

1 **Valorisation of N and P from waste water by using natural reactive hybrid sorbents: nutrients**
2 **(N,P,K) release evaluation in amended soils by dynamic experiments**

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13 **Abstract**

14 The removal of nutrients (nitrogen (N), phosphorous (P)) from waste water has become a resource
15 recovery option in recent regulations worldwide, as observed in the European Union. Although both
16 of these nutrients could be recovered from the sludge line, more than 70-75% of the N and P is
17 discharged into the water line. Efforts to improve the nutrient recovery ratios have focused on
18 developing low-cost technologies that use sorption processes. In this study, a natural zeolite
19 (clinoptilolite type) in its potassium (K) form was impregnated with hydrated metal oxides and used to
20 prepare natural hybrid reactive sorbents (HRS) for the simultaneous recovery of ammonium (NH₄⁺)
21 and phosphate (PO₄³⁻) from treated urban waste water. Three unfertile soils (e.g., one acidic and two
22 basic) amended with N-P-K charged HRS were leached with deionized water (e.g. to simulate
23 infiltration in the field) at two- and three-day time intervals over 15 different leaching cycles
24 (equivalent to 15 bed volumes). The N-P-K leaching profiles for the three charged hybrid sorbents
25 exhibited continuous nutrient release, with their values dependent on the composition of minerals in
26 the soils. In the basic soil that is rich in illite and calcite, the release of potassium (K⁺) and ammonium
27 (NH₄⁺) is favoured by-ion exchange with calcium (Ca²⁺) and accordingly diminishes the release of
28 phosphate (PO₄³⁻) due to its limited solubility in saturated calcite solutions (pH 8 to 9). The opposite is
29 true for sandy soils that are rich in albite (both acidic and basic), whereas the release of NH₄⁺ and K⁺
30 was limited and the values of both ions measured in the leaching solutions were below 1 mg/L. Their
31 leaching solutions were poor in Ca²⁺, and the release of PO₄³⁻ was higher (up to 12 mg P-PO₄³⁻/L).

1 The nutrient releases necessary for plant growth were provided continuously and were controlled
2 primarily by the soil mineral dissolution rates fixing the soil aqueous solution composition (e.g. pH
3 and ionic composition; in particular, the presence of calcite is a determinant for nutrient release,
4 especially in alkaline soils). The N-P-K charged HRS sorbents that were used for soil amendment
5 may be an alternative for avoiding nutrient leaching and reaching the goals of soil sustainability in
6 agriculture and reducing the nutrient overloading of surface waters.

7 **Keywords:** ammonium; phosphate; potassium, nutrients release; soil amendment; zeolite; resource
8 recovery.

10 **1. Introduction**

11 Soil fertility is a crucial feature in the development of agriculture for the worldwide production of food.
12 The essential plant macronutrients are nitrogen, phosphorus and potassium, which are known as the
13 NPK elements (De Castro et al., 2015). Improving the soil hydraulic conductivity and porosity
14 properties has become vital to make these nutrients available for plants (Colombani et al., 2015), and
15 conditioning soil via organic amendments is the preferred option (Laird et al., 2010). However,
16 inorganic amendments with the use of zeolites have been postulated as a better alternative due to
17 their water holding capacity (Xiubin and Zhanbin, 2001), their ability to retain and release NH_4^+ and
18 K^+ due to their high cation exchange capacity (McGilloway et al., 2003) and their ability to control
19 drainage (Bigelow et al., 2004).

20 The ever increasing population has been accompanied by a complementary increase in the demand
21 for mineral fertilizers and, accordingly, has led to increases in the production of chemicals (e.g.,
22 ammonia NH_3) and the use of non-renewable P and K. The excessive use of fertilizers has led to
23 serious problems in the sustainability of agriculture production due to land and water resource
24 degradation instead of simply achieving the purpose, which is to increase the crop yields. Therefore,
25 it is clearly necessary to develop fertilizing systems that provide a complete and controlled nutrient
26 release and simultaneously allow these nutrients to be available for uptake by plants in the short
27 term.

28 Another problem is the depletion of P, which is predicted to occur in 50 – 100 years; however, the
29 future availability of P sources has not received an appropriate amount of attention (Rasul and
30 Thapa, 2004). Thus, it is important to take advantage of the opportunities for P recovery and reduce
31 the actual demand (Cordell et al, 2009). Thus, the use of secondary sources of N and P, such as

1 those associated with urban waste waters, has been identified as an alternative for improving soil
2 fertility. Additionally, K is a macronutrient for plants; but its importance has been underestimated in
3 the agricultural field compared with those of P and N. Sewage sludge (Verstraete et al., 2009), mono-
4 incineration bottom ash (Kalmykova and Karlfeldt Fedje, 2013) and struvite (Su et al., 2014) are the
5 most successful options identified to be rich in nutrients, but such options are not always technically
6 or economically feasible and may have the potential to be banned in future (e.g., limitations on the
7 use of sludge due to presence of emerging contaminants and soil salinization risks). New solutions to
8 recover nutrients from more diluted streams (e.g., treated waste water) have been universally
9 accepted with the use of NH_4^+ and PO_4^{3-} selective sorbents. Such sorbents are known to work either
10 i) on sorption and desorption cycles to produce nutrient rich streams (Guaya et al., 2015; Thornton et
11 al., 2007) or ii) on sorption cycles and then being used in soil amendment for agricultural applications
12 (Gholamhoseini et al., 2013). Natural zeolites have been identified as the best inorganic material for
13 this purpose due to their properties; they are effective sorbents that are safe and easy to work with in
14 ion exchange applications. Zeolites are hydrated crystalline aluminium – silicate materials that
15 include micro- and mesoporosity with alkaline cations and water in their framework structure.
16 Recently, zeolites have received increased attention in the field of agriculture because their physical
17 and chemical properties make them potentially suitable candidates for soil amendments and suitable
18 carriers of plant nutrients (Król et al., 2012). However, when zeolites are applied to recover NH_4^+ from
19 waste waters, the major drawback is their ability to be regenerated. Although several types of
20 regeneration treatments have been studied, most of them are very expensive (Hedström, 2001).
21 Therefore, the direct application of natural zeolites as soil amendments has been reported to be the
22 best option for soils. These zeolites are characterized by diminished nutrient leaching, thereby
23 providing a slow-release fertilizer application (Ming and Allen, 2001), increased crop water and usage
24 efficiency (Gholamhoseini et al., 2013) and a reduced tendency for NH_3 volatilization (Latifah Omar
25 O. et al., 2010). All traditional fertilizers, including those that are specifically manufactured for the
26 slow release of nutrients, suffer from water leaching during rainfall and/or irrigation activities
27 (Badruzzaman et al., 2012). Chabazite and Clinoptilolite due to their high cation exchange capacity
28 and physical stability (Gualtieru and Passaglia, 2006; Reháková et al., 2004), have been widely used
29 as fertilizers (Coppola et al., 2002; Hong et al., 2012). However, other widely available natural
30 zeolites that have properties similar to those of clinoptilolite could be used as fertilizers but require
31 extensive trials. In the field of irrigated agriculture, zeolites have been used in addition to fertilizers to

1 retain moisture and nutrients such as N, K, Ca, magnesium (Mg) as well as other microelements in
2 the root zone for extended periods (Polat et al., 2004).
3 Additionally, new management options have been developed for use as nutrient carriers from
4 nutrient-rich waste water streams. For example, the ZeoLIFE project (Faccini et al., 2014) proposed
5 the application of NH_4^+ -charged zeolites using an Italian diagenized pyroclastic rock for soil
6 amendment (60 wt% of chabasite mixed with an NH_4^+ -rich solution of swine manure) to reduce the
7 need for fertilizers. In a previous study, a natural zeolite in its K form was modified via the
8 impregnation of hydrated metal oxides (HMO) of aluminium (ZKAl), iron (ZKFe) and manganese
9 (ZKMn) for the simultaneous recovery of NH_4^+ and PO_4^{3-} from urban waste waters. However, the
10 difficulty of regenerating these materials makes it necessary to adopt other alternatives for the further
11 utilization of the immobilized nutrients. The novelty of this work is the use of these inorganic nutrient
12 carrier materials, obtained as byproducts from a waste treatment process, as an additive for
13 agricultural amendment applications. The rationale of the study was a hypothesis (Colombani et al.,
14 2015) postulating that inorganic amendments, which improve the physical and hydraulic properties of
15 soils, can minimize the leaching of nutrients. The development of these new products could improve
16 their efficiency as fertilizers, enhance crop yields and provide secondary sources for fertilizers.
17 Therefore, the aims of this work are to (a) evaluate their use as carriers for the nutrients recovered
18 from waste water effluents and (b) assess their further application as soil amendments and slow-
19 release inorganic fertilizers (NPK) for agricultural applications. Finally, the objectives of this study are
20 to i) prepare phosphate and ammonium potassium-charged, metal hydrate impregnated clinoptilolite
21 (ZKFe, ZKAl, ZKMn) from treated waste water effluent, ii) prepare soil-N-P-K mixtures to simulate soil
22 amendment scenarios using three different types of soils (one acidic and two basics), and iii)
23 evaluate the nutrient release rates from amended soils using both batch and column leaching
24 experiments with deionized water.

