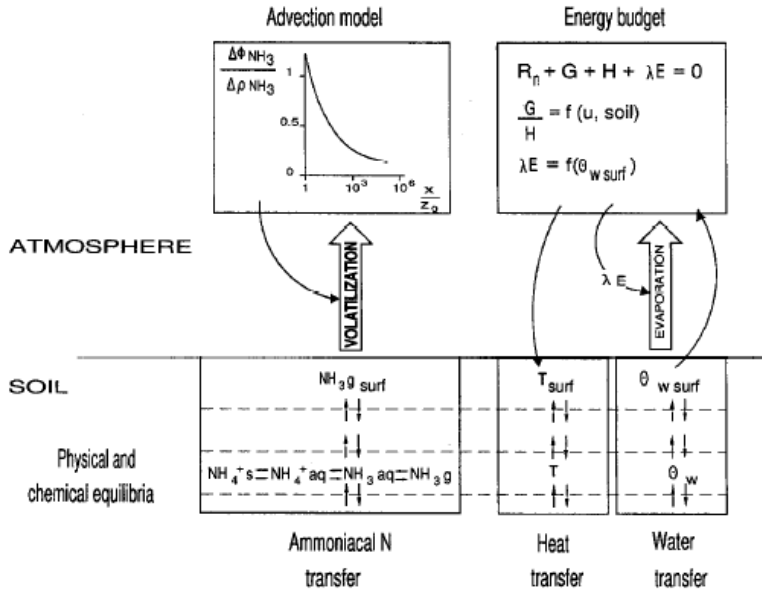
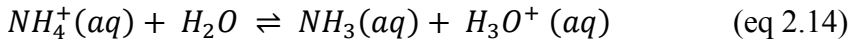


Figure 2.2. Diagram of the deterministic model Volt'Air; from Gènermont and Cellier (1997).

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 chemical 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 organication 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):



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):



(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:

$$R_n - G = H + \lambda E \quad (\text{eq 2.17})$$

where R_n is the net radiation of the surface, G the soil heat flux, H the sensible heat flux and λE 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

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

(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:

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

(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:

$$CRM = \frac{\sum_{i=1}^n O_i - \sum_{i=1}^n P_i}{\sum_{i=1}^n O_i}$$

(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.

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

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.

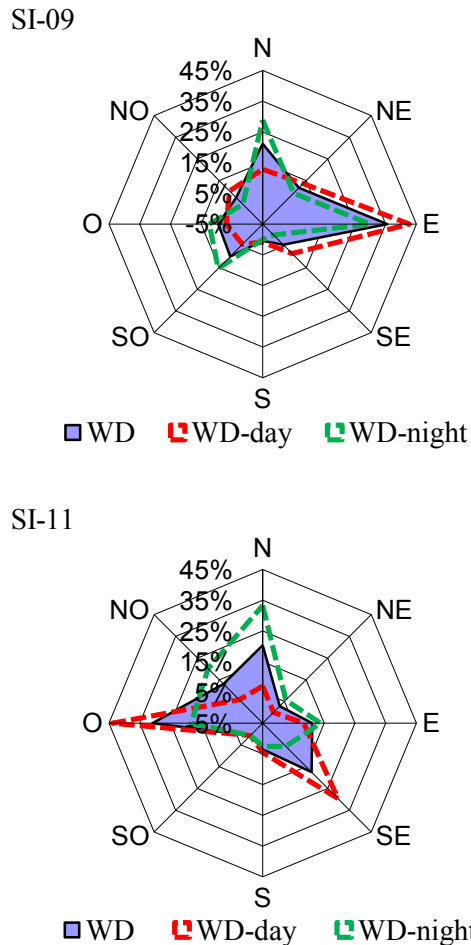


Figure 2.3. Main and day-night wind direction (WD) during the trials in Landriano in 2009 (SI-09) and 2011 (SI-11).

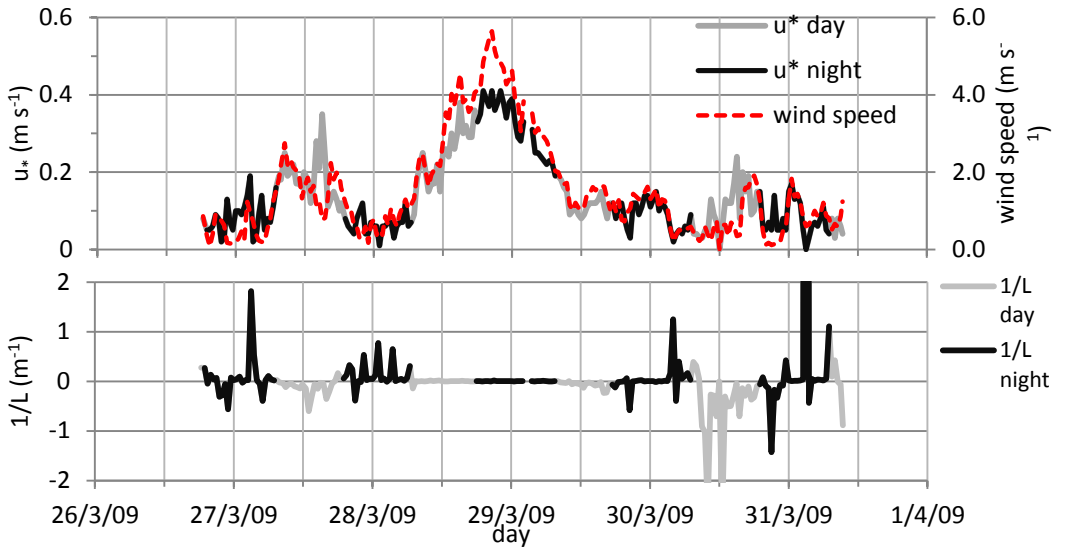


Figure 2.4. Trail in Landriano 2009 (SI-09): friction velocity (u_*) and wind speed (red dotted line) on upper panel; inverse Monin-Obukhov length ($1/L$) during day (gray line) and nighttime (black line) on lower panel.

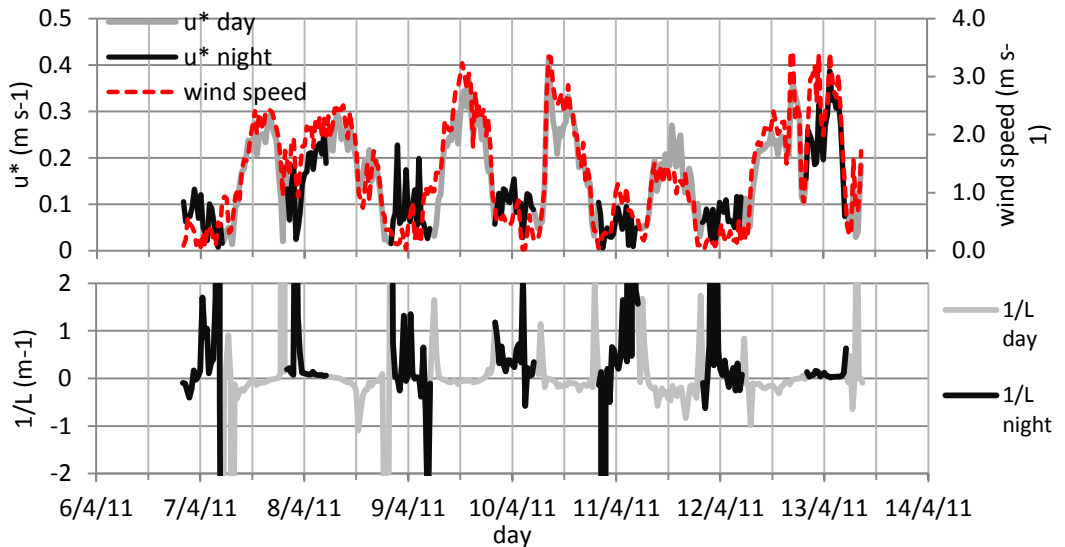


Figure 2.5. Trail in Landriano 2011 (SI-11): friction velocity (u_*) and wind speed (red dotted line) on upper panel; inverse Monin-Obukhov length ($1/L$) during day (gray line) and nighttime (black line) on lower panel.

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.

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

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 $\mu\text{g m}^{-3}$ in 2009 and 67.6 and 39 $\mu\text{g m}^{-3}$ 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.

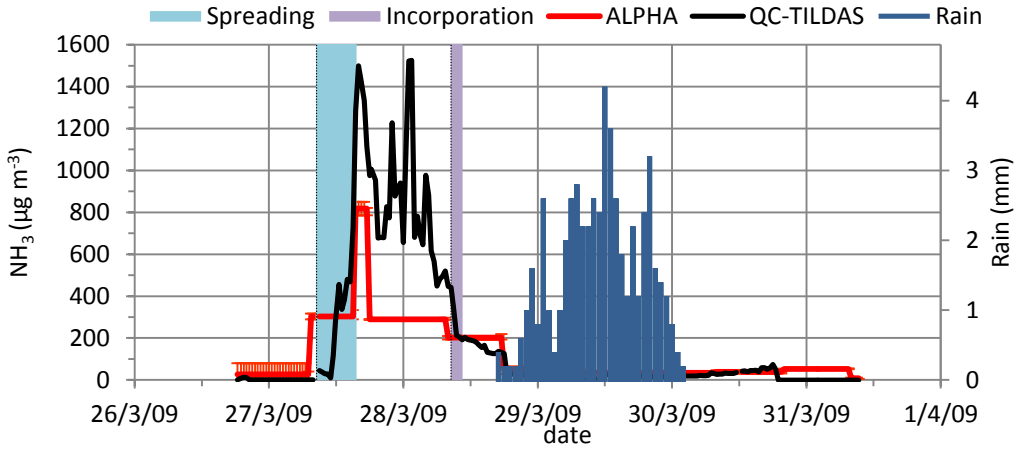


Figure 2.6. NH_3 concentration measured during the trial in Landriano in 2009 (SI-09) by the QC-TILDAS (black line), by the Alpha samplers (red lines) and rainfall. For the Alpha samplers the standard deviations are reported too.

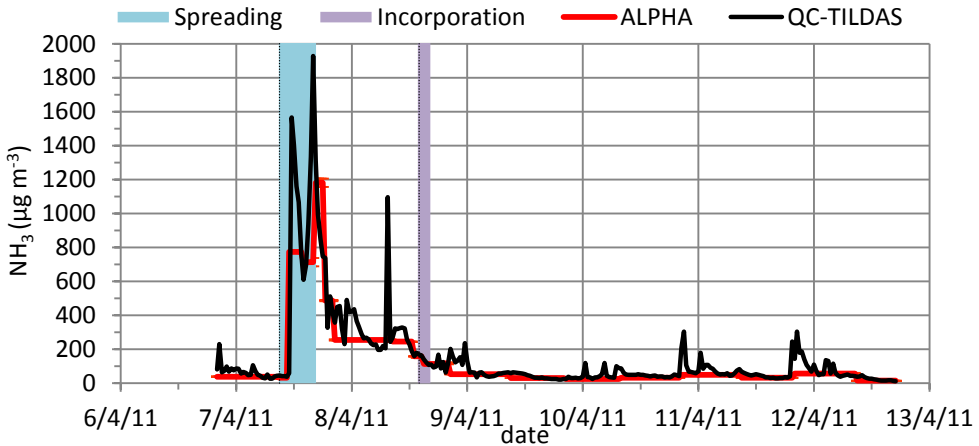


Figure 2.7. NH_3 concentration measured during the trial in Landriano in 2011 (SI-11) by QC-TILDAS (black line), by the Alpha samplers (red lines) and rainfall. For the Alpha samplers the standard deviations are reported too.

As indicated by the QC-TILDAS, the peak value of ammonia concentration in SI-09 ($1,525 \mu\text{g m}^{-3}$) was reached 1.5 hours after the slurry spreading corresponding to a mean value of $1,330 \mu\text{g m}^{-3}$ on the accumulation time of the Alpha samplers exposed in the same period. The same peak as measured by Alpha was, instead, $817 \mu\text{g m}^{-3}$ (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 rises 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 $1566 \mu\text{g m}^{-3}$ was reached 2.5 hours after the beginning, followed by a largest second peak of $1,928 \mu\text{g m}^{-3}$ reached just before the end of the application. The Alpha samplers detected the same peaks, the first of $774 \mu\text{g m}^{-3}$ and the second of $1,181 \mu\text{g m}^{-3}$, corresponding to the time-averaged values of $1,003 \mu\text{g m}^{-3}$ and $1,102 \mu\text{g m}^{-3}$ 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.

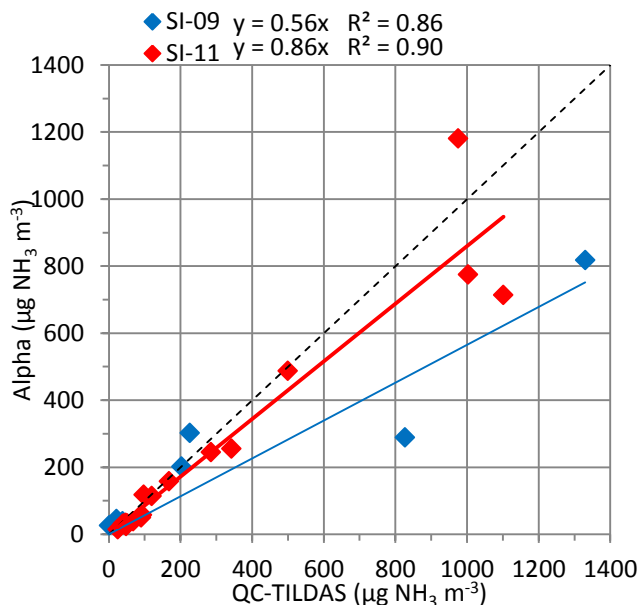


Figure 2.8. Scatter plot between the concentration measured by the Alpha and the QC-TILDAS, during the trails in Landriano 2009 (SI-09) and 2011 (SI-11). Dotted line represents 1:1 line.

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 27th March for SI-09 and on 7th April for SI-11. The maximum value of flux reached by each approach is reported, as $\text{kg N ha}^{-1} \text{ h}^{-1}$, 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 ($141,640 \text{ ng m}^{-2} \text{ s}^{-1}$). 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, $113,876 \text{ ng m}^{-2} \text{ s}^{-1}$ 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.

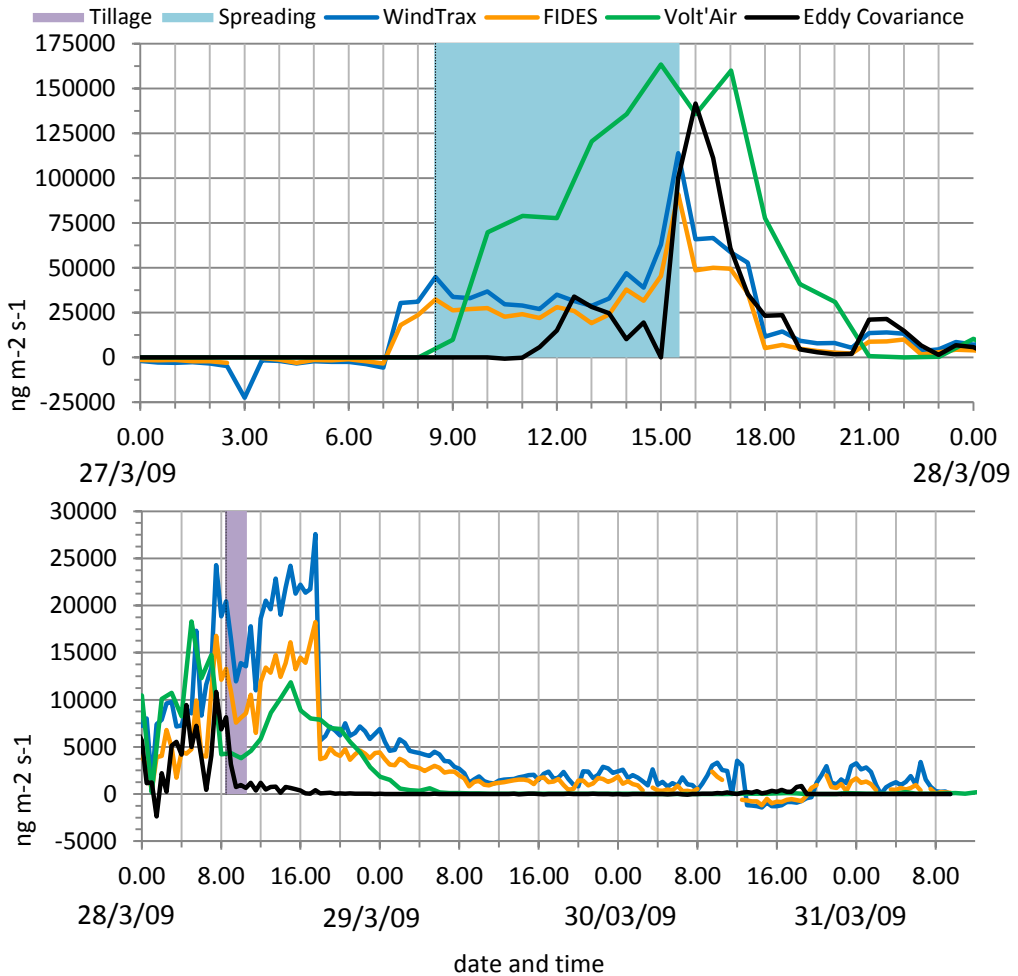


Figure 2.9. SI-09: NH₃ fluxes measured by eddy covariance technique and simulated by two inverse dispersion models (WindTrax and FIDES) and a deterministic model, Volt'Air. The vertical colour bars represent the duration of slurry spreading and incorporation. Upper panel is referred to the spreading 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 ($163,350 \text{ ng m}^{-2} \text{ s}^{-1}$), 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).

