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

Marco Carozzi^{1*}, Rossana Monica Ferrara², Mattia Fumagalli¹, Mattia Sanna¹, Marcello Chiodini¹, Alessia Perego¹, Alessandro Chierichetti¹, Stefano Brenna³, Gianfranco Rana², Marco Acutis¹

Abstract: Po Valley (Northern Italy) is one of the major ammonia (NH₃) emitting regions of Europe, where the slurry spreading causes high NH₃ volatilisation, reducing its agronomic value and becoming a potential cause of environmental concerns. In autumn 2011 a field trial was conducted to estimate the NH₃ losses from the application of dairy slurry at rate of 57 m³ 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. NH₃ 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 NH₃ losses equal to 44% of the total ammoniacal nitrogen (TAN) applied. Results showed and confirmed that surface application involves high NH₃ 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 ammoniacale (NH₃), riducendo il loro valore agronomico e causando problemi ambientali. L'obiettivo di questo studio è la stima dell'emissione di NH₃ a seguito di una distribuzione superficiale di 57 m³ 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'NH₃ 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 ammoniacale 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 NH₃ 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 ammoniacale e che quindi deve essere incentivato l'uso di tecniche alternative.

Parole chiave: emissioni di ammoniacale, modelli a dispersione, distribuzione superficiale dei reflui, campionatori passivi.

INTRODUCTION

Agriculture is the primary source of gaseous ammonia (NH₃) 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 NH₃ 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 NH₃ 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; Erismann *et al.*, 2001; Harper, 2005). Moreover, by 2020 NH₃ 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 NH₃ 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

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

NH₃ 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, NH₃ 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 NH₃ is often expensive, extensive and time consuming (Aneja 1997; Harper and Sharpe, 1998). Nowadays among all the available techniques for measuring or estimating NH₃, 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 NH₃ 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; Gènermont 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 NH₃ emissions caused by surface spreading of dairy slurry by using a concentration-based dispersion model. The quantification of the NH₃ 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 m³ ha⁻¹ was applied on 10th of October using a 20 m³ 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 = NH₄⁺ + NH₃). 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 (NH₄-N) and nitrate (NO₃-N) nitrogen, pH and water content were daily measured at 0-5 cm and 5-15 cm soil depth. Particularly, concentrations of soil NH₄-N and NO₃-N were performed with a KCl extraction and determined by spectrometric detection (FIAsstar 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 NH₃ 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 NH₃ on acid support coated with citric acid. These tools are designed to measure NH₃ 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 NH₃ concentration from the slurry application (C) and 1 km away from the field and from any other known source of NH₃.

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 $\text{NH}_4\text{-N}$ (mg L^{-1}). The air NH_3 concentration ($\mu\text{g m}^{-3}$) was then calculated by multiplying the $\text{NH}_4\text{-N}$ concentration, the volume of air sampled in one hour ($V_a = 0.003241315 \text{ m}^3 \text{ h}^{-1}$), the time of exposure (hours) (Sutton *et al.*, 2001b; Tang *et al.*, 2008), and the stoichiometric ratio between $\text{NH}_4\text{-N}$ 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):

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

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:

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

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 $w' T'$ is the covariance between w and T .

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

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

where U is the magnitude of the horizontal component of wind speed (m s^{-1}) and Ψ_m is a Monin-Obukhov universal function for momentum, estimated from the approach described by Flesch *et al.* (2004). The u_* and L were further filtered ($u_* > 0.2 \text{ m s}^{-1}$ and $|L| > 5 \text{ m}$) 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 ($\mu\text{g m}^{-2} \text{ s}^{-1}$), emitted from the fertilised surface, on the basis of the NH_3 measured concentrations (C and C_{bgd} , in $\mu\text{g m}^{-3}$), from the relationship:

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

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 NH₃ samplers in the space (see eq. 5).

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

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 NH₃ 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