25

26 **2. Materials and methods**

27 **2.1. Soil sampling**

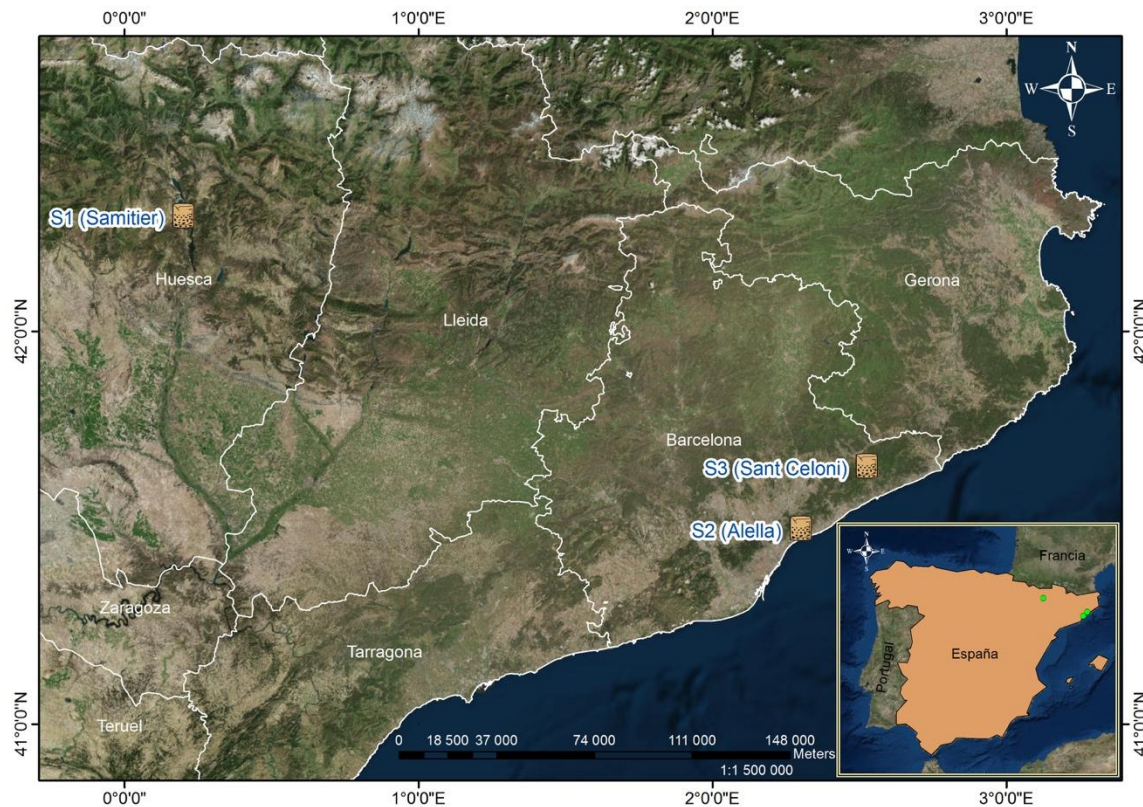
28 Three different bulk soils samples were collected from the plough layer (top 30 cm) in agricultural
29 field areas of NE Spain, as denoted in Figure 1, three replicates were obtained from each site, and
30 the sites were Samitier, Huesca (S1) (Longitude -1.4863; Latitude 0.0000), Alella (S2) (Longitude
31 2.3009; Latitude 41.5001) and Sant Celoni, Barcelona (S3) (Longitude 2.5258; Latitude 41.6592). S1

1 soil is located in the northern limit of the Ebro Depression. This is an agricultural soil developed over
2 marls on dry continental Mediterranean climate (annual temperature of 11.4 °C and 660 mm of
3 precipitation). S1 soil's main characteristics include pH of 8.5, 40% of CaCO₃, medium content of
4 organic matter (8%) due to de agricultural practices leaving harvest residues on the topsoil silty-clay
5 texture and a Ca dominated cation exchange complex with values of 25 cmol(+) kg⁻¹. S2 and S3 soils
6 are located in the Litoral Catalan mountain ranges both soils developed over granites of the
7 Paleozoic. S2 and S3 soil are agricultural soils that developed in a sub-humid Mediterranean climate
8 (annual temperature of 15.5 °C and 737 mm of precipitation). The S2 soil's main characteristics
9 include alkaline pH (9.2) due to the aerosol salt transport from the Mediterranean Sea, organic
10 matter-poor, sandy loam texture and cation exchange capacity of 30 cmol (+) kg⁻¹. The S3 soil's main
11 characteristics include pH slightly acidic/neutral (6.8), sandy loam texture (12% of clay) and cation
12 exchange capacity of 12 cmol (+) kg⁻¹. S1, S2 and S3 were classified into the Xerorthent group,
13 Entisol order (USDA, 1999).

14 The soil samples were air-dried at room temperature (20 °C) for 72 hours. The detectable vegetal
15 and animal impurities were separated from the soil samples before sieving to < 2 mm. Soils were
16 characterized for pH, moisture, bulk density, and soil organic matter (SOM). The soil pH was
17 measured using a 1:1 (w/v) soil-water suspension that was shaken for 1 h based on the ASTM
18 D4972 - 13 (Standard test method for pH of soils). Bulk density was determined using the method
19 described by ASTM D4531 - 15 (Standard test methods for bulk and dry density of peat and peat
20 products). Finally, according to the ASTM D2974 - 14 (Standard test methods for moisture, ash, and
21 organic matter of peat and other organic soils), moisture was determined by drying soil for 24 h at
22 105 °C. In addition, the organic matter content was determined by using the loss on ignition method
23 at 600 °C during 8 hours and calculated by Eq 1.

$$24 \text{ SOM (\%)} = \frac{(w_i - w_c)}{w_c} \times 100 \quad (1)$$

25 where w_i is the soil weight before calcination and w_c is the soil weight after calcination.



1
2 Figure 1. Map of the locations where the soil samples were collected.

3
4 **2.2. Preparation of ammonium and phosphate charged clinoptilolite using treated domestic**
5 **waste water**

6 A natural clinoptilolite (NC) (Zeocem Company (Slovak Republic)), was ground to fine powder
7 (particles <74 μm) and then converted to its K form. Subsequently, it was impregnated with Fe
8 (KZFe), Al (ZKAl) and Mn (KZMn) hydrated oxides as described previously (Guaya et al., 2016).
9 Weighted amounts of HMO impregnated K-zeolite samples (6.5 g of ZKAl, ZKFe, ZKMn) were
10 equilibrated with 500 mL of real treated water (pH 7.5±0.5), at 500 rpm and under room temperature
11 conditions (21±1 °C). The treated water used in the experiments was collected from the effluent
12 stream of the secondary treatment plant at the El Prat waste water treatment plant (WWTP)
13 (Barcelona Spain); the chemical composition of the water is listed in Table 1.

14
15 Table 1. Chemical composition of the effluent stream from secondary treatment at the El Prat
16 wastewater treatment plant (WWTP) used for sorption experiments.

ICP - MS elements

	Na	Ca	S	K	Mg	Sr	Al	Si	Fe	Ba
mg/L	246	127	81	36	35	1.3	0.2	0.03	0.03	0.02
	Li	B	Ti	V	Cr	Mn	Co	Ni	Cu	Zn
µg/L	19	257	6	12	0.9	3.1	2	28	5	58
	As	Se	Rb	Mo	Sn	Sb	Ba	W	Pb	U
µg/L	3	3	16	15	0.3	3	19	3	0.2	1.7
	Be, Sc, Ga, Ge, Y, Zr, Nb, Cd, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Tl, Bi, Th									
µg/L	<0.2									
	TOC elements									
	NPOC		NT		TOC		TC		IC	
mg/L	12		590		10		50		42	
	Ionic Elements									
	NH ₄ ⁺		PO ₄ ³⁻		NO ₃ ⁻		Cl ⁻			
mg/L	500		500		51		542			

1 Sodium (Na); Calcium (Ca); Sulfure (S); Potassium (K); Magnesium (Mg); Strontium (Sr); Aluminium (Al); Silicon (Si); Iron (Fe); Barium (Ba); Lithium
2 (Li); Boron (B); Titanium (Ti); Vanadium (V); Chromium (Cr); Manganese (Mn); Cobalt (Co); Nickel (Ni); Copper (Cu); Zinc (Zn); Arsenic (As); Selenium
3 (Se); Roberidium (Rb); Molybdenum (Mo); Tin (Sn); Antimony (Sb); Barium (Ba); Tungsten (W); Lead (Pb); Beryllium (Be); Scandium (Sc); Gallium (Ga);
4 Germanium (Ge); Yttrium (Y); Zirconium (Zr); Niobium (Nb); Cadmium (Cd); Cesium (Cs); Lanthanum (La); Cerium (Ce); Praseodymium (Pr);
5 Neodymium (Nd); Samarium (Sm); Europium (Eu); Gadolinium (Gd); Terbium (Tb); Dysprosium (Dy); Holmium (Ho); Erbium (Er); Thulium (Tm),
6 Ytterbium (Yb), Lutetium (Lu), Hafnium (Hf), Tantalum (Ta), Thallium (Tl), Bismuth (Bi), Thorium (Th); Non-purgeable organic carbon (NPOC); Total
7 carbon (TC); Total organic carbon (TOC); Inorganic carbon (IC); and Total nitrogen (NT); Ammonium (NH₄⁺), Phosphate (PO₄³⁻); Nitrate (NO₃⁻); Chloride
8 (Cl).
9

10 Nutrient loads on impregnated clinoptilolites were enhanced by increasing the NH₄⁺ (500 mg N-
11 NH₄⁺/L) and PO₄³⁻ (500 mg P-PO₄³⁻/L) concentrations in the waste water effluent (by adding NH₄Cl
12 and NaH₂PO₄·2H₂O, respectively). The suspension was settled to separate the solid content, which
13 was dried at 60 °C for 24 h and stored for further use. Equilibrium tests were performed several times
14 until 250 g of each charged impregnated clinoptilolite was obtained. The NH₄⁺ and PO₄³⁻
15 concentrations were determined in the initial and final aqueous solutions after filtration with a 0.45 µm
16 cellulose membrane filter.
17

18 2.3. Ammonium and phosphate batch and column leaching assays

19 The NH₄⁺ and PO₄³⁻ release assays were performed in continuous mode. Column studies were used
20 to simulate the release of nutrients from the charged impregnated clinoptilolites used for soil
21 amendment at the field scale. These experiments were performed in polyethylene columns (100 mm

1 length x 40 mm internal diameter) to simulate the natural soil arrangement, as shown in Figure 2.
 2 Twelve soil columns were used according to the descriptions given in Table 2.