	Flux		Emission Factors	
	cumulated kg N ha^{-1}	maximum $\text{kg NH}_3 \text{ ha}^{-1} \text{ h}^{-1}$	%TKN	%TAN
WindTrax	26	0.27 ± 0.04	14 ± 3.1	28 ± 6.1
FIDES	18	0.21 ± 0.03	9.8 ± 1.8	19 ± 3.6
Volt'Air	48	0.59 ± 0.07	20.8	41
Eddy Covariance	12	0.34 ± 0.04	6.4	12.7

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 ($169,482 \text{ ng m}^{-2} \text{ s}^{-1}$, 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.

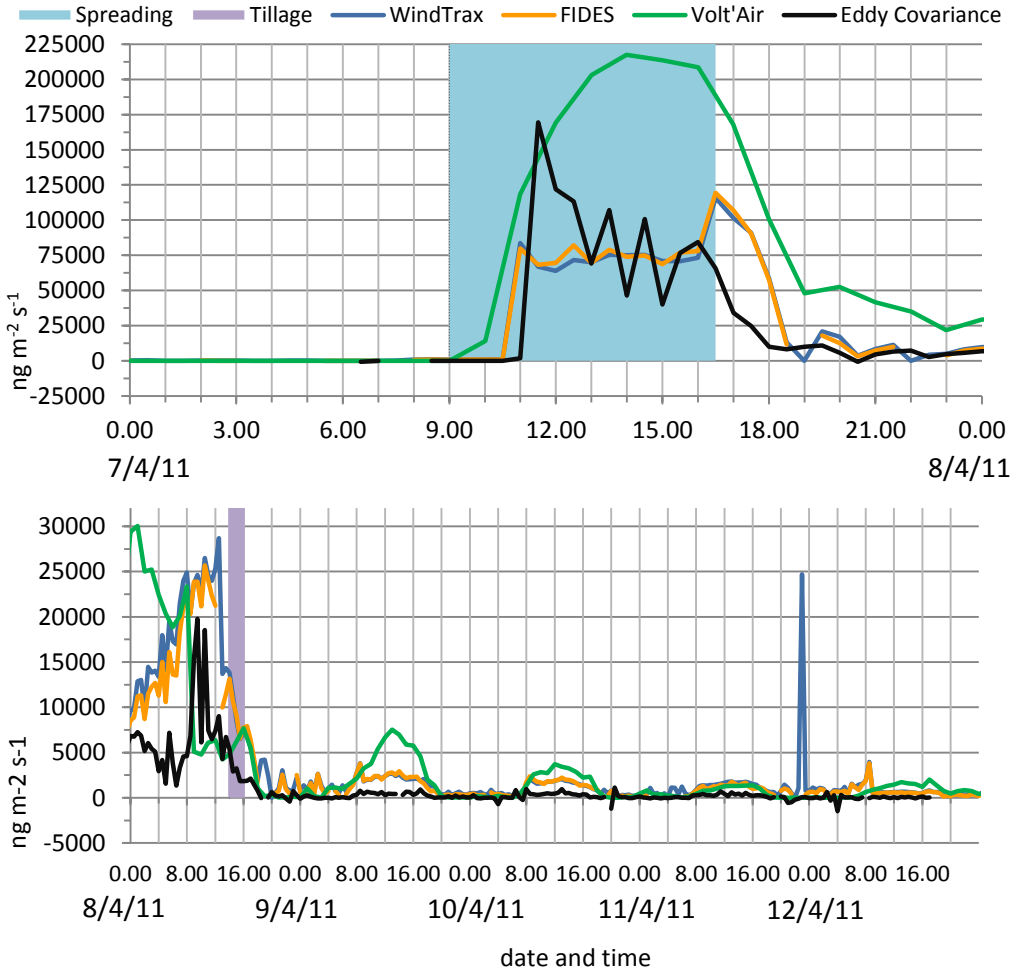


Figure 2.10. SI-11: NH_3 fluxes measured by the eddy covariance technique and simulated by two inverse dispersion models (WindTrax and FIDES) and a deterministic model, Volt'Air. The vertical colour bars represent the duration of slurry spreading and incorporation. Upper panel is referred to the spreading day, lower panel represent the days after fertilisation.

The models described a similar trend. In particular, the inverse models described the peak ($119,483 \text{ ng m}^{-2} \text{ s}^{-1}$ for FIDES and $115,830 \text{ ng m}^{-2} \text{ s}^{-1}$ 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 $217,510 \text{ ng m}^{-2} \text{ s}^{-1}$ 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).

	Flux		Emission Factors	
	cumulated kg N ha^{-1}	maximum $\text{kg NH}_3 \text{ ha}^{-1} \text{ h}^{-1}$	%TKN	%TAN
WindTrax	31	0.32 ± 0.05	14 ± 0.2	28 ± 0.4
FIDES	29	0.34 ± 0.05	13 ± 0.1	26 ± 0.1
Volt'Air	72	0.78 ± 0.14	26.6	54.4
Eddy Covariance	20	0.43 ± 0.05	9.1	18.6

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 $\pm 14\%$ and $\pm 30\%$ 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.

	RRMSE	E	CRM	Slope	Intercept	R^2	Mean measured (EC)	Mean simulated
SI-09								
Fides	189	0.78	0.1	0.9	0.0	0.79	3.7	5.8
Windtrax	307	0.45	-1.0	0.7	4.9	0.55	3.7	8.1
Volt'air	694	-1.91	-2.3	1.6	6.0	0.55	3.7	11.8
SI-11								
Fides	270	0.59	-0.7	0.8	2.9	0.64	4.8	6.9
Windtrax	280	0.55	-0.7	0.7	3.4	0.60	4.8	6.8
Volt'air	618	-1.40	-3.0	2-0	3.9	0.78	4.8	12.7

Also the Volt'Air model compared to the other approaches showed good R^2 , 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

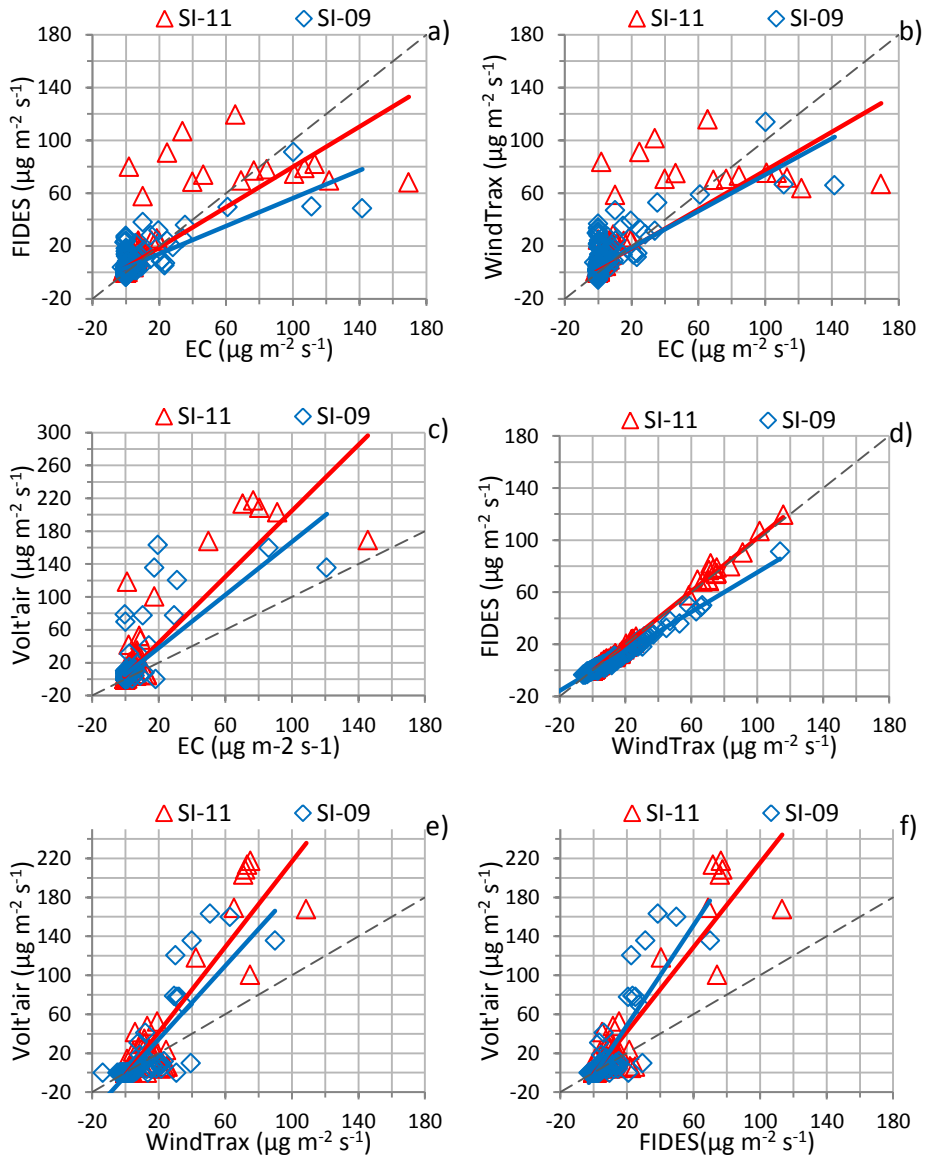


Figure 2.11. Scatter plot between eddy covariance (EC) and the models reported in the text: (a) FIDES, (b) WindTrax and (c) Volt'Air, during the trials in Landriano 2009 (SI-09) and 2011 (SI-11). (d) is the scatter plot between WindTrax and FIDES; (e) is the scatter plot between Volt'Air and Windtrax; (f) is the scatter plot between Volt'Air and FIDES. Dotted line represents 1:1 line.

f) indicated that Volt'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 NH_3 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 loss 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

- Ammann, C., 1999. On the Applicability of Relaxed Eddy Accumulation and Common Methods for Measuring Trace Gas Fluxes, *Zürcher Geographische Schriften*, 73, Geographisches Institut ETH, Zürich, Switzerland, 229 pp.
- Ammann, C., Brunner, A., Spirig, C. and Neftel, A., 2006. Technical note: Water vapour concentration and flux measurements with PTR-MS. *Atmospheric Chemistry and Physics*, 6: 4643-4651.
- Asman W. A. H., Sutton M. A., Schjørring J. K., 1998. Ammonia: emission, atmospheric transport and deposition, *New Phytol.*, 139, 27–48.
- Aubinet, M., Grelle, A., Ibrom, A., Rannik, Ü., Moncrieff, J., Foken, T., Kowalski, et al., 2000. Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology, *Adv. Ecol. Res.*, 30, 113–175
- Baldocchi, D., B. Hicks, and T. Meyers. 1988. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. *Ecology* 69, 1331-1340.
- Bolt, G.H., 1976. Transport and accumulation of soluble soil components. In: Bolt, G.H., Bruggenwert, M.G.M. (Eds.), *Soil Chemistry. A. Basic elements*. Elsevier, New York, pp. 126-140.
- Bouwmeester R.J.B., and Vlek P.L.G. 1981. Wind-tunnel simulation and assesment of ammonia volatilization from ponded water. *Agronomy Journal* 73:546-552
- Brodeur J.J., Warland J.S., Staebler R.M., Wagner-Riddle C., 2009. Technical note: laboratory evaluation of a tunable diode laser system for eddy covariance measurements of ammonia flux. *Agricultural & Forest Meteorology*, 149, 385–391.
- Businger, J. A. and Delany, A. C., 1990. Chemical Sensor Resolution Required for Measuring Surface Fluxes by Three Common Micrometeorological Techniques, *J. Atmos. Chem.*, 10, 399–410.
- Clapp, R.B., and Homberger, G.M., 1978. Empirical equations for some soil hydraulic properties. *Water Resour. Res.* 14, 60-604.
- Clarisse, L., Clerbaux, C., Dentener, F., Hurtmans, D., and Coheur, P., 2009. Global ammonia distribution derived from infrared satellite observations, *Nat. Geosci.*, 2, 479–483.
- Denmead, O.T. 1983. Micrometeorological methods for measuring gaseous losses of nitrogen in the field. In: *Gaseous loss of nitrogen from plant-soil systems* (Eds J.R. Freney & J.R. Simpson), pp 133-157.

- Dragosits U., Hallsworth S., Sutton M.A., 2010. Ammonia emissions from UK non-agricultural sources in 2008: contribution to the National Atmospheric Emission Inventory. Edinburgh, NERC/Centre for Ecology and Hydrology, 15pp. (CEH Project number: C03614)
- Dragosits, U., Theobald, M. R., Place, C. J., Lord, E., Webb, J., Hill, J., ApSimon, H. M. and Sutton, M. A. 2002 Ammonia emission, deposition and impact assessment at the field scale: A case study of sub-grid spatial variability. *Environ.Pollut.*, 117, 147–158.
- Duyzer, J. H., Verhagen, H. L. M., Weststrate, J. H., Bosveld, F. C., and Vermetten, A. W. M., 1994. The dry deposition of ammonia onto a Douglas fir forest in the Netherlands, *Atmos. Environ.*, 29, 1241–1253.
- EMEP/CORINAIR, 2007. Atmospheric Emission Inventory Guidebook. Technical report No 16/2007.
- EMEP/EEA, 2009. Air Pollutant Emission Inventory Guidebook. EEA. Technical report No 9/2009.
- Erismann J.W., Bleeker A., Hensen A., Vermeulen A., 2008. Agricultural air quality in Europe and the future perspectives, *Atmos. Environ.*, 42, 3209–3217.
- Eugster, W. and Senn, W., 1995. A Cospectral Correction Model for Measurement of Turbulent NO₂ Flux, *Boundary-Layer Meteorol.* 74, 321–340.
- Finnigan JJ, Clement R, Malhi Y, Leuning R, Cleugh HA (2003) A re-evaluation of long-term flux measurement techniques – Part I: Averaging and coordinate rotation. *Bound-Layer Meteorol* 107: 1–48.
- Flechard, C. R., Spirig, C., Neftel, A., and Ammann, C., 2010. The annual ammonia budget of fertilised cut grassland – Part 2: Seasonal variations and compensation point modeling, *Biogeosciences*, 7, 537–556.
- Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P. and Sharpe, R.R., 2004. Deducing ground-to-air emissions from observed trace gas concentrations: A field trial. *Journal of Applied Meteorology*, 43(3): 487-502.
- Fowler, D., Pilegaard, P., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, et al., 2009. Atmospheric composition change: Ecosystems – Atmosphere interactions, *Atmos. Environ.*, 43, 5193–5267.
- Gash JHC. 1986. A note on estimating the effect of limited fetch on micrometeorological evaporation measurements. *Boundary-Layer Meteorology* 35, 409-14

- Génermont, S., and P. Cellier, 1997: A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. *Agricultural and Forest Meteorology*, 88:145-167.
- Guyot G., 1998. *Physics of the environment and climate*. Chichester: John Wiley & Sons, 632 pp.
- Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., and Lindinger, W., 1995. Proton-Transfer Reaction Mass-Spectrometry–Online Trace Gas-Analysis at the ppb Level, *Int. J. Mass Spectrom.*, 149, 609–619.
- Harper L.A., 2005. Ammonia: Measurement Issues. *Agronomy Mono-graph No. 47*. In: Hatfield, J.L., Baker, J.M. (Eds.), *Micrometeorology in Agricultural Systems*. ASA-CSSA-SSSA, Madison, WI, pp. 345–380.
- Hensen, A., Loubet, B., Mosquera, J., van den Bulk, W.C.M., Erisman, J.W., Daemmgen, U. *et al.* 2009a. Estimation of NH₃ emissions from a naturally ventilated livestock farm using local-scale atmospheric dispersion modelling. *Biogeosciences*, 6, 825–862.
- Hensen, A., Nemitz, E., Flynn, M. J., Blatter, A., Jones, S. K., Sørensen, L. L., Hensen, B., Pryor, S. C., Jensen, B., Otjes, R. P., Cobussen, J., Loubet, B., Erisman, J. W., Gallagher, M. W., Neftel, A., and Sutton, M. A., 2009b. Inter-comparison of ammonia fluxes obtained using the Relaxed Eddy Accumulation technique, *Biogeosciences*, 6, 2575–2588.
- Huang, C.H., 1979. A theory of dispersion in turbulent shear flow. *Atmospheric Environment*, 13: 453-463.
- Itier B., and Perrier A., 1976. Présentation d'une étude analytique de l'advection: I. Advection liée aux variations horizontales de concentration et de température. *Annales Agronomiques* 27:111-140.
- ISPRA, 2011. Italian emission inventory 1990-2009. Information inventory report 2011. *Rapporti 138/2011*. Available at: <http://www.eea.europa.eu/publications/european-union-emission-inventory-report>.
- Jarvis S. C., Pain B. F., 1990. Ammonia volatilization from agricultural land. *Proceedings 298*, The Fertilizer Society, Peterborough, UK, 35 pp.
- Jørgensen S., Kamp-Nielsen L., Chirstensen T., Windolf-Nielsen J., Westergaard B., 1986. Validation of a prognosis based upon a eutrophication model. *Ecol. Modell.* 32 (1–3) 165–182.
- Kaimal, J. C., Finnigan J. J., 1994: *Atmospheric Boundary Layer Flows: Their Structure and Measurement*. Oxford University Press, 289 pp.

