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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 mean 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 the 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 the amended soil columns. The rationale of the study lies in the belief that inorganic amendments, that improve the physical and hydraulic properties of soils, can lead to minimize the leaching of nutrients.

Keywords: soil conditioning, natural zeolites, leaching, modeling, nitrate.

1. Introduction

So far, many research effort 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 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), the 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 period (Baerlocher et al., 2001). Theoretically, soil properties could be positively changed by Chabazite conditioning but, apart from 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 field or 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 chemicals fluxes in the saturated zone, is the application of process-based mathematical models, like CXTFIT (Toride et al., 1999).

In this respect, both tracer tests with flow interruption and modelling were used to obtain information on 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) can 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 on nutrients 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 include 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 the transportation at 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 triplicates (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 1wt %, NH_4^+ content up to 2 g/l

1 and mildly alkaline pH) in a specifically conceived prototype (Coltorti et al., 2012) in order to gain

2 an NH_4^+-charged zeolitite (CZ) to be employed as soil amendment in the ZeoLIFE field site. CZ

3 acquired an average of 6 mg/g of $N-NH_4$ during prototype treatment. Physical characterization of

4 NZ, S and SCL soils was performed in triplicates (see Table 1 for results).

5

6 *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

7

8 *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

9

10 **2.2 Batch experiments**

11 Batch leaching experiments were performed using the saturation soil extraction (SSE) methods

12 described by Schuwirth and Hofmann (2006), with use of synthetic rainwater (deionized water

13 MilliQ plus $CaCl_2$ 0.01 mM and $NaCO_3$ 0.01 mM, pH=7.6), representative of water quality

14 recharging the aquifer. The experiment was performed in a temperature-controlled laboratory at

15 20±0.5 °C. Sediments were not sterilized but air-dried at room temperature to minimize heat-driven

16 dehydration reactions and to avoid changes in the structure, in the ion exchange capacities and in

1 the dissolution characteristics of clay minerals. Samples were not washed as this would

2 preferentially remove those components that are associated with the finer and more friable minerals,

3 such as micas.

4 Six batches were run with a solid:liquid ratio of 1:10 (w/v), using 5 g of air dried sediment and 50

5 ml of synthetic rain water for the following matrices: NZ, CZ, SCL, S, $SCL_{(CZ)}$, and $S_{(CZ)}$, $SCL_{(CZ)}$,

6 and $S_{(CZ)}$ consisted of CZ mixed with natural soils (SCL, S) in a volume ratio of 1:20. For each

7 batch, triplicates were prepared to derive standard deviation of dissolved species concentration.

8 Batches were sealed and placed on a rotary shaker for 1 h at 20 °C to achieve equilibrium, prior to

9 collect samples (2 ml each) to be filtered using a 0.2 μm polypropylene filter and analysed for anion

10 by ion chromatography and NH_4^+ by UV/Vis spectrophotometry.

11

12 **2.3 Column experiments**

13 All leaching tests have been conducted at laboratory conditions (20°C) using polyethylene (PE)

14 columns with an internal diameter of 2 cm and a length of 15 cm, equipped with PE pre and post-

15 chambers consisting of 1 mm uniformly packed quartz sand and a 50 μm Nitex mesh in contact

16 with the matrix, in order to avoid material loss. Packing of air-dried sediment took place in 15–20

17 increments, and each increment was slightly packed before the next one was placed on top, until the

18 columns were completely filled. Subsequently, the columns were connected, via a system of

19 capillary Teflon tubes, to a peristaltic pump supplied by a synthetic rainwater reservoir.

20 The schematic diagram of the column experiments is shown in Fig. 1.
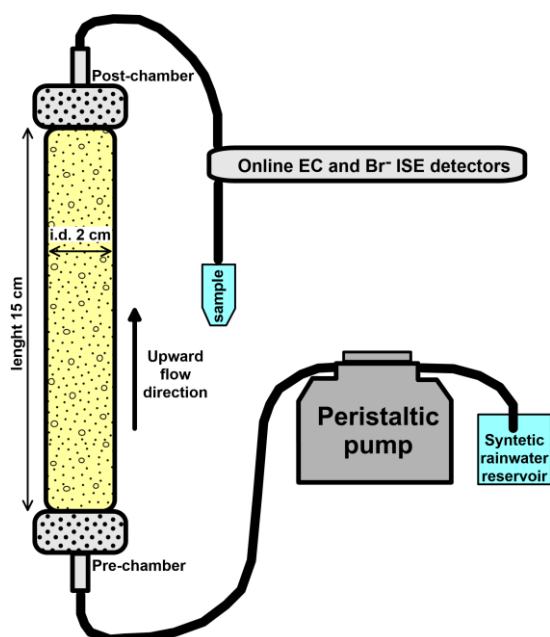
21

22

23 *Figure 1 – Scheme of the experimental setup used in the column elution and BTCs experiments.*

