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Ammonia volatilisation following urea fertilisation in an irrigated sorghum crop in Italy

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ABSTRACT

Ammonia (NH_3) fluxes were estimated by three inverse modelling methods over a *sorghum* field following the application of 240 kg N ha^{-1} of urea pills under a semi-arid Mediterranean climate. Ammonia volatilisation started following irrigation, which coincided with the third urea application. The maximum volatilisation rate was reached 7 days after irrigation. A clear dependence of the NH_3 volatilisation on irrigation and rainfall events was observed. The NH_3 fluxes ranged from −2.5 to 45 μg NH_3 m^{-2} s^{-1}. The canopy compensation point jumped from 9 μg NH_3 m^{-3} before urea hydrolysis to 131 μg NH_3 m^{-3} afterwards, while the soil compensation point varied in the meantime from 24 to 800 μg NH_3 m^{-3} on average. The soil-dominated observed NH_3 emissions were reasonably well reproduced by a two-layer resistance model. Overall, between 10% and 14% of the total nitrogen applied was volatilised.

1. Introduction

The nitrogen (N) cycle is greatly affected by human activities such as fertilizer production (Haber-Bosch process), energy production, combustion and changes in land use, generating increased amounts of reactive N (N_r) in the environment which leads to various threats to aquatic and terrestrial ecosystems, as well as to human health through atmospheric pollution (Galloway et al., 2008), while being beneficial for crop and food production.

Agriculture is responsible for over 90% of ammonia (NH_3) emissions in Europe (EMEP/EEA and guidebook, 2013) and 95% in Italy (Romano et al., 2013). In particular, field applied manure is the main source of atmospheric NH_3, followed by mineral N fertilizer use (ECETOC, 1994). Among these, urea accounts for 50% of the total world fertilizer consumption and is steadily increasing in developing countries. In Italy, about 40% of N is applied as urea, although a trend in application reduction has been recorded. Field-applied urea contributes to about 4% of the anthropogenic NH_3 emissions in Western Europe (ECETOC, 1994).

The amount of NH_3 volatilised is a variable percentage of the applied NH_3, depending on several factors such as the fertilizer type, the application technique, the soil type and humidity, the weather conditions and the crop cover (e.g. Sommer et al., 2003). NH_3 volatilisation increases with soil ammonium (NH_4^+) content, soil pH and soil temperature, while soil microbial population and organic matter content impacts the amount of NH_4^+ (van der Weerden and Jarvis, 1997).

While several studies on NH_3 volatilisation after slurry/manure spreading can be found for different environments (e.g. Carozzi et al., 2013a, 2013c; Huijsmans et al., 2003; Monteny and Erisman, 1998; Pain et al., 1998; Sintermann et al., 2012; Sommer and Hutchings, 2001), few data are available for NH_3 losses by urea under semi-arid conditions (Das et al., 2008) while these conditions would characterise approximately 12% of European and Middle Eastern land (Gao and Giorgi, 2008). Consequently, inappropriate NH_3 emission factors may be used for urea in these semi-arid conditions (20% of the N applied is used in the EMEP/EEA and guidebook, 2013). Among the few data available by micrometeorological methods in semi-arid conditions, Sanz-Cobena et al. (2008) and Pacholski et al. (2006) reported NH_3 losses of about 10% and 48% of the urea-N applied, using the integrated horizontal flux method, a method which may overestimate NH_3 emissions (Sintermann et al., 2012). Additionally, Roelcke et al. (1996) reported NH_3 losses of about 60% of surface applied urea in 13 days under semi-arid conditions, while Zhang et al. (1992) found that between 30% and 32% of the N applied as urea could be lost as NH_3 from calcareous soils in North China.

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Furthermore, understanding NH_3 volatilisation dynamics is critical to identifying best management practices and to extrapolating NH_3 losses over larger scales.

Measuring NH_3 fluxes is nevertheless still difficult. Acknowledged methods include the aerodynamic gradient (AG), the eddy covariance (EC), and the inverse modelling (IM) methods (see e.g., Loubet et al., 2010). The aerodynamic gradient method with wet denuders and conductivity analysis with gaseous separation on a semi-permeable membrane is still the reference method for measuring NH_3 fluxes (Flechard and Fowler, 1998; Flechard et al., 2010; Loubet et al., 2012; Sutton et al., 1993, 2008). Recently, the conditional time averaged gradient (COTAG) method has been developed based on time integration of the AG method conditioned by thermal stability (Famulari et al., 2009), to allow longer term and low cost monitoring of NH_3 fluxes, but these may not be well adapted yet for very unstable conditions.

The eddy covariance (EC) technique has been recently available for NH_3 with the development of highly sensitive and fast Quantum Cascade Laser (QCL) devices (Brodeur et al., 2009; Famulari et al., 2004; Ferrara et al., 2012; Shaw et al., 1998; Sintermann et al., 2011; Whitehead et al., 2008). But NH_3 flux measurement by EC with a QCL could be difficult due to the interaction of NH_3 with water and dust in the tubes.

Inverse dispersion methods are also increasingly used to evaluate NH_3 losses following slurry application using either Lagrangian Stochastic models (Flesch et al., 2007; McGinn et al., 2007; Sintermann et al., 2012; Sommer et al., 2005) or Gaussian models (Loubet et al., 2001, 2010) or both (Carozzi et al., 2013c). These methods are very well adapted for geometrically well-defined and isolated sources, and have been demonstrated as being valid when compared to reference methods in the case of high fluxes (Loubet et al., 2010; Sintermann et al., 2012).

