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Effect of zeolite application on potassium release in sandy soils amended with municipal compost

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ABSTRACT

The use of compost in enhancing organic carbon content and aggregation in soil has been widely studied in the last decades. Recently, compost is used in new environmental applications for the remediation of both contaminated groundwater and soil. However, compost addition increases by 10 orders of magnitude the soil electrical conductivity and the nutrient content such as potassium. Subsequently, nutrient leaching in groundwater may increase water salinity. The present study investigates the effect of zeolite application on potassium release in sandy soils amended with municipal compost. Kinetic experiments show that zeolite addition in soil-compost mixtures have no effect on potassium desorption rate while it results in an 18-fold increase in bio-available potassium. Column tests show that zeolite application results up to six times decrease in total potassium leaching. Experimental results show high potassium affinity for the mixture soil-compost-zeolite in $pH > 7$, which is of paramount importance, considering that soils in southern Europe (Italy, Spain, south France, Albania and Greece) exhibit slightly alkaline pH in most cases. The findings of this study may be also used to predict the potential of groundwater contamination in agricultural areas as well as during the implementation of preventive measures.

Keywords: Potassium; Zeolite; Compost; Adsorption; Sandy soil

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1. Introduction

The annual organic municipal waste production in Europe is stable, the last years at around 60 thousand tons, while compost production has increased from 31 thousand tons in 2007 to 35 thousand tons in 2012 [1]. Based on the future needs to preserve and recycle organic material and to alternatively use it as soil amendment to enhance soil quality [2–6], we expect in the near future an increase in compost production and application on soils. This predicted increase will be higher considering the application of biosolids for remediation of contaminated groundwater and removal of nutrients and heavy metals [7,8]. Municipal compost was up to 90% efficient in absorbing BTEX in groundwater [9]. In addition, high heavy metal stabilization was observed after the application of food waste in soil [10]. Bioprecipitation of heavy metals include the injection of compost in aquifers or the use of compost in permeable barriers for the creation of

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reductive conditions for sulfide precipitation and microbial enhancement [11]. However, the major concern in the use of natural residues in agriculture and/or in environmental applications is the release of excess nutrients in soil solution and subsequently in groundwater. This is particularly significant in sandy soils and sandy aquifers, which cover large parts of the developed world in transition climatic zones [12–16].

Grey and Henry [17] showed clearly the high capability of compost to release potassium, with a net loss of potassium after leaching an average of 63%. The major nutrients release from municipal compost through leaching in terms of nitrogen and potassium is comparable to this of commercial fertilizers [18]. Sharif and Renella [19] have also stressed the risks related to salinity and heavy metal release after municipal compost use in environmental and agricultural applications. Courtney and Mullen [20] showed an approximate increase in 38% in exchangeable potassium in silty sand soil amended with compost. The soil used in that study had a cation exchange capacity (CEC) of 15.9 cmol kg^{-1}, high enough to hold K firmly, which otherwise would have leached out. Bhattacharyya et al. [21] found that 42% of potassium (1,683 mg $kg^{-1)}$ was released from compost, in water exchangeable form. Mbarki et al. [22] found that the N, P, and K deficit on alfalfa roots in sandy soil (poor in adsorption sites) was 79, 46, and 77%, respectively, compared to clayey soil, after compost application in a dose of 120 t/ha. Moreover, nutrients leaching after compost application in soil can be enhanced as a result of increased application rates aiming to increase the uptake of nutrients like P or N in levels suitable for plant growth [23]. Thus, considering the increasing interest in the use of compost in environmental and agricultural applications, the properties of other compatible with compost materials need to be tested. Zeolite is a potential soil additive that has been mainly proposed for the elimination of heavy metal leaching [24]. It has also been demonstrated that in case of olive mill waste application on soil, the addition of clinoptilolite has significantly reduced the K^+, NO_3^-, Cl^-, and SO_4^{2-} release [25]. It is believed that the use of zeolite in addition to municipal compost will decrease the leaching rate of nutrients in groundwater.

The present study investigates the potassium release in mixtures of compost with zeolite and compost with zeolite and soil. No pretreatment, such as homoionic preparation to promote its use in a commercial form, were done to zeolite. Additionally, the use of K^+ zeolite takes into account the worst case scenario, since K^+ already exists in zeolite. Batch experiments were conducted for the study of potassium leaching after the addition of zeolite. The potassium adsorption/desorption on the different reactive surfaces after zeolite addition was modeled for different pH values. Column experiments were also conducted for investigating potassium leaching with simulated rain using two forms of zeolite, recoverable (zeolite stick), and not recoverable (blended with soil).