- Krupa S.V., 2003. Effects of atmospheric ammonia (NH₃) on terrestrial vegetation: a review. *Environmental Pollution*, 124, 179-221.
- Le Cadre, E. 2004. Modélisation de la volatilisation d'ammoniac en interaction avec les processus chimiques et biologiques du sol: le modèle Volt'Air., INAPG, Ecole Doctorale ABIES.
- Leith I.D., Sheppard L.J., Fowler D., Cape J.N., Jones M., Crossley A., Hargreaves K.J., Tang Y.S., Theobald M., Sutton M.A., 2004. Quantifying dry NH₃ deposition to an ombrotrophic bog from an automated NH₃ field release system. *Water, Air, & Soil Pollution: Focus* 4, 207-218.
- Loague, K., and Green R.E.. 1991. Statistical and graphical methods for evaluating solute transport models: Overview and application. *Journal of Contaminant Hydrology* 7:51-73.
- Loubet B., Générmont S., Ferrara R., Bedos C., Decuq C., Personne E., Fanucci O., Durand B., Rana G., Cellier P., 2010 - An inverse model to estimate ammonia emissions from fields. *European Journal of Soil Science*, 61, 5, 793–805.
- Loubet B., Générmont S., Personne E., Massad R.S., 2011. Can we estimate ammonia emissions by inverse modelling with time averaged concentrations? *Proceedings of Nitrogen & Global Change Key findings – future challenges*, Edinburgh April 11 – 15, 2011 [Unpublished].
- Loubet B., Milford C., Hensen A., Daemmgen U., Erisman J.W., Cellier P., Sutton M.A. - 2009 Advection of NH₃ over a pasture field and its effect on gradient flux measurements. *Biogeosciences*, 6, 1295-1309.
- Loubet, B. and Cellier, P., 2001. Experimental assessment of atmospheric ammonia dispersion and short range dry deposition in a maize canopy. *Water, Air and Soil Pollution: Focus*, 1: 157-166.
- Loubet, B., Milford, C., Sutton, M.A. & Cellier, P. 2001. Investigation of the interaction between sources and sinks of atmospheric ammonia in an upland landscape using a simplified dispersion-exchange model. *Journal of Geophysical Research*, 106, 24183–24195.
- Massman, W.J. 2000. A simple method for estimating frequency response corrections for eddy covariance systems. *Agricultural and Forest Meteorology*. 104: 185-198.
- McBain, M.C. & Desjardins, R.L. 2005. The evaluation of a backward Lagrangian stochastic (bLS) model to estimate greenhouse gas emissions from agricultural sources using a synthetic tracer source. *Agricultural & Forest Meteorology*, 135, 61–72.

- Milford, C., Theobald, M. R., Nemitz, E., Hargreaves, K. J., Horvath, L., Raso, J., Dämmgen, U., Neftel, A., Jones, S. K., Hensen, A., Loubet, B., Cellier, P., and Sutton, M. A., 2009. Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived from an inter-comparison of gradient measurements, *Biogeosciences*, 6, 819–834.
- Misselbrook T.H., Nicholson F.A., Chambers B.J., 2005. Predicting ammonia losses following the application of livestock manure to land. *Bioresource Technology* 96:159-168.
- Moal J.F., J. Martinez F. Guiziou, Coste C.M., 1995. Ammonia volatilization following surface-applied pig and cattle slurry in France. *Journal of Agricultural Science* 125:245-252.
- Moore, C.J., 1986. Frequency response corrections for eddy correlation systems. *Boundary-Layer Meteorol.* 37,17–35
- Mozurkewich M., 1993. The Dissociation-Constant of Ammonium-Nitrate and Its Dependence on Temperature, Relative-Humidity and Particle-Size, *Atmos. Environ.*, 27, 261–270.
- Nash, J. E. and Sutcliffe J. V. ,1970. River flow forecasting through conceptual models part I — A discussion of principles, *Journal of Hydrology*, 10 (3), 282–290.
- Nemitz, E., Sutton, M. A., Gut, A., San Jose, R., Husted, S., and Schjørring, J. K., 2000. Sources and sinks of ammonia within an oilseed rape canopy, *Agr. Forest Meteorol.*, 105, 385–404
- Nemitz, E, Dorsey, JR., Flynn, MJ., Gallagher, MW., Hensen, A., Erisman, JW., Owen, SM., Dammgen, U., Sutton, MA., 2009. Aerosol fluxes and particle growth above managed grassland. *Biogeosciences*. Vol. 6, pp. 1627-1645.
- Norman M., Spirig C., Wolff V., Trebs I., Flechard C., Wisthaler A., Schnitzhofer R., Hansel A., Neftel A., 2009. Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland), *Atmos. Chem. Phys.*, 9, 2635–2645.
- Norman, M., Spirig, C., Wolff, V., Trebs, I., Flechard, C., Wisthaler, A., Schnitzhofer, R., Hansel, A., and Neftel, A., 2009. Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland), *Atmos. Chem. Phys.*, 9, 2635–2645.
- Owen P.R., Thompson W.R., 1963. Heat transfer across rough surfaces. *Journal of Fluid Mechanics* 15, 321-334
- Philip J.R.. 1959. The theory of local advection: 1. *J. Meteorol.*, 16, 535-547.

- Pinder R.W., Walker J.T., Bash J.O., Cady-Pereira K.E., Henze D.K., Luo M., Osterman G. B., and Shephard M. W., 2011. Quantifying spatial and seasonal variability in atmospheric ammonia with in situ and space-based observations, *Geophys. Res. Lett.*, 38, L04802
- Rachhpahl-Singh, Nye, P.H., 1986. A model of ammonia volatilization from applied urea: I. Development of the model. *J. Soil Sci.* 37, 9-20.
- Raupach M.R., J.J. Finnigan & Y. Brunet. 1996. Coherent eddies and turbulence in vegetation canopies: The mixing-layer analogy. *Boundary Layer Meteorology*, 78, 351-382.
- Raupach, M. R.: A practical lagrangian method for relating scalar concentrations to source distribution in vegetation canopies, *Q. J. Roy. Meteor. Soc.*, 115, 609–632, 1989.
- Rothman, L.S., Barbe, A., Chris Benner, D., Brown, L.R., Camy-Peyret, C., Carleer, K.C.M.R., et al., 2001. *J. Quant. Spectrosc. Radiat. Transfer*, 82: 5-44.
- Sanz, A., Misselbrook, T., Sanz, M. J., and Vallejo, A.: Use of an inverse dispersion technique for estimating ammonia emission from surface-applied slurry, *Atmos. Environ.*, 44, 999–1002.
- Sintermann J., Neftel A., Ammann C., Häni C., Hensen A., Loubet B. and Flechard C. R., 2011a. Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories? *Biogeosciences Discuss.*, 8, 10069-10118.
- Sintermann, J., Spirig, C., Jordan, A., Kuhn, U., Ammann, C. and Neftel, A., 2011b. Eddy covariance flux measurements of ammonia by high temperature chemical ionisation mass spectrometry. *Atmospheric Measurement Techniques*, 4(3): 599-616.
- Skjøth C. A., C. Geels, H. Berge, S. Gyldenkærne, H. Fagerli, T. Ellermann, L.M. Frohn, J. Christensen, K. M. Hansen, K. Hansen, and O. Hertel, 2011. Spatial and temporal variations in ammonia emissions – a freely accessible model code for Europe. *Atmos. Chem. Phys.*, 11, 5221–5236.
- Søgaard, H.T., Sommer S.G., Hutchings N.J., Huijsmans J.F.M., Bussink D.W., Nicholson F., 2002: Ammonia volatilization from field-applied animal slurry - the ALFAM model, *Atmospheric Environment*, 36, 3309–3319.
- Sommer S.G., Hutchings N.J., 2001. Ammonia emission from field applied manure and its reduction - invited paper. *European Journal of Agronomy* 15:1-15.

- Sommer S.G., Olesen J.E., Christensen B.T., 1991. Effects of temperature, wind speed and air humidity on ammonia volatilization from surface applied cattle slurry. *Journal of Agricultural Science* 117, 91-100.
- Sommer, S. G., McGinn, S. M., and Flesch, T. K.: Simple use of the backwards lagrangian stochastic dispersion technique for measuring ammonia emission from small field-plots, *Eur. J. Agron.*, 23, 1–7, 2005.
- Stull, R.B., 1988. *An Introduction to Boundary Layer Meteorology*. Klumer Academic Publishers, Boston, Massachusetts, 666 pp.
- Sutton, M., A., Burkhardt, J., Guerin, D., Nemitz, E., Fowler, D., 1998. Development of resi stance models to describe measurements of bi-directional ammonia surface atmosphere eschange. *Atmos. Environ.*, 32(3), 473-480.
- Sutton M.A., Dragosits U., Tang Y.S., Fowler D., 2000. Ammonia emissions from non-agricultural sources in the UK, *Atmospheric Environment* 34, p.855-869.
- Sutton M.A., Tang Y.S., Miners B., Fowler D., 2001b. A new diffusion denuder system for long-term, regional monitoring of atmospheric ammonia and ammonium. *Water, Air and Soil Pollution: Focus*, 1, Part 5/6, 145-156.
- Sutton, M. A., E. Nemitz, J. W. Erisman, C. Beier, K. B. Bahl, P. Cellier, W. de Vries, F. Cotrufo et al., 2007. Challenges in quantifying biosphere-atmosphere exchange of nitrogen species. *Environmental Pollution*, 150:125-139.
- Sutton, O. G., 1932. A theory of eddy diffusion in the atmosphere, *Proc. R. Soc. A*, 135, 143–165,.
- Tang, Y.S., Cape, J.N. and Sutton, M.A. 2001. Development and Types of Passive Samplers for Monitoring Atmospheric NO₂ and NH₃ Concentrations. In *Proceedings of the International Symposium on Passive Sampling of Gaseous Pollutants in Ecological Research*. TheScientificWorld, 1, 513-529
- Thomson, D.J., 1987. Criteria for the selection of stochastic models of particle trajectories in turbulent flows. *Journal of Fluid Mechanics*, 180: 529-556.
- Todd, R.W., Cole N.A., Clark R.N., Flesch T.K., Harper L.A. and Baek B.H.. 2008. Ammonia emissions from a beef cattle feedyard on the southern High Plains. *Atmos. Environ.* 42:6797–6805.
- Valli, L., Fabbri, C., and Bonazzi, G., 2001 A national inventory of ammonia and greenhouse gas emissions from agriculture in Italy, in: *Proceedings of the 9th Int. Conference on the FAO ESCORENA Network on recycling of agricultural, municipal and industrial residues in agri- culture*, 153–159, Gargano, Italy.

- Van der Molen, J., Beljaars, A.C.M., Chardon, W.J., Jury, W.A., van Faassen, H.G., 1990. Ammonia volatilization from arable land after application of cattle slurry: 2. Derivation of a transfer model. *Neth. J. Agric. Sci.* 38, 239-254.
- van Genuchten M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Sci. Soc. Am. J.* 44 (1980), pp. 892–898.
- von Bobruzki, K., Braban, C. F., Famulari, D., Jones, S. K., Blackall, T., Smith, T. E. L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M. R., Percival, C. J., Whitehead, J. D., Ellis, R., Murphy, J., Mohacsi, A., Junninen, H., Pogany, A., Rantanen, S., Sutton, M. A., Nemitz, E., 2009. Field inter-comparison of eleven atmospheric ammonia measurement techniques, *Atmos. Meas. Tech. Discuss.*, 2, 1783–1836.
- Webb, E. K., Pearman, G. I., and Leuning, R., 1980. Correction of flux measurements for density effects due to heat and water vapour transfer, *Q. J. Roy. Meteorol. Soc.*, 106, 85–100.
- Weber, R. O., 1999. Remarks on the definition and estimation of friction velocity. *Bound.-Layer Meteor.*, 93, 197–209.
- Zahniser M.S., Nelson D.D., McManus J.B., Shorter J.H., Herndon S., Jimenez R., 2005. Development of a Quantum Cascade Laser-Based Detector for Ammonia and Nitric Acid. Final Report, U.S. Department of Energy, SBIR Phase II.

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 NH₃ 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 NH₃ emissions to the atmosphere (Sommer and Hutchings, 2001; Sogaard *et al.*, 2002; Huijsmans *et al.*, 2003; Rotz, 2004).

Even if NH₃ volatilisation following application of organic fertilisers has been widely investigated (i.e. Générmont and Cellier, 1997; Générmont *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 NH₃ 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 NH₃ 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 NH₃ flux measurements.

The inverse dispersion modelling has also been long used (Wilson *et al.* 1982, 1983) for estimating the NH₃ emission using NH₃ 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 NH₃ 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 NH₃ 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 NH₃ 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 m³ m⁻³ and the soil pH was 7.5. The field was spread with 68.5 m³ ha⁻¹ of fresh cattle manure the 24th 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 m³, 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-NH₃ ha⁻¹, while the total Kjeldahl nitrogen (TKN), as the sum of organic nitrogen, NH₃ and ammonium (NH₄⁺), was 192 kg N ha⁻¹ (Table 3.1).

Table 3.1. Main characteristics of the slurries applied during Bigarello 2009 (INJ-09) and Cornaredo 2010 (SI-10) field trials.

	Dry matter g kg ⁻¹	pH	TAN kg N-NH ₄ ⁺ ha ⁻¹	TKN kg N ha ⁻¹
INJ-09	34	8.0	139	192
SI-10	55	6.5	92	204

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 $0.25 \text{ m}^3 \text{ m}^{-3}$ while the pH was 5.5. The field was spread with $54 \text{ m}^3 \text{ ha}^{-1}$ of fresh dairy slurry the 17th 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 $91.5 \text{ kg N-NH}_3 \text{ ha}^{-1}$, while the TKN was 203 kg N ha^{-1} (see Table 3.1).

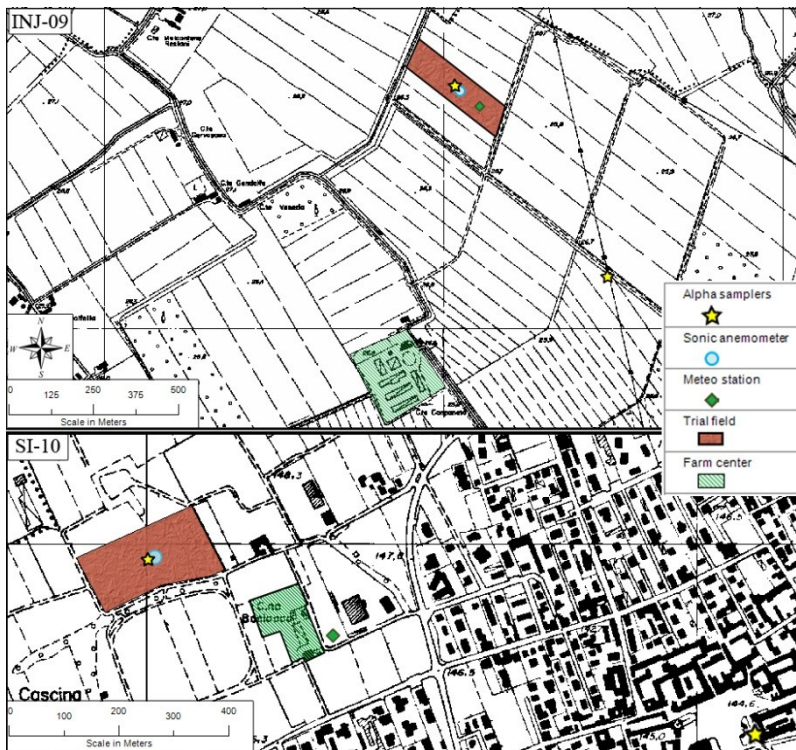


Figure 3.1. Site map of experimental fields during the trials in Bigarello in 2009 (INJ-09; top) and Cornaredo 2010 (SI-10; bottom).

Representative slurry samples (3 dm³) 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):

$$u_* = \sqrt{-|\overline{u'w'}|} \quad (\text{eq. 3.1})$$

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:

$$L = -\frac{u_*^3 T}{k g \overline{w'T'}} \quad (\text{eq. 3.2})$$

where T ($^{\circ}\text{K}$) is the mean air temperature within the surface boundary layer, k is the von K arm an'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:

$$z_0 = \frac{z}{\exp\left(\frac{U k}{u_* - \Psi}\right)} \quad (\text{eq. 3.3})$$

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 Ψ 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 (°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.

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

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 ($V_a = 0.003241315 \text{ m}^3$) multiplied for the time exposure t (hours) (Sutton *et al.*, 2001b; Tang *et al.*, 2008). The mean concentration and relative standard deviation (σ) of the three replicates were calculated for background ($\sigma_{C_{bgd}}$) and field measurements (σ_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:

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

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:

$$\begin{aligned}
 U(z) &= az^p \\
 K_z(z) &= bz^n \\
 D &= \frac{Q(t)}{\sigma_y \sqrt{2\pi}} \exp\left(-\frac{(Y)^2}{2\sigma_y^2}\right) \times \frac{(zz_s)^{(1-n)/2}}{b\alpha X} \times \exp\left(-\frac{a(z^\alpha + z_s^\alpha)}{b\alpha^2 X}\right) \times I_{-v}\left(\frac{2a(zz_s)^{\alpha/2}}{b\alpha^2 X}\right) \\
 \sigma_y &= \frac{1}{\sqrt{2}} C_y x^{\frac{2-m}{2}}
 \end{aligned} \quad (\text{eq. 3.6})$$

where $\alpha = 2 + p + n$, $v = (1 - n) / \alpha$, and I_{-v} is the modified Bessel function of the first kind of order $-v$, 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:

$$D = \frac{1}{N} \sum \left| \frac{2}{w_0} \right| \quad (\text{eq. 3.7})$$

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 σ_u , σ_v , σ_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 (σ_S), due to the uncertainty on NH_3 concentration measurements was estimated using equation (3.8) (Bevington and Robinson, 2002):

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

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:

$$(C_{1.1}, C_{1.2}, C_{1.3}; C_{2.1}, C_{2.2} \dots C_{n.3}) \left\{ \begin{array}{l} (\bar{C}_1^* \times \bar{D}_1; \bar{C}_2^* \times \bar{D}_2; \dots \bar{C}_n^* \times \bar{D}_n) \rightarrow \Sigma S_1^* \\ (\bar{C}_1^* \times \bar{D}_1; \bar{C}_2^* \times \bar{D}_2; \dots \bar{C}_n^* \times \bar{D}_n) \rightarrow \Sigma S_2^* \\ \dots \\ (\bar{C}_1^* \times \bar{D}_1; \bar{C}_2^* \times \bar{D}_2; \dots \bar{C}_n^* \times \bar{D}_n) \rightarrow \Sigma S_n^* \end{array} \right.$$

(eq 3.9)

where $C_{n:3}$ are all the field NH_3 concentrations including replications, and \bar{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.

