Field-scale ammonia emissions from surface spreading of dairy slurry in Po Valley

Marco Carozzi[1], Rossana Monica Ferrara[2], Mattia Fumagalli[1], Mattia Sanna[1], Marcello Chiodini[1], Alessia Perego[1], Alessandro Chierichetti[1], Stefano Brenna[3], Gianfranco Rana[2], Marco Acutis[1]*

Abstract: *Po Valley (Northern Italy) is one of the major ammonia (NH_3) emitting regions of Europe, where the slurry spreading causes high NH_3 volatilisation, reducing its agronomic value and becoming a potential cause of environmental concerns. In autumn 2011 a field trial was conducted to estimate the NH_3 losses from the application of dairy slurry at rate of 57 m^3 ha^{-1} on bare soil. The emissions were estimated from surface application of dairy slurry by using an inverse dispersion modelling technique associated with long term exposure passive samplers and the measure of the atmospheric turbulence. NH_3 emissions levels resulted high within the first 24 hours from the spreading, reaching the 73% of the entire losses, with a maximum value of 163 μg m^{-2} s^{-1} after 3 hours and 20 minutes, whereas the 50% of the emissions was achieved after 10 hours. The phenomenon stopped after 168 hours with a total NH_3 losses equal to 44% of the total ammoniacal nitrogen (TAN) applied. Results showed and confirmed that surface application involves high NH_3 emissions and then alternative low-emission techniques have to be adopted.*
Keywords: *ammonia emissions, inverse dispersion modeling, surface slurry application, passive samplers.*

Riassunto: *In pianura Padana la distribuzione superficiale dei reflui zootecnici determina elevate emissioni di ammoniaca (NH_3), riducendo il loro valore agronomico e causando problemi ambientali. L'obiettivo di questo studio è la stima dell'emissione di NH_3 a seguito di una distribuzione superficiale di 57 m^3 ha^{-1} di reflui zootecnici su suolo nudo nell'autunno 2011. La stima è stata effettuata mediante l'applicazione di un modello per la dispersione degli inquinanti, associato alla misura della concentrazione dell'NH_3 mediante esposizione in pieno campo di campionatori a diffusione passiva e all'utilizzo di un anemometro sonico per la misura della turbolenza atmosferica. L'emissione di ammoniaca è stata elevata nelle prime 24 h dalla distribuzione, evidenziando un picco massimo dopo 3 ore e 20 minuti (163 μg m^{-2} s^{-1}), laddove il 50% dell'intera emissione è stato raggiunto già a 10 ore dalla distribuzione. L'emissione di NH_3 è stata pari al 44% del totale di azoto ammoniacale applicato. I risultati mostrano e confermano come la distribuzione superficiale sia un metodo che determina alte perdite di ammoniaca e che quindi deve essere incentivato l'uso di tecniche alternative.*
Parole chiave: *emissioni di ammoniaca, modelli a dispersione, distribuzione superficiale dei reflui, campionatori passivi.*

INTRODUCTION

Agriculture is the primary source of gaseous ammonia (NH_3) in atmosphere and its emissions are mainly originated from the field application of animal manure and fertilisers (Gènermont *et al.*, 1998; Sommer *et al.*, 2001; Asman *et al.*, 2004), animal waste and grazing (Jarvis and Pain, 1990).

Ambient NH_3 assumes an important role and growing interest among different atmospheric nitrogen reactive species as a key to mitigate the impact of nitrogen (N) on terrestrial ecosystems (Sutton, 2006). The environmental issues due to NH_3 emissions include mainly acidification of soils, eutrophication of water with loss of biodiversity, respiratory diseases 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 NH_3 is expected to be the largest single contributor to acidification, eutrophication and formation of secondary particulate matter (Ammann *et al.*, 2005).

The need of reliable NH_3 measurements at field-scale becomes decisive (i) to promote abatement strategies, (ii) to derive emission factors to be used in national and international emission inventories, (iii) to validate models, (iv) to evaluate the ammonia exchange over natural surfaces in the continuum soil-plants-atmosphere domain, (v) to quantify the value of agronomic N-fertilisers.

The ammoniacal losses from agriculture contributes to over 90% in Europe (EEA, 2011), where Po Valley (Northern Italy) is one of the most emitting region of the whole area (Skjøth *et al.*, 2011). Nevertheless, the lack of measured data at

* Correspondig author Marco Carozzi
e-mail: marco.carozzi@unimi.it
[1] Dipartimento di Scienze Agrarie e Ambientali, Università degli Studi di Milano.
[2] CRA – SCA, Unità di ricerca per i sistemi colturali degli ambienti caldo-aridi, Bari.
[3] Ente Regionale per i Servizi alla Agricoltura e Foreste, Milano

field scale in such region (Valli *et al.*, 2001), was only recently filled (Carozzi, 2011).

