



Direct measurement of dissolved dinitrogen to refine reactive modelling of denitrification in agricultural soils

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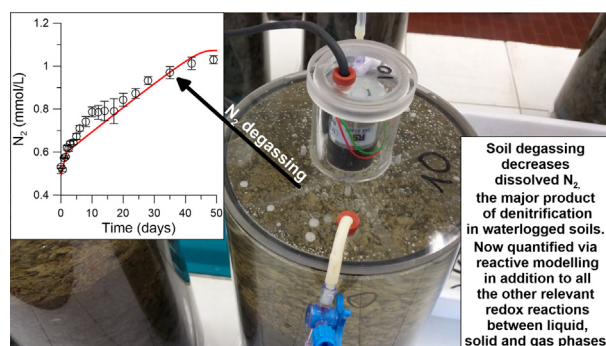
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HIGHLIGHTS

- Soils' denitrification rate increased when supplied with acetate.
- Soils showed high N₂ degassing, responsible for the low dissolved N₂ concentrations.
- This is the first model calibrated versus dissolved N₂ and all other redox species.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen fertilizers used in agriculture often cause nitrate leaching towards shallow groundwater, especially in lowland areas where soil permeability, ploughing, clay content, and the flat topography minimizes surface runoff. The introduction of good agricultural practices to reduce the nitrate amount entering the groundwater system is crucial to ameliorate the kinetic control on nitrate denitrification capacity. With this aim, a series of anaerobic mesocosms, consisting of loamy and clay soils and nitrate rich water, were modelled using acetate and natural organic matter as electron donors. Acetate was chosen because it is the main intermediate in many biodegradation pathways of organic compounds, and hence it is a suitable carbon source for denitrification. To account for the spatial variability of soil parameters, the experiments were performed in triplicates. The geochemical code PHREEQC(3) was used to simulate kinetic denitrification, and equilibrium reactions of gas and mineral phases. The reactive modelling results highlighted a rapid acetate and nitrate degradation rate, a rapid production of dissolved inorganic carbon and dinitrogen, and a steady concentration of dissolved iron and sulphate, suggesting that the main pathway of nitrate attenuation is through denitrification; concomitantly excluding the occurrence of other processes leading to nitrate consumption. In the absence of acetate, the loamy soil, poor of natural organic matter, did not allow to complete the denitrification process.

This modelling study investigates in detail the relationship between the denitrification process in natural soils, with excess and in limitation of organic substrates, and the occurrence and fate of dissolved dinitrogen analysed with a high precision membrane inlet mass spectrometer. Results demonstrate that modelling nitrate degradation processes as a whole, using geochemical datasets and codes, will improve the estimates of agricultural landscapes denitrification and support better nitrogen management, especially in lowland environments.

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1. Introduction

Nitrate (NO_3^-) is considered as the most widespread inorganic contaminant in both surface waters and groundwater due to agricultural fertilization practices (Puckett et al., 2011) and other sources like industrial and sewer systems (Wakida and Lerner, 2005) or wet and dry deposition (Bauer et al., 2007). It has been shown that the agricultural fertilization practices have risen the reactive nitrogen (N) inputs into the terrestrial biosphere up to a factor two respect to the 1860 levels (Galloway et al., 2004). It is also renowned that the ecological and toxicological effects generated by inorganic N pollution in aquatic ecosystems are detrimental (Camargo and Alonso, 2006). Recently, it has been shown that the vadose zone can be considered as a large NO_3^- reservoir, actually unaccounted in the global N cycle (Ascott et al., 2017). Thus, to understand the processes that occur in both the vadose and saturated zones, accurate data sets are needed to unravel NO_3^- fate from the application to the eventual leaching or transformation. Reactive N attenuation from surface to groundwater systems may take place via bacterial heterotrophic denitrification, using NO_3^- as electron acceptor and a carbon (C) source as electron donor, with the production of N gases (Rivett et al., 2008). This process has been extensively studied in superficial ecosystems, showing that the increasing trend of anthropogenic reactive N inputs can be overwhelming for the freshwater ecosystems (Seitzinger, 2008). Besides, other reactive gasses like N_2O and NO are often produced in well drained and tilled agricultural fields via incomplete denitrification (Mosier et al., 1998; Loick et al., 2016; Charles et al., 2017). Although, N_2O and NO production became less important in anaerobic conditions, while N_2 is the dominant denitrification product (Firestone and Davidson, 1989). To prevent such a disaster, best management practices of agricultural lands are more and more required and adopted by single nations or by international agencies (Tilman et al., 2002). One of the possible way out is to try to augment the labile organic content of soils, which in turn can diminish NO_3^- leaching via denitrification or by establishing wetlands or biofilters (Dinnes et al., 2002). Acetate is a good candidate as electron donor, since it is the main intermediate species in many biodegradation pathways of organic compounds, thus it is an appropriate C source to trigger denitrification processes (Castaldelli et al., 2013a). Beside denitrification, other processes can occur in the subsurface altering the reactive N fate, like the dissimilatory NO_3^- reduction to ammonium (NH_4^+) (Rütting et al., 2011), anammox and co-denitrification by fungi (Long et al., 2013) or autotrophic NO_3^- reduction (Chen et al., 2018). Then, new studies must take into account the role of different pathways that can affect NO_3^- in soils. In the recent past, to understand the chemical and biological processes responsible for the natural reduction of NO_3^- in soils and groundwater, a number of laboratory experiments and reactive-transport modelling studies have been performed (Mastrocicco et al., 2011; Yan et al., 2016). Numerical models are now also configured to incorporate isotopic fractionation processes controlled by kinetic and equilibrium conditions (Rodríguez-Escales et al., 2014; Vavilin and Rytov, 2015), but actually there is still a lack of accurate measurements and modelling of gaseous end-product of denitrification, like dinitrogen (N_2).