2. Methodology

2.1. Sample preparation and characterization

Three mixed samples of soil/compost (SC), soil/compost/zeolite (SCZ), and zeolite/compost (ZC) were prepared. The mixtures were composed of a sandy soil sample (S) from a fluvial basin in Crete, compost (C) from the Chania municipal wastewater treatment plant, and zeolite (Z) from the Milos island quarries of the S&B Industrial Mineral company. The soil has been characterized in earlier studies as fluvisol with sandy loam texture [26]. All samples were sieved below 2 mm and dried at 40˚C before use. The compost/soil application ratio used in the present study (SC mixture) was 200 t/ha of dry weight (90.6% w/w soil and 9.4% w/w compost). The rates of compost application considered in the present study were within the ranges examined regarding compost application in recent soil remediation studies in soils with low organic content [27–29]. The SCZ sample was produced by mixing SC with 30% w/w zeolite according to one of the highest ratio appeared in literature [25,30–32], while the ZC sample contained 90.6% w/w zeolite and 9.4% w/w compost. The 30% w/w ratio of zeolite to SC sample was selected for enhancing and thus assessing the effect of zeolite addition. Since the zeolite was not homo-ionized, a lower adsorption capacity was expected and that was a critical factor for selecting a high dose of zeolite in order to enhance the zeolite adsorption effect. Finally, the ZC sample was prepared specifically to investigate the direct interaction of zeolite with compost and compare it with the SC sample. Thus, the ZC is by no means recommended as a treatment ratio.

Bulk chemical analysis was performed on the soil fraction <2 mm by X-ray fluorescence spectroscopy using the spectrometer S2 Ranger by Bruker. Minerals were determined with the D8 Advance X-ray diffractometer (Bruker). The data obtained at 2θ range from 4˚ to 70˚ with a step size of 0.019˚ (Anode: Cu 1.54 Å, 35 kV, 35 mA). The qualitative and quantitative evaluation of the data was done by Diffrac Plus and TOPAS software, respectively, from Socabim. The amorphous material was determined using corundum as an internal standard. pH and electrical conductivity (EC) were determined with a pH/conductivity meter (WTW, 340i) in the supernatant of soil to deionized water mixture 1:2. Organic content was determined according to Gelman et al. [33]. CEC was calculated using the ammonium acetate method by adjusting pH at 7 [34]. Bioavailable K^+ was determined with ammonium acetate extraction for 1 h [35,36].

2.2. Samples characterization

The chemical and physical characteristics of both raw and mixture sample are shown in Table 1. The soil sample has neutral pH, low organic content (1.3%), and EC (92 μS cm^{-1}). CEC is very low (1.9 cmol kg^{-1}) due to the absence of clays (sandy loam texture). The CEC of the zeolite is high (188 cmol kg^{-1}) and close to the values reported (130–167 cmol kg^{-1}) by others [24,37]. Moreover, compost has relatively high CEC (28 cmol kg^{-1}) also within the range reported in the literature (ca 30–130 cmol kg^{-1}) [8,38]. The EC of the mixtures SC, SCZ, and ZC and of the C sample is 10 to 200 orders of magnitude higher compared to those of soil and zeolite. In all mixtures, the potassium content is higher than that of natural soil (S). Compost exhibits the higher calcium content that is related with the calcite addition during the maturity process. The addition of compost in the samples SC, SCZ, and ZC increases the EC and the potassium content in soil.

Mineralogical analysis is presented in Table 2. The zeolite consists of 86% clinoptilolite. The quantitative analysis reveals the presence of other minerals such as orthoclase and muscovite. The compost mineralogical analysis shows high calcite content related to the compost maturity process as it has been mentioned above. The amorphous material present in the compost consists mainly of organic matter, while in the zeolite of amorphous glass (Table 2). The soil high quartz content (52%) is attributed to the sandy texture of the fluvial deposits, while other minerals are either authigenic such as phillipsite, calcite, and dolomite or erosion products such as paragonite and muscovite.