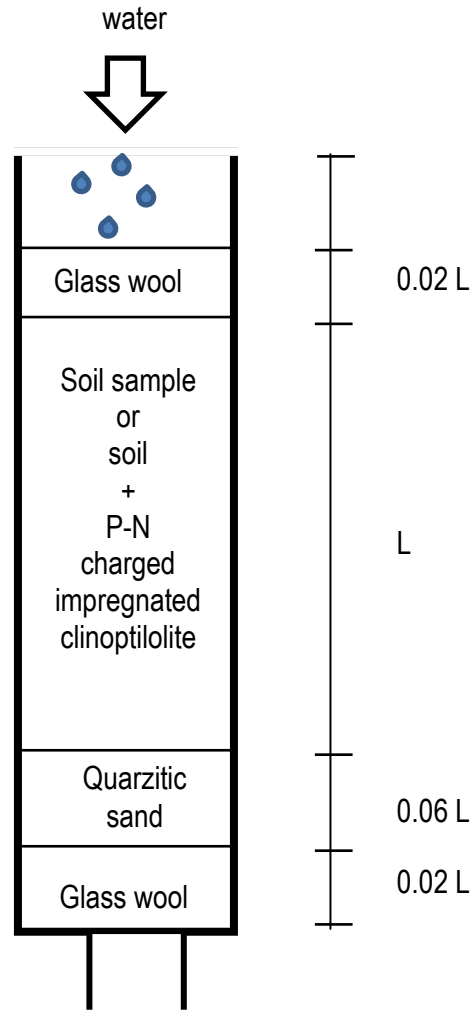
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4 Table 2. Descriptions of the column experiments including soil columns (CS1, CS2 and CS3) and
 5 amended samples of soils with charged HMO impregnated clinoptilolites (ZKAl, KZFe and KZMn).

Column	Code	Description
1	C-S1	Column S1 control sample
2	C-S1ZKAl	Column S1 sample and P-N charged Al impregnated clinoptilolite
3	C-S1ZKFe	Column S1 sample and P-N charged Fe impregnated clinoptilolite
4	C-S1ZKMn	Column S1 sample and P-N charged Mn impregnated clinoptilolite
5	C-S2	Column S2 control sample
6	C-S2ZKAl	Column S2 sample and P-N charged Al impregnated clinoptilolite
7	C-S2ZKFe	Column S2 sample and P-N charged Fe impregnated clinoptilolite
8	C-S2ZKMn	Column S2 sample and P-N charged Mn impregnated clinoptilolite
9	C-S3	Column S3 control sample
10	C-S3ZKAl	Column S3 sample and P-N charged Al impregnated clinoptilolite
11	C-S3ZKFe	Column S3 sample and P-N charged Fe impregnated clinoptilolite
12	C-S3ZKMn	Column S3 sample and P-N charged Mn impregnated clinoptilolite

6

7 An amendment equivalent to 100 kg P.ha⁻¹ of soil sample (Kleinman et al., 2002) was established to
 8 dose the P-N charged impregnated clinoptilolite in each soil column, and it contained 5.7 mg P and
 9 6.4 mg N in 0.9 g ZKAl; 5.6 mg P and 6.8 mg N in 1 g ZKFe and 5.8 mg P and 4.4 mg N in 0.6 g
 10 ZKMn. Moreover, simulating an average rainfall of 1.8 mm/d in Europe, deionized water was
 11 continuously fed to the soil column. Soil samples were selected from three different regions with an
 12 average annual rainfall between 1.8 and 2.0 mm/d. A 25-mL sample of liquid samples released from
 13 each column was collected every three days, and a total of fifteen cycles were performed. Samples
 14 were filtered through a 0.45 µm cellulose membrane filter and stored at 5 °C for further analytical
 15 measurements. In addition to the NH₄⁺ and PO₄³⁻ released from the soil columns, the other anions,
 16 cations and heavy metals, present in the effluent were quantified.



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Figure 2. Schematic of the column used in the experiment: a mixture of soil and NPK charged hybrid sorbents of depth L (m) is placed over a quartzitic sand layer (0.06 L) and a glass wool layer (0.02 L).

2.4. Analytical methods

2.4.1. Liquid samples

Standard methods were used for the PO_4^{3-} and NH_4^+ determinations (APHA, 2000). The vanadomolybdophosphoric acid colorimetric method (4500-P C) and the ascorbic acid method (4500-P E) were used for PO_4^{3-} quantification, and the ammonia-selective electrode method (4500-NH3 D) was employed for NH_4^+ determination. The ions were quantified using a Thermo Scientific Ionic Chromatograph (Dionex ICS-1100 and ICS-1000). An elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), Thermo Scientific - ICAP 6500) and inductively coupled plasma mass spectrometry or ICP-MS (ICP-MS, Thermo Scientific – X-series

1 II). The non-purgeable organic carbon (NPOC), total carbon (TC), total organic carbon (TOC),
 2 inorganic carbon (IC) and total nitrogen (NT) were determined in a total organic carbon analyser
 3 (Shimadzu, TOC-V_{CPH}).

4
 5 **2.4.2. Solid samples**

6 The chemical composition and morphology of the soil samples were determined by a Field Emission
 7 Scanning Electron Microscope (JEOL JSM-7001F) coupled to an Energy Dispersive X-ray (EDX)
 8 Spectroscopy system (Oxford Instruments X-Max). Four individual EDX measurements were
 9 performed at different positions. The infrared absorption spectra of soils were recorded in a Fourier
 10 Transform FTIR 4100 (Jasco) spectrometer in the range of 4000 – 550 cm⁻¹. A powder X-ray
 11 Diffractometer (D8 Advance A25 Bruker) was used for the X-ray diffraction (XRD) characterization of
 12 soil samples.

13
 14 **3. Results and discussion**

15 **3.1. Soils characterization**

16 The main mineralogical phases as well as the physical properties for each soil sample are
 17 summarized in Table 3. The XRD results of the soil samples are shown in Supplementary Figure S1.
 18 The sodic soils S1 and S2 with pH 8.5 and 9.2, respectively; can be described as mixed calcareous
 19 soils due to their high contents of Ca, Al, Fe and Mg with high contents of quartz and illite in S1 and
 20 albite in S2 (Gunkel-Grillon et al., 2015). In contrast, the soil sample S3 was characterized as a
 21 slightly acidic soil with pH 6.8, so it is considered a pure ferralitic soil due its higher contents of Fe, Al
 22 and Mn as it was rich in albite and quartz.

23
 24 Table 3. Chemical and physical characterization of soil samples (S1, S2 and S3).

Properties	S1	S2	S3
Minerals	Quartz SiO ₂ , Calcite CaCO ₃ , Illite (K,H3O)Al ₂ Si ₃ AlO ₁₀ (OH) ₂ , Clinocllore (Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈ , Microcline (KAlSi ₃ O ₈) Albite (NaAlSi ₃ O ₈)	Quartz SiO ₂ , Albite (Na,Ca)Al(Si,Al) ₃ O ₈ , Microcline KAlSi ₃ O ₈ , (NaAlSi ₃ O ₈), Calcite CaCO ₃ , Magnetite 2Fe ²⁺ ₃ O ₄ , Montmorillonite ((Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ •n(H ₂ O))	Quartz SiO ₂ , Albite (Na,Ca)Al(Si,Al) ₃ O ₈ , Microcline (KAlSi ₃ O ₈), Nontronite (Na _{0.3} Fe ³⁺ ₂ Si ₃ AlO ₁₀ (OH) ₂ •4(H ₂ O))

pH	8.5±0.1	9.2±0.1	6.8±0.1
Humidity (%)	3.3±0.3	1.1±0.2	2.4±0.2
Bulk density (g/cm ³)	1.1±0.2	1.4±0.2	1.2±0.2
Organic matter (%)	8.8±0.5	2.4±0.4	5.4±0.4

(±) The plus-minus sign has been used to denote the standard deviation

3.2. Preparation of charged ammonium and phosphate HMO impregnated potassium zeolites using treated domestic waste water

NH₄⁺ and PO₄³⁻ were selectively sorbed from waste water by the impregnated clinoptilolites compared to the other ions that were present in the aqueous solution (e.g., Na⁺, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻, HCO₃⁻, NO₃⁻, Cl⁻). The sorption capacities for ZKAl, ZKFe and ZKMn are presented in Table 4. Considering the acid base properties of the impregnated clinoptilolites (with pH_{pzc} values of 7.3 ZKAl, 6.4 ZKFe and 6.9 ZKMn) (Guaya et al., 2016) compared to the pH of 7.5 observed for the treated effluent used for the adsorption experiments, it can be suggested that the sorption involved in the removal of both ions are ion exchange (e.g., NH₄⁺) and complexation (e.g., H₂PO₄⁻). It may be postulated that the removal of both NH₄⁺ and PO₄³⁻ is favoured under these conditions. The extractions of both ions are pH dependent, as confirmed in previous studies (Guaya et al., 2016), with maximum extraction rates at neutral pH range, decreasing at pH values below 4 and above 10. Analysis of treated waste water after the sorption experiments revealed that K⁺ and Na⁺ were released from the impregnated clinoptilolite, which could be due to their ion exchange with NH₄⁺ ions. In particular, in the ZKMn clinoptilolite, the higher sorption capacities for PO₄³⁻ and Mg²⁺ compared with the two other clinoptilolite forms, could be associated with a precipitation reaction in the PO₄³⁻ and Mg²⁺ minerals on the clinoptilolite surface, as revealed by soil sample characterization studies. Cl⁻, SO₄²⁻, and NO₃⁻ ions as well as NPOC and TOC showed minimal sorption on the three modified clinoptilolites (Table 4). Other elements found in the treated waste water were negligibly sorbed.

1 Table 4. Sorption capacity for the major components of treated waste water of modified clinoptilolite
 2 (ZKAl, ZKFe, ZKMn) (The solid to aqueous phase ratio used was 6.5 g in 500 mL).

