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title: The role of the unsaturated zone in determining nitrate leaching to groundwater

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INTRODUCTION

Nitrate leaching from agricultural sources is a worldwide concern and in Europe a large part of farmed areas are affected by nitrate pollution since decades. In Italy, the Po River valley is the largest and more intensively farmed alluvial plain, heavily impacted by agricultural pollution and especially by NO_3^- groundwater contamination (Onorati et al., 2006; Cinnirella et al., 2005; Giuliano, 1995) and surface water eutrophication (Provini et al., 1992; Palmieri et al., 2005). With the enactment of the European Directive for water protection (2000/60 CE), a large portion of the Po river valley has been declared vulnerable to nitrate from agricultural sources and limitations to the use of N fertilizers have been applied. However, in agricultural practices, the types of soils and soil tillage, different crops and irrigation techniques and different nitrogen fertilizers, which may be synthetic, as ammonium nitrate and urea, or natural, as manures and sludge from different animal farming, form a variety of terms emphasizing site specificity of WFD application and results. Moreover, the general knowledge of key factors governing patterns and processes of N transport and transformations through the vadose zone to the water table are not fully clarified. Within this multidisciplinary framework, for any applied research finalised to reduce nitrogen losses , it is essential to fix a benchmark to star from, which in our view is aquifer recharge assessment, i.e. to quantify water resources and flux toward aquifers (Scanlon et al., 2002). Presently, the most effective tool to quantify recharge flux is to model the unsaturated soil water dynamics, although this process faces many challenges in field conditions (Youngs, 1995).

In order to identify the dominant processes affecting nitrate leaching in the Po River Delta area, a series of tracer tests were performed to determine conservative mass transfer and the fate and transport of nitrogen species.

MATERIALS AND METHODS

Each field site was equipped with: tensiometers and soil moisture probes for continuous monitoring of soil water potential; meteorological stations recording rainfall, wind speed, solar radiation, temperature and humidity; drains and suction cups to collect water samples for anions and cations analysis; core logs down to 2 m b.g.l. were collected to define soil water content, soil texture, organic matter content and bulk density; piezometers (2.5 cm inner diameter) screened from 1.5 to 4.5 m b.g.l., were monitored (via multi level samplers) to quantify the presence of nitrogen dissolved species in the shallow unconfined aquifer. Monitoring started in February 2008 and is still on, not at a constant frequency but following rainfall (on a monthly frequency, increased to daily in occasion of important event). Bromide was applied at the surface as a NaBr salt and nitrogen was applied as urea at a rate of 300 kg/ha, in a sandy and a loamy sites cultivated with maize (Andreotti et al., 2009). According to local practices, the sandy soil had been amended with chicken manure (70 q/ha) from organic breeding in the previous year, while the loamy soil had not. The major cations, anions (Na+, K+, Ca2+, Mg2+, F-, Cl-, NO3-, SO42-) and oxianions (acetate and formate) were determined by an isocratic dual pump ion chromatography ICS-1000 Dionex, equipped with AS9-HC 4 × 250 mm high capacity column and ASRS-ULTRA 4mm self-suppressor for anions and CS12A 4 × 250 mm high capacity column and CSRS-ULTRA 4mm self-suppressor for anions. An AS-40 Dionex auto-sampler was employed to run analysis, Quality Control (QC) samples were run every 10 samples. The flow and transport processes were quantified by inverse modeling with the finite element numerical code HY-

DRUS-1D (Šimunek et al., 2008). The numerical grid was discretized in 200 nodes of 0.01 m each to form a regular grid 2 m long and a surface area of 1 m^2. The grid was subdivided into 2 regions representing the upper and the lower soil horizons, initial water content conditions of collected soil cores (every 0.25 m) at each site, were measured via gravimetric methods and linearly interpolated along the vertical axis. At the soil surface, an atmospheric boundary condition with a maximum surface layer of 0.01 m was selected. As lower boundary condition variable pressure heads were specified in every model using groundwater levels. The transport boundary condition at the surface was a prescribed concentration and at the lower boundary was a zero concentration gradient (free drainage) condition. Input concentrations of Br^- and NO_3^- were gained from soil extracts collected at the soil surface (0-5 cm) throughout the monitoring period. Ammonia volatilisation was estimated in lab by using flow trough system microcosms and evolved ammonia was captured in acid traps (Bolado Rodríguez et al., 2005).