1 Elution experiments started with a slow saturation of every column with synthetic rainwater; matrix

2 and porewater were then left equilibrating for 24 hours. After the equilibration period, a peristaltic

3 pump with a constant flow rate of 100 ml/h was employed to pump the synthetic rainwater in each

4 column; an effluent tube was fixed to a fraction collector of 2 ml, which were then divided into two

5 1-ml aliquots for the analysis of anions and NH_4^+. The sample volume was appositely chosen to be

6 "minimal" in order to avoid dilution and cross contamination between successive samples. After 5-6

7 pore volumes, the pump was stopped and turned on again after 1 day to evaluate the amount of

8 nutrients leached after the flow interruption. Extra column volume was taken into account when the

9 experimental elution curves were constructed, by correcting the arrival volumes of the effluents.

10 Tracer tests were performed on every column after elution experiments; a solution of 100 mg/l of

11 NaBr dissolved into synthetic rainwater was injected for 1 minute into the column, and immediately

12 afterwards, the synthetic rain water reservoir was turned on. A small flow through cell was used to

13 monitor electrical conductivity (EC) at the column outflow and the NaBr concentration (mg/l) via a

14 Br^- ion selective electrode (ISE). An additional tracer test with flow interruption was performed on

15 every column to examine the effect of diffusive mass transfer on solute transport (Brusseau et al.,

16 1989, 1997). The experiments resulted in a tracer breakthrough, given as BTCs. The experimental

17 BTCs were corrected by subtracting the measured extra-column volume of the tubing (2 ml) and the

18 flow-through chambers (5 ml).

19 The probe was able to express the concentration, in ppm, of the ions Br-transited inside. Finally the

20 volume was measured extra-column, for the calculation of the effective porosity (n_e) via the

21 formula:

22 $$n_e = \frac{q_s}{v} \tag{1}$$

23 where q_s is the specific flow rate (volumetric flow divided by the area of the column) measured at

24 the output from each column in ml/min and v is the velocity of the non-reactive tracer (Br^-)

25 expressed in cm/min, calculated dividing the column length by the Br^- median arrival time.

26

27 **2.4 Analytical Techniques**

28 Particle size curves were obtained using a sedimentation balance for the coarse fraction and an X-

29 ray diffraction sedigraph 5100 Micromeritics for the finer fraction; the two regions of the particle

30 size curve were connected using the computer code SEDIMCOL (Brambati et al., 1973). The soil

31 organic matter was measured by dry combustion (Tiessen and Moir, 1993). Carbonate content in

32 soil were determined with a Chittick gasometrical apparatus (Dreimanis, 1962). Soil and porewater

33 pH were measured using a Hanna meter model pH211 with the glass-body combination pH probe

34 HI 1131B, incorporating a temperature probe for compensation.

Constant pressure head tests were used to infer the average hydraulic conductivity of each column, while bulk density and water content were determined gravimetrically. The gravimetric water content was measured for saturated condition after elution of 10 pore volumes. The residual water content was measured gravimetrically in triplicates on air dried sediments after being heated for 24 hours at 105 °C. The porosity, n (cm^3/cm^3) of the soil was calculated as follows (Danielson and Sutherland, 1986):

$$n = 1 - \frac{\rho_p}{\rho_b} \tag{2}$$

where ρ_p is the particle density (g/cm^3) and ρ_b is the bulk density (g/cm^3).

Online parameters on the leaching solutions were determined with a HIcell-21 electrode conductivity cell for EC measurements, Hanna Instrument[®] and with a dissolved Br^- ISE, Nextsens[®]. The latter has a USB cable to store Br^- concentration data into a personal computer; the record was set every 1 second to obtain an almost continuous BTC. Leaching solutions were filtered through 0.22 μm Dionex vials caps. Major anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were determined by an isocratic dual pump ion chromatography ICS-1000 Dionex, equipped with an AS9-HC 4×250 mm high capacity column and an ASRS-ultra 4-mm self-suppressor. An AS-40 Dionex autosampler was employed to run the analysis; quality control (QC) samples were run every ten samples. The standard deviation for all QC samples run was better than 4%, whereas the accuracy is reported as the average of the relative differences between the measured and known standards, which was 5% for anions. The detection limit was 2 μg/L for F^- and lower than 50 μg/L for all the analysed anions and cations. The dissolved NH_4^+ concentration in water was determined with a CADAS 100 UV/Vis spectrophotometer (Hach-Lange, UK), with a detection limit of 100 μg/L.

