Tracing nitrification and denitrification processes in a periodically flooded shallow sandy aquifer

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Abstract. The study defines the transfer mechanisms of nutrients and heavy metals from soil to groundwater operating in periodically water saturated soils. The study site is located in Lomellina (Po plain, Northern Italy), which is intensively cultivated with rice. Soils are dominantly constituted by sands, with acidic pH and low organic carbon content. The region generally displays low nitrate contamination in shallow groundwater, despite the intensive land use, while Fe and Mn often exceed drinking water limits. Monitoring performed through a yearly cycle closely followed the water table fluctuations in response to periodical flooding and drying of cultivated fields. pH, conductivity and Eh were measured in the field. Water samples were analysed for major ions, trace elements, nutrients and stable isotopes of DIN. Results evidence the seasonal migration of nutrients, the redox and associated metal cycling, and allow defining nitrification and denitrification processes.

1. Introduction

The Po plain, located in Northern Italy, supports most of the agricultural and industrial activities of Northern Italy, which are associated with groundwater exploitation and pollution mainly in the shallower aquifers. The Lomellina region represents a limited portion of the Po plain, of approximately 900 km^2 (Fig.1). The investigated aquifer is constituted by sediments belonging to the continental depositional system of Plio-Pleistocenic age [1, 2] and is made of gravels and sands with interbedded clay layers. This formation, reaching a depth of 150-200 m, creates a multilayer aquifer system with a water table a few meters deep; it is an aquifer of great importance for the lateral extension and for high transmissivity, of about 10^{-2} m^{2}s^{-1}. Two units can be locally recognised due to the presence of a discontinuous, impervious, silt and clay layer to a depth of 60-80 m. Groundwater flow direction is roughly oriented N to S, but, in the phreatic aquifer, is strongly controlled by draining action of the Po, Sesia and Ticino rivers (Fig. 1).

The Lomellina region is characterised by an elevated potential infiltration [3] and is intensively cultivated with, mainly, rice and corn fields. The recharge areas for the multilayer aquifer are located in the Alpine piedmont, but severe recharge takes place from seepages of channel network and from rice ponds. Soils are arenosols and luvisols, with acidic pH, mainly constituted by quartz and feldspars. A strong depletion of Mn and Fe in the topsoil is often observed in rice paddies, together with the formation, at a depth greater than 80 cm, of Fe and Mn oxi-hydroxides [4]. Soil Fe-Mn precipitates and nodules are formed within the soil pore network as a result of seasonal changes in the soil redox potential and pH. Under reducing conditions, Fe and Mn oxides release Fe(II) and Mn(II) ions to the soil solution. When the soil dries out, Fe(II) and Mn(II) oxidise and precipitate, forming new metal oxides [5]. Manganese is more mobile than Fe and requires a higher oxidation potential compared with Fe(II), leading to the formation of alternate layers of Fe-rich and Mn-rich material [6].
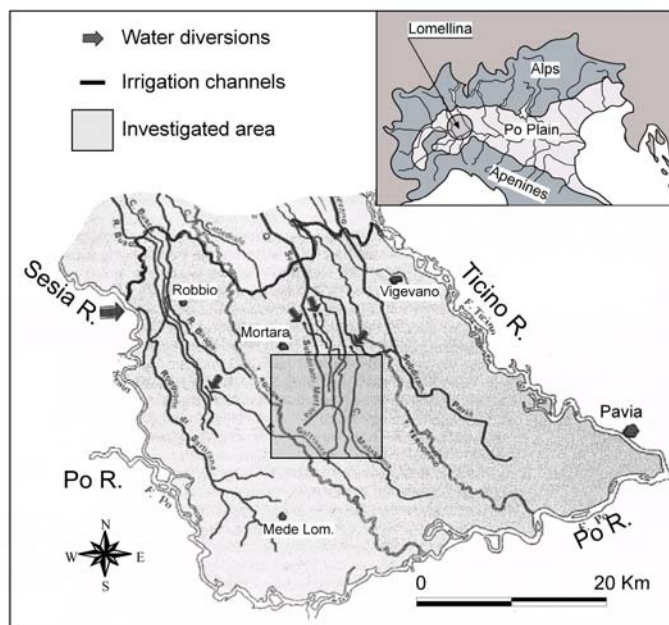
FIG. 1. Location of the investigated area