NH$_3$ losses from field-applied manure, particularly slurry, were measured in many European experiments (Søgaard *et al.*, 2002; Sintermann *et al.*, 2011a). Due to the sticky characteristics given by its polar configuration, NH$_3$ is capable to bind and to be released from solid surfaces, resulting in biased measurement of the emission. However, despite many techniques have been developed (Brodeur *et al.*, 2009), a standardized method is not yet available. The different techniques vary with regard to sensitivity, selectivity and speed; furthermore measuring NH$_3$ is often expensive, extensive and time consuming (Aneja 1997; Harper and Sharpe, 1998). Nowadays among all the available techniques for measuring or estimating NH$_3$, the most popular are (i) fluxes measurement approaches, as enclosure methods (Mosier, 1989) and micrometeorological methods (Kaimal and Finnigan, 1994), (ii) concentration-based dispersion modelling, Lagrangian (Flesch *et al.*, 2004), Eulerian (Loubet *et al.*, 2010) or Gaussian (Gash, 1985) types, and (iii) ammonia emission models (Gènermont and Cellier, 1997).

The emission of NH$_3$ at field-scale depends on the interaction of various factors which contribute to decrease or increase the losses: fertiliser type (nitrogen content, pH, dry matter), soil type (water content, soil reaction), cultivation techniques (amount and application methods of fertilisers) and climatic conditions (temperature, wind speed, rainfall) (Sommer *et al.*, 1991; Moal *et al.*, 1995; Génermont and Cellier, 1997; Sommer *et al.*, 2001; Sommer and Hutchings 2001; Søgaard *et al.*, 2002; Misselbrook *et al.*, 2005).

The aim of this study was to estimate the NH$_3$ emissions caused by surface spreading of dairy slurry by using a concentration-based dispersion model. The quantification of the NH$_3$ fluxes was obtained by applying the backward Lagrangian Stochastic model (bLS) WindTrax (Flesch *et al.* 1995; 2004), since it has been increasingly employed in the last years (Sintermann *et al.* 2011b; Ni *et al.* 2012). The model was implemented by the use of passive diffusion samplers (Tang *et al.*, 2001) and the measure of atmospheric turbulence.

MATERIALS AND METHODS

The experimental site

The trial was performed from the 9th to 17th of October 2011 in Bigarello (MN), (Lat. 45°11' N, Long. 10°54' E, Alt. 23 m a.s.l.) in a field of 4.3 ha

characterized by silty-clay soil (Hypercalcic Calcisol). Maize crop was previously harvested in September and stubbles were chopped and left on the surface. A uniform dairy slurry application rate of 57 m^3 ha^{-1} was applied on 10th of October using a 20 m^3 tank equipped with a splash plate. The spreading started from the longitudinal row passing to the centre of the field, close to measuring devices, towards the upwind edge, and then from the centre to the downwind side of the field. The slurry application (started at 8.15 a.m. and lasted 4 hours) supplied 68 kg N ha^{-1} of total ammoniacal nitrogen (TAN = NH$_4^+$ + NH$_3$). The TAN content was the 63% of the total slurry N content, while the values of the dry matter and the pH were 30 g kg^{-1} and 7.5, respectively.

Meteorological data were collected by a standard weather station, located close to the field. During the trial air temperature ranged from 0 to 25°C (mean value: 12.3°C), relative humidity was 29 to 98% (mean value: 65.5%). The mean of wind speed was 1.2 m s^{-1} with a maximum value of 4.7 m s^{-1}, whereas the main wind direction was SW. No rain events occurred in the sampling period.

During the experiment ammoniacal (NH$_4$–N) and nitrate (NO$_3$–N) nitrogen, pH and water content were daily measured at 0-5 cm and 5-15 cm soil depth. Particularly, concentrations of soil NH$_4$–N and NO$_3$–N were performed with a KCl extraction and determined by spectrometric detection (FIAstar 5000 Analyzer, Foss Tecator, Denmark). These analysis were in agreement with the ISO 11732 (1997) and ISO 13395 (1996) procedures. The values of soil pH were obtained in water solution with a soil-to-solution ratio of 1:2.5 (weight/volume), whereas the soil water content (SWC) was determined gravimetrically for each soil sample by the oven-drying method.

Air ammonia measurements

The air NH$_3$ concentration was quantified through the exposure of the passive samplers ALPHA (Adapted Low-cost Passive High Absorption) developed by Tang *et al.* (2001) and Sutton *et al.* (2001a). The operating principle of ALPHA samplers is the capture of gaseous NH$_3$ on acid support coated with citric acid. These tools are designed to measure NH$_3$ air concentration less than 1 µg m^{-3} (Leith *et al.*, 2004) to over 4 mg m^{-3} (Carozzi, 2011).

Samplers were placed both in the centre of the field to measure the NH$_3$ concentration from the slurry application (*C*) and 1 km away from the field and from any other known source of NH$_3$.

The latter sampling point was used to measure the background level of NH_3 concentration (C_{bgd}). Samplers were exposed in three replicates at the height (z) of 1.25 m from the displacement height $d = 0$, corresponding to the ground. The positions of the ALPHA samplers and the shape of the fields were mapped using a GPS device.

