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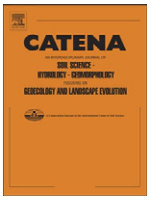

Batch and column experiments on nutrient leaching in soils amended with Italian natural zeolitites

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ABSTRACT

This paper describes the application of the Italian chabazite-rich tuff of Sorano (Grosseto) as a soil conditioner and slow nutrient fertilizer to a silty-clay soil and a sandy soil. The study was developed by means of batch and column experiments. The objectives of the study were: (1) to evaluate and compare the physical and hydraulic properties of mixtures of soil and natural zeolitite (95:5% v/v) with those of unamended soils, (2) to determine the effects of applying NH_4^+-enriched zeolitites on soils and (3) to model water and solutes movement in two different scenarios, with and without amendment incorporation. Results of column experiments were then modelled to obtain the physical–chemical and hydraulic parameters representative of the soils amended with the NH_4^+-enriched zeolitites. Using synthetic rainwater as eluent, NH_4^+ was never detected in the water phase of batches and columns; NO_3^- and PO_4^{3-} were both present at high concentrations in batch tests and were leached in column elution tests. NO_3^- displayed very high concentrations at the beginning of the elution whereas PO_4^{3-} showed low concentrations and retarded peaks in both amended soil columns. The rationale of the study lies in the belief that inorganic amendments, which improve the physical and hydraulic properties of soils, can lead to minimized leaching of nutrients.

1. Introduction

So far, many research efforts have been spent to focus on innovative management strategies to improve soil fertility and simultaneously limit nutrient loss to surface and groundwater (Stark and Richards, 2008), which in the end lead to eutrophication (Edmeades, 2003). The most common method to increase the soil water and nutrient retention is through soil conditioning with organic amendments (Bigelow et al., 1999; Laird et al., 2010; McCoy, 1992). Although organic amendment decay can decrease hydraulic conductivity and porosity (Haynes and Naidu, 1998), inorganic amendments like zeolites have been proposed to improve the waterholding capacity (Huang and Petrovic, 1994; Xiubin and Zhanbin, 2001), drainage control (Bigelow et al., 2004) and the retention and release of ammonium (NH_4^+) due to their high cation exchange capacity (CEC) (Bish and Ming, 2001; McGilloway et al., 2003). The application of natural zeolites has been reported to diminish nutrient leaching and to increase crop water use efficiency (Coltorti et al., 2012; Gholamhoseini et al., 2013; Ming and Allen, 2001; Polat et al., 2004). Besides, natural zeolites could also decrease ammonia volatilization (He et al., 2002; Latifah et al., 2010). Chabazite is one of the most useful natural zeolites due to its high CEC (Mumpton, 1999; Sheta et al., 2003), selective reversible sorption for NH_4^+ (Gualtieri and Passaglia, 2006) and structure stability over long periods (Baerlocher et al., 2001). Theoretically, soil properties could be positively changed by chabazite conditioning but, apart from a few examples (Coppola et al., 2002; Hong et al., 2011), so far detailed studies are still needed.

In this paper, batch and column leaching experiments were performed on silty clay loam and sandy soils amended with NH_4^+-charged natural zeolitites with very high chabazite content (Faccini et al., 2014). These experiments aim at simulating the leaching (dissolution, desorption and degradation) behaviour of nutrients during the water–soil interaction (Mastrocicco et al., 2009). The comparison between the amounts of nutrients leached from different soils, natural or amended, will provide fundamental information in understanding the geochemical behaviour of zeolite-bearing minerals. To improve the knowledge of nutrient leaching within the water–soil continuum, a clear picture of the flow dynamics is a prerequisite.

To characterise the flow and transport properties on the field or at the laboratory scale, tracer tests are usually employed (Mao and Ren, 2004), and flow interruption techniques are performed to assess the physical non-equilibrium behaviour (Brusseau et al., 1989, 1997). Moreover, the numerical transport modelling of the abovementioned tracers can help to discern dilution and dispersion processes from reactions between the water and the solid phase (Appelo et al., 1990). The most widely used method to determine water and chemical fluxes in the saturated zone is the application of process-based mathematical models, like CXTFIT (Toride et al., 1999).