2.5 Modelling Approach

Assuming a uniform water content and steady-state flow conditions, the one-dimensional transport non equilibrium advection–dispersion equation (ADE), including first-order degradation reaction, can be written as (van Genuchten and Wierenga, 1976):

$$\theta_m \frac{\partial C_m}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - J_w \frac{\partial C_m}{\partial x} - \alpha(C_m - C_{im}) - (\theta_m \mu_m)C_m \tag{3}$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) - (\theta_{im} \mu_{im})C_{im} \tag{4}$$

where subscripts $_m$ and $_{im}$ pertain to the mobile and immobile region, respectively. C (ML^{-3}) denotes solute concentrations as a function of distance x (L) and time t (T). D_m (L^2T^{-1}) is the hydrodynamic dispersion coefficient for the mobile region, J_w (LT^{-1}) the volumetric water flux density and the

1   volumes θ (L^3L^{-3}), θ_m, (L^3L^{-3}) and θ_{im} (L^3L^{-3}) are the total, mobile and immobile water content. For

2    $\theta_m=\theta$, Eq. 1 reduces to the single-domain ADE. The solute-mass transfer between mobile and

3   immobile regions is limited by the first-order rate coefficient α (T^{-1}). The dispersion coefficient D_m

4   provides a measure of solute spreading and D_m can be extrapolated empirically by $D=\lambda_L+D^*$ where

5   λ_L (L) is the longitudinal dispersivity and D^* (L^2T^{-1}) is the effective diffusion coefficient.

6   The main characteristics that distinguish the dual domain approach (DD) from ADE BTCs of a

7   tracer are the so called "early breakthrough", related to accelerated transport via preferential

8   pathways and "tailing", due to diffusion driven processes into stagnant zones. Thus, more the

9   sediments are characterized by preferential pathways and stagnant zones, more the behaviour of

10   solute transport can be approximated by DD approach, while the ADE cannot be successfully used.

11   In the numerical models, the 15 cm long experimental columns were discretized in a 200 cell grid.

12   The hydraulic conductivities and porosities attributed to this grid are listed in Table 1. A constant

13   head boundary was used at both the influent and effluent end of the column to simulate steady state

14   flow rates. The tracer pulse was simulated as a time pulse input boundary condition for the infinite

15   dilution injections. While a multiple pulse input was selected to simulate the frontal analysis

16   injections, that consisted of continuous tracer injection for 2 pore volumes. CXTFIT was run in

17   inverse mode to estimate (i) λ_L where the BTCs were simulated via single-domain ADE and (ii) λ_L,

18   θ_{im}, α where the DD approach was employed.

19

20   **3. Results and discussion**

21

22   **3.1 Batch experiments**

23   NZ have small amount of leachable nutrients and Cl^-, while CZ have an extremely high NO_3^- and

24   Cl^- content, and a remarkable NH_4^+ and PO_4^{3-} contents (Table 3).

25   These high concentrations are due to the swine manure used to charge the zeolitite, although the

26   manure is rich in NH_4^+ but poor in NO_3^- (Tab. 2). The predominant presence of NO_3^- over NH_4^+ in

27   CZ was due to the oxic conditions during and after the charging process. In fact, the charged

28   zeolitites were stored in a large open tank near the mixing prototype; here, the residual manure

29   fraction present on the zeolitite's grain surfaces was subject to nitrification (Stumm and Morgan,

30   1996):

31   $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ (5)

32   usually resulting in a pH lowering if carbonates are not present to buffer the reaction. In this case,

33   carbonates were present in all the sediment matrixes (Table 1) and the measured pH in each batch

34   experiment did not decrease with respect to the soil pH (Table 3).

Table 3. Rainfall leachable NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, Cl^- fractions (mg/kg) and pH (-) for the different matrixes analysed and their standard deviation from triplicate samples.

	NH_4^+ (mg/kg)	NO_3^- (mg/kg)	NO_2^- (mg/kg)	PO_4^{3-} (mg/kg)	Cl^- (mg/kg)	pH (-)
NZ	<0.5±0.0	3.9±1.3	1.0±0.4	<0.5±0.0	13.0±3.4	7.2±0.1
CZ	35.0±8	3840±1020	2.7±0.8	36.4±18	723±287	7.3±0.2
Manure	2224±255	0.3±0.1	7.5±5.9	98.6±32	1106±166	8.0±0.4
S	<0.5±0.0	26.3±3.3	0.2±0.1	0.6±0.1	6.2±0.9	7.4±0.1
S$_{(CZ)}$	<0.5±0.0	354±54	0.6±0.1	2.2±0.4	101.1±12	7.4±0.2
SCL	<0.5±0.0	40.2±5.0	1.3±0.4	1.5±0.3	15.2±2.1	7.0±0.2
SCL$_{(CZ)}$	<0.5±0.0	589±76	1.8±0.6	3.6±0.7	68.5±13	7.1±0.2

NH_3 volatilization of the residual manure fraction present on the zeolitite's grain surfaces was surely an active process during the storage period, although this process was not monitored in the field. During the small incubation time of the batches, the gross NH_3 volatilization could be considered negligible (Rochette et al., 2009; Van der Stelt et al., 2007).