	ZKAl	ZKFe	ZKMn
	(mg/g)		
PO ₄ ³⁻	6.3±0.8	5.6±0.6	9.6±1.2
NH ₄ ⁺	7.1±1.2	6.9±1.3	7.3±1.1
Na ⁺	-7.0±1.1	-6.6±0.9	-9.3±1.0
K ⁺	-11.3±1.2	-11.6±1.1	-8.4±1.0
Mg ⁺	0.8±0.1	0.5±0.1	1.2±0.1
Cl ⁻	0.2±0.1	0.00±0.1	0.8±0.1
SO ₄ ²⁻	0.04±0.01	0.04±0.01	0.07±0.01
NO ₃ ⁻	0.02±0.01	0.01±0.01	0.00±0.01
NPOC	0.2±0.1	0.2±0.1	0.2±0.1
TOC	0.3±0.2	0.1±0.1	0.1±0.1
TC	0.1±0.1	0.03±0.02	0.03±0.01
IC	-0.2±0.1	-0.1±0.1	-0.03±0.01

3 (-) A negative value indicates release from the K-HMO impregnated zeolites

4 (±) The plus-minus sign has been used to denote the standard deviation

5

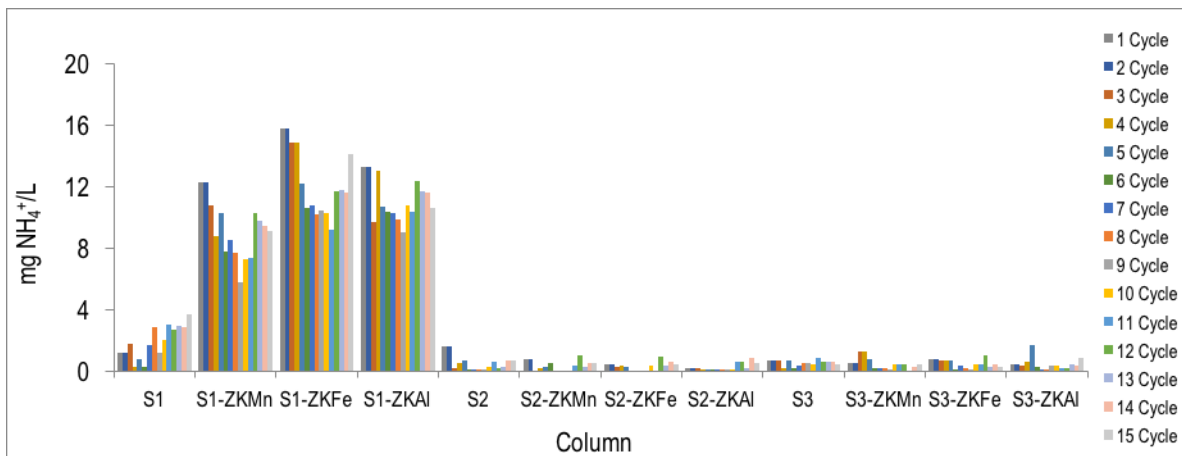
6 3.3. Release of NPK and trace elements from clinoptilolite amended soils using column tests

7 A sequence of 15 different leaching cycles simulating infiltration in the field test was carried out, and
 8 the composition of the effluent collected from each column is plotted in Figures 3 to 9.

9 3.3.1 Release of NH₄⁺, PO₄³⁻ and K⁺

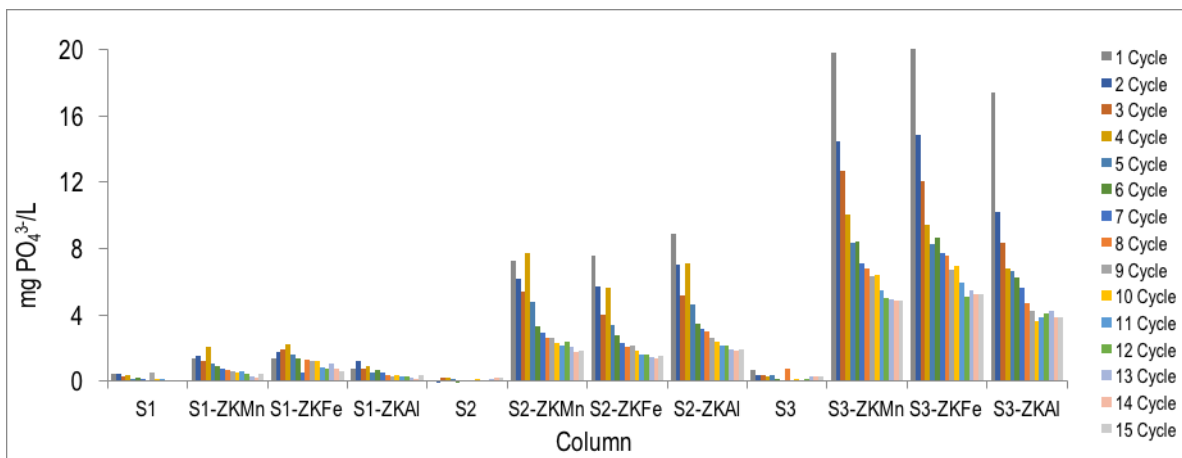
10 The results plotted in Figure 3 clearly show the release of higher amounts of nutrients (N, P, K) from
 11 the amended soil filled columns compared with the non-amended soil filled columns, and the results
 12 are in agreement with those reported in batch tests. Although the NH₄⁺ and PO₄³⁻ release capacities
 13 are similar for ZKAl, ZKFe and ZKMn, different leaching profiles were observed for these compounds,
 14 being coupled with the release profiles of NH₄⁺ and K⁺ but uncoupled with those of PO₄³⁻.

1 a)



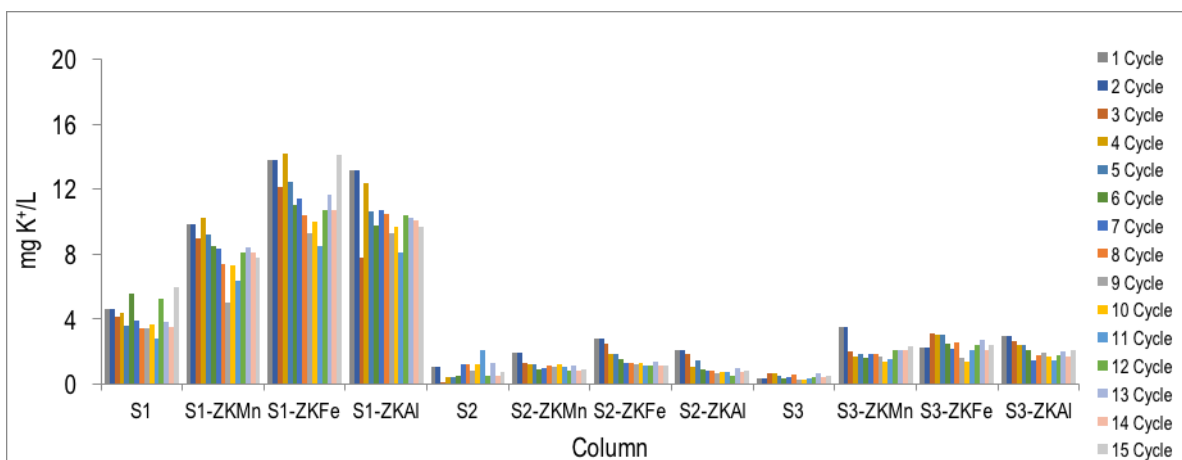
2

3 b)



4

5 c)



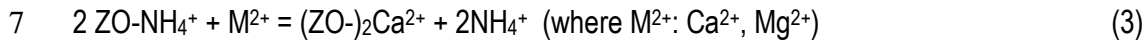
6

7 Figure 3. Amount of NH_4^+ (a), PO_4^{3-} (b) and K^+ (c) leached from non-amended and amended soil
8 columns through 15 continuous cycles.

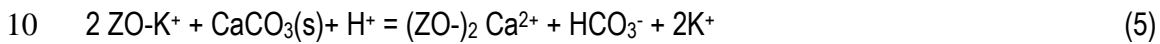
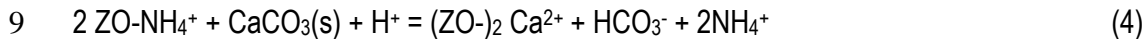
9

1 The measured leaching values were found to be controlled by ion-exchange and complexation
2 reactions involving the K-HMO impregnated clinoptilolites described in Eqs. 2 – 6 and by the mineral
3 dissolution reactions in Eqs. 7 - 11.

4 As soil S1 is rich in calcite and illite, the increase in the content of K^+ , Ca^{2+} and Mg^{2+} , favours the
5 exchange of the sorbed NH_4^+ , as described in reactions 2 - 3:



8 The interaction with calcite could be described by the following global reactions:



12 The ion-exchange selectivity of impregnated clinoptilolites follows the sequence: $NH_4^+ > K^+ > Na^+ >$
13 $Ca^{2+} > Mg^{2+}$. The higher selectivity for NH_4^+ can be attributed to the fact that the background
14 concentration of NH_4^+ in the solution is below 0.5 mg/L, as shown on the columns with only soil
15 (Figure 3). For soil S1, the Ca^{2+} and K^+ leaching profiles generated by the dissolution of the illite and
16 calcite are one order of magnitude higher than the other two soils. In the case of S2, although it has a
17 high calcite content, its higher pH value decreases the calcite solubility, thereby causing a decrease
18 in the measured values. As a consequence the exchange of NH_4^+ and K^+ ions from the charged
19 impregnated clinoptilolite is increased, and the leaching test values of K^+ and NH_4^+ in solution range
20 from 15 to 10 mg/L for both NH_4^+ and K^+ . Additionally, soils that are rich in Na-clays and calcite such
21 as S1 could provide a continuous release of NH_4^+ and K^+ for plant roots. However, the high Ca^{2+}
22 concentration values reduce the release of PO_4^{3-} values measured below 2 mg/L over the 15 cycles
23 (e.g., 15 BV) for S1.