ALPHA were replaced a minimum of twice per day, after dawn and just before sunset, in order to monitor the change of atmospheric turbulence, which affects the dispersion of pollutants. During the daylight hours of the spreading day and the day after, the samplers replacement was done every three hours to have a more detailed time step. On the third day the replacement was done each 6 hours and subsequently every 12 hours.

The exposed filters were leached with deionised water (3 mL) and then analysed by spectrometric detection (FIAstar 5000 system, FOSS, Denmark) through a gas semi permeable membrane (ISO 11732, 1997), in order to measure the concentration of NH_4-N (mg L^{-1}). The air NH_3 concentration (µg m^{-3}) was then calculated by multiplying the NH_4-N concentration, the volume of air sampled in one hour (V_a = 0.003241315 m^3 h^{-1}), the time of exposure (hours) (Sutton *et al.*, 2001b; Tang *et al.*, 2008), and the stoichiometric ratio between NH_4-N and NH_3. The mean concentration and the standard deviation of the three replicates were calculated both for background (σ_{bgd}) and field measurements (σ_C).

Micrometeorological measurements
Micrometeorological measurements were performed to supply the parameters of atmospheric turbulence to the bLS model WindTrax (see section 2.4). The friction velocity (u^*), the Monin-Obukhov length (L) and the surface roughness length (z_0), together with wind speed (U) and wind direction (WD), were derived from a three-dimensional ultrasonic anemometer (USA-1, METEK GmbH, Elmshorn, Germany). The sampling frequency was 10 Hz and the device was set in the centre of the field at the same height of the ALPHA samplers. Friction velocity (m s^{-1}) is derived from the Weber's formula (1999):

$$u_* = \sqrt{-\overline{u'w'}} \qquad \text{[eq. 1]}$$

where u' and w' indicate the fluctuations of the wind components u and w along the three directions of the wind. The Monin-Obukhov length L [m] was derived from the Monin and Obukhov similarity theory (MOST, Stull, 1988) under horizontally homogeneous and steady state conditions:

$$L = -\frac{u_*^3 \ T}{k \ g \ \overline{w'T'}} \qquad \text{[eq. 2]}$$

where T [K] is the mean air temperature within the surface boundary layer, k is the von Kàrmàn's constant (0.41), g is the acceleration of gravity (9.81 m s^{-2}) and $\overline{w'T'}$ is the covariance between w and T.

The roughness length was derived from the wind speed profile relationship, as:

$$z_0 = \frac{z}{\exp\left(\dfrac{k \cdot U(z)}{u_*} - \Psi_m (z/L)\right)} \qquad \text{[eq. 3]}$$

where U is the magnitude of the horizontal component of wind speed (m s^{-1}) and Ψ_m is a Monin–Obuhkhov universal function for momentum, estimated from the approach described by Flesch *et al.* (2004). The u_* and L were further filtered ($u^* > 0.2$ m s^{-1} and $|L| > 5$ m) to guarantee the condition for the MOST application (Flesch *et al.*, 2004; Hensen *et al.*, 2009; Loubet *et al.*, 2009). Moreover, to parameterise the bLS model, a constant value of z_0 (0.028 m) was calculated as the median value of eq. 3 over the experimental period.

The backward Lagrangian Stochastic model WindTrax
The WindTrax model (Thunder Beach Scientific, Halifax, Canada) is based on the backward Lagrangian stochastic dispersion theory described by Flesch *et al.*, (1995; 2004) and it has been employed to estimate the transfer coefficient D (s m^{-1}). The transfer coefficient is used to derive the flux of NH_3, S (µg m^{-2} s^{-1}), emitted from the fertilised surface, on the basis of the NH_3 measured concentrations (C and C_{bgd}, in µg m^{-3}), from the relationship:

$$S = (C - C_{bgd}) \times D^{-1} \qquad \text{[eq. 4]}$$

where D is retrieved by the model as the number of the interactions (N_{source}) between the source area and the thousands of trajectories (N)

generated by the model and located upwind from the position of the two NH_3 samplers in the space (see eq. 5).

$$D = \frac{1}{N} \sum_{N_{source}} \left| \frac{2}{w_0} \right| \qquad [\text{eq. 5}]$$

where (w_0) is the vertical wind speed of those trajectories that intersect the source area. The dispersion model used with the long term exposure samplers can be applied only with short time intervals (typically 30 min or 1 hour), because of the strong change of the atmospheric stability over a timescale of few hours. In the same way, the estimation of S is possible considering only the periods of atmospheric stationarity reached by short integration time of the turbulence parameters (u^*, L and z_0), as the MOST theory states. For the determination procedure of S three hypotheses have to be assumed: (i) non-reactivity of the emitted NH_3 in the atmosphere, (ii) spatial homogeneity of the flux from the surface and (iii) steadiness of z_0 (Loubet and Cellier, 2001; Loubet et al., 2009; Nemitz et al., 2009).

