Agricultural Water Management 98 (2011) 1441–1450

Contents lists available at ScienceDirect

Agricultural Water Management

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

Nitrate fate in a Mexican Andosol: Is it affected by preferential flow?

B. Prado[a,*], C. Duwig[b], J. Etchevers[c], J.P. Gaudet[d], M. Vauclin[e]

[a] *Instituto de Geología, Universidad Nacional Autónoma de México, Cd. Universitaria, CP 04510, México, DF, Mexico*
[b] *IRD/UJF-Grenoble 1/CNRS/G-INP, LTHE UMR 5564, Grenoble, F-38041, France*
[c] *Colegio de Postgraduados, Laboratorio de Fertilidad de Suelo, CP 56230 Montecillo, Mexico*
[d] *UJF-Grenoble 1/CNRS/IRD/G-INP, LTHE UMR 5564, Grenoble, F-38041, France*
[e] *CNRS/UJF-Grenoble 1/IRD/G-INP, LTHE UMR 5564, Grenoble, F-38041, France*

ARTICLE INFO

Article history:
Received 14 July 2010
Accepted 26 April 2011
Available online 19 May 2011

Keywords:
Anion adsorption
Physical non-equilibrium
Variable charge soil
Isotopic tracer

ABSTRACT

Andosols are the dominant soils in the Valle de Bravo basin, the origin of a significant amount of Mexico City's drinking water. The main land use is agriculture and most of the existing surface water bodies are eutrophic. Nitrogen fertilizer is used extensively. There have been very few studies on nitrate (NO_3^-) fate in this type of soil and region. Comprehensive laboratory studies were conducted to determine the fate of NO_3^- in an Andosol profile from Valle de Bravo, in order to assess the risk of water resources contamination. Nitrate retention was analysed statically (using batch experiments) and dynamically (using intact and packed soil columns) at different soil depths and its competition with Cl^- was evaluated. Complementary laboratory experiments were conducted to study water transport through the columns and nitrogen transformations in the soil. In batch and columns, NO_3^- adsorption was linear in the range of concentrations studied and higher in the deepest soil layer. Preferential flow pathways were found in the unaltered deeper soil layers, while tillage activity in the top layer destroyed the pore continuity. In spite of the deeper soil layer's greater capacity for NO_3^- retention, the presence of preferential flow pathways coupled with high rainfall intensities, makes the NO_3^- mobile below the root zone at 1 m depth and increases the risk of groundwater contamination. The results illustrate the complexity of nitrate fate in Andosols and can be used to improve agricultural practices in the central Mexico region.

1. Introduction

Extensive research on preferential flow has been conducted on temperate soils. A complete review of the principles and controls on preferential flow and transport in soil has been published by Jarvis (2007). Preferential flow and transport phenomena can occur at all scales from the pore scale of 10^{-3} m to large regions of 10^6 m (Clothier et al., 2008). There is a great emphasis on how these flows heterogeneously transport a range of substances, including nitrate (Seo and Lee, 2005), organic compounds (Wehrer and Totsche, 2008), biota, pesticides (Kahl et al., 2008), and colloids (Burkhardt et al., 2008). However studies on preferential flow in soils from volcanic origin are scarce and do not find consistently preferential flow in this soil type. Preferential flow has been observed in Andosols using fluorescent tracers (McLeod et al., 1998; Duwig et al., 2008) and by infiltrometry on undisturbed cores (Clothier et al., 2000). Maruyama et al. (2003), Eguchi and Hasegawa (2008) and Prado et al. (2009) found that the flow bypassed a part of the soil matrix, and that preferential flow occurred in tubular macropores. On the contrary, neither Magesan et al. (2003) nor Sansoulet et al. (2007) found preferential flow in their study on intact cores. Preferential flow in soils is associated with the earlier appearance of agrochemicals in groundwater than in soils with homogeneous wetting. It poses a particular problem in agricultural areas used as catchments for water supply. This is the case with the Cutzamala system which provides 21% (19 $m^3 s^{-1}$) of Mexico City's water supply.