2.3. Kinetic K^+ desorption experiments

The aim of these experiments was to assess the kinetics of K^+ release from the soil and the samples. Thus, K^+ desorption experiments were conducted for all samples at a solid to solution ratio of 1/20 at different time periods of 1 h, 3 h, 6 h, 9 h, 24 h, 3 d, 9 d, 15 d, and 30 d. The solution used in all experiments was synthetic rain of specific ionic strength (5.6×10^{-4} mole L^{-1}) and pH (5.39), according to the chemical analysis of rain from Samara et al. [39]. The salts that were used for the preparation of synthetic rain comprised $CaSO_4.2H_2O$, KCl, $MgCl_2.6H_2O$, and $NaNO_3$, while HCl and H_2SO_4 (0.1 M) were used for pH adjustment. The added K^+ through the synthetic rain was considered negligible (1.3×10^{-6} cmole L^{-1}).

After soil/liquid separation by filtration using a 0.45 μm filter, the filtrates were analyzed for potassium. The residual solids from the kinetic desorption experiments were dried, and extraction with ammonium acetate was applied for the determination of bioavailable K^+. All experiments were conducted in duplicate at 25˚C. Ammonium acetate extraction in the kinetic experiment residuals was named Am1 experiment, while the bioavailable extraction in the unprocessed fresh samples was named Am2.

All the duplicate trials were tested with *F*-test and *T*-test for having equal variance and identical mean values, while the Pearson correlation coefficient was calculated. The statistical tests were performed with the Statistical Analysis Tool of the Excel Microsoft Software.

2.4. pH-edge experiments and modeling

The pH experiments were conducted at pH 4, 5, 6, and 9 under continuous agitation. The pH was monitored and adjusted twice a day, for a seven day period. The solid to solution ratio was the same as in the kinetic experiments. After the end of the experiment, the solution was separated by filtration using a 0.45 μm filter, and the filtrates were analyzed for potassium content. The results were modeled for adsorption/desorption regarding the different samples with the use of MINEQL+ [40]. The triple layer model was applied to describe surface speciation, while the ROH (concentration of host sites in the organic matter) and the SOH (concentration of host sites in the oxides) for the compost were calculated from the determined organic matter content (Table 1) and from the sites content of Fe and Mn oxides, which were calculated from the adsorption capacity presented in other studies [41–43]. The Fe and Mn oxides sites varied (50–600 mg kg^{-1}); however, for the modeling trials we used the highest values of Fe and Mn oxides content as to investigate the K leaching assuming the highest oxide content. Model trials showed that the oxide concentration in compost from low to high values was not capable to severely influence the amount of K release. The ROH and SOH host sites in the soil were estimated from its organic matter content (Table 1) and from the content of Fe and Mn oxides

Table 1
Chemical and physical parameters of the soil (S), zeolite (Z), compost (C), and mixtures (SC, SCZ, and ZC)

Sample	Na_2O (%)	MgO (%)	K_2O (%)	CaO (%)	TiO_2 (%)	MnO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	P_2O_5 (%)	LOI (%)	pH	EC, µS cm^{-1}	[a]OC %	CEC cmol kg^{-1}
S	0.9	1.7	1.5	2.7	0.8	0.1	4.7	10.5	61.5	0.2	7.1	7.25	92	1.3	1.9
Z	2.1	1.5	3.4	2.7	0.1	0.1	0.9	10.1	73.3	0.1	10.1	8.26	184	n.d	188
C	4.3	0.1	2.7	20.5	0.4	<0.01	2.5	2.7	14.0	1.1	52.9	7.62	21,000	20.5	28
SC	1.0	1.5	1.8	2.7	0.7	0.1	4.7	11.3	60.3	0.4	10.2	6.86	1900	2.8	5.9
SCZ	1.7	1.5	2.3	2.8	0.6	0.1	3.8	10.9	65.1	0.3	11.8	6.80	2,200	1.9	55
CZ	2.5	1.3	3.3	3.8	0.1	0.1	0.9	9.0	70.2	0.2	14.4	7.64	2,400	1.6	140

Note: n.d: not determined.
[a]OC: organic carbon.

(approximately 8,000 mg kg^{-1}) taken from Moraetis et al. [26]. The soil/solution ratio (g L^{-1}) was set to 50 and the specific surface for the different mixtures was set for zeolite, compost and soil to 20, 16, and 2.7 $m^2\ g^{-1}$, respectively [44–46]. Finally the "Zeo" component added in the model to include zeolite which adsorbs potassium.

The K^+ reactions assumed in the present study were the K^+ adsorption/desorption on organic matter (ROH-K) and oxides (SOH-K) for all samples and the K^+ adsorption/desorption on zeolite (Zeo-K) for the SCZ and ZC mixtures. As initial K^+ concentration in the modeling trials the maximum K^+ concentration attained in the pH experiments at pH 4 was used.