RESULTS

Micrometeorological conditions
The trends of u^* and the atmospheric stability parameter (z/L) measured together with their statistics, are shown in Fig. 1 and Tab. 1, respectively. Friction velocity marked the typical high peak values during the daylight hours and the
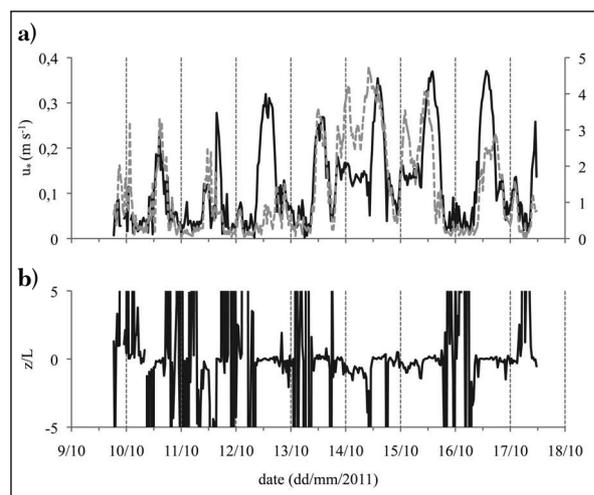
Fig. 1 - a) friction velocity (u^*) and wind speed (grey dotted line) over the experiment; b) atmospheric stability parameter (z/L).
Fig. 1 - a) velocità di frizione (u^*) e velocità del vento (linea grigia tratteggiata) per la durata dell'esperimento; b) parametro di stabilità atmosferica (z/L).

		min	max	mean	median	σ
u_*	m s⁻¹	0.00	0.37	0.12	0.09	0.09
z/L		-43403	1492	-143	0	2331
Wind speed	m s⁻¹	0.0	4.7	1.3	0.8	1.2
C	µg m⁻³	9	820	96	29	173
C_{bgd}	µg m⁻³	8	35	15	14	8
S (flux)	µg m⁻² s⁻¹	0	163	6	1	17

Tab. 1 - Main statistics of atmospheric turbulence parameters (u^* and L), NH_3 concentration measured in the fertilised field (C) and its background level (C_{bgd}), Wind speed and the estimates NH_3 flux (S).
Tab. 1 - Principali statistiche dei parametri della turbolenza atmosferica (u^* e L), concentrazione di NH_3 misurata al centro del campo (C) e di background (C_{bgd}), velocità del vento (Wind speed) e del flusso di NH_3 stimato (S).

minimum values over the night time, where the amplitude and the magnitude of the peaks are directly related to the presence of horizontal wind. The negative peaks of z/L indicated the daily instability whereas positive peaks showed the nocturnal stability. Night and early mornings were characterized by phases of stability conditions, excepted for 14th and 15th of October where cloud cover and a strong and persistent wind occurred.

Ammonia concentrations
Fig. 2 shows the concentrations of NH_3 (µg m⁻³) measured over the experimental period in the centre of the field and present as background. Before the application of the fertiliser, the concentration was 1.7 µg m⁻³ higher than the background value. In the first three hours after the spreading, the field NH_3 concentration rose up to 505 µg m⁻³, followed by a fast increase to 820 µg m⁻³ in the subsequent three hours. In the following measurement period (6 to 15 h), the concentration decreased down to 300 µg m⁻³ and then increased during the night time hours to 539 µg m⁻³. After the first 24 hours the concentration gradually decreased, reaching the background concentration after further 60 hours. In the last measurement period (84 to 168 h) the magnitude measured in the centre of the field and as background was coincident. Tab. 1 shows the statistics relative to such NH_3 concentrations.
The variability (σ) of the three ammonia samplers ranged from 0.2 to 31.8 µg m⁻³. In Fig. 3 the
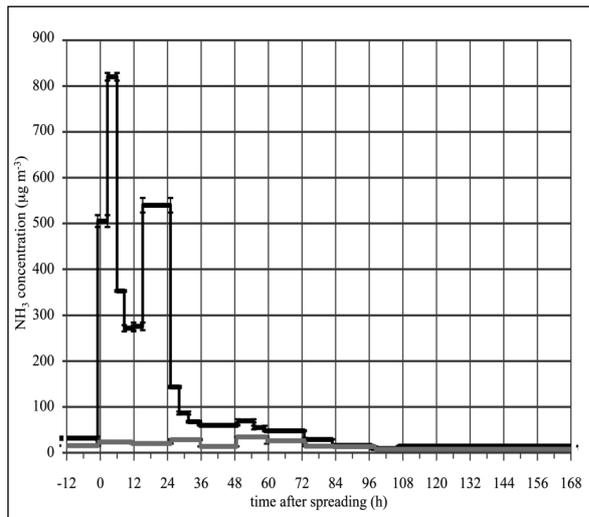
Fig. 2 - NH_3 concentrations measured in the centre of the fertilised field (dark line) and in its background values (gray line). The error bars show standard deviations.
Fig. 2 - Concentrazioni di NH_3 misurate nel centro del campo fertilizzato (linea nera) e come background (linea grigia). Le barre di errore mostrano le deviazioni standard.
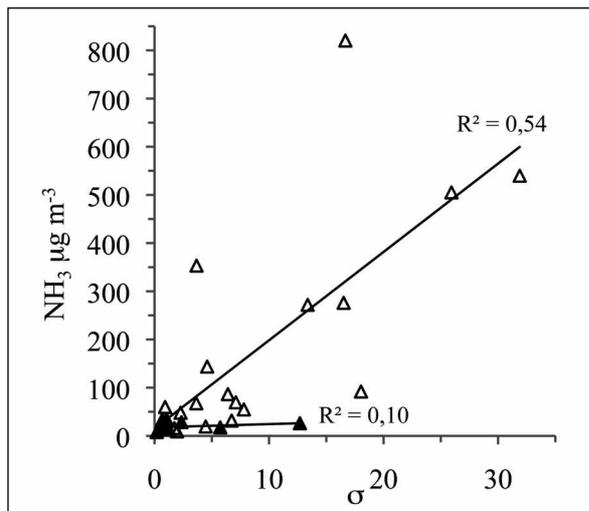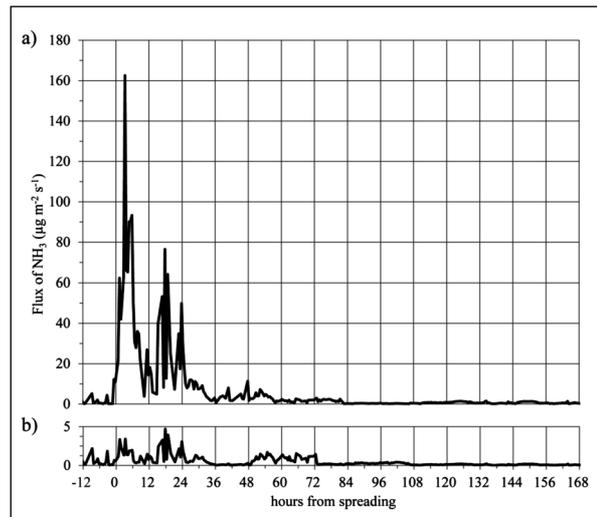