RESULTS AND DISCUSSION

Unsaturated zone modelling

A good model fit of water content and head pressure at various depth was achieved in each site. A robust estimation of cumulative infiltration and evapotranspiration has been derived and the obtained water balance is considered reliable (R^2: 92% for the loamy soil and 84% for the sandy soil). In the loamy soil, NO_3^- and Br^- percolated downwards very slowly, with sharp peaks located approximately 0.3 m below ground level after the harvest (Fig.1).

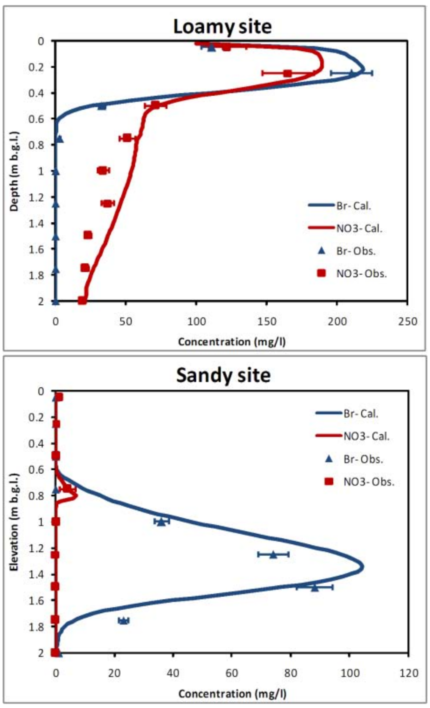

Figure 1. Observed and calculated Br^- and NO_3^- concentrations along the soil profile in the loamy and sandy site after 120 day from the fertilization.

In the sandy soil NO_3^- disappeared within the first meter of soil, while the Br^- peak was recovered approximately 1.5 m below ground level (Fig.1). The fast migration of Br^- in the sandy site was due to the elevated hydraulic conductivity of the soil (Tab. 1), while the disappearance of NO_3^- was essentially due to root uptake and denitrification (Fig.2).

A good match between calculated and observed bromide concentrations was obtained in both sites via the inverse modeling procedure encoded in HYDRUS-1D. A robust reconstruction of the field velocity and of the dispersion coefficient was achieved matching observed and calculated Br^-concentrations.

Table 1. hydraulic and transport parameters used in the numerical models for the two soil horizons of each site.

Parameter	Loam (0-0.75 m)	Loam (0.75-2 m)	Sand (0-0.55 m)	Sand (0.55-2 m)
K_s (m/d)	0.02	0.053	8.1	15.4
θ_s (m³/m³)	0.41	0.38	0.36	0.31
θ_r (m³/m³)	0.05	0.06	0.039	0.025
α (1/m)	0.12	0.51	8.50	11.21
n (-)	1.45	1.53	2.21	2.42
Disper. (m)	0.01	0.001	0.002	0.001
Diff. (m²/d)	$1e^{-4}$	$1e^{-4}$	$1e^{-4}$	$1e^{-4}$
μNO_3^- (1/d)	0.003	0.004	0.01	0.1

Very small vertical dispersivity values were obtained (Tab. 1) in both sites, to account for the sharp concentration gradients observed in both fields. Mass recovery of bromide was near 90% for sandy and loamy soils, suggesting that homogeneous transport processes were present at the field scale.

