Catena 166 (2018) 200–208

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Soil type and microclimatic conditions as drivers of urea transformation kinetics in maize plots

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ARTICLE INFO

Keywords:
Urea fertilizer
Nitrification rate
Ammonia volatilization
Numerical modelling
Relative humidity
Cation exchange capacity

ABSTRACT

This study presents a multidisciplinary approach (hydrological, microbiological, agronomic) to determine the dynamics of transformation of synthetic urea applied as soil fertilizer during maize production. The approach consisted in field and laboratory experiments on urea hydrolysis, ammonia volatilisation and nitrification, in four soil types (named Silty-loam, Silty-clay, Peat and Sand) intensively fertilized with synthetic urea. The field plots were modelled with HYDRUS-1D to determine the fate and transport of N species in the top soils. The numerical models successfully captured the main N transformations throughout the simulated period. In addition to the field monitoring of nitrogen species, microbial C and N, and urease activity were screened in each soil. The field soil sampling highlighted that the kinetics of ammonification was consistent with the hydrolysis of urea except for the sandy soil; kinetics of ammonification decreased in the order: Silty-clay > Peat ≫ Silty-loam > Sand. The differences of urease activities and nitrification potential rates between soils supported the measured field nitrification rates, and were as follow in order of decreasing rate: Silty-clay > Silty-loam ≥ Peat > Sand. The lowest nitrification rates pertained to the inherently more vulnerable sandy soil due to the scarcity of nitrifiers. The performance of volatilization was as follow in order of decreasing rate: Sand ≫ Silty-loam ≥ Peat > Silty-clay; but in general very low volatilization rates were found. This was imputed to the concurrence of both elevated soil CEC that promoted ammonium sorption and to low wind speed in the monitored plots. The presented multidisciplinary approach should be employed in many other agricultural settings to obtain robust data for numerical models simulations on the fate and transport of reactive N species in agricultural lands.

1. Introduction

In the last decades, the use of nitrogen fertilizer has increased exponentially at a global scale (Vitousek, 1997; Galloway, 2008) with detrimental consequences on freshwater and marine ecosystems (Jorgensen and Richardson, 1996; Ongley, 1996), on nitrous oxide emissions and greenhouse effect (Turner, 1991; Gruber and Galloway, 2008) and on groundwater and drinking water quality. This has caused serious health problems worldwide, such as methemoglobinemia or "Blue Child Syndrome" (Fan and Steinberg, 1996), congenital malformations (Dorsch et al., 1984) and different forms of cancer (Hill et al., 1973; Ward et al., 1996).

In the last three decades nitrate and ammonium based fertilizers have been progressively abandoned in favour of the use of urea (FAO-IFA, 2001; Gilbert et al., 2006). Nevertheless, only few studies have focused on urea transformations in different soil types, and the consequences on nitrogen fate in surface and groundwater pollution.

Literature reports that urea hydrolysis is rapid and usually occurs within three days after distribution (Yadav et al., 1987; Sankhayan and Shukla, 1976). Factors as timing and modalities of application (Al-Kanani et al., 1991; Khakural and Alva, 1995), soil moisture (Sankhayan and Shukla, 1976; Prasertsak et al., 2001; Wali et al., 2003), soil type (Sturnpe et al., 1984; Khalil et al., 2009) and air temperature (Bolado Rodríguez et al., 2005) have been evidenced to have a predictable effect on urea hydrolysis. Other relationships remain somehow controversial, as in the case of organic matter, which in some soils seems to increase urease activity (Kanchikerimath and Singh, 2001; Liang et al., 2014; Yadav et al., 1987) and in others to decrease it (Sankhayan and Shukla, 1976).

Once hydrolysis has occurred, several processes regulate nitrogen

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https://doi.org/10.1016/j.catena.2018.04.009
Received 26 April 2017; Received in revised form 4 April 2018; Accepted 6 April 2018
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fate. Released ammonia may adsorb onto soil particles, be assimilated by crops, volatilized to the atmosphere or be nitrified to nitrate (Pan et al., 2016; Sommer and Hutchings, 2001). Particularly, ammonia volatilization is of great concern since it can be greatly influenced by micrometeorological patterns, crop and soil types (Ferrara et al., 2014; Li et al., 2017). The nitrate not assimilated by crops is likely to be lost in runoff water, leached to groundwater (Ju et al., 2006; Mastrocicco et al., 2011) and/or be denitrified to N_2 and N_2O (Jahangir et al., 2012; Zhang et al., 2015). All these processes may be influenced at microscale by all above cited parameters regulating urea hydrolysis, in a series of interconnected microbiological, physical and hydrogeological processes, which should be considered as a whole to understand and predict reactive nitrogen fate, but are very difficult to tackle when working in the field. In fact, incomplete description of processes involved and the difficulty of having unambiguous input parameters remain the main limitations in describing urea and nitrogen fate in soils, as pointed out with dedicated model simulations (Marjerison et al., 2016; Michalczyk et al., 2014; Tan et al., 2015). In order to improve process based numerical models of reactive nitrogen emission and leaching, scientific literature must still gather studies with accurate and realistic data on reactive nitrogen emission and leaching mechanisms.

This paper presents the results of an interdisciplinary study on nitrogen transformations and fate achieved through field and laboratory experiments on urea hydrolysis, ammonia volatilization and nitrification, in four soil types intensively fertilized with synthetic urea. The aim of this study is to quantify the kinetics of urea transformation observed in the field by means of a deterministic numerical model, and highlight the role of soil type and local meteorological conditions in driving the reactive nitrogen speciation in topsoils.