24 The highest NH_4^+ release was found in soil solutions S1, and it was almost negligible for both S2 and
25 S3. The soil solution S1 demonstrated the highest release of NH_4^+ , and a similar behaviour was
26 observed for the other cations (Ca^{2+} , Mg^{2+}) present in the charged impregnated clinoptilolites. The
27 increase in the cation contents in the solutions could be an effect of the occurrence of their aqueous
28 complexation to dissolved organic matter, which prevented their fixation to soil (Fisher-Power et al.,
29 2016). Soil sample S1 revealed the highest organic matter content and a basic pH 8.2 that favoured
30 the release of organic matter in soil solution (Dijkstra et al., 2004) due to the deprotonation of organic
31 molecules, which made them more negatively charged and hydrophilic. The low content of NH_4^+ in

1 soil solutions S2 and S3 could be explained in terms of the attachment of the NH_4^+ ions to the
2 colloidal particles of soil samples, which is in accordance with previous reports (Moradzadeh et al.,
3 2014). The NH_4^+ retention has previously been demonstrated to occur on the ion exchange sites of
4 the soils as exchangeable cations (Na^+ , Mg^{2+}) were released (Colombani et al., 2015). It is worth
5 noting that other mechanisms in soil environments should be ruled out (e.g., volatilization,
6 nitrification) as should the interlayer fixation of NH_4^+ ions due to the short duration of the experiments
7 (e.g., weeks)

8 Colombani et al., 2015 carried out two column experiments to evaluate the inorganic N leaching from
9 a zeolite enriched in NH_4^+ from swine manure or NH_4Cl solutions by flushing with synthetic rainwater
10 under saturated conditions. The NH_4^+ content in the leachate solution of the first column was higher
11 than of the second column, but in both cases, it represented less than 9% of the total exchangeable
12 NH_4^+ . The PO_4^{3-} content in the soil solutions was low which is in accordance with previous reports on
13 the low mobility of inorganic P in soils (Marofi et al., 2015). This is attributable to the chemical
14 processes of inorganic P in soils such as complexation, solubilization and sorption and the interaction
15 with other ions which influence the P migration (Han et al., 2016) or the formation of metal complexes
16 with Fe and Al (Rashid et al., 2016) and the chemical precipitation of some Ca, Mg, Fe and Al
17 phosphates (Lombi et al., 2004). Soil samples S1 and S2 contain calcite in their mineralogical
18 compositions, which is known to affect the PO_4^{3-} mobility to a greater degree (Afif et al., 1993). In this
19 study the highest availability of PO_4^{3-} in solutions is from S3; this can be attributed to its pH of 6.8,
20 which caused the inorganic forms of P to be soluble, in agreement with a previous study (Anda et al.,
21 2015). This result can be attributed to the higher availability of some metals on the surface layers of
22 basic soils that promote PO_4^{3-} fixation compared to acidic soils. Moreover, the oxidizing conditions for
23 the existing metal (oxy)hydroxides can favour the PO_4^{3-} fixation, whereas the reducing conditions can
24 promote PO_4^{3-} release due to the dissolution of these (oxy)hydroxides, as shown for the behaviour of
25 arsenic, an anion similar to PO_4^{3-} , in soils (Rinklebe et al., 2016). Additionally, the redox potential has
26 a strong influence on the P mobility in soils because under the reducing conditions P(V) is reduced to
27 P(III) which is less reactive with the (oxy)hydroxides (Song et al., 2015). However, the evaluation of
28 the redox potential in the leaching test was outside the scope of this study.

29 For soils S2 and S3, which are characterized by lower contents of calcite and higher contents of Na-
30 rich clay minerals such as albite, a higher release of PO_4^{3-} , with values from 5 to 2 $\text{mgPO}_4^{3-}/\text{L}$ for S2
31 and from 15 to 5 $\text{mgPO}_4^{3-}/\text{L}$ for S3 (Figure 3), is observed. Additionally, due to the lower solubility

1 values of albite, there is a consequent reduction in the amounts of Na⁺ ions in solution, causing a
 2 further reduction in the release of NH₄⁺ and K⁺ ions from the charged impregnated clinoptilolite.
 3 In the cases of S2 and S3, for which albite is the richest mineral in the soil solution, thus providing
 4 higher values of Na⁺ in solution with a consequently lower selectivity in the presence of NH₄⁺, the
 5 NH₄⁺ leached values were found to be less than 1 mg NH₄⁺/L after 15 cycles and 15 BV of leaching
 6 solution. This indicates that in soils with high contents of Na-rich clays, charged impregnated
 7 clinoptilolites showed good properties of providing a slow release of NH₄⁺ compared to the illite rich
 8 soils (e.g., S1). This result suggests that the NH₄⁺ - K⁺ exchange is favoured over the NH₄⁺ - Na⁺
 9 exchange in the clinoptilolites used for soil amendment. The clinoptilolite selectivities for certain
 10 cations and their competition were observed in a previous study (Ming and Dixon, 1987). The NH₄⁺
 11 ion receives preference over the Na⁺ ion due to the former's smaller size in occupying the ion
 12 exchange sites of clinoptilolite; it explains the difficulty of releasing NH₄⁺ from the clinoptilolites in the
 13 amended soils with high contents of Na-rich clays (S2 and S3). In contrast, in the soil with high
 14 content of K-rich clays, the small size of both NH₄⁺ and K⁺ species promoted their easy ion exchange.
 15 The use of charged NPK HMO impregnated clinoptilolites as soil fertilizers effectively provided a
 16 gradual release of nutrients in aqueous solutions over the 15 cycles. It was found that the amount of
 17 PO₄³⁻ released from each column was influenced by both the nature of the soil and the use of
 18 charged impregnated clinoptilolite as the soil amendment (Table 5). In the case of PO₄³⁻ for S1, lower
 19 concentrations were measured compared with S2 and S3.

20

21 Table 5. Release in solution of PO₄³⁻ from each column of continuous tests (values of K⁺ and NH₄⁺
 22 release were not calculated, as the K⁺ and NH₄⁺ released by the clinoptilolite could not be
 23 distinguished from those released from the dissolution of minerals present in the soils).

System	Release P(%)	System	Release P(%)	System	Release P(%)
C-S1	3.5	C-S2	0.6	C-S3	4.0
C-S1ZKMn	8.3	C-S2ZKMn	31.5	C-S3ZKMn	87.2
C-S1ZKFe	8.9	C-S2ZKFe	31.9	C-S3ZKFe	93.4
C-S1ZKAl	4.6	C-S2ZKAl	37.7	C-S3ZKAl	75.7

24

1 In the case of soil S2, with the highest pH value (approximately 9), the PO_4^{3-} ions demonstrated a
2 total release of 32-38% after the 15 cycles; similarly, for soil S1 at pH value of approximately 8, the
3 release amount was 5-9%. In contrast, for acidic soils, in which the sorption of ions is less favoured,
4 up to 87-93% of the loaded P- PO_4^{3-} was desorbed.

5 As mentioned earlier, the leaching behaviour of K^+ revealed a similarity with that of NH_4^+ , so the
6 highest K^+ release was found for soil S1. The processes that influenced the NH_4^+ release for the
7 organic matter content and ion exchange capacity of soil, are also pertinent for K^+ release. In
8 addition, the existence of illite as mineral clay in soil S1 may contribute to the K^+ release in solution
9 (Wang et al., 2015). Zwingmann et al. (2009) evaluated a zeolite for sandy soils with low water and
10 nutrient retention capacities and concluded that the zeolite soil amendment was highly suited for land
11 use, including horticulture and turf, because of its capacity to reduce the leaching losses of NH_4^+
12 fertilizers. The use of a zeolite synthesized by caustic treatment of kaolin at 80–95 °C (Mesolite),
13 which had a moderately low surface area (9–12 m^2/g) but a very high cation exchange capacity in
14 column experiments, showed that the addition of 0.4% Mesolite to a sandy soil greatly reduced (90%)
15 the leaching of added NH_4^+ compared to that of a non-amended soil. The zeolite was 11 times more
16 efficient in retaining NH_4^+ than were natural zeolites, and the loaded NH_4 -Mesolite showed a slow
17 release of NH_4^+ into the soil solution.

18 Therefore, the N-P-K charged impregnated clinoptilolite is likely to be an effective slow release
19 fertilizer that could help address the issue of essential nutrient deficiency in soils. Furthermore, this
20 system could constitute an effective and cheap source of macronutrients and may be an option for
21 the economic and social sustainability of agriculture. It would also help avoid the surface runoff and
22 nutrient overloading, promoted by waste water discharges and the arbitrary use of fertilizers.

23

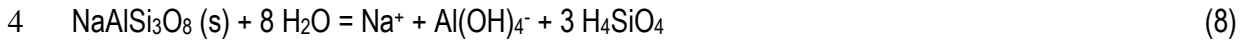
24 **3.3.2 Release of Na^+ , Ca^{2+} and Mg^{2+}**

25 The chemical compositions of the leaching solutions from the columns throughout the leaching cycles
26 reported a minimal variation, as shown in Figure 4. Basic soils S1 and S2 with a high content of
27 CaCO_3 reported pH values between 8.3 and 8.9 throughout the leaching cycles, and the values were
28 found to be similar to those measured in the batch tests (8.2 and 8.9, respectively) (Supplementary
29 information Figure S2). The pH is controlled by the dissolution of $\text{CaCO}_3(\text{s})$ and silicate base minerals
30 present in the soils. According to the mineral composition of the three soils (Table 1), the principal
31 phases and their dissolution reactions can be expressed by Eqs. 7 to 11.