From the equation 5, 1 mole of NH_4^+ produce 1 mole of NO_3^- thus, from table 3, the NH_4^+ present in the slurry pig manure should have produced 7644±877 mg/kg of NO_3^-. Despite of this, only half of the expected NO_3^- concentration was found in the CZ batches. This inconsistency was probably imputable to the extremely high variability of the NO_3^- concentrations observed in the CZ batches, or to incomplete nitrification. In any case, comparing the conservative species Cl^- in the pig manure and in the CZ batches (Table 3), a dilution factor of 1.5 is appreciable, indicating that the manure/zeolite ratio was well below the unity. An even higher dilution factor of 2.7 is appreciable for the PO_4^{3-} since this species has a greater affinity for the solid matrix (Griffioen, 1994).

The same behaviour described above is shown by the S$_{(CZ)}$ and SCL$_{(CZ)}$ batches, although here a further dilution factor of all the recorded concentrations is appreciable (Table 3), since the CZ was mixed with natural soils with a volumetric ratio of 1:20. The large variability of the observed concentrations is also reflected in the standard deviations of both S$_{(CZ)}$ and SCL$_{(CZ)}$. The corresponding natural soil standard deviations are relatively small, but just because the measured concentrations are lower. From the S$_{(CZ)}$ and SCL$_{(CZ)}$ batch experiments is clear that only NO_3^- could be significantly leached by rainfall or irrigation events after the CZ amendment. NO_3^- could be derived from the manure residua coating the zeolitite grains (the CZ production process in the prototype does not foresee the washing of the material) and/or from the nitrification of a small amount of the NH_4^+ trapped in the zeolitite (at most the 15% of the total exchangeable N). In this

1   last case, the exchange is most probably caused by the release in the solution of cations (Na^+, K^+)

2   from the manure residua.

3

4   **3.2 Column experiments**

5   In the first column experiments, a comparison between the Br^- BTCs of unamended and amended

6   soils was done for both S and SCL soils. Figure 2 shows the results of the frontal analysis BTCs: it

7   is evident that for the S and $S_{(CZ)}$ columns the results were quite similar, whereas for the SCL and

8    $SCL_{(CZ)}$ columns some differences are visible. First of all, the SCL BTC was affected by large

9   oscillations due to the physical heterogeneities of the porous structure, while the addition of zeolites

10   diminished this effect and changed the dispersivity of the porous matrix. From these preliminary

11   column experiments it seems obvious that the physical transport properties of the S soil could not

12   be greatly altered, while for SCL soil some differences have been caused, although not very intense.

13   A comparison was made between IC Br^- concentrations collected in five discrete samples and ISE

14   Br^- concentrations collected via continuous logging, to test if the very small flow-through chamber

15   of the ISE detector was able to produce reliable data. The results gave a linear regression coefficient

16   (R^2) of 0.991, proving a good reliability of the ISE set up. Nevertheless, ISE recalibration was

17   needed every new BTC test. Online EC values were also compared with online ISE Br^-

18   concentrations, giving a R^2 of only 0.934, since EC is not influenced by the Br^- but also by other

19   cations that could be exchanged from the solid matrix (Mastrocicco et al., 2011).Thus, EC values
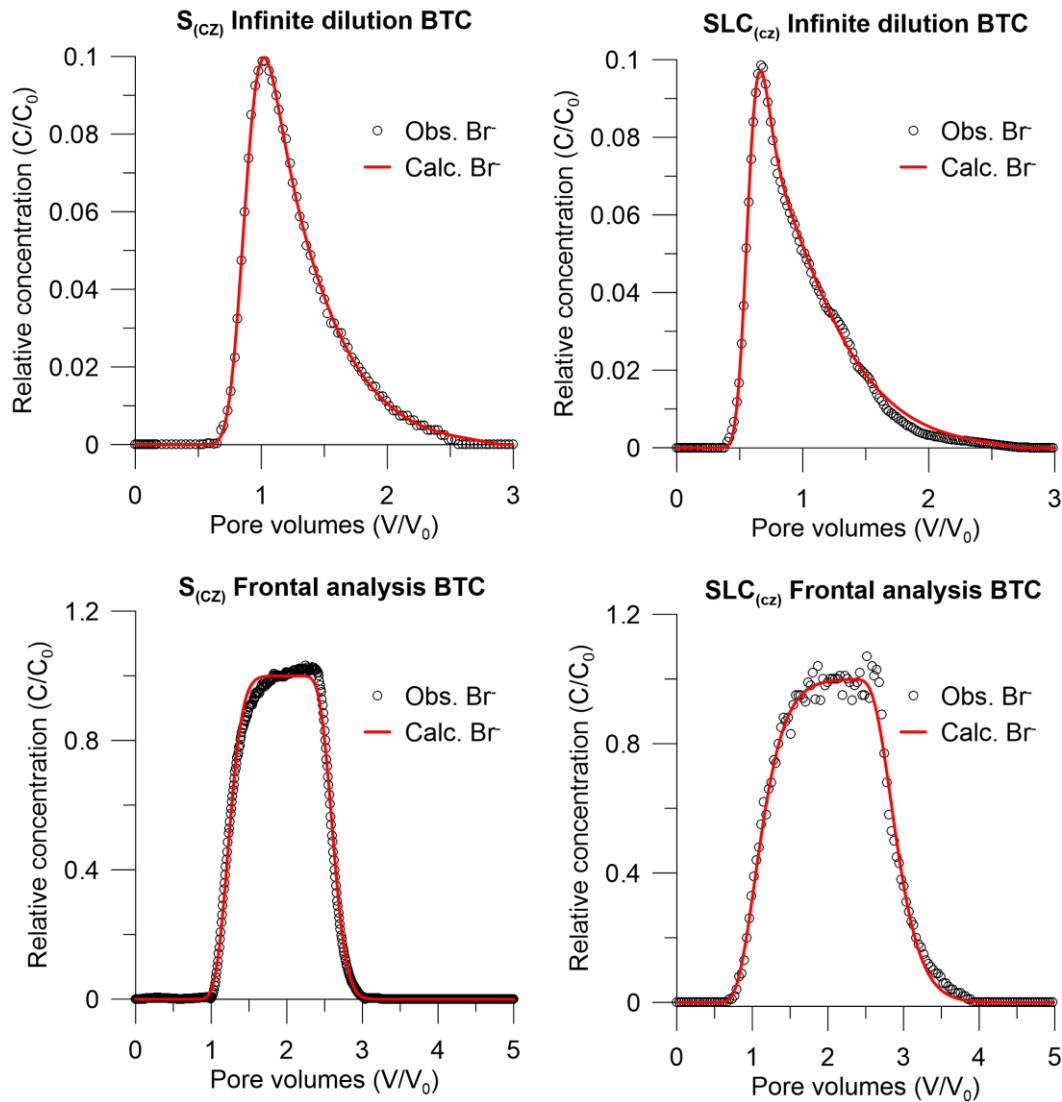
20   were not used for model fitting.