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 NH_3 concentration measured in the fertilised field (C) and its background level (C_{bgd}), during Bigarello 2009 (INJ-09) and Cornaredo 2010 (SI-10).*

		u^* m s^{-1}	L m	C $\mu\text{g m}^{-3}$	C_{bgd} $\mu\text{g m}^{-3}$
INJ-09	<i>min</i>	0.01	-586	12.3	9.6
	<i>max</i>	0.38	1,144	95.2	42.7
	<i>mean</i>	0.10	-1.42	35.1	22.8
	<i>median</i>	0.07	0.18	30.5	22.5
	σ	0.09	106	21.3	9.8
SI-10	<i>min</i>	0.001	-4,083	0.9	3.8
	<i>max</i>	0.33	75,724	315.2	15.3
	<i>mean</i>	0.08	198	13.4	7.7
	<i>median</i>	0.06	-0.01	3.8	6.7
	σ	0.07	105	74.9	8.9

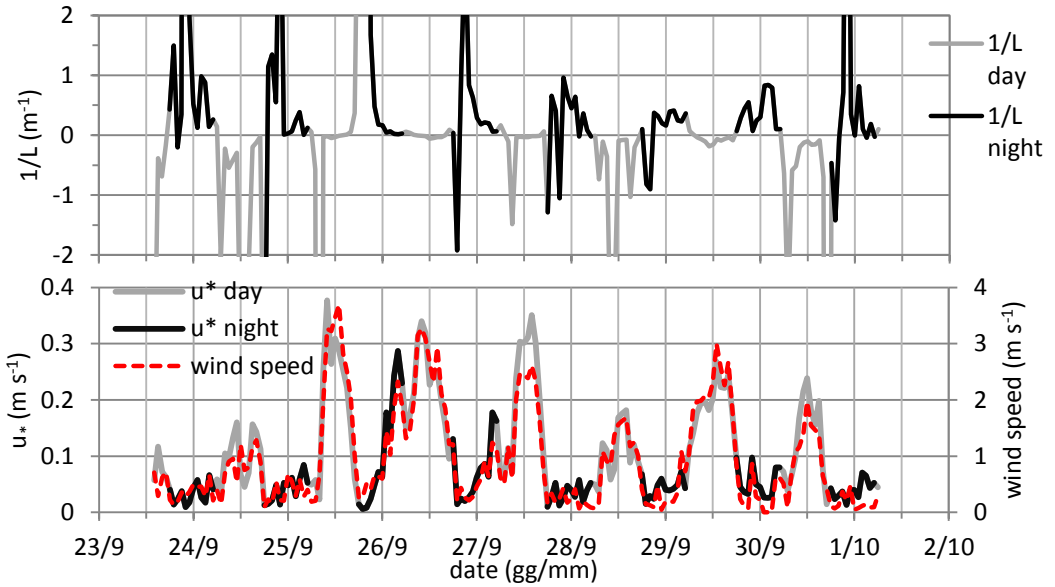


Figure 3.2. Inverse Monin-Obukhov length ($1/L$) during day and nighttime (upper panel); friction velocity (u_*) and wind speed (lower panel) in Bigarello 2009 (INJ-09) trial.

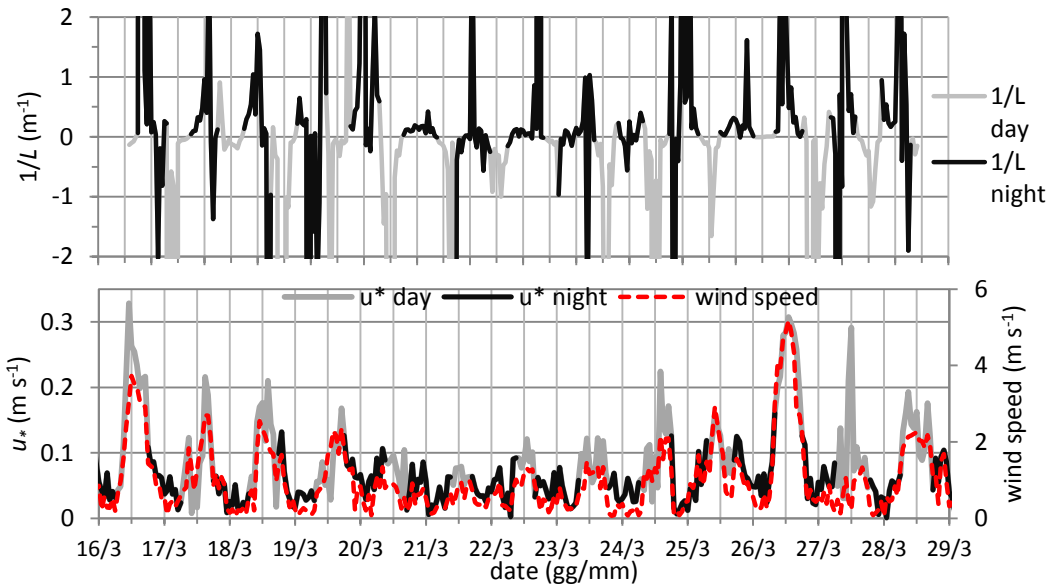


Figure 3.3. Inverse Monin-Obukhov length ($1/L$) during day and nighttime (upper panel); friction velocity (u_*) and wind speed (lower panel) in Cornaredo 2010 (SI-10) trial.

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 L/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 $5 \mu\text{g m}^{-3}$ 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 $95.2 \mu\text{g m}^{-3}$ (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 $315.2 \mu\text{g m}^{-3}$ (2 hours averaged) after a rapid increase after the start of the slurry spreading, and fell at night to $46 \mu\text{g m}^{-3}$ (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 $99 \mu\text{g m}^{-3}$ 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.

COMPARISON OF TWO INVERSE DISPERSION MODELS

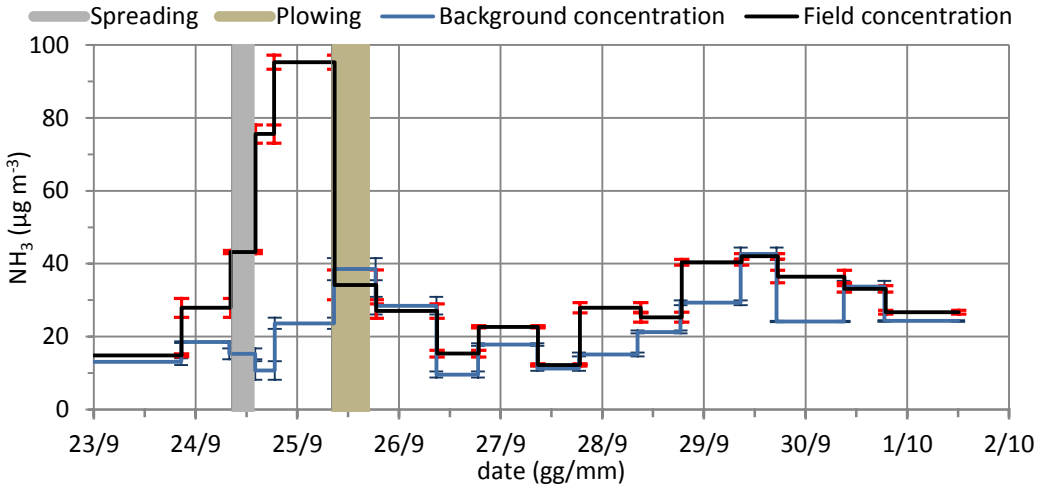


Figure 3.4: NH_3 concentrations measured in the centre of the fertilised field and in its background values in Bigarello 2009 (INJ-09). The vertical colour bars show the duration of slurry spreading and ploughing. The error bars show standard deviations.

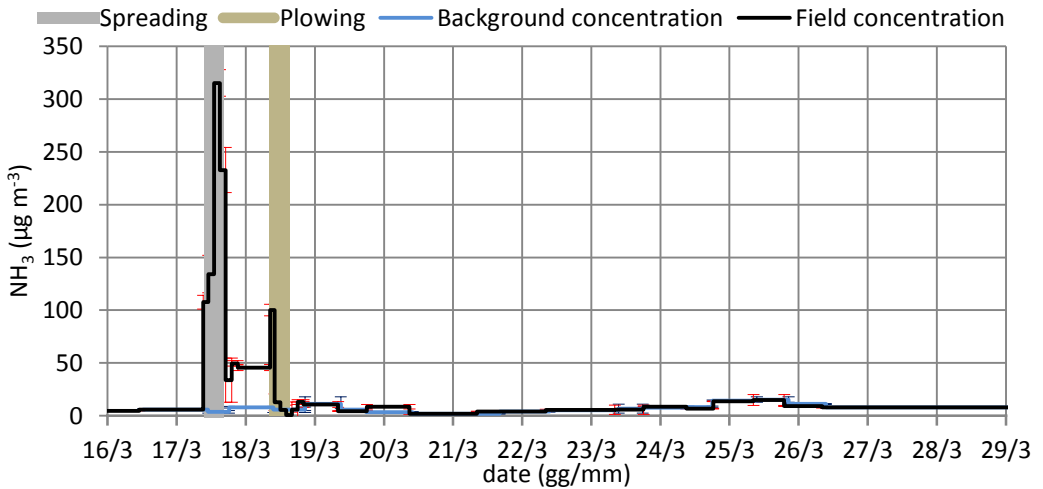


Figure 3.5: NH_3 concentrations measured in the centre of the fertilised field and in its background in Cornaredo 2010 (SI-10). The vertical colour bars show the duration of slurry spreading and ploughing. The error bars show standard deviations.

3.3.3 Uncertainties in ammonia concentrations

The measure of variability (σ), relative to the mean each three ALPHA exposed, ranged from 0.4 to 8.1 $\mu\text{g m}^{-3}$ in INJ-09, with an averaged value of 2.5 $\mu\text{g m}^{-3}$. For SI-10, the mean variation of σ was 6.7 $\mu\text{g m}^{-3}$ with values between 0.07 and 41.8 $\mu\text{g m}^{-3}$. Figure 3.6 a) and 3.6 b) shows the relations existing between the σ 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 σ (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 σ 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 σ . 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.

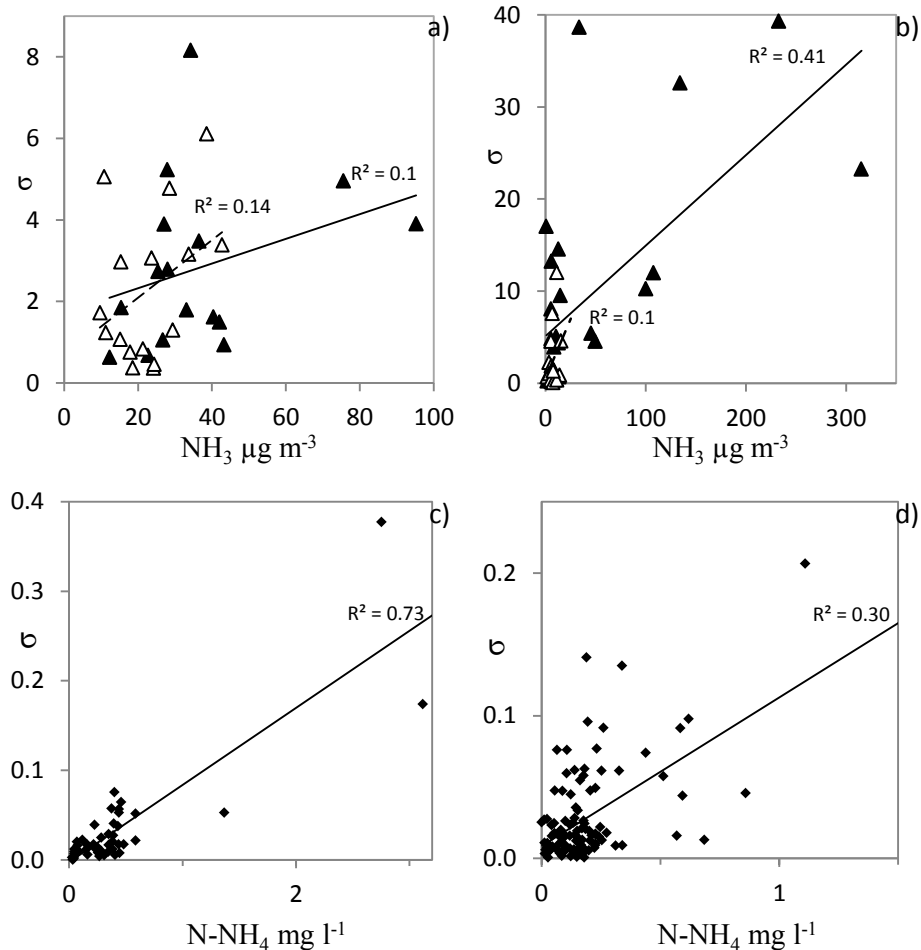


Figure 3.6. Scatter plots reporting the average of NH_3 concentration and relative standard deviation (σ) for measurements in the field (\blacktriangle) and at the background (\triangle) in (a) Bigarello 2009 (INJ-09) and (b) Cornaredo 2010 (SI-10). Regression between the mean of N-NH_4^+ concentration from all the samples analysed (\blacklozenge) 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 $7,745 \pm 4,106$ $\text{ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$ using D and $5,039 \pm 1,466$ $\text{ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$ using \bar{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 $33,021 \pm 186$ $\text{ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$ using D and $29,760 \pm 688$ $\text{ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$ using \bar{D} ; (Table 3.5). INSERT table 3.4 and 3.5 and FIGURE 7, 8.

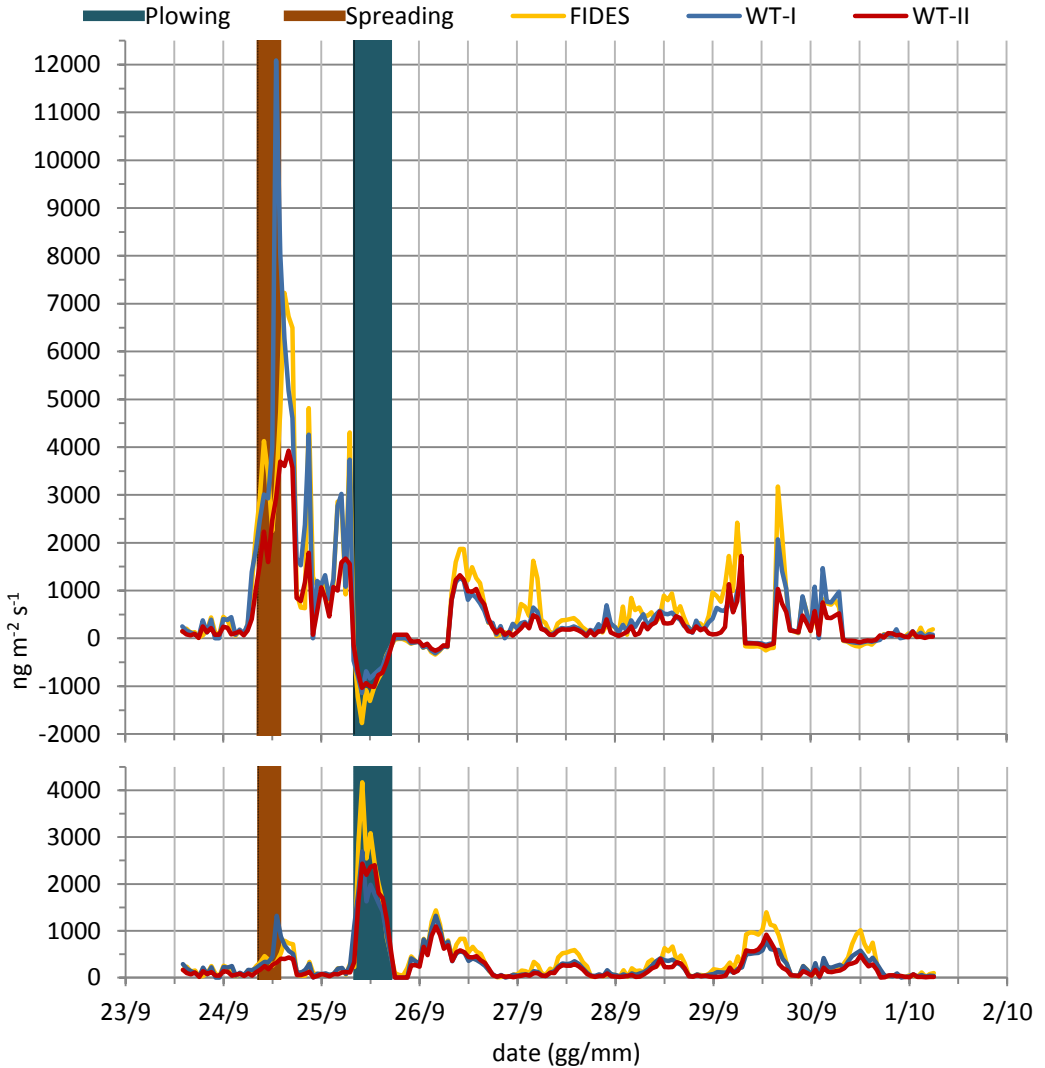


Figure 3.7: Upper panel: NH_3 flux during Bigarello 2009 (INJ-09) simulated by the inverse dispersion models: WindTrax using the turbulence parameters (WT-I); WindTrax using the three components of wind speed (WT-II); and FIDES. Lower panel: uncertainty in the modelling approaches employed due to the uncertainty in the concentrations measurements. The vertical colour bars represent the duration of slurry distribution and ploughing.