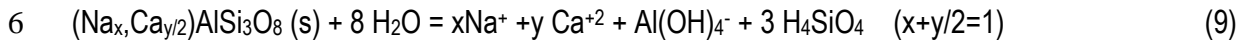
1 Illite:



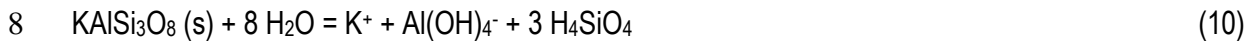
3 Albite:



5 Albite Ca rich:



7 Microcline:

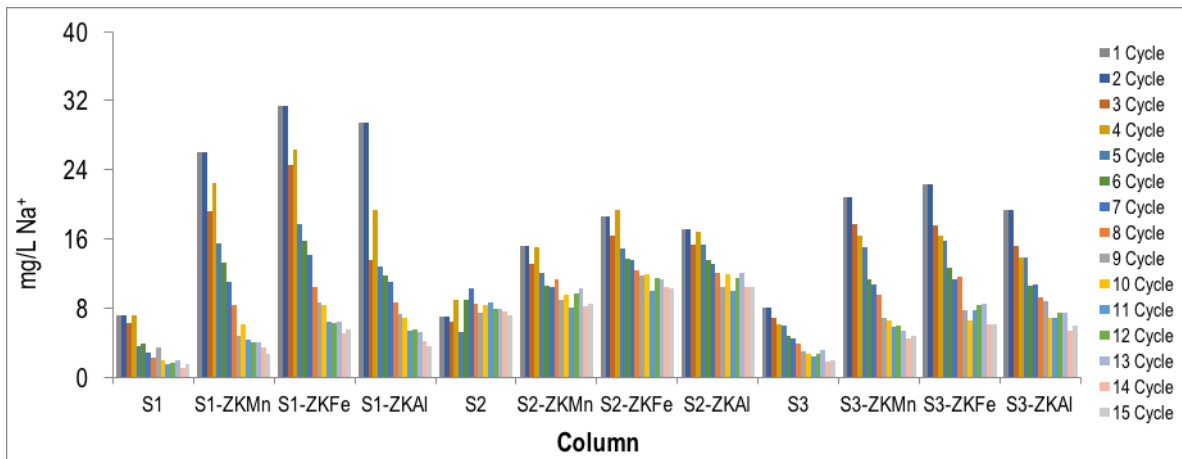


9 Calcite:



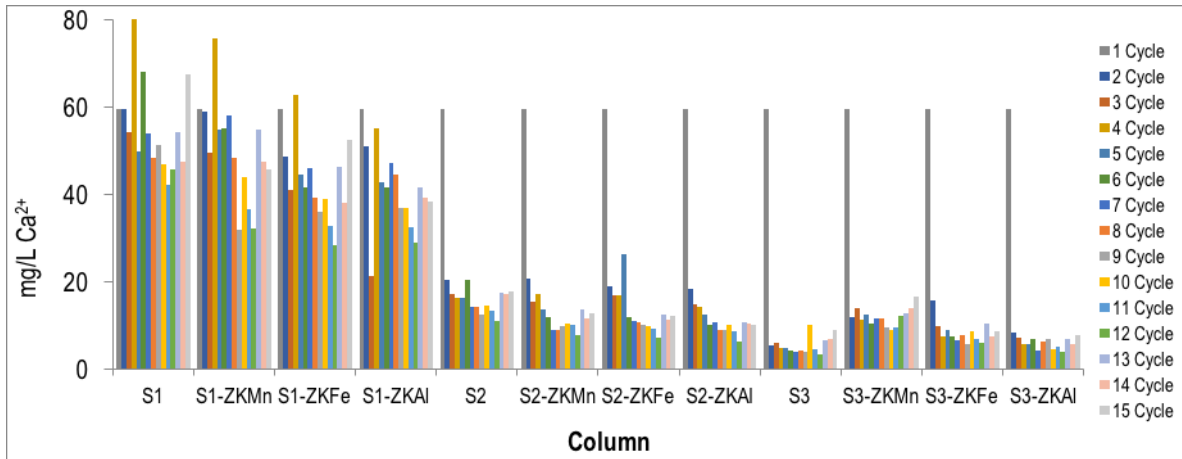
11 The dissolution profiles for Na^+ , Ca^{2+} and Mg^{2+} ions (Figure 4) shown consistently higher values of
12 Na^+ for the three non-amended and amended columns and higher values of Ca^{2+} for S1, with values
13 as high as 50 $mgCa^{2+}/L$.

14 a)



15

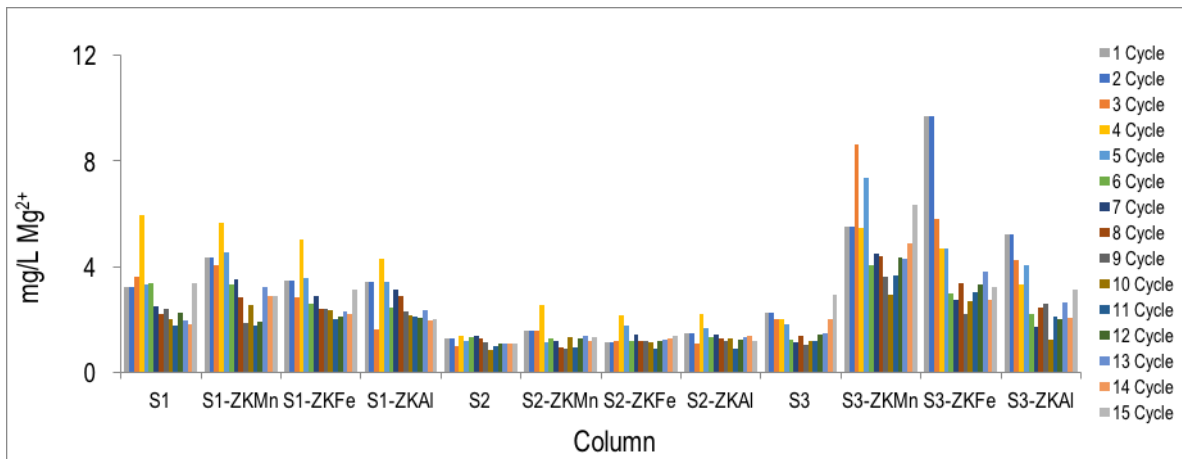
16 b)



1

2

c)



3

4 Figure 4. Leaching profiles of Na^+ (a), Ca^{2+} (b) and Mg^{2+} (c) from non-amended and amended soil
 5 columns through 15 continuous cycles (equivalent to 15 BV).

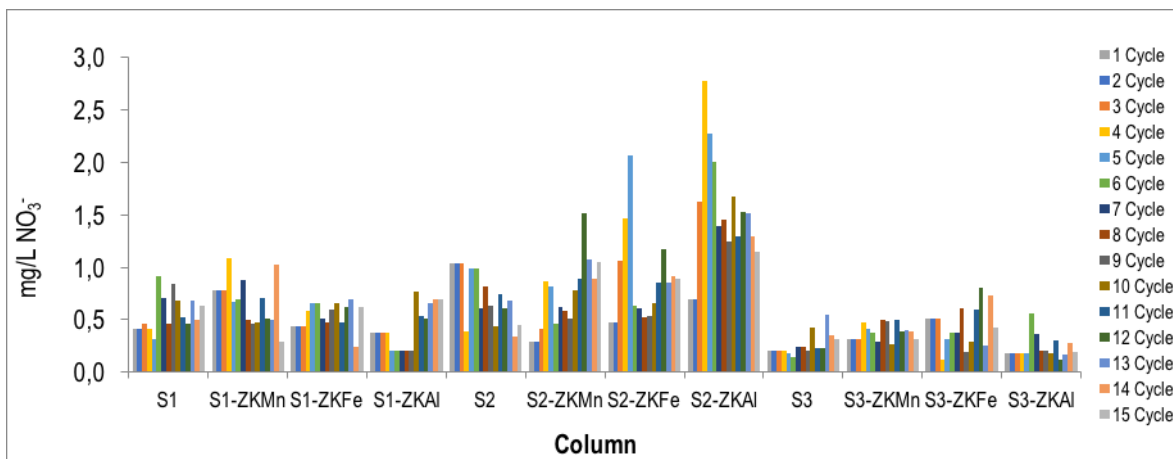
6 Lower values were measured for Mg^{2+} because the content of magnesium containing minerals was
 7 lower. The variation between non-amended and amended soils is controlled by the mineral
 8 dissolution rates and the cation exchange reactions, the quantifications of which were outside the
 9 scope of this study.

10 The N-P-K charged impregnated clinoptilolites used in this study were demonstrated to be sources of
 11 soil other nutrients, specifically exchangeable cations (e.g. Na^+ , Ca^{2+} and Mg^{2+}) which are
 12 conventionally depleted by nutrient uptake and subsequent harvest and removal of biomass
 13 (Berthrong et al., 2009). Therefore, their use would be an interesting way to reach soil equilibrium,
 14 avoiding soil acidification via the long-term use of fertilizers and the leaching process that occurs in
 15 high-rainfall areas (Fageria and Baligar, 2008).