Fig. 4 - a) NH_3 flux simulated by the inverse dispersion model WindTrax. b) uncertainty in the modelling approaches employed due to the uncertainty in the concentrations measurements.
Fig. 4 - a) flussi di NH_3 stimati attraverso l'impiego del modello a dispersione WindTrax. b) incertezza nella stima dei flussi attraverso il modello, dovuti alla incertezza nella misura delle concentrazioni.

Fig. 3 - Scatter plots reporting the average of NH_3 concentration and relative standard deviation (σ) for measurements in the field ($\triangle$) and at the background ($\blacktriangle$).
Fig. 3 - Grafico a dispersione riportante la media delle concentrazioni di NH_3 e la deviazione standard (σ) misurate nel centro del campo ($\triangle$) e come background ($\blacktriangle$).

relation between σ and the mean values of concentration measured in the field and as background is displayed for each measurement period. The relation between C_{bkg} and σ_{bgd} was not significant ($R^2 = 0.10$, $P>0.05$), while a significant relationship was detected between C and its σ_C ($R^2 = 0.54$, $P<0.01$).

Ammonia emissions from slurry spreading

The flux estimated by the bLS model WindTrax and the error due to the dispersion of the NH_3 concentration mean value are displayed in Fig. 4. The emission trend showed high peaks immediately after the spreading, with a maximum value (163 µg m^{-2} s^{-1}) reached after 3 hours and 20 minutes (see Tab. 1). Subsequently, the emission decreased quickly to rise again during the night time hours (15 to 21 h). The last high peak occurred after 24 hours because of the increase of the solar radiation. In the last measurement period (24 to 168 h) a gradual reduction to low values (2 µg m^{-2} s^{-1}) was detected. Errors ranged from 0 to 4.7 µg m^{-2} s^{-1}, with a mean value of 0.4 µg m^{-2} s^{-1}.

Dynamics of soil NH_4-N, NO_3-N and pH

The dynamics of N into the soil as ammonium and nitrate form, together with the trends of SWC and pH at 0-5 and 5-15 cm depth, are displayed in Fig. 5a and 5b, respectively. The measurement period ranged from -72 to 96 hours with a time step of 24 hours, where time 0 represented the time immediately before the manure spreading. Samplings at -48 and -24 hours were not carried out because of the high soil moisture. The content of NH_4-N in the soil profile (0-15 cm) was constant before the slurry application (around 1 mg L^{-1}, from 0 to -72 hours) and rose up after the fertilisation, particularly in the first layer (0-5 cm).
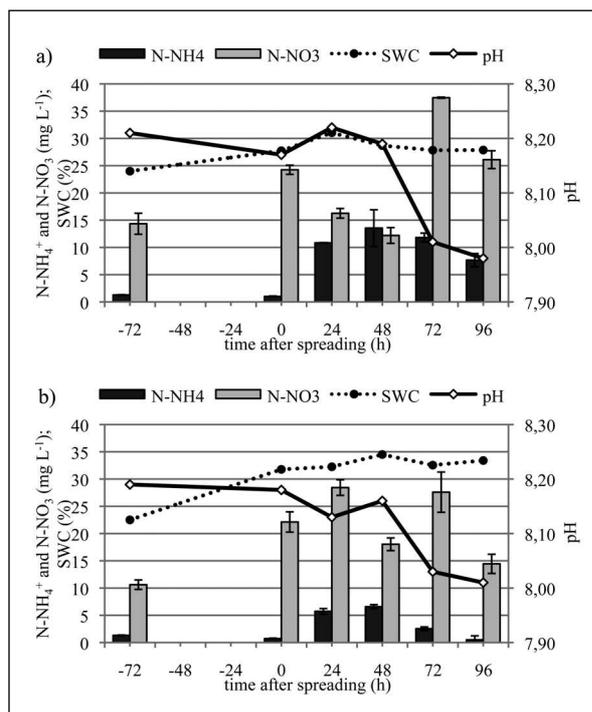
Fig. 5 - Trend of soil N-NH$_4^+$, N-NO$_3^-$, pH and water content (SWC) during the time after slurry spreading in the field trial: a) 0 – 5 cm depth; b) 5 – 15 cm depth.
Fig. 5 - Andamento del valore di pH e del contenuto di N-NH$_4^+$ e N-NO$_3^-$ e acqua (SWC) nel suolo durante le ore dello spandimento del liquame in campo: a) profilo 0 – 5 cm di profondità; b) profilo 5-15 cm di profondità.