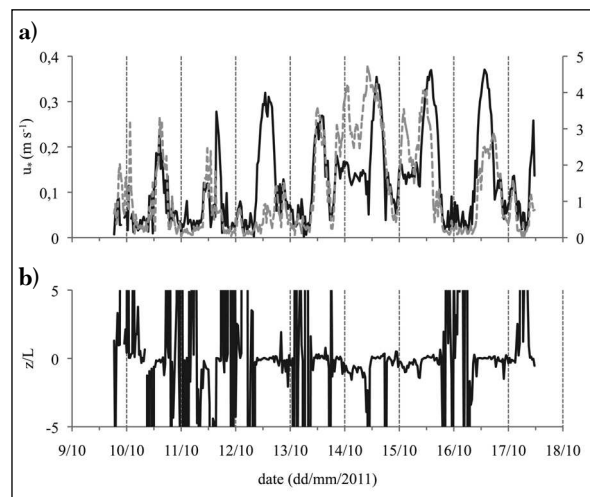


Fig. 1 - a) friction velocity (u^*) and wind speed (grey dotted line) over the experiment; b) atmospheric stability parameter (z/L).
Fig. 1 - a) velocità di frizione (u^*) e velocità del vento (linea grigia tratteggiata) per la durata dell'esperimento; b) parametro di stabilità atmosferica (z/L).

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

Tab. 1 - Main statistics of atmospheric turbulence parameters (u^* and L), NH₃ concentration measured in the fertilised field (C) and its background level (C_{bgd}), *Wind speed* and the estimates NH₃ flux (S).

Tab. 1 - *Principali statistiche dei parametri della turbolenza atmosferica (u^* e L), concentrazione di NH₃ misurata al centro del campo (C) e di background (C_{bgd}), velocità del vento (*Wind speed*) e del flusso di NH₃ 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 NH₃ ($\mu\text{g m}^{-3}$) measured over the experimental period in the centre of the field and present as background. Before the application of the fertiliser, the concentration was $1.7 \mu\text{g m}^{-3}$ higher than the background value. In the first three hours after the spreading, the field NH₃ concentration rose up to $505 \mu\text{g m}^{-3}$, followed by a fast increase to $820 \mu\text{g m}^{-3}$ in the subsequent three hours. In the following measurement period (6 to 15 h), the concentration decreased down to $300 \mu\text{g m}^{-3}$ and then increased during the night time hours to $539 \mu\text{g m}^{-3}$. 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 NH₃ concentrations.

The variability (σ) of the three ammonia samplers ranged from 0.2 to $31.8 \mu\text{g m}^{-3}$. In Fig. 3 the

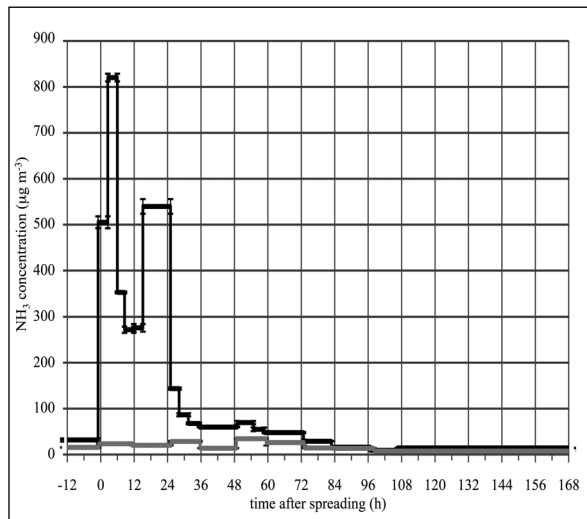


Fig. 2 - NH_3 concentrations measured in the centre of the fertilised field (dark line) and in its background values (gray line). The error bars show standard deviations.

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.

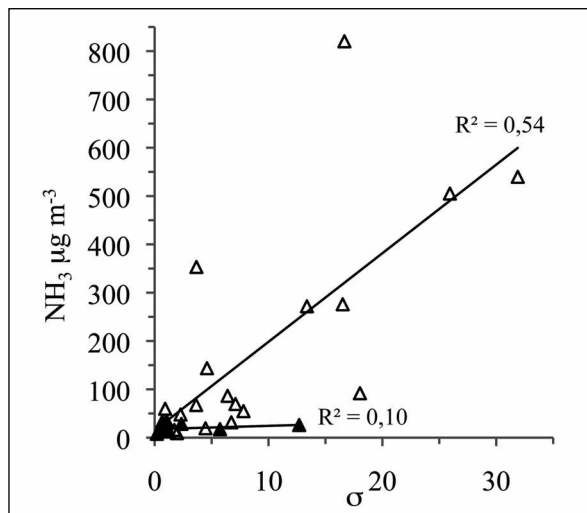


Fig. 3 - Scatter plots reporting the average of NH_3 concentration and relative standard deviation (σ) for measurements in the field (Δ) and at the background (\blacktriangle).

Fig. 3 - Grafico a dispersione riportante la media delle concentrazioni di NH_3 e la deviazione standard (σ) misurate nel centro del campo (Δ) 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_{bkd} was not significant ($R^2 = 0.10$, $P > 0.05$), while a significant relationship was detected between C and its σ_C ($R^2 = 0.54$, $P < 0.01$).