2. Methods of investigation

Eleven very shallow wells (< 20 m depth) were selected in a limited area (50 km^2) for water level, hydrochemical and isotopic monitoring. The water table depth was measured daily at the centre of the investigated area. Groundwater sampling closely followed the agronomical practices and was performed approximately once per month, from March 2006 to January 2007. Analyses included: pH, Eh, temperature, conductivity, major ions, trace metals, and, stable isotopes of dissolved nitrates. The pH, redox potential, temperature and conductivity were measured in situ. Chemical analyses were performed at the Dipartimento di Scienze della Terra, University of Pavia. Anions and cations were determined by ion chromatography and trace metals by ICP-AES. All reported values have ionic balance within 5%. Samples for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ analysis were collected and prepared according to standard procedures [7, 8]. All gases were analysed on a Finningan™ MAT 250 Mass Spectrometer at ISO4 s.s., Turin, Italy. The analytical errors are ±0.2 and ±1 ‰ respectively.

3. Results

In the Lomellina region, the phreatic aquifer displays waters of poor quality: high salinity, high nitrate, sulphate and chloride contents and, locally, detectable amounts of heavy metals (Fe, Mn, As) and pesticides [9]. The seasonal fluctuation of the water table (Fig. 2) shows a steep rise of the water table of 1.6 m, related to field waterlogging, rising the piezometric surface to about 1.5 m below the surface. Data collected from local irrigation agencies allowed calculating for the entire season a recharge of about 38,000 m^3/ha, highly exceeding natural recharge from precipitation. The seasonal variation of groundwater quality includes a rise in temperature and conductivity, and a decrease in pH, a typical evolution for shallow groundwater. On the other hand, Eh is highly variable from well to well, ranging from 450 to 210 mV and indicating the presence of localised oxido-reduction phenomena. Based on hydrochemical characteristics and seasonal evolution two groups of waters may be distinguished:

— Group 1 (wells 5, 6, 7, 8, 10, 11 and 12, empty symbols in all figures). After soil flooding, this group of wells shows a progressive decrease in Eh and dissolved nitrates (DIN), increase in alkalinity and Fe content. Mn is always low and Zn content may rise up to 2.6 mg/l.

— Group 2 (wells 1, 4, 9 and 3, full symbols in all figures). These wells show an inverse seasonal evolution, i.e. an increase in Eh, dissolved nitrate and Mn contents, decrease in Fe and low Zn content. These wells also show very high K contents (up to 60 mg/l).
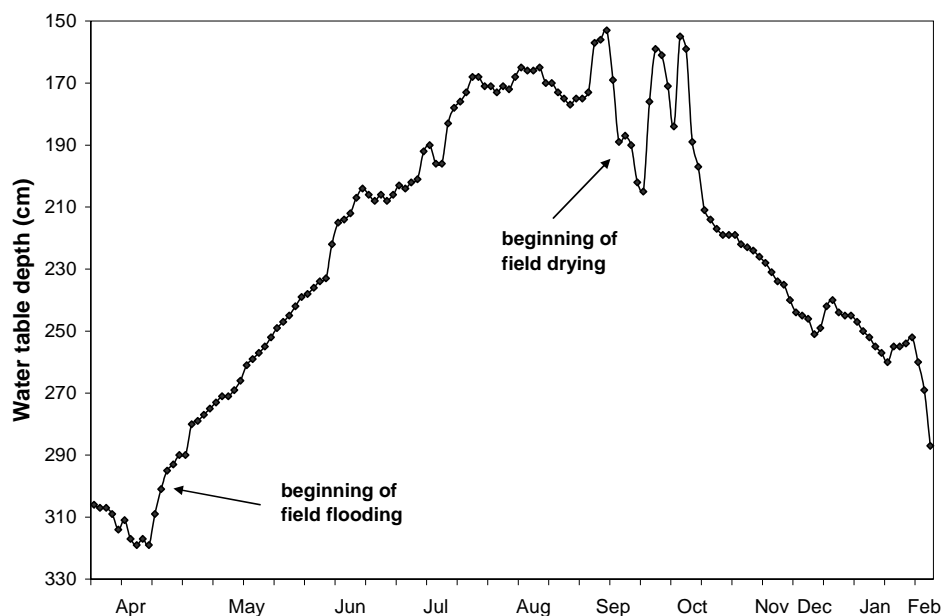
FIG. 2. Water table level fluctuation in response to soil flooding