The highest values in the two soil layers were observed 48 hours after the spreading.
The values of NO$_3$-N concentration did not seem to have a specific trend over time. In both layers the maximum values were reached at 72 h, showing the highest values in the lower layer (5-15 cm). At 72 and 96 hours the NO$_3$-N concentration appeared to be higher in the 0-5 cm depth (+26% and +44%, respectively).
The values of pH were reduced by 0.23 and 0.19 units in the 0-5 and 5-15 cm, respectively. The pH fast decrease started after 48 hours. The SWC showed values ranging from 24 to 31% in the 0-5 cm profile, with the maximum value observed 24 hours after the spreading. In the deeper layer a wider variation of SWC occurred (from 22% at -72 hours to 35% at 48 hours).

DISCUSSION

The NH$_3$ volatilisation estimated over the field trial followed the typical trend reported elsewhere (i.e. Sommer and Hutchings 2001; Powell *et al.*, 2011). The highest emission rate was recorded immediately after the slurry application.

Subsequently, it quickly fell down because the concentration of TAN in soil surface decreased as consequence of emission itself, infiltration, absorption in the soil matrix, or nitrification (van der Molen *et al.*, 1990; Sommer *et al.*, 2004). Cumulative NH$_3$ loss observed at the end of the trial was visibly exhausted and equal to 30.2 kg N ha^{-1}, corresponding to an emission factor (EF) of 44.4% of the TAN applied. The emission ranged from 40% to 53% between 6 to 12 hours from the spreading. Similar findings were obtained by other authors, measuring a range of total loss between 30 and 70% of the TAN (Sommer and Hutchings, 1995; Meisinger and Jokela, 2000). After 24 and 48 hours the total loss reached 73% and 88%, respectively, getting to the 100% of the emission at the end of the trial at 168 hours. The trend of the cumulate emission can be represented by the Michaelis-Menten equation (eq. 6) already used in this context by Søgaard *et al.* (2002):

$$N(t) = N_{max} \frac{t}{t + K_m} \qquad [\text{eq. 6}]$$

where N_{max} is the total loss of NH$_3$ (fraction of TAN applied) and K_m [h] is the time t satisfying $N(t) = \frac{1}{2} N_{max}$. A low value of K_m indicates that a high proportion of the total NH$_3$ loss occurs soon after application, whereas a high K_m value indicates that losses occur over a longer period. In our case after 10 hours the 50% of the total NH$_3$ was emitted (K_m = 10 hours). The EF obtained in this field trial is coherent with what has been reported in the recent literature (see the review by Sintermann *et al.*, 2011b). Furthermore, applying the regressive model ALFAM (Søgaard *et al.*, 2002), based on the data deriving from 800 experiments and on the Michelis-Menten equation type described above, the EF obtained resulted 40% of the TAN.
The fluxes estimated by the bLS model WindTrax showed high levels of emission when z/L parameter assumed negative values, or else when the atmosphere is in unstable condition. That was evident during the hours immediately close to the application of the slurry, characterized by high levels of concentration. The high fluxes observed during the night time hours of the spreading day (15 to 24 h) were due both by high levels of ammonia concentration (see Fig. 2) and the alternation of the atmosphere conditions. In fact, over the night, atmospheric condition can range from high stability, where the vertical gradients of ambient concentration are enhanced to very small