2. Materials and methods

2.1. Study sites

This study was conducted in the Po Plain lowlands, which are intensively farmed due to the flat topography and to the abundance of surface water for irrigation. Here, the primary land use is maize cropping. In the study area, located in Ferrara Province (Italy) at an altitude ranging from 5 to −3 m above sea level, four sites (named Silty-clay, Silty-loam, Peat and Sand) were selected to monitor nitrogen transformations and transport in the unsaturated zone (Fig. 1).

For field site setup and characterization, see Mastrocicco et al. (2010) and Mastrocicco et al. (2012). Meteorological stations recording rainfall, wind speed, air temperature and relative humidity every hour are located from 0.5 to 1.5 km far from the field sites and are available on-line from the meteorological regional service (www.smr.arpa.emr.it/dext3r). Each field site was selected far from towns and buildings to avoid microclimatic effects induced by concrete pavements and surfaces, and to be representative of microclimatic conditions in agricultural environments. Although, sites are relatively near to each other with linear distances between 17 and 30 km (Fig. 1), the microclimates of Silty-clay and Silty-loam sites are influenced by the Po river, while the microclimates of Peat and Sand sites are influenced by the Adriatic Sea (Pavan et al., 2008). A medium maturing maize hybrid (*Zea mays* L., FAO 500, 125 days), commonly employed in this area, was selected to be grown in the four field sites, at density of 7 plants m^{-2}. Three replicate plots of 10 × 20 m were cultivated at each site and used to derive urea transformation and its standard deviation. The application of urea fertilizer was performed following the suggested best management practices delivered by the Emilia-Romagna Region, using the software CRITERIA that takes into account crop type, soil type, crop rotation and residual nitrogen in soil. The field experiments were conducted from the beginning of May 2008 to the end of August 2008, the urea was applied using the classical broadcast spreading, in previously ploughed fields to be representative of the local farmers' practices. The urea was applied 10 days before the maize seedling growth stage. Ploughing was performed before winter and consisted of a fall mouldboard ploughed down to 40 cm followed by disc harrow with no additional tillage operations prior to seeding and soil sampling. The applied urea-N rates were: 200 kg-N/ha for the Silty-clay, 230 kg-N/ha for the Silty-loam, 270 kg-N/ha for the Peat and 250 kg-N/ha for the Sand.

2.2. Field measurements

2.2.1. Soil characterization

From collected core samples, particle size curves were obtained using a settling tube for the sandy fraction and an X-ray Micromeritics Sedigraph 5100 for the finer one. Organic matter content (SOM) was measured by loss of ignition method, while dry bulk density and porosity were determined gravimetrically. Soil pH was determined using 1:1 soil/water ratio. $CaCO_3$ and CEC data were sourced from the soil online database of Emilia-Romagna region (https://agri.regione.emilia-romagna.it/Suoli).

2.2.2. C and N microbial biomass in soils

Twelve soil samples were collected (3 for each field site) in duplicates two days after fertilization, sealed in vacuum bags to maintain soil water content at field condition, stored in a cool box at 4 °C and immediately transported to the laboratory. The soil samples were adjusted to field capacity according to the estimates published by Saxton and Rawls (2006), and conditioned for 7 days at 22 °C.

For the extraction of C and N microbial biomass (C_{mic}, and N_{mic}, respectively), two sets of soil samples, one fumigated with ethanol-free chloroform for 24 h in the dark at 25 °C in a desiccator and the other non-fumigated, were treated according to the procedure proposed by Vance et al. (1987) for C_{mic} and to the procedure proposed by Horwath and Paul (1994) for N_{mic}.

The concentration of organic C in the extract was determined with a carbon analyzer (Carbon Analyzer Shimadzu TOC-V-CSM) after acidification with one drop of 2 M HCl to remove any dissolved carbonate.

C_{mic} was calculated as follows (Vance et al., 1987):

$$C_{mic} = \frac{E_C}{k_{EC}} = \frac{(C_{fs}) - (C_{nfs})}{k_{EC}} \quad (1)$$

where C_{fs} is the organic C extracted from fumigated soil and C_{nfs} is the organic C extracted from non-fumigated soil, while k_{EC} (0.45) is a proportionality factor for converting the E_C (extracted carbon) value to C_{mic} (Wu et al., 1990).

The concentration of NH_4^+-N and NO_3^--N in the extract were determined using a double beam Jasco V-550 UV/VIS spectrophotometer.

N_{mic} was calculated as follows (Jenkinson, 1988):

$$N_{mic} = \frac{E_N}{k_{IN}} = \frac{(N_{fs}) - (N_{nfs})}{k_{IN}} \quad (2)$$

where N_{fs} is the flush of NH_4^+-N due to fumigation and N_{nfs} is the NH_4^+-N produced in the non-fumigated soil during the 10 d of incubation, while k_{IN} (0.54) is the proportionality factor for converting the E_N (extracted nitrogen) to N_{mic}.

2.2.3. Assay of urease activity

Subsamples for urease analysis were passed through a 2 mm sieve and kept at 4 °C until the analyses were performed. Urease activity in soils was assayed by the buffer method (Tabatabai, 1994), which involves the determination of the NH_4^+-N released when a soil sample is incubated with THAM buffer at the optimal pH (pH 9.0) with or without toluene, and urea (0.2 M) at 37 °C for 2 h. When chloroform fumigation was used, urease activity was assayed within 1 h after removing the chloroform fumes by evacuation. The urease microbial activity was calculated by subtracting from the total urease activity the extracellular one.

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