Modeling was first applied for the compost sample with the aim to calculate the equilibrium constant (logK) for the SOH-K and ROH-K (Table 3) describing the sorption sites in oxides (SOH) and organic matter (ROH). Then, these equilibrium constants were used for the calculation of the equilibrium constant for the K^+ adsorption/desorption on zeolite (Zeo-K). The shaded values in Table 3 are the calculated constants.

2.5. Column desorption experiments

Three plexiglas columns of internal diameter 3 cm and length of 15 cm containing 175 g of samples were used in column studies. The first two columns contained the SC and the SCZ samples named SC and

Table 2
Mineralogical analysis of the raw materials used for the preparation of the mixtures (%)

Mineral percentage	Compost	Zeolite	Soil
Amorphous	20.3	1.5	
Calcite	50.1		2.1
Clinoptilolite		86	
Chlorite			5.0
Dolomite	6.2		3.3
Feldspars[a]		6.1	5.0
Goethite	0.01		
Hydroxylapatite	0.8		
Illite			3.4
Kaolinite	3.9		8.0
Magnetite	0.9		
Muscovite		6.4	13.2
Paragonite			2.1
Phillipsite			5.6
Quartz	15.7		52.4

[a]Feldspar for zeolite is orthoclase, whereas for soil is albite.

Table 3
LogK for the species in the pH-edge modeling for the compost sample (C), SC mixture, SCZ mixture, and the ZC mixture. Shaded values are calculated. Components concentration (in cmol L^{-1})

	C	SC	SCZ	ZC
Species	log *K*			
Zeo-K	–	–	−4.5	−4.5
ROH-K	1.8	1.5	1.5	1.5
SOH-K	3.0	3.0	3.0	3.0
SOH-OH	−10.8	−10.8	−10.8	−10.8
SOH-H	7.29	7.29	7.29	7.29
OHROH	−4.5	−4.5	−4.5	−4.5
OH^-	−13.997	−13.997	−13.997	−13.997
$CaOH^+$	−12.697	−12.697	−12.697	−12.697
$MgOH^+$	−11.397	−11.397	−11.397	−11.397
HSO_4^-	1.99	1.99	1.99	1.99
$CaNO_3^+$	0.5	0.5	0.5	0.5
$CaSO_4$ (aq)	2.36	2.36	2.36	2.36
KSO_4^-	0.85	0.85	0.85	0.85
$MgSO_4$ (aq)	2.26	2.26	2.26	2.26
$NaSO_4^-$	0.73	0.73	0.73	0.73
Components	cmol L^{-1}			
SOH	5.77E–03	3.65E–02	2.58E–02	5.99E–03
ROH	1.79E	3.74E–01	2.48E–01	1.86E–01
Zeo	–	–	3.36E	1.00E–01
Ca	4.06E–02	4.06E–02	4.06E–02	4.06E–02
Cl	4.79E–03	4.79E–03	4.79E–03	4.79E–03
K	1.28E	1.21E–01	7.70E–02	4.28E–01
Mg	8.28E–03	8.28E–03	8.28E–03	8.28E–03
Na	4.78E–03	4.78E–03	4.78E–03	4.78E–03
NO_3	4.78E–03	4.78E–03	4.78E–03	4.78E–03
SO_4	4.06E–02	4.06E–02	4.06E–02	4.06E–02

SCZ1, respectively. The third column (named SCZ2) contained the same proportions of soil to compost and zeolite as in column SCZ1, but zeolite was placed into a fine nylon membrane (aperture diameter 200 μm) to allow soil solution infiltration. The use of nylon membrane also facilitates zeolite recovery and has the benefit of avoiding zeolite-soil mixing. The capability of regeneration would be an asset in agricultural practices as it has also been mentioned by Doula et al. [25] for soils receiving wastes continuously. The column desorption experiment simulated one year rainfall of 495 mm, typical for many coastal Mediterranean areas. Artificial rain was applied in each column for one week to investigate potassium leaching from the zeolite samples and compare the two different techniques of zeolite application to soil (not recoverable and recoverable). The total volume of rain applied over a period of 7 d was 350 mL (50 mL per day). Soils remained wet through the experiment and rain was allowed to infiltrate through gravity. Leachates were collected from the bottom of the column. The total infiltration time was approximately 50 min for the SC and 60 min for the SCZ1 and SCZ2 samples.