21
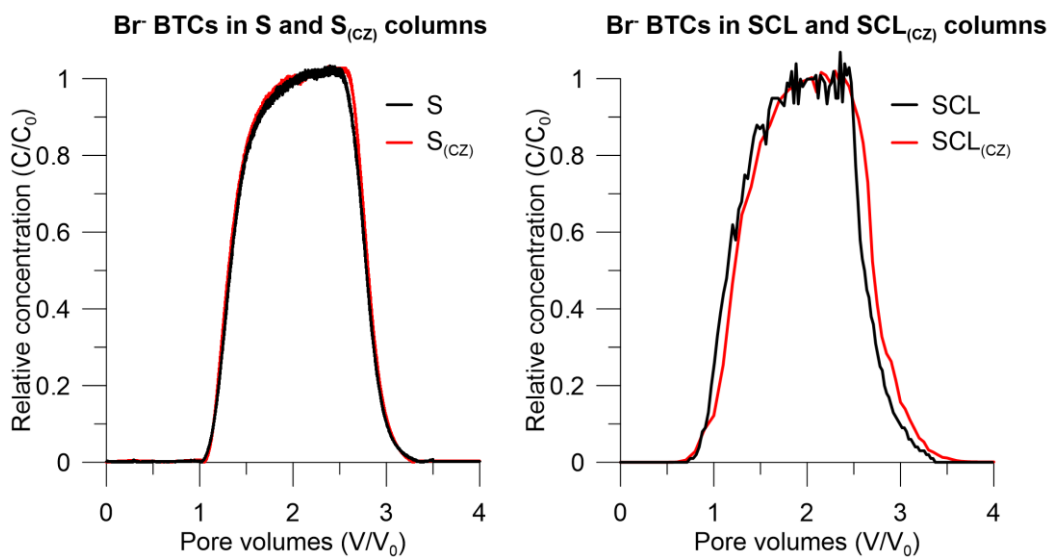
24   *Figure 2 – Comparison of Br^- BTCs in S and $S_{(CZ)}$ columns (left plot), SCL and $SCL_{(CZ)}$ columns*

25   *(right plot).*

Figure 3 – Observed and calculated Br⁻ concentrations in $S_{(CZ)}$ and $SCL_{(CZ)}$ columns for both infinite dilution BTCs (upper plot) and frontal analysis BTCs (lower plots).