The behaviour of heavy metals is closely connected to that of DIN (Fig. 3), although the two groups display an opposite seasonal trend. Most wells show an inverse correlation between Fe and DIN. In addition, samples of group 2 containing high Mn show a direct correlation between Mn and DIN. Zn contents up to 2 mg/l are observed in wells of group 1; group 2 displays lower Zn contents, showing a positive correlation with Fe (and negative correlation with DIN).
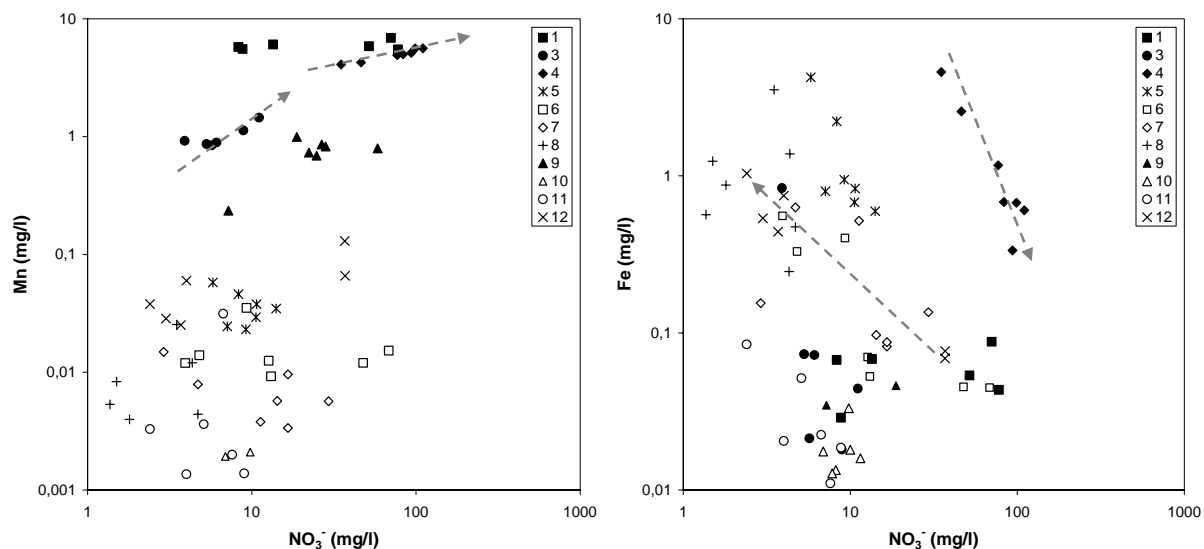

FIG. 3. Seasonal evolution of DIN and heavy metals. Grey arrows indicate the seasonal trends observed in different wells. Group 1 = empty symbols, group 2 = full symbols

The isotopic composition of dissolved nitrates also clearly differentiates the two groundwater types (Fig. 4). Group 1 shows $\delta^{15}N$ ranging from +4 to +13 ‰, and several samples fall in the compositional field of soil organic matter; group 2 shows more enriched values for both stable isotopes and aligns along the slope of the denitrification trend.
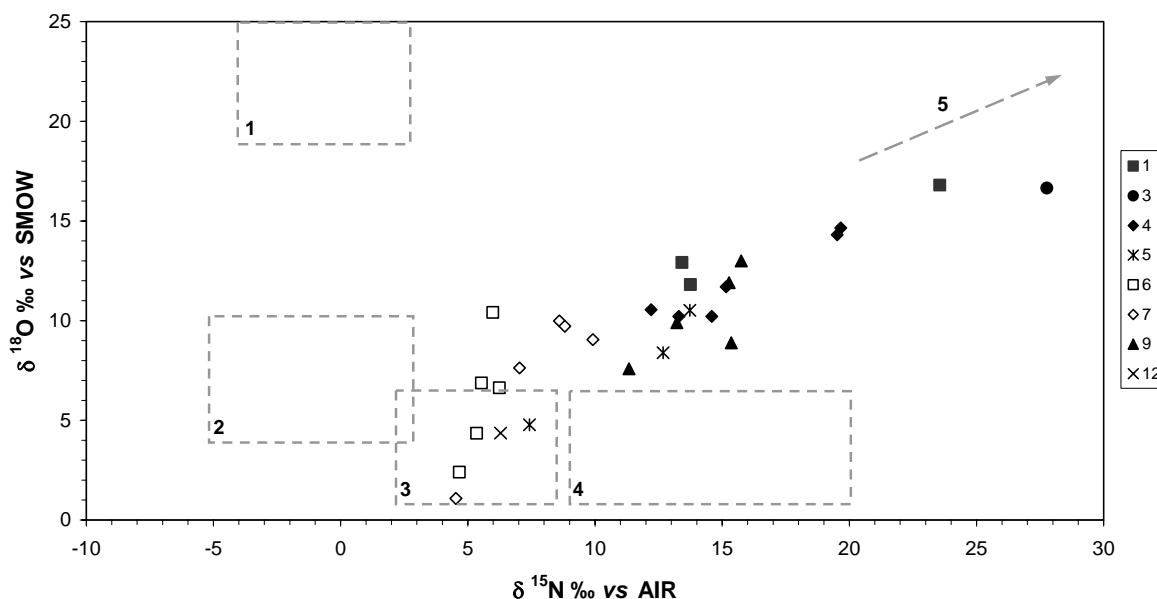