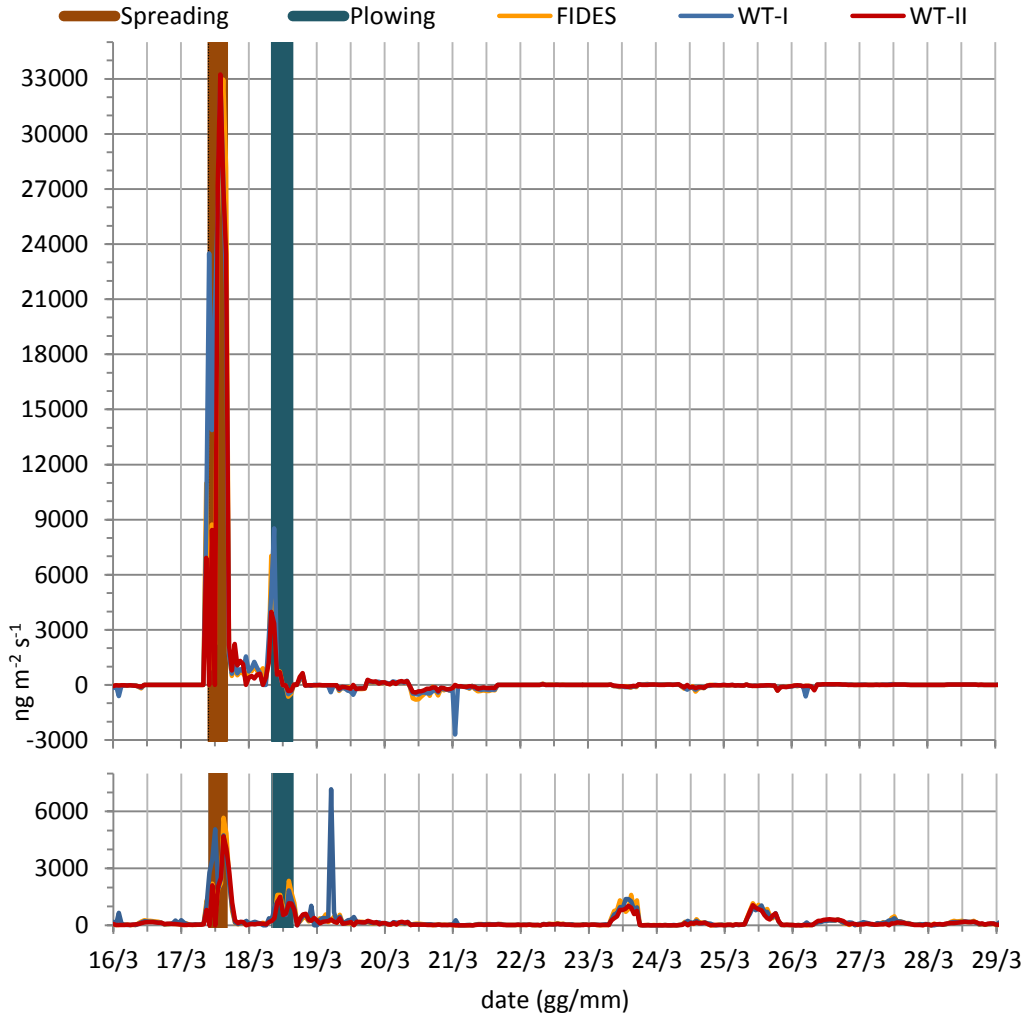


Figure 3.8: Upper panel: NH₃ fluxes during Cornaredo 2010 (SI-10) simulated by the inverse dispersion models: WindTrax using the turbulence parameters (WT-I); WindTrax using the three components of the wind (WT-II); and FIDES. Lower panel: uncertainty in the modelling approaches employed due to the uncertainty in the concentrations measurements. The vertical colour bars represent the duration of slurry spreading and ploughing.

COMPARISON OF TWO INVERSE DISPERSION MODELS

Table 3.4. Cumulated and maximum NH₃ 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 (\pm err%) is reported as percentage of TAN and TKN. The results are relative to simulation using the transfer coefficient, and its time averaged on exposition time (\bar{D}).

INJ-09	Flux		Emission Factors	
	cumulated kg N-NH ₃ ha ⁻¹	maximum kg N-NH ₃ ha ⁻¹ h ⁻¹	%TKN	%TAN
WT-I	3.4	0.36 ± 0.02	1.77 ± 0.44	2.46 ± 0.61
WT-II	2.1	0.12 ± 0.01	1.11 ± 0.39	1.53 ± 0.54
FIDES	3.5	0.21 ± 0.01	1.81 ± 0.57	2.51 ± 0.79
WT-I \bar{D}	2.9	0.19 ± 0.01	1.48 ± 0.41	2.06 ± 0.57
WT-II \bar{D}	1.6	0.10 ± 0.01	0.83 ± 0.30	1.15 ± 0.42
FIDES \bar{D}	2.5	0.15 ± 0.01	1.31 ± 0.37	1.81 ± 0.51
mean ± σ	0.28 ± 0.07	[0.19 ± 0.01 [#]] ± 0.01	[1.44 ± 0.51 [#]] ± 0.43	[2.00 ± 0.71 [#]] ± 0.60

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 NH₃ 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 (\pm err%) is reported as percentage of TAN and TKN. The results are relative to simulation using the transfer coefficient, and its time averaged on exposition time (\bar{D}).

SI-10	Flux		Emission Factors	
	cumulated kg N-NH ₃ ha ⁻¹	maximum kg N-NH ₃ ha ⁻¹ h ⁻¹	%TKN	%TAN
WT-I	5.9	0.97 ± 0.04	2.88 ± 0.70	6.41 ± 1.57
WT-II	4.3	0.99 ± 0.04	2.12 ± 0.49	4.71 ± 1.10
FIDES	4.7	0.98 ± 0.08	2.31 ± 0.60	5.14 ± 1.33
WT-I \bar{D}	5.7	0.86 ± 0.03	2.80 ± 0.59	6.23 ± 1.32
WT-II \bar{D}	4.7	0.89 ± 0.03	2.32 ± 0.45	5.17 ± 1.01
FIDES \bar{D}	4.3	0.90 ± 0.08	2.12 ± 0.45	4.73 ± 1.00
mean ± σ	0.49 ± 0.07	0.93 ± 0.05	[2.43 ± 0.57 [#]] ± 0.56	[5.40 ± 1.27 [#]] ± 1.26

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 $2.0 \pm 0.7\%$ and $5.4 \pm 1.3\%$, 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).

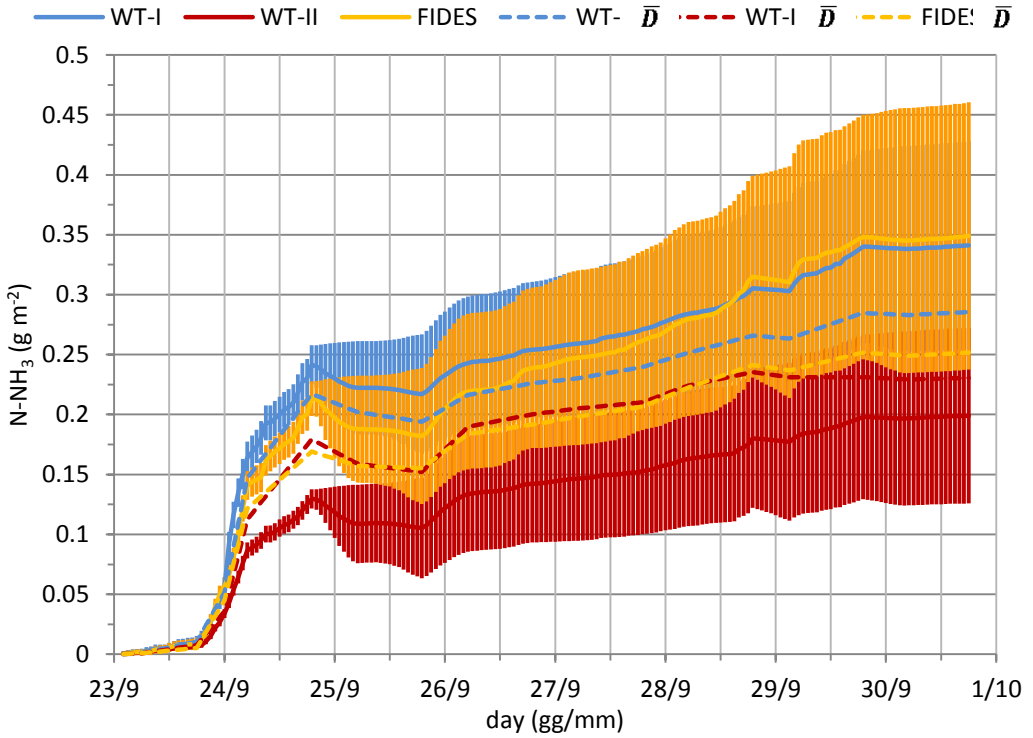


Figure 3.9: Cumulated NH_3 volatilisation (g m^{-2}) for Bigarello 2009 (INJ-09) obtained by the three inverse dispersion models: WindTrax using the three components of the wind (WT-II), WindTrax using the turbulence parameters (WT-I) and FIDES. The solid lines are relative to hourly output of the models, while dotted lines are relative to output obtained using the mean of the mass transfer coefficient (\bar{D} ; dotted line). In the graph are indicated the cumulated uncertainties (vertical bars).

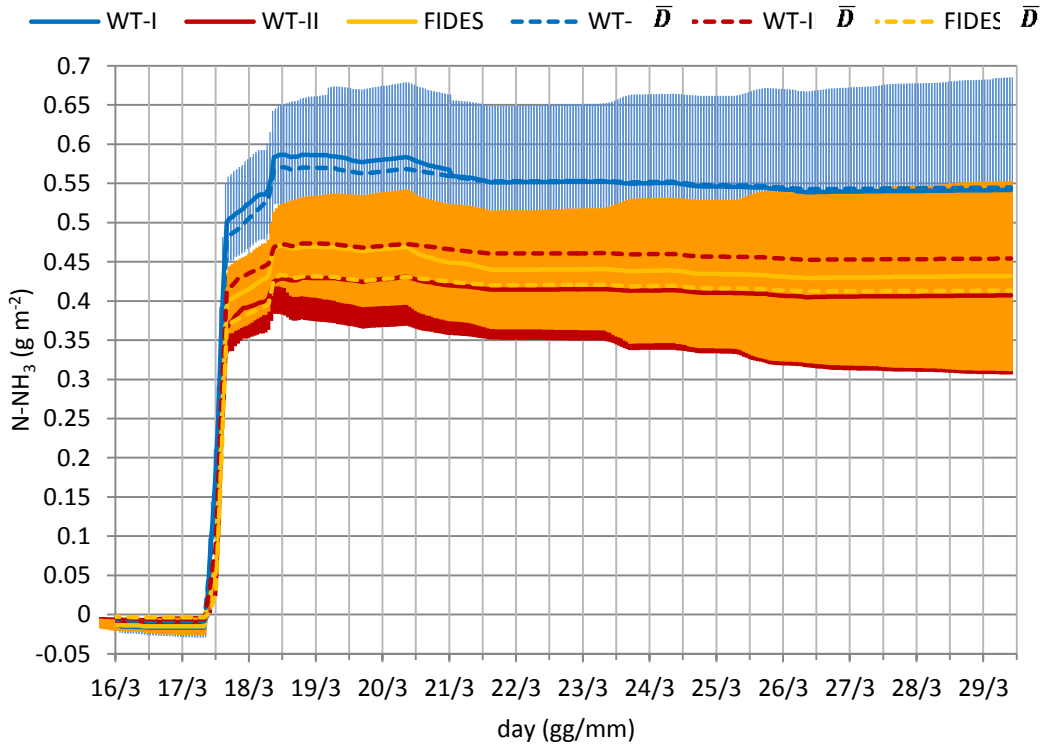


Figure 3.10: Cumulated NH_3 fluxes (g m^{-2}) in Cornaredo 2010 (SI-10) obtained from WindTrax using the three components of the wind (WT-II), WindTrax using the turbulence parameters (WT-I) and FIDES. The solid lines are relative to hourly output of the models, while dotted lines are relative to output 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 NH₃ volatilisation

Passive samplers employed in this study are appropriate tool for determining long term NH₃ 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 NH₃ 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 σ 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 NH₃ 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.

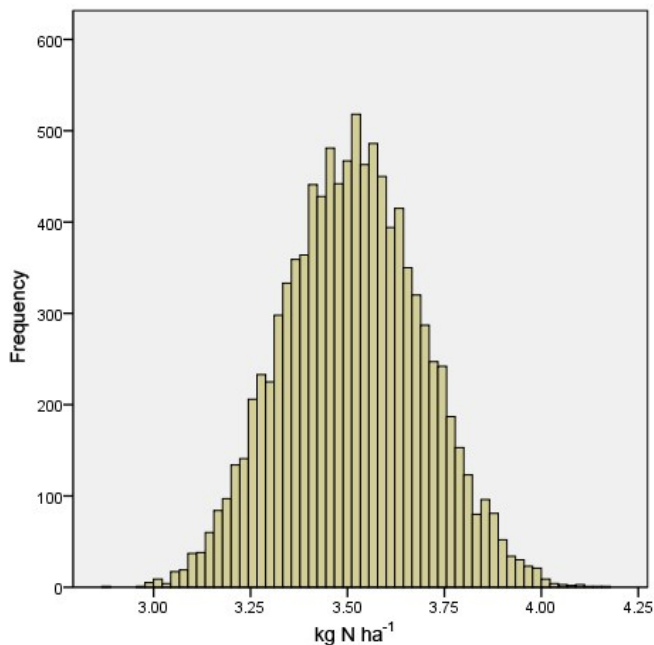


Figure 3.11. Frequency distribution of cumulated NH₃ loss as kg N ha⁻¹ calculated in Cornaredo 2010 (SI-10) with a bootstrap analysis, using WindTrax approach with the turbulence parameters.

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 through 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 NH₃ volatilisation following slurry spreading

In INJ-09, the main peak in NH₃ 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 NH₃ 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 NH₃ 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 NH₃ 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 NH₃ volatilisation, which stopped just after incorporation.

3.4.3 Ammonia emission factors

The NH₃ 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 NH₃ losses following the application of manure, abatement strategies have been investigated, considering all the factors involved in NH₃ volatilisation. In particular, manure application methods have been shown to be among the most cost-effective practice available to farmers to reduce NH₃ emissions. For example, NH₃ 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 NH₃ 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 NH₃ 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 $5.4 \pm 1.27\%$ 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; Søgaaard *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 NH₃ volatilisation through different measurement techniques, wide range of weather, soil and agronomic situations, making difficult the comparison. For example, Søgaaard *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.

References

- Asman W.A.H., Sutton M.A. and Schjoerring J.K., 1998: Ammonia: emission, atmospheric transport and deposition. *New Phytologist* 139, 27-48.
- Battye, W., Pistikopoulos, P., & Samaras, Z. 2003. Evaluation and improvement of ammonia emissions inventories. *Atmospheric Environment*, 37(18), 3873-3883.
- Bevington, P.R., Robinson, D.K., 2002. *Data Reduction and Error Analysis for the Physical Sciences*, 3rd Ed., McGraw-Hill. ISBN 007119926
- Bittman, S., L. van Vliet J. P., Kowalenko C. G., McGinn S., Hunt D. E., Bounaix F., 2005. Surface-banding liquid manure over aeration slots: A new low-disturbance method for reducing ammonia emissions and improving yield of perennial grasses. *J. Agron.* 97:1304.
- Bleeker A., Sutton M. A., Acherman B., Alebic-Juretic A., Aneja V. P., Ellermann T., Erismann J. W., Fowler D., Fagerli H., Gauger T., Harlen K. S., Hole L. R., Horvath L., Mitosinkova M., Smith R. I., Tang Y. S., van Pul A., 2009. Linking Ammonia Emission Trends to Measured Concentrations and Depositions of Reduced Nitrogen at Different Scales. *Atmospheric Ammonia: Detecting emission changes and environmental impacts. Results of an Expert Workshop under the Convention on Long-range Transboundary Air Pollution*. Springer, 123-180.
- Bouwman A.F., Goldewijk K. K., Van der Hoek K.W., Beusen A.H.W., van Vuuren D.P., Willems W.J., Rufino M.C., Stehfest E., 2011. Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900-2050 period. *Proceedings of the National Academy of Sciences of the United States of America (PNAS)*, 05/2011.
- Brodeur, J.J., Warland, J.S., Staebler, R.M. & Wagner-Riddle, C. 2009. Technical note: Laboratory evaluation of a tunable diode laser system for eddy covariance measurements of ammonia flux. *Agricultural and Forest Meteorology*, 149, 385-391.
- CRPA, Research Centre on Animal Production, Italy – National ammonia emissions and emission scenarios from the agronomic land spreading and the use of nitrogen fertilizers in Italy. 2011. ISBN: 978-88-904312-3-4.
- Denmead, O.T., Raupach, M.R. 1993. Methods for measuring atmospheric gas transport in agricultural and forest systems. In: L.A. Harper, A.R. Mosier, J.M, Duxbury and D.E. Rolston (eds.) *Agricultural Ecosystem Effects on Trace*

- Gases and Global Climate Change. ASA Spec. Publ. 55. American Society of Agronomy, Madison, pp. 19-43
- EEA, 2010. European Union emission inventory report 1990–2008 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP). Technical report No 7/2010. <http://www.eea.europa.eu/publications/european-union-emission-inventory-report>.
- EEA, 2011. NEC Directive status report 2010. Technical report No 3/2011. <http://www.eea.europa.eu/publications/nec-directive-status-report-2010>.
- Famulari, D., Fowler, D., Hargreaves, K., Milford, C., Nemitz, E., Sutton, M. & Weston, K. 2005. Measuring eddy covariance fluxes of ammonia using tunable diode laser absorption spectroscopy. *Water, Air, & Soil Pollution: Focus*, 4 (6), 151-158.
- Ferm, M., Galle, B., Klemedtsson, L., Kasimir-Klemedtsson, Å., Griffith, D. W. T., 2000. Comparison of different techniques to measure ammonia emission after manure application. Swedish Environmental Research Institute. Rapport/report 1383.
- Flesch, T., Wilson, J.D., Yee, E., 1995. Backward-time Lagrangian stochastic dispersion models, and their application to estimate gaseous emissions. *J. Appl. Meteor.* 34, 1320–1332.
- Flesch, T. K., J. D. Wilson, L. A. Harper, B. P. Crenna, R. R. Sharpe, 2004: Deducing Ground-to-Air Emissions from Observed Trace Gas Concentrations: A Field Trial. *J. Appl. Meteor.*, 43, 487–502.
- Fox, D.G. 1981. Judging air quality model performance: a summary of the AMS workshop on dispersion models performance. *Bull. Am. Meteorol. Soc.*, 62:599-609.
- Galloway, J.N., Aber J.D., Erisman J.W., Seitzinger S.P., Howarth R.W., Cowling E.B., Cosby B.J., 2003. The Nitrogen Cascade. *Bioscience* 53: 341-356.
- Genermont, S., and Cellier P., 1997. A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. *Agricultural and Forest Meteorology* 88:145-167.
- Genermont, S., Cellier, P., Flura, D., Morvan, T., Laville, P., 1998. Measuring ammonia fluxes after slurry spreading under actual field conditions. *Atmos. Environ.* 32, 279–284.
- Hensen A., Loubet B., Mosquera J., van den Bulk W. C. M., Erisman J. W., Dämmgen U., Milford C., Löpmeier F. J., Cellier P., Mikuška P., Sutton M. A., 2009. Estimation of NH₃ emissions from a naturally ventilated livestock