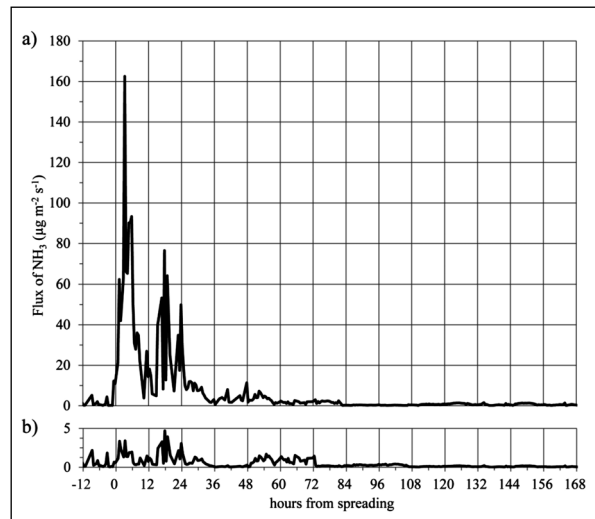


Fig. 4 - a) NH_3 flux simulated by the inverse dispersion model WindTrax. b) uncertainty in the modelling approaches employed due to the uncertainty in the concentrations measurements.

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.

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 ($163 \mu\text{g m}^{-2} \text{s}^{-1}$) 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 ($2 \mu\text{g m}^{-2} \text{s}^{-1}$) was detected. Errors ranged from 0 to $4.7 \mu\text{g m}^{-2} \text{s}^{-1}$, with a mean value of $0.4 \mu\text{g m}^{-2} \text{s}^{-1}$.

Dynamics of soil $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ 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 $\text{NH}_4\text{-N}$ 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).

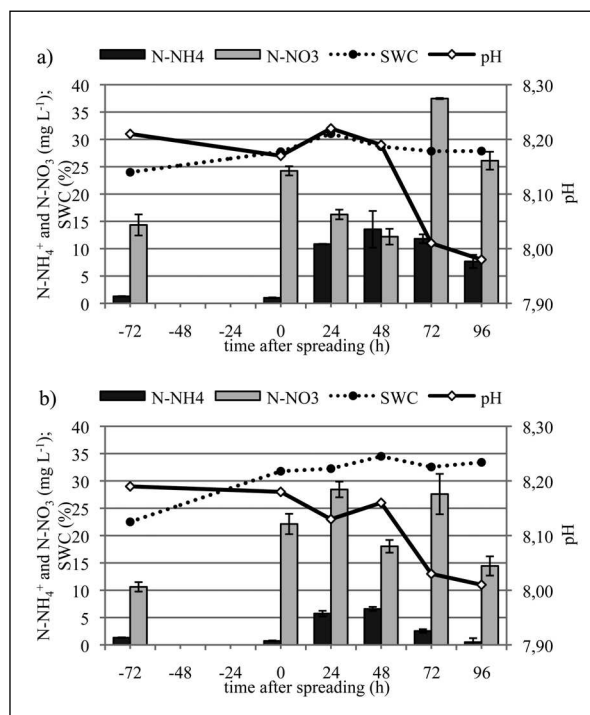


Fig. 5 - Trend of soil $N-NH_4^+$, $N-NO_3^-$, pH and water content (SWC) during the time after slurry spreading in the field trial: a) 0 – 5 cm depth; b) 5 – 15 cm depth.

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 Søggaard *et al.* (2002):

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

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 for similar conditions (see the review by Sintermann *et al.*, 2011b). Furthermore, applying the regressive model ALFAM (Søggaard *et al.*, 2002), based on the data deriving from 800 experiments and on the Michaelis-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 NH₃ 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 NH₃ 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 NH₃ emission was not expected to be larger than 5 to 10% ($\pm 5\%$) in a 100 m² 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 NH₃ fluxes at field scale (Ferrara *et al.*, 2012; Carozzi, 2011).

Despite the low sampling frequency, an increase of the NH₄-N concentration into the soil after the application of the slurry was recorded. As emissions ended also the NH₄-N concentration decreased, whereas the NO₃-N concentration started to increase due to the nitrification process (which was most evident at 0-5 cm depth soil profile). As reported by Générumont and Cellier (1997) and Misselbrook *et al.*, (2005) NH₃ 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 NH₄⁺ to NH₃ 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 NH₃ 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.

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