diffusivity, to unstable conditions, in which concentration gradients are small due to the intense turbulent activity of the surface layer (Erisman *et al.*, 1988; Famulari *et al.*, 2009). Another factor affecting ammonia emissions was the vertical wind speed (w), whereas the horizontal wind speed is not involved. In fact, as occurred from 14th to 15th October, the strong horizontal wind speed recorded did not affect the emissions that remained at low level. On the opposite, during the night time hours of the spreading day, when the value of vertical wind speed was high, an increase of emission occurred. The pattern of NH_3 emissions followed the trend of the measured concentrations and the high emission peaks took place in correspondence with the high values of concentration. Over the spreading daylight hours and the subsequent two days, the frequency of the ALPHA samplers change (3 hours in the first two days and 6 in the third, instead of 12 hours) allowed to obtain a more detailed ammonia concentrations and fluxes. In fact, integrating these concentrations over a time of 12 hours, the peaks of emission resulted lower and the final EF decreased by 5% (from 44 to 39% TAN). Therefore the temporal detail in the acquisition of the NH_3 concentration is a crucial point for a correct determination of the emission (Carozzi *et al.*, 2012). Loubet *et al.* (2010) found that for an exposure time between 2 and 12 hours, the underestimation of NH_3 emission was not expected to be larger than 5 to 10% ($\pm$ 5%) in a 100 m^2 surface area. Moreover, the use of inverse dispersion models, coupled with long term exposure concentration samplers, produced similar results if compared to the fastest and error-prone Eddy Covariance approach, when measuring NH_3 fluxes at field scale (Ferrara *et al.*, 2012; Carozzi, 2011).

Despite the low sampling frequency, an increase of the NH_4-N concentration into the soil after the application of the slurry was recorded. As emissions ended also the NH_4-N concentration decreased, whereas the NO_3-N concentration started to increase due to the nitrification process (which was most evident at 0-5 cm depth soil profile). As reported by Gènermont and Cellier (1997) and Misselbrook *et al.*, (2005) NH_3 emission and soil pH are directly related. In our case they started to decrease at the same time (after 24 h). Such behaviour was probably due to the release of protons (H^+) caused by the transition from NH_4^+ to NH_3 in the nitrification process (van Breemen *et al.*, 1982; Freney *et al.*,

1983). Lastly the increase of the SWC due to the slurry application was observed in the first 24 hours in the 0-5 cm layer, whereas in the 5-15 cm layer the effect was extended till 48 hours.

CONCLUSIONS

Surface application of dairy slurry determined high ammonia emission levels within the first 24 hours, followed by a first rapid and then gradual decrease to low emission levels in the subsequent days. Ammonia losses were the 44% of the total TAN applied. The results obtained highlighted the need of low-emission techniques, such as surface spreading with incorporation and injection, which are supported by scientific data showing the reduction of ammonia emission under experimental conditions. However, the incorporation of slurry should be done as soon as possible because the 50% of the total ammonia emission occurred within 10 hours. Reliable NH_3 quantification has to be considered a central aspect for decision makers, to promote abatement strategies and to derive emission factors used in national and international emission inventories.

REFERENCES

Ammann C., Bertok I., Cofala J., Gyarfas F., Heyes C., Klimont Z., Schöpp W., Winiwarter W., 2005. Baseline Scenarios for the Clean Air for Europe (CAFE) Programme. Final Report, IIASA, Laxenburg, Austria.

Aneja V.P., 1997. Summary of discussion and research re-commendations. 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., Hutchings N.J., Sommer S.G., Andersen J., Münier B., Génermont S., Cellier P., 2004. Emissions of ammonia. In: Emissions of Air Pollutants (eds R. Friedrich & S. Reis), pp. 111-143. Springer, Berlin.

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.

Carozzi M., 2011. Ammonia Emissions From Arable Lands In Po Valley: Methodologies,

Dynamics And Quantification. Università degli Studi di Milano, PhD thesis, 194 pp.

Carozzi M., Ferrara R.M., Acutis M., Rana G., 2012. Dynamic of ammonia emission from urea spreading in Po Valley (Italy): relationship with nitrogen compounds in the soil. In: Proceeding of 17th International Nitrogen Workshop. Wexford, 26-29 June 2012.

EEA, 2011. NEC Directive status report 2010. Technical report No 3/2011. http://www.eea.europa.eu/publications/nec-directive-status-report-2010. Accessed on 2th Aug 2012.

Erisman J.W., Otjes R., Hensen A., Jongejan P., van den Bulk P., Khlystov A., Möls H., Slanina S., 2001. Instrument development and application in studies and monitoring of ambient ammonia. Atmospheric Environment, 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.

Famulari D., Fowler D., Nemitz E., Hargreaves K.J., Storeton-West R.L., Rutherford G., Tang Y.S., Sutton M.A., Weston K.J., 2009. Development of a low-cost system for measuring conditional time-averaged gradients of SO_2 and NH_3. Environmental Monitoring and Assessment 161, 11-27.

Ferrara R.M., Loubet B., Di Tommasi P., Bertolini T., Magliulo V., Cellier P., Eugster W., Rana G., 2012. Eddy covariance measurement of ammonia fluxes: Comparison of high frequency correction methodologies. Agricultural and Forest Meteorology, 158: 30-42.

Flesch T.K., Wilson J.D., Harper L.A., Crenna B.P., Sharpe R.R., 2004. Deducing ground-to-air emissions from observed trace gas concentrations: A field trial. Journal of Applied Meteorology, 43(3): 487-502.