- farm using local-scale atmospheric dispersion modeling. *Biogeosciences*, 6, 2847–2860
- Huijsmans, J.F.M., de Mol R.M., 1999. A model for ammonia volatilization after surface application and subsequent incorporation of manure on arable land. *Journal of Agricultural Engineering Research* 74: 73-82.
- Huijsmans, J.F.M., Hol, J.M.G., Vermeulen, G.D., 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. *Atmos. Environ.* 37, 3669–3680.
- ISPRA, 2011. Italian emission inventory 1990-2009. Information inventory report 2011. *Rapporti* 138/2011. Available at: <http://www.eea.europa.eu/publications/european-union-emission-inventory-report>.
- ISTAT, 2011. Istituto nazionale di statistica, 6° censimento generale dell'agricoltura. Risultati provvisori. Available at: <http://censimentoagricoltura.istat.it/fileadmin/template/main/res/comunicato-censimento-agricoltura.pdf>
- Kaimal, J. C., Finnigan J. J., 1994: *Atmospheric Boundary Layer Flows: Their Structure and Measurement*. Oxford University Press, 289 pp.
- Kruit, R.J.W., van Pul, W.A.J., Otjes, R.P., Hofschreuder, P., Jacobs, A.F.G. and Holtslag, A.A.M., 2007. Ammonia fluxes and derived canopy compensation points over non-fertilized agricultural grassland in The Netherlands using the new gradient ammonia - high accuracy - monitor (GRAHAM). *Atmospheric Environment*, 41(6): 1275-1287.
- Leith, I.D., Sheppard, L.J., Fowler, D., Cape, J.N., Jones, M., Crossley, A., Hargreaves, K.J., Tang, Y.S., Theobald, M., Sutton, M.A., 2004. Quantifying dry NH₃ deposition to an ombrotrophic bog from an automated NH₃ field release system. *Water Air and Soil Pollution: Focus* 4, 207–218.
- Loubet B., Générumont S., Ferrara R., Bedos C., Decuq C., Personne E., Fanucci O., Durand B., Rana G., Cellier P. - 2010 - An inverse model to estimate ammonia emissions from fields. *European Journal of Soil Science*, 61, 5, 793–805.
- Loubet B., Générumont S., Personne E., Massad R.S., 2011. Can we estimate ammonia emissions by inverse modelling with time averaged concentrations? *Proceedings of Nitrogen & Global Change Key findings – future challenges*, Edinburgh April 11 – 15, 2011 [Unpublished].

- Loubet, B., Cellier, P., Milford, C., and Sutton, M. A., 2006. A coupled dispersion and exchange model for short-range dry deposition of atmospheric ammonia, *Q. J. Roy. Meteorol. Soc.*, 132, 1733–1763.
- Loubet, B., Milford, C., Hensen, A., Daemmgen, U., Erisman, J.-W., Cellier, P., and Sutton, M. A., 2009. Advection of NH₃ over a pasture field, and its effect on gradient flux measurements, *Biogeosciences Discussions* 6, n°. 1: 163-196.
- Meisinger, J. J., and W. E. Jokela. 2000. Ammonia volatilization from dairy and poultry manure. *Managing, Nutrients and Pathogens from Animal Agriculture*. Natural Resource, Agriculture, and Engineering Service, Ithaca, NY. 130, 334–354
- Milford, C., Theobald, M.R., Nemitz, E., Hargreaves, K.J., Horvath, L., Raso, J., Damngen, U., Neftel, A., Jones, S.K., Hensen, A., Loubet, B., Cellier, P. and Sutton, M.A., 2009. Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived from an inter-comparison of gradient measurements. *Biogeosciences*, 6(5): 819-834.
- Moal, J.F., Martinez, J., Guiziou, F., Coste, C.M., 1995. Ammonia volatilization following surface-applied pig and cattle slurry in France. *J. Agric. Sci.* 125, 245–252.
- Monteny, G. J. and Erisman J. W., 1998. Ammonia emission from dairy cow buildings: A review of measurement techniques, influencing factors and possibilities for reduction. *Netherlands Journal of Agricultural Science* 46:225-247.
- Pain B. F., Phillips V. R., Clarkson, C. R., Klarenbeek, J. V. 1989. Loss of nitrogen through ammonia volatilization during and following the application of pig or cattle slurry to grassland. *Journal of the Science of Food and Agriculture* 47: 1-12.
- Pinder, R. W., Walker J. T., Bash J. O Cady-Pereira, K. E., Henze D. K., Luo M., Osterman G. B. and Shephard M. W., 2011. Quantifying spatial and seasonal variability in atmospheric ammonia with in situ and space-based observations, *Geophys. Res. Lett.*, 38.
- Rotz, C. A. 2004. Management to reduce nitrogen losses in animal production. *J. Anim. Sci.* 82 (E. Suppl.): E119-E137.
- Schaeffer, D.L. 1980. A model evaluation methodology applicable to environmental assessment models. *Ecol. Model.*, 8:275-295.
- Sintermann J., Neftel A., Ammann C., Häni C., Hensen A., Loubet B. and Flechard C. R., 2011a. Are ammonia emissions from field-applied slurry substantially

- over-estimated in European emission inventories? *Biogeosciences Discuss.*, 8, 10069-10118.
- Sintermann, J., Spirig, C., Jordan, A., Kuhn, U., Ammann, C. and Neftel, A., 2011b. Eddy covariance flux measurements of ammonia by high temperature chemical ionisation mass spectrometry. *Atmos. Meas. Tech.* 4(3), 599-616.
- Skjøth C. A., Geels C., Berge H., Gyldenkerne S., Fagerli H., Ellermann T., Frohn L.M., Christensen J., Hansen K. M., Hansen K, Hertel O., 2011. Spatial and temporal variations in ammonia emissions – a freely accessible model code for Europe. *Atmos. Chem. Phys.*, 11, 5221–5236.
- Søgaard H.T., Sommer S.G., Hutchings N.J., Huijsmans J.F.M., Bussink D.W., Nicholson F., 2002. Ammonia volatilization from field-applied animal slurry—the ALFAM model. *Atmospheric Environment* 36, 3309–3319.
- Sommer, S. G., and N. Hutchings. 1995. Techniques and strategies for the reduction of ammonia emission from agriculture. *Water Air Soil Poll.* 85, 237–248.
- Sommer, S. G., and N. Hutchings. 2001. Ammonia emission from field applied manure and its reduction—invited paper. *European Journal of Agronomy* 15, 1–15
- Sommer, S. G.; Olesen; J. E., 1991. "Effects of Dry Matter Content and Temperature on Ammonia Loss", *Journal of Environmental Quality* 20, 679-683.
- Sommer, S.G., Genemont, S., Cellier, P., Hutchings, N.J., Olesen, J.E. and Morvan, T., 2003. Processes controlling ammonia emission from livestock slurry in the field. *European Journal of Agronomy*, 19(4): 465-486.
- Sommer, S.G., McGinn, S.M. and Flesch, T.K., 2005. Simple use of the backwards Lagrangian stochastic dispersion technique for measuring ammonia emission from small field-plots. *European Journal of Agronomy*, 23(1): 1-7.
- Sommer, S.G., McGinn, S.M., Flesch, T.K., 2005. Simple use of the backwards Lagrangian stochastic dispersion technique for measuring ammonia emission from small field-plots. *European Journal of Agronomy* 23, 1–7.
- Sommer, S.G., Olesen, J.E., 2000. Modelling ammonia emission from animal slurry applied with trail hoses to cereals. *Atmos. Environ.* 34, 2361–2372.
- Stull, R.B., 1988. *An Introduction to Boundary Layer Meteorology*. Klumer Academic Publishers, Boston, Massachusetts, 666 pp.
- Sutton M.A., Miners B., Tang Y.S., Milford C., Wyers G.P., Duyzer J.H. and Fowler D., 2001a. Comparison of low-cost measurement techniques for long-term monitoring of atmospheric ammonia. *J. Env. Monit.*, 3, 446-453.

- Sutton M.A., Tang Y.S., Miners B., Fowler D., 2001b. A new diffusion denuder system for long-term, regional monitoring of atmospheric ammonia and ammonium. *Water, Air and Soil Pollution: Focus*, 1, Part 5/6, 145-156.
- Sutton, M.A., Tang, Y.S., Miners, B. and Fowler, D., 2001. A new diffusion denuder system for long-term regional monitoring of atmospheric ammonia and ammonium. *Water Air and Soil Pollution: Focus(1)*: 145-156.
- Svensson, L., Ferm, M., 1993. Mass-transfer coefficient and equilibrium concentration as key factors in a new approach to estimate ammonia emission from livestock manure. *Journal of Agricultural Engineering Research* 56, 1–11.
- Tang Y. S., van Dijk N., Love L., Dragosits U., Vieno M., Smith R.I., Ripey B., Sutton M. A., 2004. Ammonia Monitoring in Northern Ireland. Final Report. Available at: <http://www.environmentalresearch.info/search/DatabaseSearchBin.aspx?outputid=88325&type=pdf>.
- Tang Y.S., van Dijk N., Love L., Simmons I., Dore T., Dragosits U., Vogt E., Cape J.N., Smith R.I., Sutton M.A., 2008. Analysis of temporal and spatial patterns of NH_3 and NH_4^+ over the UK - 2006, (ed.), Centre for Ecology and Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK, pp. 30.
- Tang, Y.S., Cape, J.N. and Sutton, M.A. 2001. Development and Types of Passive Samplers for Monitoring Atmospheric NO_2 and NH_3 Concentrations. In *Proceedings of the International Symposium on Passive Sampling of Gaseous Pollutants in Ecological Research*. TheScientificWorld, 1, 513-529.
- Tang, Y.S., Simmons, I., van Dijk, N., Di Marco, C., Nemitz, E., Dammgén, U., Gilke, K., Djuricic, V., Vidic, S., Gliha, Z., Borovecki, D., Mitosinkova, M., Hanssen, J.E., Uggerud, T.H., Sanz, M.J., Sanz, P., Chorda, J.V., Flechard, C.R., Fauvel, Y., Ferm, M., Perrino, C. and Sutton, M.A., 2009. European scale application of atmospheric reactive nitrogen measurements in a low-cost approach to infer dry deposition fluxes. *Agriculture Ecosystems & Environment*, 133(3-4): 183-195.
- Thompson, R.B., Meisinger. J.J. 2002. Management factors affecting ammonia volatilization from cattle slurry following land application in the mid-Atlantic USA. *Journal of Environmental Quality* 31, 1329–1338.
- Thomson, D.J., 1987. Criteria for the selection of stochastic models of particle trajectories in turbulent flows. *Journal of Fluid Mechanics*, 180: 529-556.

- Todd, R.W., Cole, A.N., Clark, N.R., Flesch, T.K., Harper, L.A., Baek, B.H., 2008. Ammonia emissions from a beef cattle feedyard on the southern High Plains. *Atmospheric Environment* 42, 6797–6805.
- Twigg, M.M., House, E., Thomas, R., Whitehead, J., Phillips, G.J., Famulari, D., Fowler, D., Gallagher, M.W., Cape, J.N., Sutton, M.A. and Nemitz, E., 2011. Surface/atmosphere exchange and chemical interactions of reactive nitrogen compounds above a manured grassland. *Agricultural and Forest Meteorology*, In Press, Corrected Proof.
- Valli L., Fabbri C., Bonazzi G., 2001. A national inventory of ammonia and greenhouse gas emissions from agriculture in Italy. RAMIRAN 2000 Proceedings of the 9th International Workshop of the Network General Theme: “Technology Transfer”, Gragnano (Italy), 6-9 September 2000, 153-159.
- von Bobrutzki, K., Braban, C.F., Famulari, D., Jones, S.K., Blackall, T., Smith, T.E.L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M.R., Percival, C.J., Whitehead, J.D., Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M.A. and Nemitz, E., 2010. Field inter-comparison of eleven atmospheric ammonia measurement techniques. *Atmospheric Measurement Techniques*, 3(1): 91-112.
- Weber, R. O., 1999. Remarks on the definition and estimation of friction velocity. *Bound.-Layer Meteor.*, 93, 197–209.
- Whitehead, J.D., Twigg, M., Famulari, D., Nemitz, E., Sutton, M.A., Gallagher, M.W. and Fowler, D., 2008. Evaluation of laser absorption spectroscopic techniques for eddy covariance flux measurements of ammonia. *Environmental Science & Technology*, 42(6): 2041-2046.
- Wilson, J.D., Catchpoole, V.R., Denmead, O.T. and Thurtell, G.W., 1983. Verification of a simple micrometeorological method for estimating the rate of gaseous mass transfer from the ground to the atmosphere. *Agricultural Meteorology*, 29: 183-189.
- Wilson, J.D., Thurtell, G.W., Kidd, G.E. and Beauchamp, E.G., 1982. Estimation of the rate of gaseous mass transfer from a surface source plot to the atmosphere. *Atmospheric Environment*, 16(8): 1861-1867.
- Wyers, G.P., Otjes, R.P. and Slanina, J., 1993. A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia. *Atmospheric Environment*, 27A: 2085-2090.

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 abatement 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 (NH_3), contributing 50% of global NH_3 emissions (Bouwman *et al.*, 1997), over 90% in Europe (EEA, 2011). The reduction of atmospheric NH_3 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, NH_3 , 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 NH_3 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 NH_3 emission from field-applied manure draws attention since it contributes largely to the overall NH_3 volatilization from livestock production. Knowledge of NH_3 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; Søggaard *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; Søggaard *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 4.1. Main characteristics of the trials.

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

(i) Surface spreading of cattle slurry:

- The “SS-11” field 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 $0.22 \text{ m}^3 \text{ m}^{-3}$ and 8.2, respectively. The field was spread on surface with $57 \text{ m}^3 \text{ ha}^{-1}$ of fresh dairy slurry on 10th of October, using a 20 m^3 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 = $\text{NH}_4^+ + \text{NH}_3$) 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 $0.17 \text{ m}^3 \text{ m}^{-3}$ and pH of 7.1. The field surface was spread with $87 \text{ m}^3 \text{ ha}^{-1}$ 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 $0.25 \text{ m}^3 \text{ m}^{-3}$

while the pH was 5.5. On 17th of March 2010 fresh dairy slurry was applied ($54 \text{ m}^3 \text{ ha}^{-1}$) 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 $0.21 \text{ m}^3 \text{ m}^{-3}$ and 6.4, respectively. Dairy slurry was applied on 7th April at the rate of $75 \text{ m}^3 \text{ ha}^{-1}$, 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 then 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 Vulgare L.* The field was spread in 3.5 hours with $55 \text{ m}^3 \text{ ha}^{-1}$ 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 $0.22 \text{ m}^3 \text{ m}^{-3}$ and a pH of 8.

(iii) Injection of cattle slurry

- “INJ-09” was conducted from 22th September to 1st 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 $0.36 \text{ m}^3 \text{ m}^{-3}$ and the soil pH was 7.5. The field was fertilised with $68.5 \text{ m}^3 \text{ ha}^{-1}$ of fresh cattle slurry the 24th 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 14th June 2010 in Landriano on a 10 ha sandy-loam field cultivated with maize and ended the 17th of July 2010. Urea in granular form was surface spread the 18th 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 $0.15 \text{ m}^3 \text{ m}^{-3}$ 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).

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

^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), NH_3 concentration measured in the fertilised field (C) and ammonia background level (C_{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).

		SS-11	SI-09	SI-10	SI-11	SIC-11	INJ-09	UR-10
u_*	$m s^{-1}$							
	min	0	0	0	0	0	0	0
	max	0.37	0.41	0.33	0.41	0.65	0.38	0.50
	mean	0.10	0.14	0.08	0.15	0.13	0.10	0.15
	median	0.09	0.12	0.06	0.14	0.10	0.07	0.14
L	m							
	min	-557	-1816	-4083	-259	-572	-586	-3,293
	max	735	8,216	75,724	7,269	735	1,144	182,962
	mean	3.8	135	198	50	2.2	-1.42	249
	median	-0.05	6	-0.01	0	-0.05	0.18	-1.20
C	$\mu g m^{-3}$							
	min	9	8	0.7	12	4.5	10.1	1.3
	max	820	886	259.6	973	236	78.4	59
	mean	169	197	11	191	46	28.9	18.7
	median	67	53	3.1	48	36	25.1	16.6
C_{bgd}	$\mu g m^{-3}$							
	min	7.7	2	3.1	8	7.7	7.9	3.6
	max	34	84	12.6	29	34	35.2	41.2
	mean	19	39	6.3	16	19	18.8	16.3
	median	16	26	5.5	15	16	18.5	16.6
z_0	m							
	min	0	0	0	0	0	0	0
	max	0.25	0.45	0.30	0.35	0.6	0.08	0.99
	mean	0.05	0.09	0.02	0.06	0.18	0.03	0.7
	median	0.03 ^a	0.02 ^a	0.06 ^a	0.04 ^a	0.04 ^a	0.03 ^a	0.4 ^a

^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.

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

^acumulate 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 $\mu g m^{-3}$ (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

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 NH₃ (C_{bgd}) a sample point was located more than 600 m away from the investigated fields and away from any possible NH₃ sources. The value of air NH₃ 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 :

$$C = D \times S + C_{bgd} \quad (\text{eq 4.1})$$

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

$$S = (C - C_{bgd}) \times D^{-1} \quad (\text{eq 4.2})$$

The hypotheses are: (i) no reaction of NH₃ 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 where 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:

$$D = \frac{1}{N} \sum_{N_{\text{source}}} \left| \frac{2}{w_0} \right| \quad (\text{eq 4.3})$$

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.