FIG. 4. Isotopic composition of DIN. 1= synthetic fertilisers; 2 = mineralised synthetic fertilisers; 3 = soil organic matter; 4 = manure and septic tank effluents; 5 = slope of the denitrification trend

4. Interpretation

Fig. 5 shows the seasonal trends observed in DIN content and isotopic composition for the two groups of samples. After soil flooding, group 1 shows a marked decrease in nitrate contents associated to enrichment in the nitrogen isotopic composition. This trend is easily interpreted as a denitrification, operated *via* the oxidation of the dissolved inorganic matter and producing an increase in alkalinity. Samples with the highest nitrate concentrations show $\delta^{15}N$ composition typical of the soil organic matter and a $\delta^{18}O$ composition in equilibrium with the water isotopic composition ($\delta^{18}O \approx$ -9‰) [10]. On the other hand, the observed increase in $\delta^{18}O$ of DIN cannot be justified by a contribution from enriched nitrates or by the reopening of the system to atmospheric O_2. It is therefore suggested that the Fe oxi-hydroxides may play a role in modifying this isotopic signal. During denitrification, the increase in Fe content is probably due to the destabilization of Fe oxi-hydroxides, as it is not coupled to a parallel increase in sulphates: therefore a denitrification operated *via* pyrite oxidation can be excluded.

Previous studies have highlighted the important role of Fe and Mn dynamics in trace metal mobilisation in soils. A marked increase in the soil solution concentrations of metals like Cu, Zn or Cd, related to Mn and Fe reduction and mobilization as effect of lowered Eh in flooded soils is reported [11]. This mechanism could explain the direct relationship observed between Fe and Zn in several wells.