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In this respect, both tracer tests with flow interruption and modelling were used to obtain information on the mobility of the selected reactive species. The first objective of these tests was to determine whether the physical equilibrium approach described by the classical advection dispersion equation (ADE) could be assumed or if non-equilibrium processes (preferential flows) were relevant for the column experiments. Once this issue was solved, the main target was to quantify the physical parameters that deterministically describe the flow and transport process to gain insights into nutrient leaching behaviour.

2. Materials and methods

2.1. Soil collection

The soil material was sourced from the top layer of the ZeoLIFE experimental site (Coltorti et al., 2012; Di Giuseppe et al., 2014), located 40 km east of Ferrara, Italy (45°50′33″N and 12°05′40″E) and 15 km from the Adriatic Sea in a reclaimed land at an average altitude of −3 ± 0.3 m above sea level (a.s.l.). The experimental site included recent alluvial deposits, mainly silty-clay loam (SCL) and medium fine sand (S) according to the USDA-SCS (1984) textural classification (Bondesan et al., 1995; Mastrocicco et al., 2013).

A series of soil samples for SCL and S were collected from different locations within the field site to minimize soil heterogeneity. The soil samples were stored in PE bags under vacuum in the field and maintained refrigerated during transportation to the Sedimentology Laboratory of the University of Ferrara. In the laboratory, the soil samples were homogenized at room temperature and a physical characterization was performed for the resulting mixture of SCL and S in triplicate (see Table 1 for results).

The zeolitite comes from a thick deposit of volcanoclastic products close to Sorano (Grosseto, IT); it has chabazite (68.5 ± 0.9%), phillipsite (1.8 ± 0.4%) and analcime (0.6 ± 0.3%) as the main zeolites, and K-feldspar (9.7 ± 0.7%), mica (5.3 ± 0.6%), pyroxene (2.9 ± 0.4%) and volcanic glass (11.2 ± 1.0%) (Faccini et al., 2014). To assess the zeolitite chemical composition (see Table 2), triplicates were completely oven-dried at 50 °C, powdered, homogenized in an agate mortar and analysed by X-ray fluorescence (XRF) on powder pellets, using a wavelength-dispersive automated ARL Advant'X spectrometer. Loss on ignition (LOI) was evaluated after overnight heating at 950 °C (LOI_{950}). This natural potassic chabazite zeolitite (NZ) is a granular (Ø < 3 mm) by-product of quarrying activity; its high CEC, low Na content and very high and constant total zeolitic content, make it the most suitable material for ammonium (NH_4^+) exchange and re-use for agricultural purposes. Therefore, NZ was mixed with swine manure (with a solid fraction of about 1 wt.%, NH_4^+ content up to 2 g/l and mildly alkaline pH) in a specifically conceived prototype (Coltorti et al., 2012) in order to gain an NH_4^+-charged zeolitite (CZ) to be employed as soil amendment in the ZeoLIFE field site. CZ acquired an average of 6 mg/g of N-NH_4 during prototype treatment. Physical characterization of NZ, S and SCL soils was performed in triplicate (see Table 1 for results).

Table 1
Sediment characteristics and their standard deviation from triplicate samples.

Parameter	SCL	S	NZ
Grain size (%)			
Coarse sand (630–2000 μm)	0.0 ± 0.0	5.0 ± 0.8	10.1 ± 1.1
Medium sand (200–630 μm)	0.0 ± 0.0	45.1 ± 3.4	22.5 ± 0.6
Fine sand (63–200 μm)	19.1 ± 1.3	33.1 ± 2.8	32.4 ± 2.4
Silt (2–63 μm)	41.9 ± 3.1	12.0 ± 0.2	22.2 ± 0.2
Clay (<2 μm)	39.0 ± 2.4	4.8 ± 0.5	12.8 ± 0.5
Hydraulic conductivity (cm/d)	10.1 ± 2.1	146 ± 22	116 ± 18
Bulk density (kg/m^3)	1.1 ± 0.1	1.5 ± 0.1	1.4 ± 0.1
Residual water content (%)	13.0 ± 0.2	5.8 ± 0.3	8.1 ± 0.5
Total porosity (%)	59.0 ± 0.4	43.4 ± 0.4	41.3 ± 0.2
Organic matter (%)	8.1 ± 0.4	1.1 ± 0.1	0.0 ± 0.0
Soil pH (–)	6.6 ± 0.6	7.6 ± 0.3	6.9 ± 0.2
Carbonates (%)	7.0 ± 2.0	7.0 ± 2.0	1.5 ± 0.6