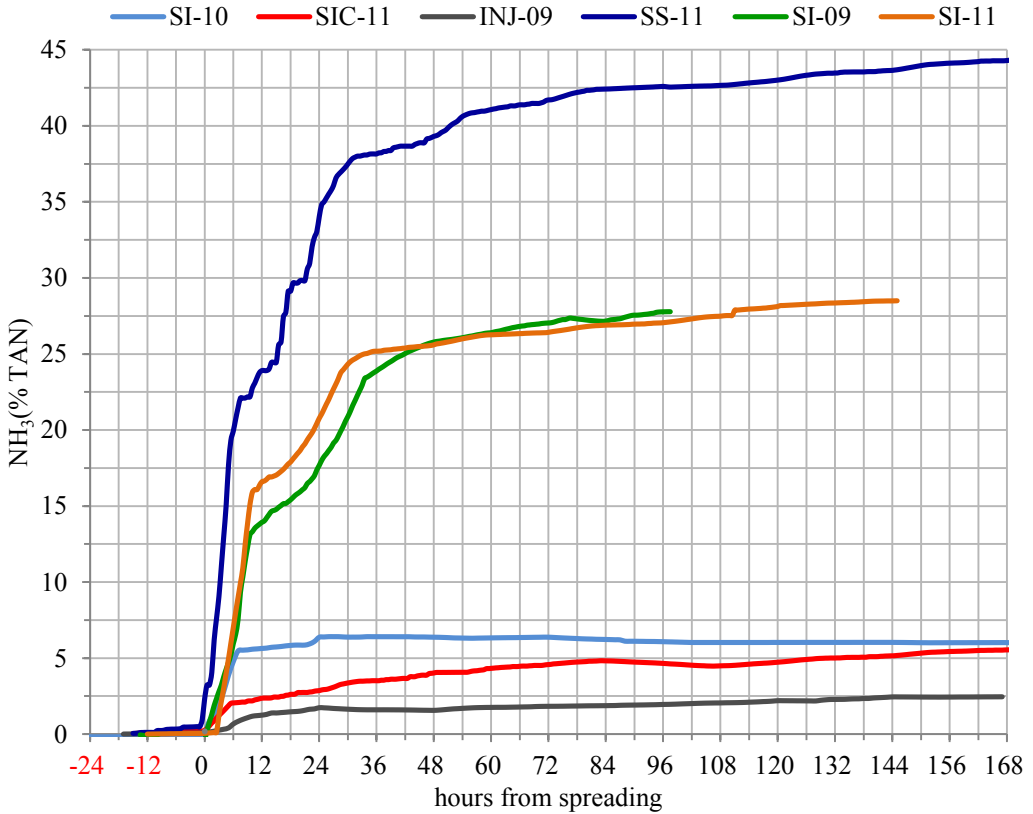


Figure 4.1. Cumulated NH_3 fluxes (%TAN) obtained using WindTrax (see text for explanation of the model) for different slurry spreading technique: surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SIC-11); injection (INJ-09).

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 ($54 \text{ m}^3 \text{ ha}^{-1}$). 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 NH_3 peak, cumulated 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)

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

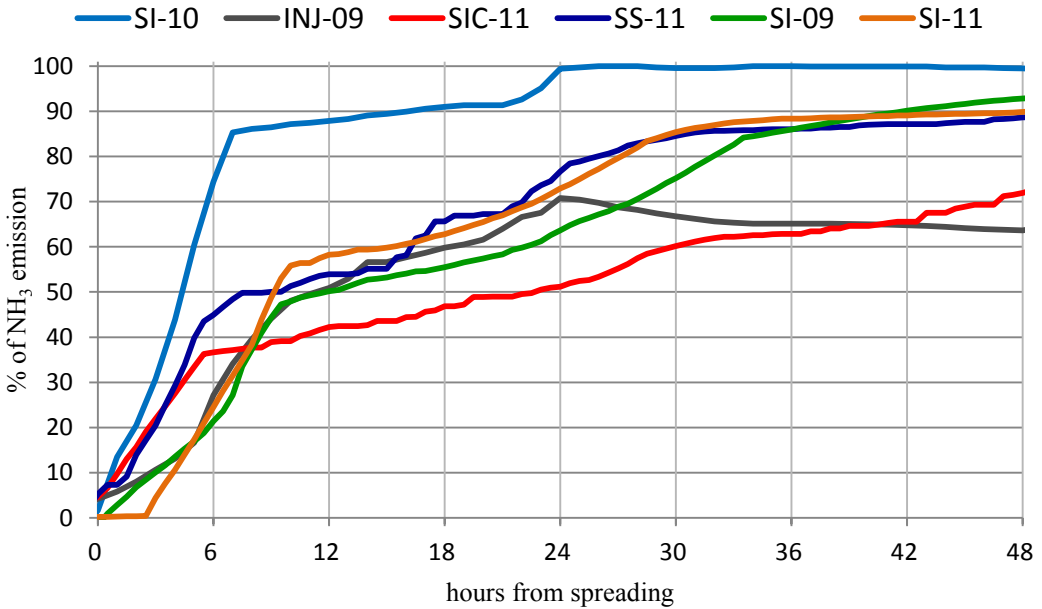


Figure 4.2. Cumulated NH_3 fluxes from WindTrax (see text for explanation of the model) reported as % of total emission during the first 48 hours from the beginning of the slurry spreading: surface spreading (SS-11); surface incorporation (SI-09, SI-10, SI-11, SIC-11); injection (INJ-09).

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 $0.6\% \text{ h}^{-1}$; 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 $6\% \text{ h}^{-1}$ in SS-11, $4\% \text{ h}^{-1}$ in SI-09 and SIC-11, $5\% \text{ h}^{-1}$ in SI-11 and INJ-09, while SI-10 reaching the highest values of $12\% \text{ h}^{-1}$. The maximum hourly loss in terms of N was $3.2 \text{ kg ha}^{-1} \text{ h}^{-1}$ in SS-11 and SI-11, 4 hours and 8 hours after the beginning of the spreading, respectively; about $2.7 \text{ kg ha}^{-1} \text{ h}^{-1}$ in SI-09 at 7 hours; $1.0 \text{ kg ha}^{-1} \text{ h}^{-1}$ in SI-10 at 4 hours; $0.23 \text{ kg ha}^{-1} \text{ h}^{-1}$ in SIC-11 at 2 hours; and $0.36 \text{ kg ha}^{-1} \text{ h}^{-1}$ 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 $1\% \text{ h}^{-1}$ in SS-10 and SIC-11, to $3\% \text{ h}^{-1}$ in SI-09 and INJ-09, $0.5\% \text{ h}^{-1}$ in SI-10, while remain constant for SI-11 ($5\% \text{ h}^{-1}$). During the first night of each trial, the rate of emissions reduced to values around $1.0 \pm 0.5\% \text{ h}^{-1}$, 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

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 is 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 comparison, 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 NH₃ 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 times 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⁻¹) could be responsible of an inhibition of NH₃ volatilization due to absence of mass transport Sommer *et al.* (1991). In this regard and Huijsmans *et al.* (2003) showed that NH₃ losses increased when wind speed increased from 2 to 5 m s⁻¹ resulted on average in a 74% increase in total volatilisation for surface incorporation. Moreover, NH₃ emissions were reported to be very sensitive to slurry and soil pH condition, where the losses increase by increasing of pH values (Freney *et al.*, 1983; Genermont and Cellier,

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; Générmont 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_3 volatilization from urea is reported as cumulative 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_3 emissions after the surface application of urea that increased exponentially from 6 to 24 hours, reaching the maximum emission peak of $170 \text{ g N ha}^{-1} \text{ h}^{-1}$. 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).

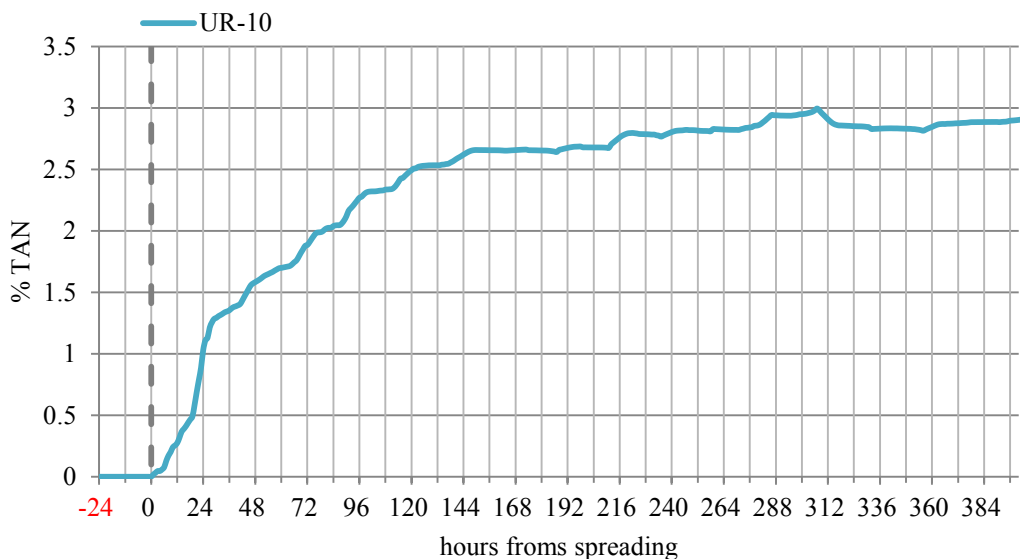


Figure 4.3. Cumulated NH_3 fluxes (%TAN) from WindTrax (see text for explanation of the model) for urea spreading (UR-10).

During the first 24 hours, 35% of the total emission was recorded, with averaged NH_3 losses of $1.7 \mu\text{g m}^{-2} \text{s}^{-1}$. Starting from the day after, the NH_3 emission decreased, remaining always below $1 \mu\text{g m}^{-2} \text{s}^{-1}$ 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 $1 \mu\text{g m}^{-2} \text{s}^{-1}$ 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 $4 \mu\text{g m}^{-2} \text{s}^{-1}$ following surface application of 120 kg N ha^{-1} , while Meyers *et al.* (2006) reported maximum fluxes of about $2.6 \mu\text{g m}^{-2} \text{s}^{-1}$ 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 $0.4\% \text{ h}^{-1}$, equivalent to a loss of $10 \text{ g N ha}^{-1} \text{ h}^{-1}$. At 120 hours the NH_3 loss was 83% of the total one. Starting from the 5th day, until the reaching of the maximum value of the accumulation (307 h), the emission rate was further reduced to values around $2.6 \text{ g N ha}^{-1} \text{ h}^{-1}$, 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 NH_3 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 NH_3 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

- Amberger, A., 1991. Ammonia emission during and after land spreading of slurry. In: Nielsen, V.C., Voorburg, J.H., L'Hermite, P. (Eds.), *Odour and Ammonia Emissions from Livestock Farming*. Elsevier Applied Science, London, pp. 126–131.
- Asman, W. A. H. 1992. Ammonia emission in Europe: Update emission and emission variations. Report 228471008. National Institute of Public health and Environmental protection, Bilthoven, The Netherlands.
- Bouwman, A.F., Boumans, L.J.M., Batjes, N.H., 2002. Estimation of global NH₃ volatilization loss from synthetic fertilisers and animal manure applied to arable lands and grasslands. *Global Biogeochemical Cycles* 16 (2), 1024.
- Bouwman, A.F., et al., 1997. A global high-resolution emission inventory for ammonia. *Global Biogeochemical Cycles* 11, 561–587.
- Bowman, D. C., Paul J. L., Davis W. B. and Nelson S. H., 1987. Reducing ammonia volatilization from kentucky bluegrass turf by irrigation. *Hortscience* 22(1): 84-87.
- Braschkat, J., Mannheim, T., Marschner, H., 1997. Estimation of ammonia losses after application of liquid cattle manure on grassland. *Z. Pflanz. Bodenk.* 160, 117-123.
- Brunke, R., Alvo, P., Schuepp, P., Gordon, R., 1988. Effect of meteorological parameters on ammonia loss from manure in the field. *Journal of Environmental Quality* 17, 431–436.
- Businger, J. A. and Oncley, S. P.: Flux Measurements with Conditional Sampling, *J. Atmos. Oceanic Technol.*, 7(2), 349–352, 1990.
- Bussink, D.W., J.F.M. Huijsmans & J.J.M.H Ketelaars, 1994. Ammonia volatilization from nitric-acid-treated cattle slurry surface applied to grassland. *Netherlands Journal of Agricultural Science* 42: 293-309.
- Clarisse, L., C. Clerbaux, F. Dentener, D. Hurtmans and P.F. Coheur (2009), Global ammonia distribution derived from infrared satellite observations, *Nat. Geosci.*, 2(7), 479–483.
- Court, M.N., Stephen R.C. and Waid. J.S., 1964. Toxicity as a cause of the inefficiency of urea as a fertilizer. *J. Soil Sci.* 15:42-48.
- CRPA, 2006. Progetto MeditAIRaneo: settore Agricoltura. Relazione finale. Technical report on the framework of the MeditAIRaneo project for the Agriculture sector, Reggio Emilia – Italia

- ECETOC, 1994. Ammonia emissions to air in Western Europe. Technical report No. 62. European Centre for Ecotoxicology and Toxicology of Chemicals. Brussels, Belgium, 196pp.
- EEA, 2011. NEC Directive status report 2010. Technical report No 3/2011. <http://www.eea.europa.eu/publications/nec-directive-status-report-2010>
- EMEP/CORINAIR, 2007. Atmospheric Emission Inventory Guidebook. Technical report No 16/2007.
- EMEP/EEA, 2009. Air Pollutant Emission Inventory Guidebook. Technical report n. 9/2009.
- EUROSTAT, 2011. Livestock in UE-27 Available at http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=food_in_pagr1&lang=en, accessed on 17/01/2012.
- Ferguson, R.B., McInnes, K.J., Kissel, D.E., Kanemasu, E.T., 1987. Comparison of methods of estimating ammonia volatilization in the field. *Fertilizer Res.* 15, 55–69.
- Ferm, M., Kasimir-Klemedtsson, A., Weslien, P., Klemedtsson, L., 1999. Emission of NH₃ and N₂O after spreading of pig slurry by broadcast or band spreading. *Soil Use and Management*, 15, 27-33.
- Ferrara, R. M., 2008. Study of the soil-crop-atmosphere continuum under Mediterranean climate: role of H₂O, CO₂ and NH₃ emissions from arable land. PhD thesis. Seconda Università Degli Studi Di Napoli.
- Flesch, T., Wilson, J.D., Yee, E., 1995. Backward-time Lagrangian stochastic dispersion models, and their application to estimate gaseous emissions. *J. Appl. Meteor.* 34, 1320–1332.
- Flesch, T.K., J.D. Wilson, L.A. Harper, and Crenna, B.P.. 2005. Estimating gas emission from a farm using an inverse-dispersion technique. *Atmospheric Environ.* 39:4863-4874
- Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P. and Sharpe, R.R., 2004. Deducing ground-to-air emissions from observed trace gas concentrations: A field trial. *Journal of Applied Meteorology*, 43(3): 487-502.
- Fowler, D., Sutton, M.A., Smith, R.I., Pitcairn, C.E.R., Coyle, M., Campbell, G., Stedman, J., 1998. Regional mass budgets of oxidized and reduced nitrogen and their relative contribution to the nitrogen inputs of sensitive ecosystems. *Environmental Pollution* 102, 337–342.