The BTCs experiments in both amended soils (Figure 3) were fitted using the same parameter sets for the infinite dilution and frontal analysis tests (Table 4). These double tests provide much more consistent information on the column's physical properties respect to a single trial. In addition, despite the time consuming procedures to run these experiments, they could provide a robust evidence of the column set up reliability or suggest the possible source of errors, e.g. floating concentrations due to Br⁻ detector calibration failure, inconstant flow, entrapped air bubbles, etc... As shown in figure 3, the BTCs for the $S_{(CZ)}$ column display little tailing and early breakthrough, so they could be well fitted using the standard ADE equation (Table 4). The obtained λ_L value is small but it is in the range of the observed values for sandy repacked soils columns (Bromly et al., 2007), with a small standard deviation indicating little uncertainty in parameter identification. On the

1   contrary, the SCL$_{(CZ)}$ column displays longer tailing and early breakthrough, so they could be well

2   fitted only by using the DD equation (Table 4). The obtained λ_L value display a larger uncertainty

3   respect to the S$_{(CZ)}$ column, although the statistical values are quite elevated, indicating an overall

4   good degree of reliability even for this column. The high θ_{im} value obtained through inverse

5   modelling indicates that the active region of flow within the SCL$_{(CZ)}$ column is only the 62% of the

6   pore space, while the low α value indicates that the two regions exchange solutes at a relatively slow

7   rate.

8

9   *Table 4. Parameters obtained by inverse modelling for the BTCs simulations in S$_{(CZ)}$ and SCL$_{(CZ)}$*

10   *columns, and their corresponding mean square for error (MSE) and R^2. The symbol $\pm$ denotes the*

11   *standard deviation of the obtained parameter value.*

Parameter	S$_{(CZ)}$	SCL$_{(CZ)}$
λ_L (cm)	0.56±0.05	1.12±0.41
θ_{im} (-)	-	0.224±0.01
α (1/d)	-	0.07±0.008
MSE (mg/l)	0.089	0.072