Following waterlogging, group 2 shows a seasonal evolution of progressive increase in DIN and depletion in $\delta^{15}N$ and $\delta^{18}O$; this evolution is also accompanied by an increase in dissolved Mn and a decrease in dissolved Fe and alkalinity. This evolution follows the slope of the denitrification trend, but in the opposite direction, and could therefore be interpreted as a mixing process between a residual and a "fresh" nitrate source. Nevertheless, samples with the highest nitrate concentrations have an isotopic composition of about +12.5 in $\delta^{15}N$ and + 10.5 in $\delta^{18}O$ which cannot be readily attributed to any precise source.
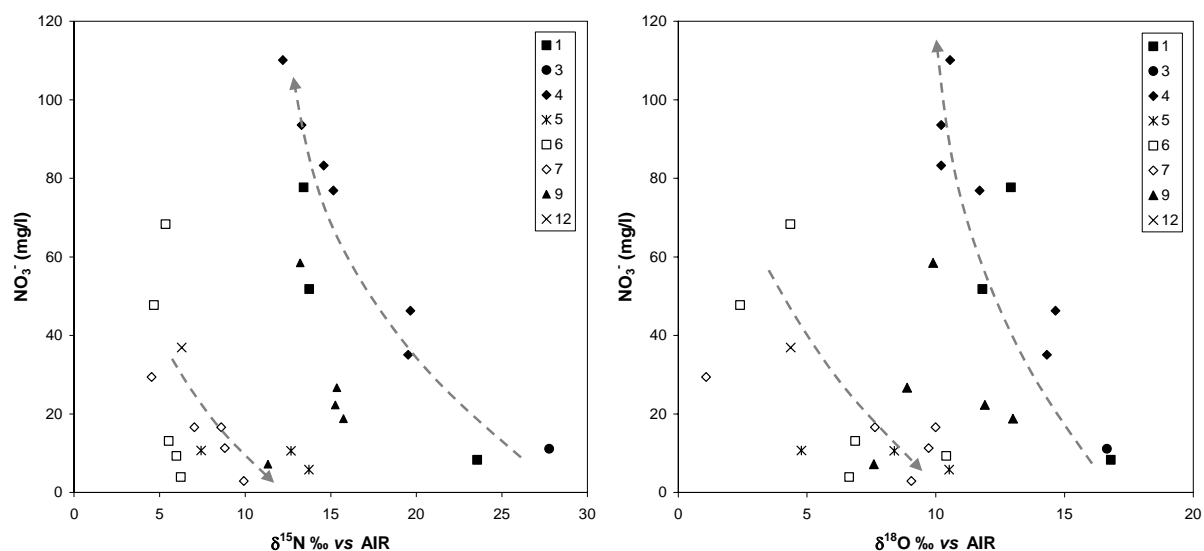
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FIG. 5. Seasonal evolution of DIN content and isotopic composition

Flooded rice paddies are microbiologically very active systems where, within few cm depths, rapid changes in the redox conditions are observed [12]. In late spring, fields are waterlogged and a reducing environment is established; two or three periods of drying up are performed to allow for pesticide and herbicide treatments, followed by re-flooding. Finally, at the end of the growing season, the field is desaturated and water is allowed to evaporate; as a consequence an oxic environment is established during winter. Rice cultivation requires the use of reduced ammonium-based fertilizers, generally urea. This compound can be oxidized to nitrate, if oxygen is present. After flooding, dissolved oxygen is rapidly consumed and nitrate is the first molecule reduced after oxygen depletion, followed by Mn(IV), Fe(III) and sulphates, according to the redox potential of the electron acceptor. Along oxic-anoxic interfaces, directly beneath the waterlogged soil, alternative electron acceptors will be regenerated because of the re-oxidation of reduced compounds [12]. The oxygen isotopic composition of biogenic manganese oxides indicate that they derive 50% of their oxygen from water and 50% from dissolved oxygen [13]. Therefore their isotopic composition is enriched in $\delta^{18}O$ with respect to water, despite the absence of fractionation during precipitation. In our case study their isotopic composition, in equilibrium with local groundwater ($\delta^{18}O \approx -9‰$) should be approximately of +6-7‰.

An enriched $\delta^{15}N$ in DIN from agricultural environments is generally attributed to manure spreading. Nevertheless ammonification, volatilization and plant uptake may enrich the isotopic signal of synthetic fertilizers of several deltas [14]. Given the close relationship observed between dissolved nitrate and Mn content in samples from group 2, it is suggested that their enriched isotopic composition could be obtained by nitrification of residual ammonium using MnO_2 as an oxygen source. A simple calculation estimates this contribution to the nitrate-oxygen to less than 1/3. On the other hand, this does not agree with the amount of dissolved Mn. Therefore, to explain the enriched oxygen isotope composition of DIN, we need to consider that the oxidation likely occurs during the drying up of the paddies, when the water isotopic composition can be enriched due to evaporation.

The difference in hydrochemical and isotopic evolution between group 1 and 2 cannot be readily justified on the basis of location, land use, permeability or redox conditions. Nevertheless, it should be noted that the conspicuous recharge from the surface likely induces a chemical stratification within the first meters of the aquifer. In addition, at the same location, the redox conditions may quickly vary with depth and time in response to soil flooding and drying episodes.

5. Conclusion

Flooded rice paddies provide a unique environment where, in ideal conditions, nitrification and denitrification processes can be traced and rates calculated. This was not possible at the end of this monitoring year, because the cycle was not completely closed by a return to the initial conditions. This is attributed to the exceptionally warm winter experienced this year, allowing the biological activity in soils to persist.

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