- Freney, J.R., J.R. Simpson and O.T. Denmead. 1983. Volatilization of ammonia. Gaseous loss of nitrogen from plant-soil systems. (Eds) J.R. Freney and J.R. Simpson. pp.1-32. Martinus Nijhoff, The Hague.
- Génermont, S., and P. Cellier, 1997: A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. *Agricultural and Forest Meteorology*, 88:145-167.
- Harper, L. A., Catchpoole, V. R., Davis, R. and Weir, K. L. 1983. Ammonia volatilization: soil, plant and microclimate effects on diurnal and seasonal fluctuations. *Agron. J.* 75: 212–218.
- Hensen A., Loubet B., Mosquera J., van den Bulk W. C. M., Erisman J. W., Dämmgen U., Milford C., Löpmeier F. J., Cellier P., Mikuška P., Sutton M. A., 2009. Estimation of NH₃ emissions from a naturally ventilated livestock farm using local-scale atmospheric dispersion modeling. *Biogeosciences*, 6, 2847–2860
- Hoff, J.D., Nelson, D.W., Sutton, A.L., 1981. Ammonia volatilization from liquid swine manure applied to cropland. *Journal of Environmental Quality* 10, 90–95.
- Huijsmans, J. F. M., Hol, J. M. G., and Vermeulen, G. D., 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land, *Atmos. Environ.*, 37, 3669–3680.
- Huijsmans, J.F.M., Hol, J.M.G., Hendriks, M.M.W.B., 2001. Effect of application technique, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to grassland. *Netherlands Journal of Agricultural Science* 49, 323–342.
- Huijsmans, J.F.M., Hol, J.M.G., Vermeulen, G.D., 2003. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. *Atmos. Environ.* 37, 3669–3680.
- IPPC, 1996. Concerning integrated pollution prevention and control. EEC/96/61, Official Journal No. L257 10.10.96, Brussels.
- Ismail, K.M., Wheaton, F.W., Douglass, L.W., Potts, W., 1991. Modelling ammonia volatilization from loamy sand soil treated with liquid urea. *Transactions of the ASAE* 34, 756–763.
- ISPRA, 2011. Italian emission inventory 1990-2009. Information inventory report 2011. Rapporti 138/2011. Available at:

- <http://www.eea.europa.eu/publications/european-union-emission-inventory-report>.
- ISTAT, 2011. Istituto nazionale di statistica, 6° censimento generale dell'agricoltura. Risultati provvisori. Available at: <http://censimentoagricoltura.istat.it/fileadmin/template/main/res/comunicato-censimento-agricoltura.pdf>
- Jarvis, S.C. and B.F. Pain. 1990. "Ammonia volatilisation from agricultural land". The fertiliser society proceedings. No. 298. pp.1-35. The Fertiliser Soc., London.
- Leith I.D., Sheppard L.J., Fowler D., Cape J.N., Jones M., Crossley A., Hargreaves K.J., Tang Y.S., Theobald M., Sutton M.A., 2004. Quantifying dry NH₃ deposition to an ombrotrophic bog from an automated NH₃ field release system. *Water, Air, & Soil Pollution: Focus* 4, 207-218.
- Loubet B., Générumont S., Ferrara R., Bedos C., Decuq C., Personne E., Fanucci O., Durand B., Rana G., Cellier P., 2010 - An inverse model to estimate ammonia emissions from fields. *European Journal of Soil Science*, 61, 5, 793–805.
- Loubet B., Générumont S., Personne E., Massad R.S., 2011. Can we estimate ammonia emissions by inverse modelling with time averaged concentrations? *Proceedings of Nitrogen & Global Change Key findings – future challenges*, Edinburgh April 11 – 15, 2011 [Unpublished].
- Loubet B., Milford C., Hensen A., Daemmgen U., Erisman J.W., Cellier P., Sutton M.A. - 2009 Advection of NH₃ over a pasture field and its effect on gradient flux measurements. *Biogeosciences*, 6, 1295-1309.
- Loubet, B. and Cellier, P., 2001. Experimental assessment of atmospheric ammonia dispersion and short range dry deposition in a maize canopy. *Water, Air and Soil Pollution: Focus*, 1: 157-166.
- McInnes, K.J., Ferguson, R.B., Kissel, D.E., Kanemasu, E.T., 1986. Field measurements of ammonia loss from surface application of urea solution to bare soil. *Agron. J.* 78, 192–196.
- Meisinger, J.J., and W.E. Jokela. 2000. Ammonia volatilization from dairy and poultry manure. p. 334-354. In: *Proc Managing nutrients and pathogens from animal agriculture*. Camp Hill, PA. 28-30 Mar., 2000. NRAES-130. Ithaca, NY
- Menzi, H., Pain, B., Sommer, S.G., 2002. Manure management: the European perspective. In: Ong, H.K., Zulkifli, I., Tee T.P., Liang, J.B. (Eds.), *Global*

- Perspective in Livestock Waste Management. Malaysian Society of Animal Production, Selangor, Malaysia, pp. 35-44.
- Meyers, T. P., Luke, W. T., and Meisinger, J. J., 2006. Fluxes of ammonia and sulfate over maize using relaxed eddy accumulation, *Agr. Forest Meteorol.*, 136, 203–213.
- Misselbrook, T. H., Smith, K. A., Johnson, R. A., and Pain, B. F., 2002. Slurry application techniques to reduce ammonia emissions: Results of some UK field-scale experiments, *Biosyst. Eng.*, 81, 313–321
- Misselbrook, T.H., J.M. Powell, G.A. Broderick, and J.H. Grabber. 2005a. Dietary manipulation in dairy cattle: Laboratory experiments to assess the influence of ammonia emissions. *J. Dairy Sci.* 88:1765–1777.
- Moal, J.F., Martinez, J., Guiziou, F., Coste, C.M., 1995. Ammonia volatilization following surface-applied pig and cattle slurry in France. *J. Agric. Sci.* 125, 245-252.
- Nemitz, E, Dorsey, JR., Flynn, MJ., Gallagher, MW., Hensen, A., Erisman, JW., Owen, SM., Dammgren, U., Sutton, MA., 2009. Aerosol fluxes and particle growth above managed grassland. *Biogeosciences*. Vol. 6, pp. 1627-1645.
- Paerl, H.W., Dennis, R.L., Whittall, D.R., 2002. Atmospheric deposition of nitrogen: implications for nutrient over-enrichment in coastal waters. *Estuaries* 25, 677–683.
- Pinder, R. W., Walker J. T., Bash J. O Cady-Pereira, K. E., Henze D. K., Luo M., Osterman G. B. and Shephard M. W., 2011. Quantifying spatial and seasonal variability in atmospheric ammonia with in situ and space-based observations, *Geophys. Res. Lett.*, 38.
- Rochette, P., J. D. MacDonald, D. A. Angers, M. H. Chantigny, M. O. Gasser and N. Bertrand, 2009. Banding of urea increased ammonia volatilization in a dry acidic soil. *Journal of Environmental Quality* 38(4): 1383-1390.
- Rotz, C. A. 2004. Management to reduce nitrogen losses in animal production. *J. Anim. Sci.* 82 (E. Suppl.): E119-E137.
- Schjørring J. K., Ferm M. & Sommer, S. G. 1992. Measurement of NH₃ emission and deposition by the gradient method: Can passive flux samplers be used to obtain the net exchange of NH₃ through periods of several days with varying wind speed and atmospheric NH₃ concentration? In Allegrini, I. (ed) *Proc from Development of Analytical Techniques for Atmospheric Pollutants Rome*, April 13-15, 1992. pp 21-34.

- Skjøth C. A., Geels C., Berge H., Gyldenkærne S., Fagerli H., Ellermann T., Frohn L.M., Christensen J., Hansen K. M., Hansen K., Hertel O., 2011. Spatial and temporal variations in ammonia emissions – a freely accessible model code for Europe. *Atmos. Chem. Phys.*, 11, 5221–5236.
- Søgaard, H.T., Sommer, S.G., Hutchings, N.J., Huijsmans, J.F.M., Bussink, D.W., Nicholson, F., 2002. Ammonia volatilization from field applied animal slurry: the ALFAM model. *Atmos. Environ.* 36, 3309-3319.
- Sommer, S. G. and Hutchings, N. J., 2001. Ammonia emission from field applied manure and its reduction – invited paper, *Eur. J. Agron.*, 15, 1–15.
- Sommer, S.G. and B.T. Christensen. 1991. Effect of dry matter content on ammonia loss from surface applied cattle slurry. *Odour and Ammonia Emissions from Livestock Farming*. (Eds) V.C. Nielsen et al. pp. 141-147. Elsevier, London.
- Sommer, S. G., McGinn, S. M., and Flesch, T. K., 2005. Simple use of the backwards lagrangian stochastic dispersion technique for measuring ammonia emission from small field-plots, *Eur. J. Agron.*, 23, 1–7.
- Sommer, S.G., Genermont, S., Cellier, P., Hutchings, N.J., Olesen, J.E. and Morvan, T., 2003. Processes controlling ammonia emission from livestock slurry in the field. *European Journal of Agronomy*, 19(4): 465-486.
- Sommer, S.G., Hutchings, N.J., Carton, O.T., 2001. Ammonia losses from field applied animal manure. Report No. 60, Plant Production, Danish Institute of Agricultural Sciences, Horsens, Denmark.
- Sommer, S.G., Jensen, C., 1994. Ammonia volatilisation from urea and ammoniacal fertilizers' surface applied to winter wheat. *Fertilizer Research* 37, 85-92.
- Sommer, S.G., Olesen, J.E., 2000. Modelling ammonia volatilization from animal slurry applied to cereals. *Atmos. Environ.* 34, 2361-2372.
- Stevens, R.J., R.J. Laughlin & J.P. Frost, 1992. Effects of separation, dilution, washing and acidification on ammonia volatilization from surface-applied cattle slurry. *Journal of Agricultural Science, Cambridge* 119: 383-389.
- Stull, R.B., 1988. *An Introduction to Boundary Layer Meteorology*. Klumer Academic Publishers, Boston, Massachusetts, 666 pp.
- Sutton M.A., Miners B., Tang Y.S., Milford C., Wyers G.P., Duyzer J.H. and Fowler D., 2001. Comparison of low-cost measurement techniques for long-term monitoring of atmospheric ammonia. *J. Env. Monit.*, 3, 446-453.

- Sutton M.A., Tang Y.S., Miners B., Fowler D., 2001b. A new diffusion denuder system for long-term, regional monitoring of atmospheric ammonia and ammonium. *Water, Air and Soil Pollution: Focus*, 1, Part 5/6, 145-156.
- Svensson L., and Ferm M. 1993. Mass transfer coefficient and equilibrium concentration as key factors in a new approach to estimate ammonia emission from livestock manure. *Journal of Agricultural Engineering Research* 56, 1-11.
- Tang Y.S., van Dijk N., Love L., Simmons I., Dore T., Dragosits U., Vogt E., Cape J.N., Smith R.I., Sutton M.A., 2008. Analysis of temporal and spatial patterns of NH₃ and NH₄⁺ over the UK - 2006, (ed.), Centre for Ecology and Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK, pp. 30.
- Tang, Y.S., Cape, J.N. and Sutton, M.A. 2001. Development and Types of Passive Samplers for Monitoring Atmospheric NO₂ and NH₃ Concentrations. In *Proceedings of the International Symposium on Passive Sampling of Gaseous Pollutants in Ecological Research*. The Scientific World, 1, 513-529.
- Thomson, D.J., 1987. Criteria for the selection of stochastic models of particle trajectories in turbulent flows. *Journal of Fluid Mechanics*, 180: 529-556.
- Todd, R.W., Cole N.A., Clark R.N., Flesch T.K., Harper L.A. and Baek B.H.. 2008. Ammonia emissions from a beef cattle feedyard on the southern High Plains. *Atmos. Environ.* 42:6797–6805.
- Turner, D. A., Edis R. B., Chen D., Freney J. R., Denmead O. T. and Christie R., 2010. Determination and mitigation of ammonia loss from urea applied to winter wheat with n-(n-butyl) thiophosphorictriamide. *Agriculture Ecosystems & Environment* 137(3-4): 261-266.
- Valli L., Còndor R.D., 2011. National ammonia emissions scenarios from the agronomic land spreading and the use of nitrogen fertilizers in Italy. CRPA, ISBN: 978-88-904312-3-4.
- Valli L., Fabbri C., Mazzotta V., Bonazzi G., 2003, "Clima, Ambiente: Tecniche di abbattimento per l'Ammoniaca e altri gas serra da allevamenti suini ed avicoli". Settima conferenza nazionale delle agenzie ambientali, Milano 2003.
- Van Der Molen, J., Van Faassen, H.G., Leclerc, M.Y., Vriesema, R., Chardon, W.J., 1990. Ammonia volatilization from arable land after application of cattle slurry. 1. Field estimates. *Journal of Agricultural Science* 38, 145–158.
- Walker, J.T., Aneja, V.P., Dickey, D.A., 2000. Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmospheric Environment* 34, 3407–3418.

- Webb, J., Pain, B., Bittman, S., and Morgan, J.: The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response-A review, *Agr. Ecosyst. Environ.*, 137, 39–46.
- Wienhold, F.G., Frahm, H., Harris, G.W., 1994. Measurements of N₂O fluxes from fertilised grassland using a fast tunable diode laser spectrometer. *Journal of Geophysical Research* 99, 16557-16568.
- Wyers, G. P., Otjes, R. P., and Slanina, J.: A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia, *Atmos. Environ.*, 27A(13), 2085–2090, 1993.
- Zhu T., Pattey E. and Desjardins R.L., 2000. Relaxed eddy-accumulation technique for measuring ammonia volatilization. *Environmental Science & Technology*, 34, 199-203.

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 Générumont and Cellier

(1997). 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 NH_3 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 NH_3 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_2O 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).

Input data	Units	Range	Information	SI-09	SI-11
Day of the beginning of the run	day of year	1 - 1000		84.000	96.833
Day of the end of the run	day of year	1 - 1000		96.958	103.375
Time step of the model	minutes	1 - 180	must correspond to the time step of weather and optional variables input files	60	60
Type of experiment		"P" or "T"	P = field T = wind tunnel	P	P
parcel length		"yes" or "no"	"oui": calculation using the configuration parcel and wind direction from weather file "non": reading the value of parcel dimension in the file weather	yes	yes
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 <i>et al.</i> (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

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).

Input data	Units	Range	Information	SI-09	SI-11
Type of application	dimensionless	0-3	0 = no application 1 = N fertiliser application organic or mineral 2 = pesticide application 3 = N fertiliser and pesticide application	1	1
Number of soil managements	dimensionless	0-5		1	1
Case of soil management, for each management					
Day and hour of soil management	day of year	1 - 1000		87.334	98.375
Type of cultivation technique	dimensionless	1	No choice for the moment: 1	1	1
Depth of cultivation	m			0.15	0.15
Proportion of incorporated soil	dimensionless	0-1	1 for commercial mineral fertilisers Eye appreciation: 0 no soil incorporation 1 totally incorporation	0.8	0.8
Number of irrigations)	dimensionless	1		0	0
Case of irrigation, for each irrigation					
Day and hour of irrigation	day of year	1 - 1000			
Water volume applied	mm = L m ⁻²	0 - 100			
Case of N fertiliser application					
Type of fertiliser	dimensionless	10-40	10 = slurry surface applied 20 = NH ₄ -NO ₃ granules surface applied 30 = urea prills surface applied 35 = urea granules surface applied 40 = N solution surface applied	10	10
Day and hour of N application	day of year	1 - 1000		86.334	97.375
If "Type of fertiliser" ≠ 10 : Rate of N applied	kg N ha ⁻¹				
If "Type of fertiliser" = 10 : Slurry applied	m ³ fresh slurry ha ⁻¹	0 - 1000	density of slurry can be assumed to be 1000 kg m ⁻³ if not available	87.18	75.20

Type of application technique	dimensionless	0-1	0 = surface 1 = bands	0	0
Case technique application bands					
Proportion covered by the product applied	dimensionless	0.01-0.99	0.33 for slurry; default is “NR”		
Case of slurry surface or incorporated = 10					
Type of modelling of the slurry layer	dimensionless	0-2	0 = slurry applied within the first layer of soil 1 = consideration of 1 individualized surface layer of slurry 2 = consideration of 2 individualized surface layers of slurry	1	1
Dry mater content of the slurry	g kg ⁻¹ fresh matter	0-1000	not directly used in the model	43.88	54.5
Total Nitrogen content of the slurry	g kg ⁻¹ fresh matter		density of slurry, assumed to be 1000 kg m ⁻³	2.160	2.970
Total Ammoniacal Nitrogen content of the slurry	g kg ⁻¹ fresh matter		density of slurry, assumed to be 1000 kg m ⁻³	1.095	1.450
Total Nitrate Nitrogen content of the slurry	g kg ⁻¹ fresh matter		if available, otherwise NR	NR	NR
Slurry pH	-	0.01-13.99	very important	8.00	7.76
Slurry CEC	cmol ⁺ kg ⁻¹ dry matter		if available, otherwise NR	NR	NR
Slurry density	kg m ⁻³	0-2000	if available, otherwise 1000 kg m ⁻³	1000	1000
Bulk density of the slurry dry matter	kg m ⁻³	0-2000	if available, otherwise 1000 kg m ⁻³	100	100
Critical application rate for uniform application	m ³ ha ⁻¹	0 - 1000	60 m3 ha-1 as a default value	60	60
Case water retention model = CH (general information)					
Infiltration correction fact for the 1 layer of soil	dimensionless	0 - 1	0.02 for liquid slurry spreading		
Case water retention model = VG (general information)					
VG parameters for the slurry: teta_sat	m ³ m ⁻³	0 - 1		0.996	0.996
VG parameters for the slurry: teta_r	m ³ m ⁻³	0 - 1		0.373	0.373
VG parameters for the slurry: alpha	m ⁻¹	> 0		3.6	3.6
VG parameters for the slurry: n	-	> 1		1.361	1.361
VG parameters for the slurry: Ksat	m s ⁻¹	> 0		8.34E-08	8.34E-08

Appendix C: Required soil inputs of Vol’Air model for the two trials described in the text (SI-09 and SI-11).

APPENDIX

Input data	Units	Range	SI-09					SI-11				
			Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5
Layer depth	m	0 - 2	0.02	0.05	0.1	0.2	0.4	0.02	0.05	0.1	0.2	0.4
Clay < 2 μm	g kg ⁻¹	0 - 1000	173	173	173	173	182	168	168	168	174	185
Silt 2-50 μm	g kg ⁻¹	0 - 1000	454	454	454	454	590	49.5	495	495	556	582
Sand 50-2000 μm	g kg ⁻¹	0 - 1000	373	373	373	373	228	337	337	337	270	233
Initial soil water content	g kg ⁻¹	0 - 1000	138	138	138	138	143.7	208	208	208	211	192
pH	-	0 - 14	7.14	7.14	7.14	7.14	7.5	6.3	6.3	6.3	6.3	6.3
Organic carbon	g kg ⁻¹	0 -1000	14.5	14.5	14.5	14.5	12.8	17.0	17.0	17.0	18.8	18.6
Initial N-NH ₄ content	mg kg ⁻¹	0 - 1000	0.72	0.72	0.72	0.72	0.80	2.22	2.22	2.22	4.69	0.84
Initial N-NO ₃ content	mg kg ⁻¹	0 - 1000	8.32	8.32	8.32	8.32	6.60	8.89	8.89	8.89	14.1	2.86
Cation exchange capacity	cmol kg ⁻¹	0 - 200	11	11	11	11	11	11	11	11	11	11
Bulk density	kg m ⁻³	0 - 3	1423	1423	1423	1423	1388	1420	1420	1420	1402	1386
Water content at saturation	m ³ m ⁻³	0 - 1000	0.425	0.425	0.425	0.425	0.436	0.463	0.463	0.463	0.461	0.459
Residual water content	m ³ m ⁻³	0 - 1000	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
alpha	m ⁻¹	> 0	0.03	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02
n	-	1 - 2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Saturation conductivity	m s ⁻¹	10 ⁻⁶ - 10 ⁻⁴	2.59×10 ⁻⁰⁶	2.59×10 ⁻⁰⁶	2.59×10 ⁻⁰⁶	2.59×10 ⁻⁰⁶	1.71 ×10 ⁻⁰⁶	2.97×10 ⁻⁰⁶	2.97×10 ⁻⁰⁶	2.97×10 ⁻⁰⁶	2.43×10 ⁻⁰⁶	2.25 ×10 ⁻⁰⁶

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.).

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