R^2	0.996	0.995

12

13   Once the parameter values for each column were estimated, these were applied to the elution

14   experiments performed on the same columns before the starting of Br$^-$ BTCs. The results are shown

15   in figure 4 for the S$_{(CZ)}$ column and in figure 5 for the SCL$_{(CZ)}$ column; the complete dataset with all

16   the monitored ions is provided as SI. The elution of conservative species like Cl$^-$ was well

17   reproduced by the numerical model, with a MSE of 1.69 mg/l and R^2 of 0.994 (Fig. 4). It has to be

18   noted that, in order to gain a good fit between observed and modelled concentrations, the initial

19   condition for the dissolved concentrations was changed from constant to stepwise. The stepwise

20   dissolved concentrations consisted of 5 discrete steps (3 cm each) in which the columns were

21   subdivided: in the first step (column inlet) the rainwater concentration was used, in the last step

22   (column outlet) the observed initial concentrations were used and in the others three intermediate

23   steps the two measured concentrations were linearly interpolated. In this way, the sudden

24   concentration drop observed for all the ions could be well reproduces. This behaviour has a simple

25   physical explanation: since the water saturation of the columns was achieved pumping from the

26   inlet the synthetic rainwater, the soluble salt were dissolved and carried by the water phase at the

27   wetting front, thus producing higher concentrations near the column outflow and lower near to the

28   column inflow. If the columns were filled with a homogenized soil saturated paste, a more

1 homogeneous initial concentration would be attained, however, this artificial homogenization
2 procedure would not have mimicked the real saturation during prolonged rainfall or irrigation
3 periods and thus it has not been done.
4
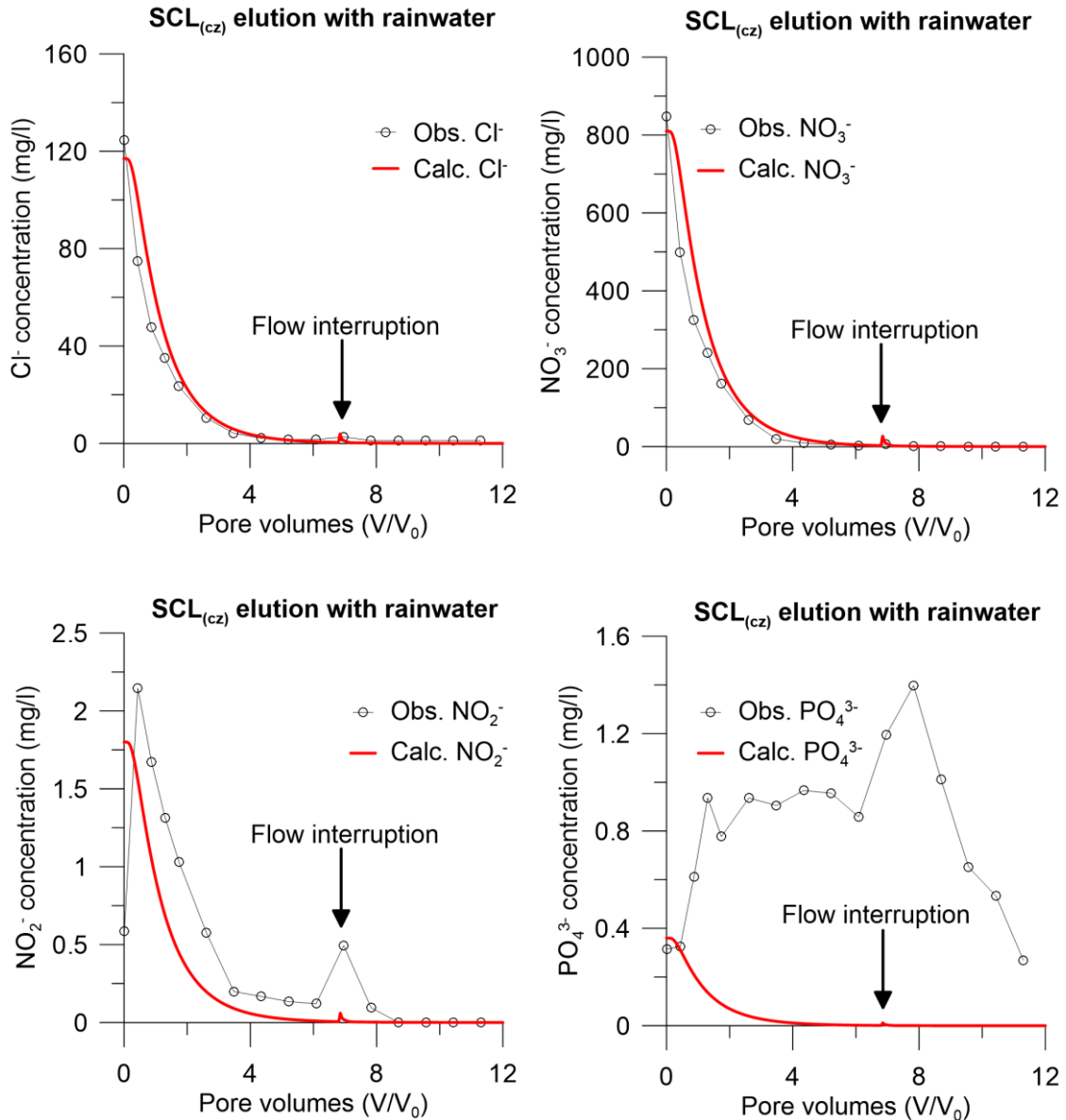
6 *Figure 4 – Observed and calculated Cl^-, NO_3^-, NO_2^- and PO_4^{3-} concentrations eluted from $S_{(CZ)}$*
7 *columns.*