The Cutzamala system is located on the west side of Mexico City in the Trans Mexican Volcanic Belt and the study site is inside Valle de Bravo watershed, the most important sub catchment of the Cutzamala river basin. Field observations (Secretaría de Ecología, 1999) showed that crop productivity in Valle de Bravo watershed is low, encouraging farmers to apply agrochemicals. Farmers often are not trained and usually do not conduct any soil fertility measurements. Olvera-Viascán et al. (1998) observed that most of the surface water bodies in the Valle de Bravo watershed were eutrophic with the highest phosphorus and nitrogen loadings entering the Valle de Bravo reservoir through the Amanalco river system. Merino-Ibarra et al. (2008) studied the physical and chemical limnology of Valle de Bravo reservoir and found high-chlorophyll-a values and cyanobacterial blooms taking place during

---

[*] Corresponding author. Tel.: +52 56224286x159; fax: +52 5555506644.
E-mail addresses: bprado@geologia.unam.mx (B. Prado), celine.duwig@ird.fr (C. Duwig), jetchev@colpos.mx (J. Etchevers), jean-paul.gaudet@ujf-grenoble.fr (J.P. Gaudet), michel.vauclin@ujf-grenoble.fr (M. Vauclin).

0378-3774/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.agwat.2011.04.013

the stratification period (February to October). They concluded that water quality in Valle de Bravo reservoir was mainly affected by eutrophication. Studies on agrochemical fate in the soil of the catchment are thus an important first step in understanding the origin of the contamination sources and reducing the water eutrophication.

Andosols show high water retention, good permeability, and generally high organic matter content. They are highly productive agricultural soils (Shoji et al., 1993; Dahlgren et al., 2004). The existence of amorphous short range compounds combined with high organic matter content confers a variable charge to Andosols (Shoji et al., 1993). The presence of these short range compounds and the high saturated hydraulic conductivity (around or above 10^{-5} ms^{-1}, Armas-Espinel et al., 2003) make the study of ion dynamics in Andosols complex. Nitrate (NO_3^-) movement through soils depends on water movement and sorption processes. Sorption of NO_3^- in Andosols has been well documented (Kinjo and Pratt, 1971a; Sansoulet et al., 2007). Transport studies have been conducted on repacked columns under transient flow in horizontal columns (Katou et al., 1996) and vertical lysimeters (Feder and Findeling, 2007), under saturated conditions in the laboratory (Qafoku et al., 2004) and field studies under unsaturated flow conditions (Payet et al., 2009). Using classical “static” laboratory methods, various authors have linked NO_3^- sorption to the positive charges of allophanes. Nitrate sorption capacity varies depending on the amount and type of allophanes (Al or Si rich allophanes) (Ryan et al., 2001), the soil solution pH (Schalscha et al., 1973), the solution ionic strength (Sposito, 1984), and competition with other anions such as Cl^- (Kinjo and Pratt, 1971a; Katou et al., 1996; Feder and Findeling, 2007). However, little work has been done on solute movement in Andosols using intact soil columns under unsaturated flow conditions (Magesan et al., 2003; Eguchi and Hasegawa, 2008; Prado et al., 2009). This is fundamental to understand what happens to NO_3^- in Andosols under field conditions.

In the present study, nitrate transport was studied in an Andosol profile to a depth of 0.9 m from the Valle de Bravo basin. The goal was threefold: (i) to assess the importance of each process affecting nitrate fate i.e. preferential flow, sorption and transformation, (ii) to compare the results obtained by different laboratory methods, under static or dynamic conditions, and (iii) to evaluate the competition between NO_3^- and Cl^-. For this purpose, a range of independent laboratory experiments were combined, making this study a more complete work than previous studies where NO_3^- and Cl^- leaching were examined on Andosols. Soil NO_3^- retention was studied both dynamically (displacement in intact and repacked soil columns) and statically (batch experiments) at three different depths. Competition between NO_3^- and chloride ions was studied by analysing Cl^- behaviour in the same experiments. Soil mineralogy, chemistry, and exchange capacities affecting NO_3^- transfer were evaluated. Bacterial NO_3^- transformations such as nitrification and denitrification were analysed using incubation experiments.