2.6. Analytical techniques

Atomic absorption spectroscopy (AAnalyst 100, Perkin Elmer) was used to determine the concentration of potassium in all experiments (kinetic experiments, pH-edge, and bioavailable K^+). The extracted ammonium for the CEC determination was measured with the use of spectrophotometer (HACH 2,800) at 425 nm.

3. Results

3.1. Kinetic desorption experiments

The results of the kinetic desorption experiments are shown in Fig. 1. The maximum desorption of potassium regarding the compost (C) takes place in the first three days (58.2 cmol kg^{-1}), followed by a

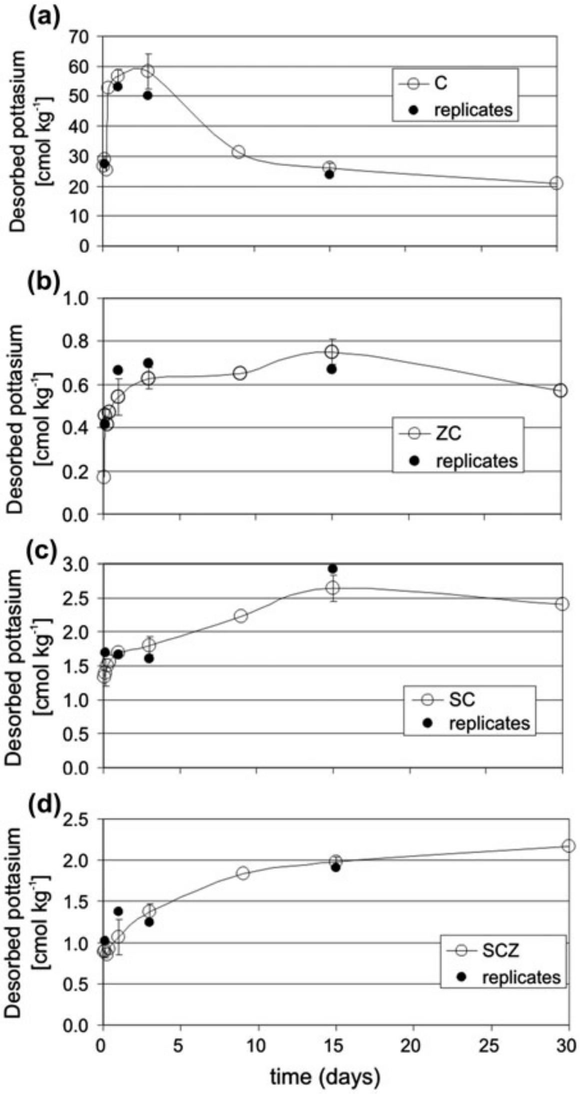

Fig. 1. Potassium release (cmol kg^{-1}) in kinetic experiments using synthetic rain for 30 d regarding (a) the sample C, (b) the mixture ZC, (c) the mixture SC, and (d) the mixture SCZ. Replicates are shown in black circles and standard deviation of the replicates is depicted with error bars.

sharp decrease up to the 13th day. Then equilibrium is gradually reached (Fig. 1(a)). The ZC samples (ZC) showed a gradual increase in potassium release up to the day 15 (0.6 cmol kg^{-1}), which then drops slowly (Fig. 1(b)). The SC samples also show a gradual increase in potassium desorption up to the day 15 (2.6 cmol kg^{-1}), which then slowly reaches equilibrium (Fig. 1(c)). The SCZ samples show a faster desorption rate until the ninth day and a much slower one thereafter, reaching 2.17 cmol kg^{-1} after 30 days (Fig. 1(d)). The results reproducibility was tested with *F*-test and *T*-test and duplicates showed equal variance and means, while the Pearson correlation varied between 80 and 99%.

The desorption rate of each sample was calculated using first-order kinetics $C = C_0e^{-krt}$, where C_0 refers to the initial potassium concentration, C is the potassium concentration at time t, and k_r is the rate constant. The calculated k_r values are 1.8, 0.53, 5.7, and 0.46 for C, SC, ZC, and SCZ, respectively.