8

9 Similarly to Cl^-, also NO_3^- was displaced after the first two pore volumes, indicating the
10 conservative behaviour of this anion in oxic conditions. NO_2^- followed the same conservative
11 behaviour just in the first pore volume, but then it was produced at a constant rate, indicating that
12 reactive soil nitrogen was constantly mineralized. NH_4^+ was always below detection limits (and thus
13 not shown in figure) as in absence of high concentrations of cations in the water phase all the NH_4^+

1 remain entrapped within the zeolite structure (Miladinovic and Weatherley, 2008). The column

2 released PO_4^{3-} with elevated variability, indicating that also reactive soil phosphorous was

3 undergoing mineralization. CZ increases the dissolution of insoluble phosphate from soils, as also

4 recently shown by Lancellotti et al. (2014); in addition, since PO_4^{3-} has a large affinity for the solid

5 matrix, its breakthrough was largely retarded, as shown by the PO_4^{3-} peak after eight pore volumes.

6 For all the analysed species, the flow interruption did not affect their concentrations.

7
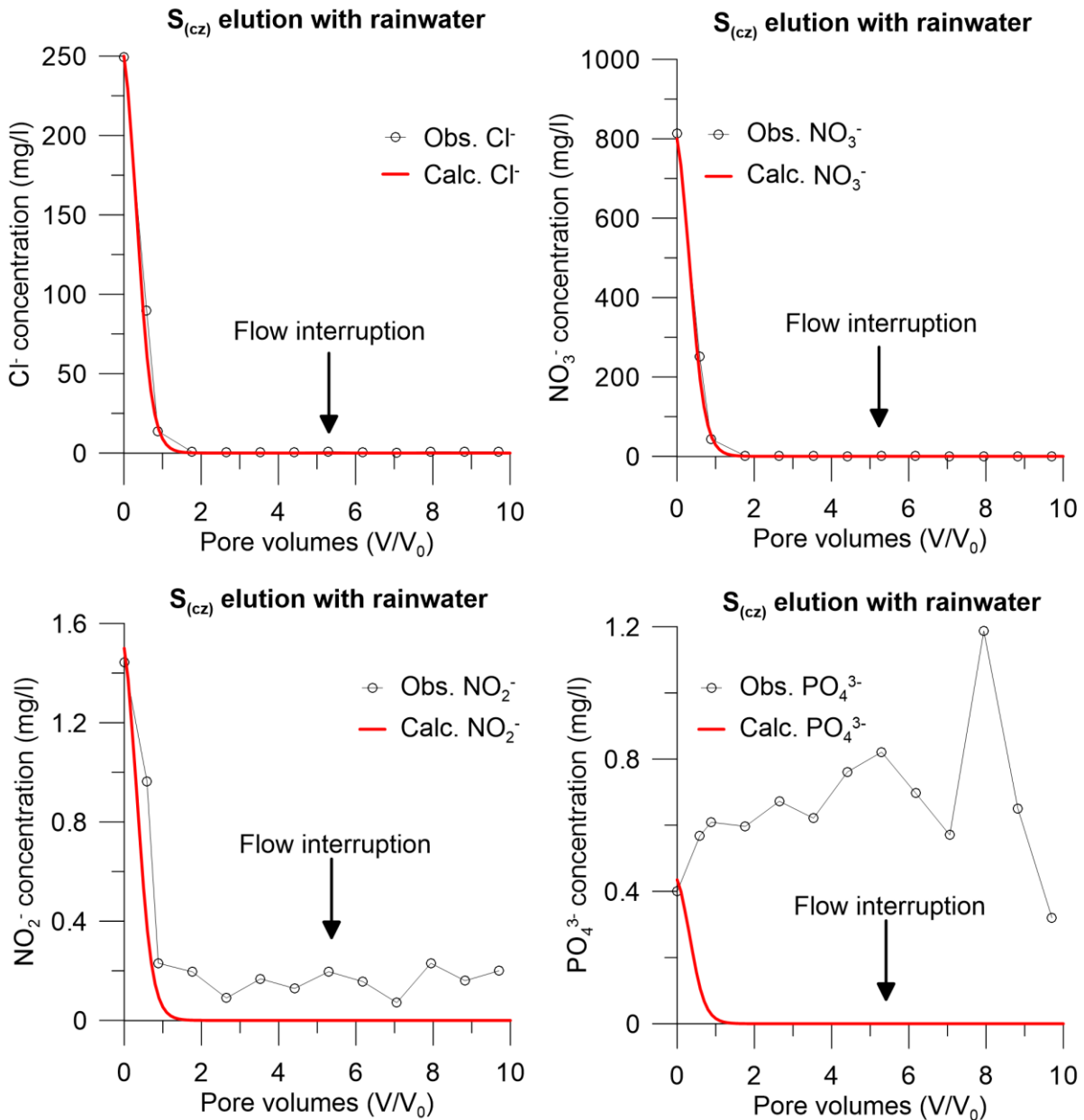
8
9

10 *Figure 5 – Observed and calculated Cl^-, NO_3^-, NO_2^- and PO_4^{3-} concentrations eluted from SCL$_{(CZ)}$*

11 *columns.*

12

Looking at figure 5, the same consideration can be drawn for the selected ions discussed before. The major differences are the longer tailing of the elution curves due to complex structure of the pore space and the model fitting, which was not as good as for the $S_{(CZ)}$ column with a MSE of 5.72 mg/l and R^2 of 0.931. In addition, here the effect of the flow interruption was at least measurable, although a much longer interruption period would be required to equilibrate the immobile and mobile regions, given the low α value.

It could be noted that the initial concentrations of Cl^- and NO_3^- were markedly higher than the concentration obtained with the batch tests for both the $S_{(CZ)}$ and $SCL_{(CZ)}$ columns. This was because these soluble salts immediately passed into solution and were flushed away in the first two pore volumes as proposed before.

By integrating the mass of each discrete sample with respect to the amount of mobile phase (water) eluted from the $S_{(CZ)}$ column, the obtained Cl^- and NO_3^- concentrations were 105 and 313 mg/kg, respectively. Similarly, the $SCL_{(CZ)}$ column behaved conservatively with concentrations integrated over the entire test of 65 mg/kg for Cl^- and 407 mg/kg for NO_3^-, respectively. Comparing these results with those of the batches reported in table 3, a good agreement between the $S_{(CZ)}$ batches and column is appreciable, whereas lower concentrations were recovered for the $SCL_{(CZ)}$ column respect to their corresponding batches. Again, this behaviour could be imputable to the complex porous structure that was disaggregated in the batches, in which all the readily available nutrients and inorganic ions passed into solution.

4. Conclusions

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. This was done via batch experiments, column elutions and column BTCs. The results of column experiments were then modelled to gain column parameters representative of the amended soils with charged zeolites. NH_4^+ was never detected in the water phase of batches and columns, using as eluent synthetic rainwater. This is very promising for natural zeolites application as soil amendments. NO_3^- and PO_4^{3-} were both present at high concentrations in batch tests and were leached in column elution tests, but the first one displayed very high concentrations at the beginning of the elution while the second showed low concentrations and retarded peaks in both the amended soil columns.

Batches typically overestimated concentrations because they brought to equilibrium various kinetics reactions that under natural conditions can be very slow. Batch experiment could be cheaper and less time consuming, but do not provide the solute concentration changes over time. Ultimately, the column experiments could be more costly in terms of time and analysis but they provided a

description closer to reality. This study suggests that natural zeolitites charged with swine manure could be a viable option to retard excess leaching of nutrients in agricultural lands and both batch and column experiments should be performed together to crosscheck and validate the obtained results.

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