Flesch T.K., Wilson J.D., Yee E., 1995. Backward-time Lagrangian stochastic dispersion models, and their application to estimate gaseous emissions. Journal of Applied Meteorology 34: 1320-1332.

Freney J.R., Simpson J.R., Denmead O.T., 1983. Volatilization of ammonia. In: Freney, J.R., Simpson J.R. (Eds.), Gaseous Loss of Nitrogen from Plant–Soil Systems. Kluwer Academic Publisher, Dordrecht, pp. 1-32.

Gash J.H.C., 1985. A note on estimating the effect of a limited fetch on micrometeorological evaporation measurements. Boundary-Layer Meteorology, 35: 409-413.

Génermont S., Cellier P., 1997: A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. Agricultural and Forest Meteorology, 88:145-167.

Génermont S., Cellier P., Flura D., Morvan T., Laville P., 1998. Measuring ammonia fluxes after slurry spreading under actual field conditions. Atmospheric Environment, 32: 279-284.

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. Atmospheric Environment, 32: 273-277.

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 NH_3 emissions from a naturally ventilated livestock farm using local-scale atmospheric dispersion modelling. Biogeosciences, 6: 825-862.

Jarvis S.C., Pain B.F., 1990. Ammonia volatilisation from agricultural land. The fertiliser society proceedings. The Fertiliser Society, London No. 298. pp.1-35.

Kaimal J.C., Finnigan J.J., 1994. Atmospheric Boundary Layer Flows: Their Structure and Measurement. Oxford University Press, 289 pp.

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 NH_3 deposition to an ombrotrophic bog from an automated NH_3 field release system. Water Air and Soil Pollution: Focus 4: 207-218.

Loubet B., Génermont S., Ferrara R., Bedos C., Decuq C., Personne E., Fanucci O., Durand B., Rana G., Cellier P., 2010. An inverse model to estimate ammonia emissions from fields. European Journal of Soil Science, 61 (5): 793-805.

Loubet B., Milford C., Hensen A., Dämmgen U., Erisman J.W., Cellier P., Sutton M.A., 2009. Advection of NH_3 over a pasture field and its

effect on gradient flux measurements. Biogeosciences, 6: 1295-1309.

Loubet B., 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.

Meisinger J.J., Jokela W.E., 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.

Misselbrook T.H., Powell J.M., Broderick G.A., Grabber J.H., 2005. Dietary manipulation in dairy cattle: Laboratory experiments to assess the influence of ammonia emissions. Journal of Dairy Science, 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. Journal of Agricultural Science, 125: 245-252.

Mosier A., 1989. Chamber and isotope techniques. In M.O. Andreae and D.S. Schimel (eds.), Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, pp.175-188. Report of the Dahlem Workshop, Berlin, Feb 19-24, 1989. John Wiley and Sons, New York.

Nemitz E., Dorsey J.R., Flynn M.J., Gallagher M.W., Hensen A., Erisman J.W., Owen S.M., Dämmgen U., Sutton M.A., 2009. Aerosol fluxes and particle growth above managed grassland. Biogeosciences, 6: 1627-1645.

Ni K., Pacholski A., Gericke D., Kage H., 2012. The measurement time required for determining total NH_3 losses after field application of slurries by trail hoses. The Journal of Agricultural Science: 1-10.

Powell J.M., Jokela W.E., Misselbrook T.H., 2011. Dairy Slurry Application Method Impacts Ammonia Emission and Nitrate Leaching in No-Till Corn Silage. Journal of Environmental Quality, 40: 383-392.

Sintermann J., Neftel A., Ammann C., Häni C., Hensen A., Loubet B., Flechard C.R., 2011a. Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories? Biogeosciences Discussion: 10069-10118.

Sintermann J., Ammann C., Kuhn U., Spirig C., Hirschberger R., Gärtner A., Neftel A., 2011b. Determination of field scale ammonia emissions for common slurry spreading practice with two independent methods. Atmospheric Measurement Techniques, 4: 1821-1840.

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. Atmospheric Chemistry and Physics, 11: 5221-5236.

Søgaard H.T., Somme 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., 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., Hutchings N.J, 1995. Techniques and strategies for the reduction of ammonia emission from agriculture. Water Air Soil Pollution, 85: 237-248.

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., 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., Schjoerring J.K., Denmead O.T. 2004. Ammonia emission from mineral fertilizers and fertilized crops. Advances in Agronomy, Volume 82, 557-622.

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. Fowler D., 2001a. Comparison of low-cost measurement techniques for long-term monitoring of atmospheric ammonia. Journal of Environmental Monitoring, 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., 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. Quarterly journal of the royal meteorological society, 119: 1047-1070.

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., 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. The Scientific World, 1: 513-529.

Valli L., Fabbri C., 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 Wit T., Ridder T.B., Reijnders H. F. R., 1982. Soil acidification from ammonium sulphate in forest canopy through fall. Nature, 288: 548-550.

van Der Molen J., Bussink D.W., Vertregt N., Van Faassen H.G., Den Boer D.J., 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.

Weber R.O., 1999. Remarks on the definition and estimation of friction velocity. Boundary.-Layer Meteorology, 93: 197-209.