3.2. Bio-available K^+

Fig. 2(a)–(d) show the bioavailable potassium in Am1 experiment, while Fig. (2(e)) shows the bioavailable potassium from the fresh mixtures and samples, which have not been subjected to the kinetic test (Am2 experiment). It is obvious that the addition of 30% w/w zeolite (SCZ) results in almost 18-fold increase in bioavailable potassium (average value in the ninth day 15.4 cmol kg^{-1}) compared to the SC sample (average value in the ninth day 0.88 cmol kg^{-1}) in the Am1 experiment (Fig. 2(c) and (d)). The same trend was observed in the Am2 experiment (Fig. 2(e)). The ZC samples show higher bioavailable potassium (average value after the ninth day 46.4 cmol kg^{-1}) compared to the C sample (average value in the ninth day 8.1 cmol kg^{-1}) in the Am1 experiment (Fig. 2(a) and (b)). Similarly, in the Am2 experiment the C sample shows less bioavailable K^+ (26 cmol kg^{-1}) compared to the ZC sample (39.2 cmol kg^{-1}). The lower K^+ desorption for the ZC samples, in the Am2 experiment (39.2 cmol kg^{-1}), compared to the Am1 experiment (46.4 cmol kg^{-1}), may be the result of inefficient homogenization and/or inherent heterogeneity of the compost within the ninth day ZC sample (Fig. 2(b)). Finally, comparing Am1 and Am2 we are able to clearly demonstrate that in samples where is no zeolite addition (SC, C), the bioavailable potassium is less in Am1 test compare to Am2 which shows that potassium has already released through the kinetic test with rain solution.

Taking into account the maximum release of K^+ in the Am2 experiment for the C sample and normalizing it according to the ZC compost content, we are able to calculate the maximum theoretical bioavailable potassium desorption from the compost in the ZC samples, which is approximately 2.4 cmol kg^{-1}. Thus, from the total 39.2 cmol kg^{-1} of bioavailable potassium released from the ZC sample in the Am2 experiment, 2.4 cmol kg^{-1} is attributed to the compost, while the rest derived from zeolite. We infer that the extra K^+ is naturally hosted in zeolite and accounts for 36.8 cmol kg^{-1}, which is approximately the 20% of the zeolite CEC. Thus, in the case of samples SCZ,

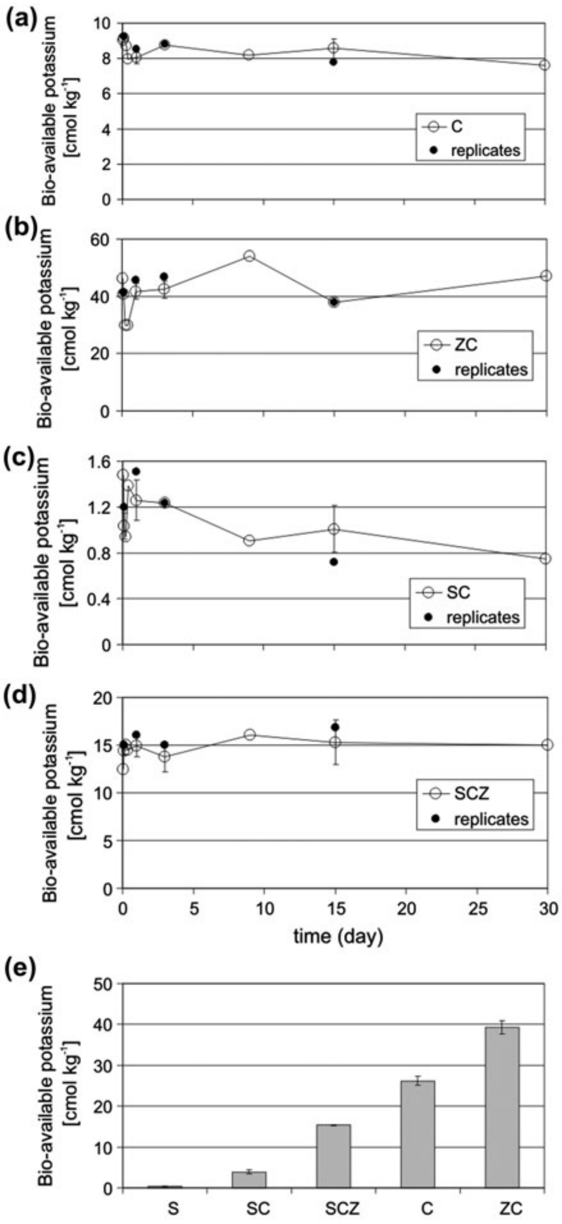

Fig. 2. Bioavailable potassium (cmol kg^{-1}) in the kinetic experiment (Am1) residues regarding (a) the sample C, (b) the mixture ZC, (c) the mixture SC, and (d) the mixture SCZ. Replicates are shown in black circles. (e) Bioavailable potassium (cmol kg^{-1}) in the fresh C sample, and ZC, SC, SCZ mixtures (Am2). Standard deviation of the replicates is depicted with error bars.