16

1 **3.3.3 Release of other nutrients (NO₃⁻ and SO₄²⁻)**

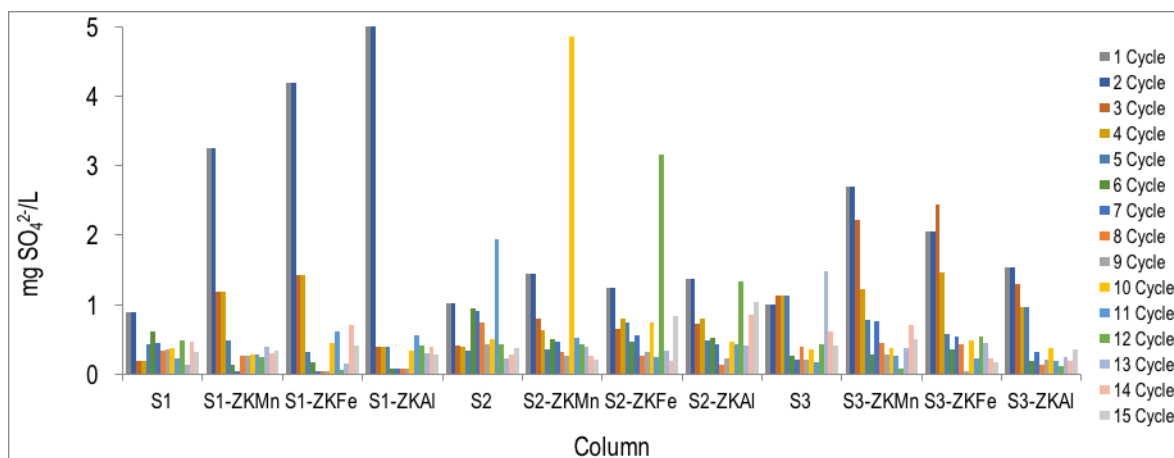
2 In this study, the NO₃⁻ concentration in the solution was lower than the NH₄⁺ concentration; this is a
3 consequence of the higher sorption selectivity for NH₄⁺ of the impregnated clinoptilolite during the
4 loading stage, as revealed in Table 4. In general, low values of NO₃⁻ were measured as the sorption
5 capacity was very limited due to the low selectivity of HMO for nitrate in the presence of PO₄³⁻. NO₃⁻ is
6 an important inorganic form of N, which is commonly up taken by plants due to its good mobility
7 (Rinklebe et al. 2016). The highest release of NO₃⁻ was observed in soil solution S2 at pH 9.2
8 followed by S1 at pH 8.2, and it was almost negligible in S3 at pH 6.3. This result is in accordance
9 with previous reports on the increase of NO₃⁻ release in soils solutions with the increase in soil pH
10 (Escydey et al., 2015). Similarly, from a chabazite bearing zeolite enriched in NH₄⁺ from swine
11 manure, it was reported that a small amount of NO₃⁻ in the column was released into solution, which
12 was attributed to its low sorption selectivity during the loading stage with manure (Colombani et al.,
13 2015).



14 Figure 5. Amount of NO₃⁻ released in solution from non-amended and amended soil columns through
15 15 continuous cycles.
16

17
18 Anions that are required in lower amounts due to their fertilizing properties, such as SO₄²⁻ exhibited a
19 minor leaching into the solutions, as shown in Figure 6, which has been attributed to their lower
20 sorption by HFO. The highest SO₄²⁻ content was found in the first cycle of study suggesting that it was
21 released almost completely in the first cycle. The SO₄²⁻ revealed the highest release in soil S1 cycle 1
22 compared with soils solutions S2 and S3, which showed a gradual release. The SO₄²⁻ retention in
23 soils S2 and S3 could be explained in terms of the electrostatic factors and inner sphere complexes,

1 but the faster release in S1 may have occurred due to the effects of dissolved organic matter, which
2 might have reduced the SO_4^{2-} retention (Escudey et al., 2015).



3
4 Figure 6. Amount of SO_4^{2-} released into solution from non-amended and amended soil columns
5 through 15 continuous cycles.

6

7 Therefore, the N-P-K charged impregnated clinoptilolites used for soil amendment could be a slow
8 releaser of NO_3^- and may be an effective system for avoiding NO_3^- leaching and denitrification, which
9 are critical factors that determine the N bioavailability to plants and impact the environmental quality
10 due to eutrophication. Additionally, these amendment materials could be an alternative way to
11 provide the relatively low concentration of SO_4^{2-} that is needed by plants and to overcome S
12 deficiencies in soils. This may be especially useful because S deficiencies decrease the crop yield
13 and, in certain instances, reduce the crop nutritional value and quality (Huang et al., 2012).

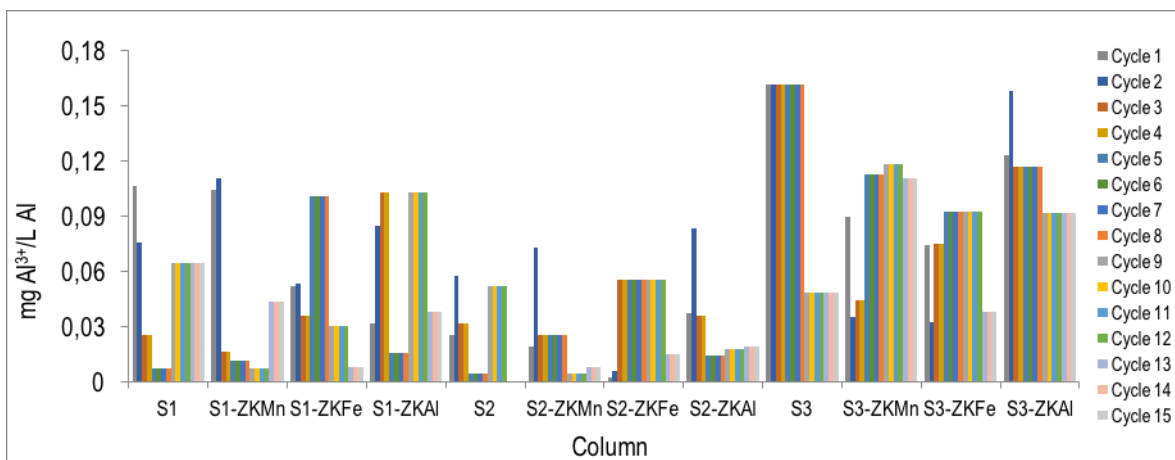
14

15 **3.3.4 Release of other micronutrients and trace pollutants from zeolite amended soils**

16 Regarding the presence of metal transition ions including the presence of those used in the
17 impregnation of the clinoptilolite, very low contents of Fe, Al and Mn were observed in all solutions,
18 as shown in Figure 7. In particular, low amounts of Al were released from the three soils evaluated
19 (e.g. below 0.18 mg/L). Al is considered a serious problem because it inhibits root growth at small
20 concentrations, and it is a primary factor that limits plant growth via the root apex, which reduces the
21 yields and crop quality, especially in acidic soils (Zheng, 2010). In addition, Fe is another important
22 micronutrient that was released from the three soils; values of almost 1 mgFe/L were reached by the
23 soil that had the highest content of organic matter (i.e., S1). That result is in accordance with previous
24 reports regarding the low solubility of Fe oxides in soils, which is often responsible for the deficiency

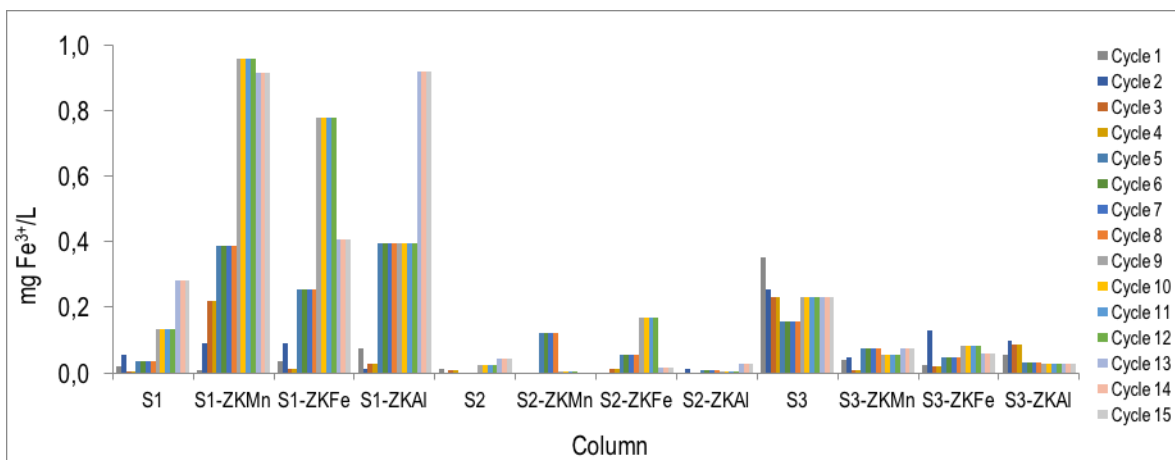
1 of Fe in plants; however, Fe availability may be increased by the effects of organic matter in soils
 2 (Hansen, 2006). Mn an essential micronutrient that is involved in several metabolic processes of
 3 plants, was released mainly by S1 and S3. This behaviour also seems to be related to the organic
 4 matter content of those soils, which would promote the dissolution of Mn oxides. However, in excess,
 5 Mn is harmful due to its toxicity, which results in a reduction of biomass and photosynthesis that
 6 commonly affects plant tops (Millaleo et al., 2010).
 7 Finally, the application of HMO of Al, Fe and Mn forms impregnated on the clinoptilolites as soil
 8 amendment materials have a clear advantage because they had very low solubility values under the
 9 expected pH conditions of the leaching solution, which were typically between 6.5 and 9. Therefore,
 10 they do not contribute to the accumulation of both Al and Mn in soils, considering their toxicity and
 11 danger at higher contents.

12 a)



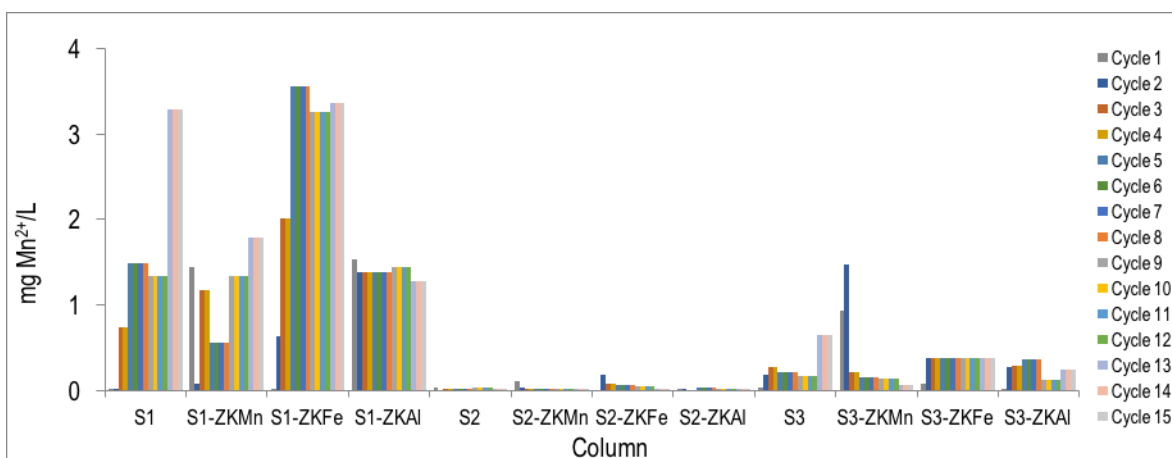
13

14 b)