In this study, we analyse ammonia fluxes above a *sorghum* crop, following application of urea pills, in the semi-arid region of Apulia (Italy). The fluxes were estimated with three inverse modelling methods. A resistance model is used to interpret the NH_3 flux dynamics and identify its soil and plant components. The canopy and soil compensation points are evaluated and compared to soil pH and NH_4^+ measurements and discussed. Finally the emission factor of NH_3 volatilisation following urea application is estimated.

2. Materials and methods

2.1. Field site and nitrogen application

The experimental campaign was carried out from 17 to 30 July 2008 in Rutigliano (41′N, 17°54′ E, 122 m a.s.l.) near Bari in Southern Italy in a 2 ha flat field of growing *Sorghum vulgare* (cv *Hay Day*) sowed on 10 June 2008 and irrigated with a sprinkler. The soil is a loamy clay (Clay 41%; Silt 44%; Sand 15%), with a porosity of 52%, a bulk density of 1.15 kg L^{-1}, a field capacity of 29% and a wilting point of 17%. The pH(H_2O) was 7.8, while the pH(KCl) was around 7.0 during the experimental campaign. The climate is semi-arid Mediterranean, with hot and dry summers and short and temperate winters with mean annual temperature of 15.7 °C and mean annual precipitation of 600 mm.

The crop was very heterogeneous with a mean leaf area index varying from 1.0 to 5.0 m^2 m^{-2} (Licor 3100, USA) and an average height from 0.72 to 1.25 m. Single sided LAI and plant height was determined 2 times per week on 10 plants. In total 240 kg N ha^{-1} of urea (46% N content commercial name; Fertilsud s.r.l., Italy) was applied in granular form in three applications: 30, 90 and 120 kg N ha^{-1} on 1, 16 and 22 July 2008. The first and second applications were done under dry conditions (applying 7.9 mm of water by irrigation only before urea spreading), while 9.3 mm of water was applied before and after the third application. The amount of urea applied was slightly larger than usual agronomic practices for irrigated *sorghum* (150–200 kg N ha^{-1}; Giardini and Vecchietti, 2000).

2.2. Site experimental monitoring

A summary of the variables monitored is given in Table 1. The meteorological data (air temperature, relative humidity, global radiation, reference evapotranspiration, wind speed, wind direction and rainfall) were measured with a standard meteorological station placed on a reference grass field located near the experimental field with all sensors at 2 m above ground. The other meteorological data (net radiation, incoming and outgoing global radiation, infrared surface temperature, wind speed and direction, air temperature and relative humidity) were measured in the middle of the experimental field every 10 s and averaged over one hour time intervals with a data logger (CR10X, Campbell Sci., Shepshed, UK). Soil samples were also collected every three to four days, at random locations at 0–0.2 and 0.2–0.4 m depths for the volumetric soil water content and at 0.2–0.4 m depth for soil available nitrate (NO_3^-), NH_4^+ and pH.

2.3. Heat, water vapour and CO_2 fluxes by eddy covariance

Heat, water vapour and carbon dioxide (CO_2) fluxes were measured by eddy covariance, with a tri-axial ultrasonic anemometer (Gill R2, Gill Instruments Ltd, UK), and a H_2O/CO_2 open path infrared absorption analyser (Li-Cor 7500, USA) located near the centre of the field at z_m = 1.3 m and z_m = 1.6 m height (changed on the 26 July). The fetch was around 120 m in the prevalent wind direction, which is a short fetch for EC measurements. The flux footprint was estimated with the Kormann and Meixner (2001) model using a roughness length z_0 of 0.06 m. The percentage of flux footprint in the field was found to range from 68% to 96% (for $u_* > 0.1$ m s^{-1}) and averaged 84%. The wind sector 240–300 deg/N was the most critical sector with only 72% of the flux footprint in the field. The eddy covariance fluxes of CO_2, latent (LE) and sensible heat (H), as well as the friction velocity (u_*) and the Obukhov length (L) were calculated as in Aubinet et al. (2000). The Eddysoft package (Kolle and Rebmann, 2007) was used to acquire and to calculate half-hourly mean eddy fluxes.

2.4. NH_3 concentrations with a QC-TILDAS

NH_3 concentration was measured with the compact QC-TILDAS-76 (SN002-U, Aerodyne Research Inc., ARI, USA; Zahniser et al., 2005). An accurate description of the device can be found in McManus et al. (2008) and Nelson et al. (2004), while Ellis et al. (2010) evaluated the performance of the instrument. In this trial, a 2.5 m long 0.75 cm inner diameter PFA tube was used as the inlet for the QC-TILDAS. The NH_3 concentrations of the QCL were calibrated to match the concentrations of the diffusion samplers, described in the following, with a calibration factor of 2.86 ± 0.09 as discussed in Ferrara et al. (2012).

2.5. Estimation of NH_3 fluxes by inverse modelling

NH_3 flux was estimated by inverse modelling using the concentration measured at the EC mast by the QCL ($C(z_m)$) and background NH_3 concentration (C_{bgd}) was estimated as the minimum of three sets of diffusion samplers (Tang et al., 2001) located at 100 m, 100 m and 300 m on the north, south and west of the field (Fig. 1) and changed weekly. The inverse modelling methods have been extensively detailed in Flesch et al. (1995, 2004, 2005a, 2005b, 2007) and the methodology used here detailed in Loubet et al. (2010)