15.4 cmol kg^{-1} in Am2 experiment derived from (a) the naturally hosted potassium in zeolite (approximately 12.2 cmol kg^{-1}) and (b) from the K^+ desorbed from the compost and the soil (approximately 3 cmol kg^{-1}). By considering the same calculations for the Am1 experiment, the SCZ zeolite potassium content was found to be 15.1 cmol kg^{-1}. Comparing the SCZ zeolite potassium content in the Am1 and Am2 experiments, we presume that 2.9 cmol kg^{-1} can be attributed to the potassium absorbed in zeolite during the kinetic experiment.

The results reproducibility for the bioavailable potassium experiment was tested with *F*-test and *T*-test and duplicates show equal variance and mean, while the Pearson correlation of the duplicates varied between 70 and 98%.

3.3. pH-edge experiments and modeling

The desorption rate of K^+ as a function of pH is shown in Fig. 3. Black circles denote experimental, while open circles modeling results. The root mean square error is depicted with error bars, while the fitting is considered satisfactory. The higher desorption of potassium was recorded at low pH values (4 and 5), while at higher pH values desorption was reduced. The samples containing zeolite (SCZ, ZC) show minimum potassium desorption (Fig. 3(b) and (d)) in high pH values, while the samples without zeolite (C, SC) show constant desorption of potassium (Fig. 3(a) and (c)).

The calculated logK for zeolite reaction with K^+ was initially set by considering the values appeared in literature, ranging from 2.54 to 2.56 [37]. However, the derived logK for the K^+ adsorption/desorption on zeolite is much lower (~4.5) compared to the one used in the initial trials.

The K^+ adsorption over different surfaces is shown in Fig. 4. Potassium shows high preference to zeolite in the SCZ and ZC sample for higher pH values (Fig. 4(a)). On the other hand, the decrease in K^+ adsorption in high pH values in the organic matter (ROH-K) and oxides sites (SOH) (Fig. 4(b) and (c)) shows that those host sites contribute K^+ on zeolite.

3.4 Column desorption experiments

The results of column experiments are shown in Fig. 5. The SCZ1 samples exhibits lower potassium desorption compared to the SC samples for the entire period subjected to simulated rain (no leachates were produced in the first day), while the SCZ2 samples exhibits higher potassium desorption compared to the SCZ1, but lower potassium desorption compared to SC for the entire experimental period except for day 1 (Fig. 5(a)). The SCZ1 and SCZ2 samples show lower total potassium release (reduction of 83 and 42%, respectively) compared to the SC sample (Fig. 5(b)). After the fourth day of rain application, potassium