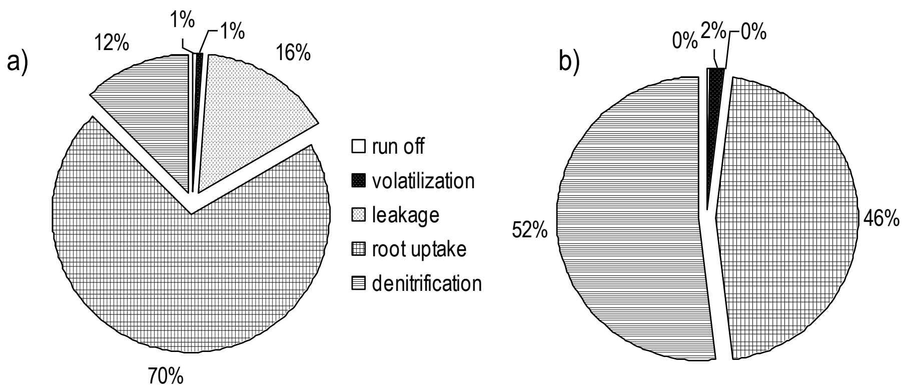

Figure 2. NO_3^- balance cake plot for: a) loamy soil; b) sandy soil.

Results for the nitrogen mass balance are in good accordance with concentrations measured in the field for the same nitrogen species at the same sampling time. NO_3^- leaching was observed in the loamy soil where the redox conditions remained oxidizing throughout the year, while in the sandy soil residual content of organic matter from fertilization with manure in the previous year (fraction of organic carbon: 0.042 and acetate: 34 mg/l) very likely decreased the redox potential to reducing conditions and favored excess nitrate removal via denitrification preventing its migration towards the saturated zone (Fig. 2).

Nitrate leaching to groundwater

Figure 3 shows a largely variable groundwater table in the loamy site, where the groundwater flow is linked with canals level, while, in the sandy site groundwater fluctuations were less pronounced, since it is located near the coast and fluctuations are smoothed. In the loamy soil nitrate mass transfer to the unconfined aquifer was slow as shown in Fig. 1 and concentrated at the end of the winter season, when the water table rise and bring in solution the available NO_3^- (Fig. 3).

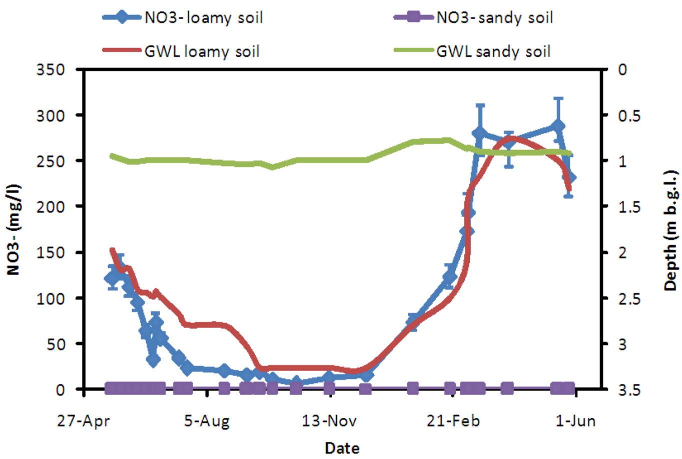

Figure 3. groundwater level fluctuations and NO_3^- trends in groundwater in loamy soil and sandy soil throughout the year.

In the sandy site, despite the fast transfer of mass, NO_3^- was never detected, confirming the results from the unsaturated zone (Paragraph "Unsaturated zone modeling").

CONCLUSIONS

Results highlight the reliability of the use of conservative tracers and numerical modeling jointly, to understand nitrate mass transfer rate and mass balance.

For the practical interest of WFD application, this approach has evidenced that in the sandy soil, more permeable and intrinsically more vulnerable, the relatively low amount of organic matter lasting from manure use in the previous year, was sufficient to prevent nitrate leaking, by removing the excess via denitrification. This result highlights the need to pay attention to the kind of manure used and to the relative degradation kinetics which may also be heavily affected by farming type, organic or industrial. This last term, in fact, other than impacting water quality for the presence of hormones and other undesired chemicals, may influence organic matter and nitrogen mineralization rates, interfering with bacterial activities due to the presence of antibiotics.

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