Table 2
Major elements (oxides) of the Sorano zeolitite.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	MnO	MgO	CaO	Na_2O	K_2O	LOI
wt.%	51.2	16.6	3.38	0.48	0.18	0.11	1.76	5.00	0.79	5.84	14.3

2.2. Batch experiments

Batch leaching experiments were performed using the saturation soil extraction (SSE) methods described by Schuwirth and Hofmann (2006), with the use of synthetic rainwater (deionized water MilliQ plus $CaCl_2$ 0.01 mM and $NaCO_3$ 0.01 mM, pH = 7.6), representative of water quality recharging the aquifer. The experiment was performed in a temperature-controlled laboratory at 20 ± 0.5 °C. Sediments were not sterilized but air-dried at room temperature to minimize heat-driven dehydration reactions and to avoid changes in the structure, ion exchange capacities and dissolution characteristics of the clay minerals. Samples were not washed as this would preferentially remove those components that are associated with the finer and more friable minerals, such as micas.

Six batches were run with a solid:liquid ratio of 1:10 (w/v), using 5 g of air-dried sediment and 50 ml of synthetic rainwater for the following matrices: NZ, CZ, SCL, S, $SCL_{(CZ)}$, and $S_{(CZ)}$. $SCL_{(CZ)}$, and $S_{(CZ)}$ consisted of CZ mixed with natural soils (SCL, S) in a volume ratio of 1:20. For each batch, triplicates were prepared to derive standard deviation of dissolved species concentration. Batches were sealed and placed on a rotary shaker for 1 h at 20 °C to achieve equilibrium, prior to collecting samples (2 ml each) to be filtered using a 0.2 μm polypropylene filter and analysed for anion by ion chromatography and NH_4^+ by UV/Vis spectrophotometry.

2.3. Column experiments

All leaching tests have been conducted at laboratory conditions (20°C) using polyethylene (PE) columns with an internal diameter of 2 cm and a length of 15 cm, equipped with PE pre- and post-chambers consisting of 1 mm uniformly packed quartz sand and a 50 μm Nitex mesh in contact with the matrix in order to avoid material loss. Packing of air-dried sediment took place in 15–20 increments, and each increment was slightly packed before the next one was placed on top until the columns were completely filled. Subsequently, the columns were connected, via a system of capillary Teflon tubes, to a peristaltic pump supplied by a synthetic rainwater reservoir.

The schematic diagram of the column experiments is shown in Fig. 1.

Elution experiments started with a slow saturation of every column with synthetic rainwater; matrix and porewater were then left equilibrating for 24 h. After the equilibration period, a peristaltic pump with a constant flow rate of 100 ml/h was employed to pump the synthetic rainwater in each column; an effluent tube was fixed to a fraction collector of 2 ml, which was then divided into two 1-ml aliquots for the analysis of anions and NH_4^+. The sample volume was appositely chosen to be "minimal" in order to avoid dilution and cross-contamination between successive samples. After 5 − 6 pore volumes, the pump was stopped and turned on again after 1 day to evaluate the amount of nutrients leached after the flow interruption. Extra column volume was taken into account when the experimental elution curves were constructed by correcting the arrival volumes of the effluents. Tracer tests were performed on every column after elution experiments; a solution of 100 mg/l of NaBr dissolved into synthetic rainwater was injected for 1 min into the column, and immediately afterwards, the synthetic rainwater reservoir was turned on. A small flow-through cell was used to monitor electrical conductivity (EC) at the column outflow and the NaBr concentration (mg/l) via a Br^- ion-selective electrode