15

1 c)

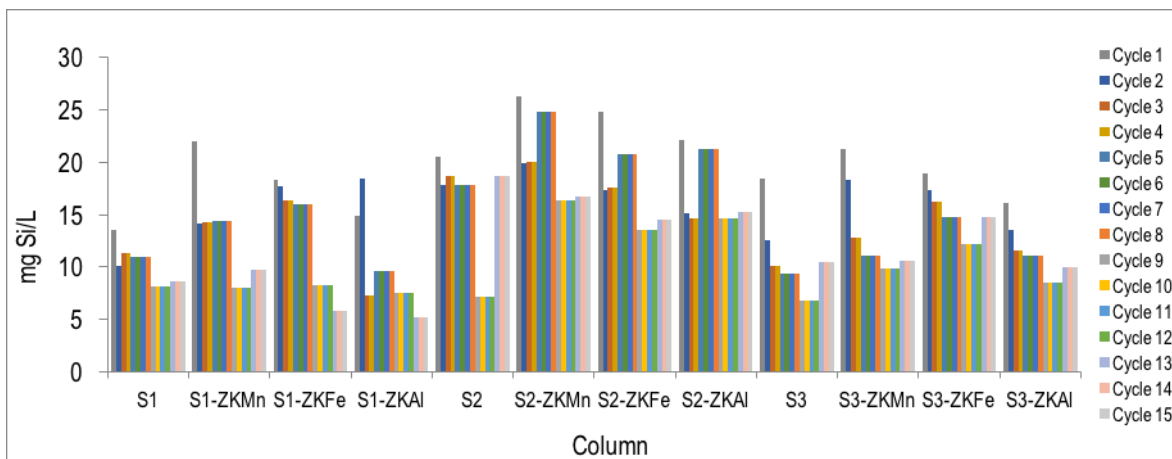


2

3 Figure 7. Amount of Al (a), Fe (b) and Mn (c) released in solution from non-amended and amended
4 soil columns through 15 continuous cycles.

5

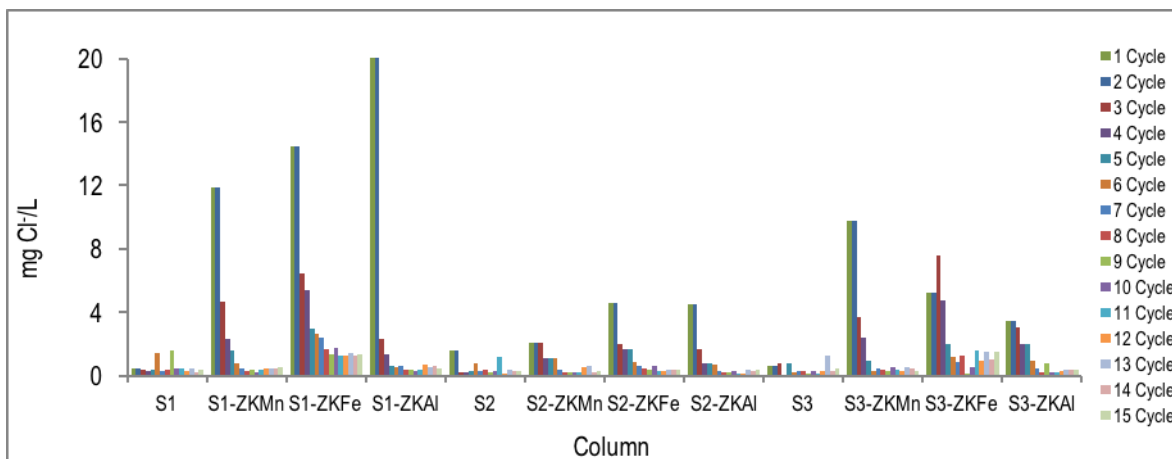
6 An important release of Si was found in solutions from the soil loaded columns, as shown in Figure 8.
7 The values of Si measured on both non-amended and amended soils solutions follow a similar trend.
8 The high release of Si could be associated with the dissolution of clay minerals present in the soils,
9 as described by equations 2 and 7, and with the formation of H_4SiO_4 ($SiO_2(s)$), which was found to be
10 higher in the soil with the higher pH values (e.g., S2 with $pH\ 9.2\pm 0.1$). In general, the values of Si in
11 the amended samples were slightly higher than those in the non-amended soils due to the higher
12 consumption of cationic species during the exchange reactions with HMO-impregnated clinoptilolites,
13 as shown in reactions 2 and 5, and due to the higher dissolution of clay minerals. However, the
14 contribution of the dissolution of clinoptilolite cannot be disregarded. Non reported values on the
15 dissolution of natural zeolites have been found; however, a previous study demonstrated that in a
16 clinoptilolite, the Si dissolution rates increased by increasing pH (e.g., S1 and S2 with $pH\ 8.5\pm 0.1$
17 and 9.2 ± 0.1 , respectively) (Cotton, 2008). Because Si release is characteristic of soil weathering, the
18 amendment materials used in this study could increase the soil silicon bioavailability. This Si
19 enhancement represents an advantage for increasing yields and providing crop resistance to
20 diseases and insect pests (Huang et al., 2012).



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Figure 8. Amount of Si released in solution from non-amended and amended soil columns through 15 continuous cycles.

The leaching values also showed the release of Cl^- ions from the amended samples, with higher values in the first leaching cycles and then decreasing exponentially to values below $1 \text{ mgCl}^-/\text{L}$ (Figure 9). The initial higher values were associated with water occluded on the clinoptilolite structure after being in contact with treated effluent or Cl^- complexed with the HMO impregnated onto the clinoptilolite samples. It should be mentioned that the treated effluent contained an initial Cl^- concentration of up to 600 mg/L , as the Barcelona Metropolitan Area has high contents of Cl^- in the water that is treated and finally distributed for human consumption (up to $250\text{-}300 \text{ mg Cl}^-/\text{L}$). This increase is mainly due to contributions from human food and the intrusion of seawater into the sewer system. In addition, it should be noted that speciation studies have indicated that chlorine occurs predominantly as Cl^- in soils and that its transport is determined by water flows. Thus, the low contents of Cl^- that are released from the soils amended with charged impregnated clinoptilolite make them appear to be efficient fertilization systems. Therefore, at the same time this essential micronutrient could be supplied for plant uptake, thus avoiding the deficiency symptoms observed in the growth rate of many plants, and it could limit the Cl^- accumulation and toxicity in the plants (White and Broadley, 2001).



1
2 Figure 9. Amount of Cl⁻ released in solution from non-amended and amended soil columns through
3 15 continuous cycles.

4
5 Finally, the aqueous solution from soil columns also showed trace levels (at the µg/L level) of some
6 elements such as alkali and alkali-earth elements (Li, Rb, Sr and Ba), non-metal ions (B, Sb, Se and
7 As) and transition metals (Ti, V, Cr, Co, Ni, Cu, Zn, Mo). The relatively low amounts of these
8 elements leached out from the soil columns represent an advantage for fertilizing applications due to
9 their low toxicity to the growth of the plants and in some cases, they are even required as
10 micronutrients. Be, Hg, Cd or Pb were also found in the soil column solutions in negligible amounts
11 (below µg/L), but such elements are known to be of potential toxicological concern for both plants
12 and humans (Supplementary information Figure S3). However, it should be noted that some of these
13 micronutrients are essential for healthy plant growth and are conventionally added to soils in small
14 proportions. Therefore, the charged impregnated clinoptilolites used in this study for soil amendment
15 is an interesting system for fertilizing that provides an opportunity to avoid the accumulation of heavy
16 metals in soils. Additionally, it could mitigate other problems such as the bioaccumulation and
17 biomagnification in the food chain by other potentially toxic elements in soils (e.g., Be, Hg, Cd or Pb)
18 that decrease crop yields in addition to the environmental risks that they present for superficial and
19 groundwater contamination (Wuana and Okieimen, 2001).

20

21 4. Conclusions

22 Three impregnated clinoptilolite forms ZKAl, ZKFe and ZKMn were used for the simultaneous
23 removal of NH₄⁺ and PO₄³⁻ from treated waste water effluent. The chemical sorption of NH₄⁺ and
24 PO₄³⁻ occurred via ion exchange, surface complexation and chemical precipitation. The sorption of

1 toxic elements by the three impregnated clinoptilolites was observed to be negligible, thus confirming
2 their high selectivity towards NH_4^+ and PO_4^{3-} . The NPK charged impregnated clinoptilolites were
3 further used for the amendment of three unfertile soil samples, and the release of nutrients was
4 evaluated in continuous cycles of natural weathering simulation conditions. The release of nutrients
5 and other elements was found to be a function of the soil properties such as, pH, mineralogical
6 composition and organic matter content. A certain amount of other fertilizing ions (NO_3^- and SO_4^{2-})
7 was also detected in the leaching columns solutions from the amended soils. Both species that were
8 originally present in the treated waste waters could have undergone complexation with HMO
9 impregnated on the clinoptilolites. Moreover, the charged impregnated clinoptilolites released
10 negligible contents of Al, Fe, Mn and other toxic elements, thus demonstrating their safety for
11 agricultural applications.

12 The use of NH_4^+ - PO_4^{3-} - K^+ charged impregnated clinoptilolite systems in agriculture seems to be a
13 promising method to reduce N leaching in the hydrological system. Amendments of soils with doses
14 on the order of kg/m^2 of N,P,K-loaded clinoptilolites would create a reservoir of exchangeable N, P
15 and K, thus allowing a reduction in the use of added fertilizers and contributing to further decreasing
16 the polluting potential of the cultivation, especially of those crops that have a high N demand. Long
17 term field results are still needed validate and quantify the efficiency of this innovative technique to
18 foster a more environmentally friendly and large scale agricultural management.

19

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31

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