The main purpose of this research was to quantify the main biogeochemical reactions governing N_2 exsolution and transport through the vadose/saturated zone interface, using laboratory mesocosms simulated via the reactive geochemical code PHREEQC(3) (Parkhurst and Appelo, 2013).

As far as the authors are aware, this is the first biogeochemical modelling study in agricultural soils constrained by major redox species, combined with a high precision membrane inlet mass spectrometer (MIMS) employed to track N_2 production.

2. Materials and methods

2.1. Study sites

In Italy, the Po River valley is the largest and most intensively farmed alluvial plain, and is heavily impacted by NO_3^- contamination in groundwater (Soana et al., 2017) and surface water (Panepinto et al., 2016). In the coastal area of the Po River valley, four sites (representative of the most common soil types) have been extensively studied in the last decade within various national and international research projects. The four sites have different soils characteristics: sandy, peaty, silty-loam and silty-clay. The sites were set to deepen the knowledge on N transformations and transport in lowland and to select the most suitable strategies to reduce N load towards surface water (Castaldelli et al., 2013b) and groundwater (Mastrocicco et al., 2009). On the base of results previously achieved by field monitoring and laboratory experiments on denitrification (Mastrocicco et al., 2011; Castaldelli et al., 2013a), to conduct the present mesocosms experiment, soils were sampled in two of the abovementioned sites, here named CCR (silty-loam) and SAP (silty-clay). These two sites were chosen since only these ones were subjected to NO_3^- leaching and NO_3^- concentrations in groundwater above the maximum admissible limits of 50 mg/L. The soil thickness in both sites is elevated and has the same grain size of the parent materials (alluvial sediments of the Po river). The water table elevation is proximal to the ground surface in winter and spring time, with the soils ephemerally saturated, due to the low soil hydraulic conductivity in both sites (Mastrocicco et al., 2010). The low value of soil hydraulic conductivity found in both sites (approximately 3.0 cm/day) usually produce a perched water table, thus enabling waterlogging conditions after prolonged rain or irrigation events. Irrigation is usually supplied only in summer period using sprinklers depending on the crops need.

2.2. Unsaturated zone sampling and mesocosms set up

Soils were manually excavated in April 2016 from the plough layer (from topsoil to 30 cm below ground level) in both CCR and SAP sites selecting three different locations each distant from another at least 50 m to provide statistical representativeness of field conditions. Both soils were near to saturated conditions when collected. The soils were then re-packed in Plexiglas columns sealed with O-rings to avoid gas losses (Fig. 1). All the mesocosms were amended with 6.40 mmol/L of NO_3^- , mimicking an intense rain event of 100 mm after the first fertilization distribution in coverage on wheat (equivalent to 90 kg-N/ha). Three replicates from each site were amended with acetate (CCR-ace and SAP-ace), with a concentration of 5.40 mmol/L, according to the stoichiometric relationship of heterotrophic denitrification via acetate (Lew et al., 2012). Three replicates from each site were left unamended (CCR and SAP) to track the eventual natural denitrification capacity of the soils. Then mesocosms were sealed with a screw cap equipped with a screw-tight rubber sealed between two PVC disks. Once sealed, each mesocosms consisted in 30 cm of soil overlaid by 10 cm of water with no headspace (Fig. 1).

2.3. Analytical methods

Technical grade (99% purity) acetate and KNO_3 salts were purchased from Merck (Darmstadt, Germany). Water samples were filtered through a 0.22 μm mesh. NO_3^- and nitrite (NO_2^-) were measured on a Technicon Auto Analyser II. NH_4^+ was determined on a double beam Jasco V-550 spectrophotometer using salicylate and hypochlorite in the presence of sodium nitroprussiate. Acetate was determined as total fatty acids on a double beam Jasco V-550 spectrophotometer after esterification with ethylene glycol and subsequent reduction with FeCl_3 . The major cations and anions of selected samples were determined by ion chromatography. Dissolved ferrous iron (Fe^{2+}) and

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