2. Material and methods

2.1. The study site

The Cutzamala system is located on the west side of Mexico City in the Trans Mexican Volcanic Belt (Prado et al., 2007). Half of the system supply of water comes from Valle de Bravo reservoir (394×10^6 m^3, Tortajada and Castelán, 2003). Valle de Bravo basin, part of the Cutzamala system, is located in the Trans-Mexican Volcanic Belt and is characterised by the predominance of volcanic rocks from the Cenozoic Era, with basalt in the lower part of the basin, and andesitic rocks in the upper part. The hydrogeology of the region is not well known and no information could be found on groundwater use and quality, but 541 springs were counted in the basin (Carrillo-Rivera, 2006). Indeed, Amanalco signifies “the place where water is born” in Otomi language. The experiment was conducted in the La Loma micro-watershed located in the Amanalco watershed, a sub-catchment of Valle de Bravo basin (Fig. 1). The site is representative of the environmental conditions and land use in the Valle de Bravo basin.

The watershed covers an area of 53 ha between 19°16′48.6″ and 19°16′11.3″ North, and 99°58′13.7″ and 99°59′13.7″ West. It has an elevation of 2500–3100 masl, a mean annual rainfall of 1300 mm, an average temperature of 10.7 °C and a mean annual evapotranspiration of 1240 mm. The raining season is between June and September and accounts for 70–85% of the total yearly rainfall.

The main crop in the La Loma micro-watershed is maize, which occupies 35% of the land area and is fertilized with 90 kg N ha^{-1} $year^{-1}$ in the form of diammonium phosphate. The remaining land use is 46% forest, 2% wheat and 17% fallow. Measurements of water and nitrogen balance were performed during four raining season under maize and forest plots and showed that the drainage and evapotranspiration constituted the main loss terms of the water balance during the studied raining seasons and that drainage accounted for more than half of the incident rainfall under the two maize plots. Nitrate losses at the base of the maize rootzone occurred mainly through leaching (unpublished data).

The soil under study was sampled in one of the maize plot and was classified as a Typic Hapludand by Prado et al. (2007) (Soil Survey Staff, 1999).

2.2. Soil characteristics affecting NO_3^- transfer

The soil's physical, chemical and mineralogical properties along with the analytical methods are described in detail in Prado et al. (2007) and summarised hereafter. Three soil depths (5–21 cm named hereafter P1; 30–46 cm: P2; and 80–96 cm: P3) from a representative soil profile were sampled. The experimental soil was a typical Andosol with a loose granular consistency in the upper 20 cm due to soil ploughing carried out 10 months before the soil core sampling. Between 20 and 80 cm, subangular blocks were observed and confirmed by thin layer micro-morphological observations (Prado et al., 2007). The whole soil profile has a silt loam texture. Hydrophobicity was assessed by comparing infiltration with ethanol and water in 5 cm diameter cylinders under constant head and no difference was observed on maize plots. Table 1 presents the main chemical and mineralogical properties known to affect NO_3^- adsorption and movement. The soil porous network properties are described in detail in Prado et al. (2009).

The main soil components are allophane (21–26%), organic matter (8.4–9.5%), Ferrhidrite (1.8–3.2%) and iron oxides (2.1–3.1%). The CEC was determined by NH_4OAc at pH 7 (Soil Survey Staff, 1999) and the AEC was determined at soil pH as described by Zelazny et al. (1996). The cation exchange capacity (CEC) and the anionic exchange capacity (AEC) remain more or less constant throughout the soil profile, at about 20 and 2 $cmol_c$ kg^{-1}, respectively. The negative value of delta pH (pH KCl − pH H_2O) (−0.4 pH unit) indicates that negative charges prevail (Parfitt, 1990). These results confirm the presence of both variable and permanent charges in the soil (Uehara and Gillman, 1981). The surface charge of allophanes is of the dual-charge particle type. Iron oxides usually have a positive net charge under the acidic conditions typical of tropical soils (Uehara and Gillman, 1981) The presence of these noncrystalline materials like allophane, explains the physico-chemical behaviour of the soil studied, i.e. the variable charge (ΔpH value varies from −0.35 to −0.45 and low values of extractable Al, around 0.05 $cmol_c kg^{-1}$) and high water retention capacity (the ratio between available water content and water content at 0.33 bar varies from 23% to 45%).