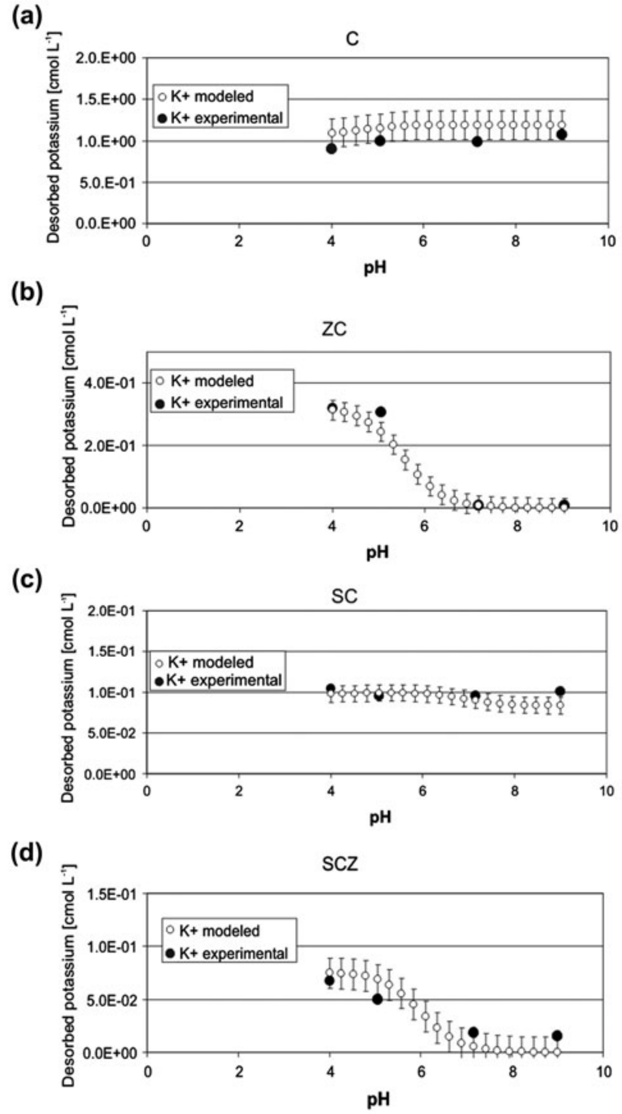

Fig. 3. Experimental (black dots) and modeled (white dots) potassium desorption in pH-edge test (cmol L^{-1}) for (a) the sample C, (b) the mixture ZC, (c) the mixture SC, and (d) the mixture SCZ. The root mean square error (RMSE) was calculated and depicted as error bars.

desorption in the SCZ1 and SCZ2 columns seem to be stabilized, while in the SC column it decreases continuously.

4. Discussion

Zeolite addition does not significantly affect K desorption rate in the SCZ compared to that of SC, while it increases the desorption rate in the ZC sample compared to that of the C and SC samples. These comparisons may infer the misleading conclusion that zeolite

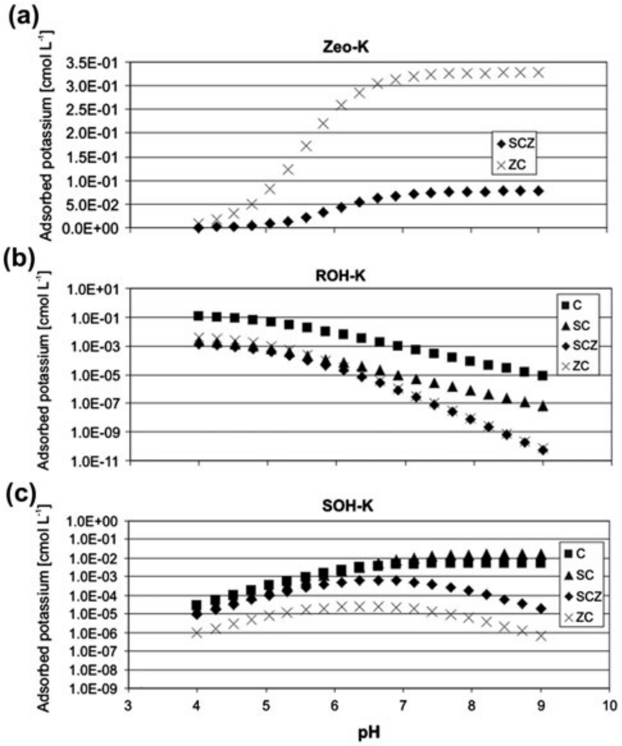

Fig. 4. Adsorbed potassium (cmol L^{-1}) on different surfaces such as (a) zeolite (Zeo-K), (b) organic matter (ROH-K), and (c) oxides (SOH-K) over the different samples (C) and mixtures (SC, SCZ and ZC).

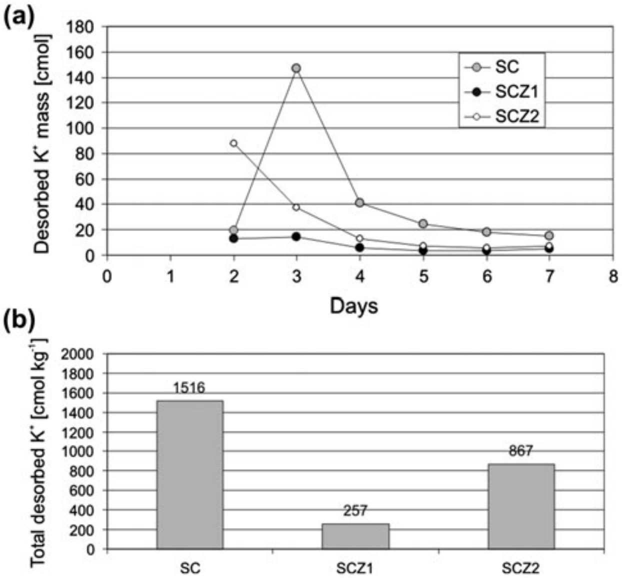

Fig. 5. (a) Potassium desorption (mole) for the columns SC, SCZ1, and SCZ2 for each day of the rain simulation. (b) Total potassium desorption (cmol kg^{-1}) in one year rain simulation (total potassium shown on the columns top).

did not adsorb potassium in the SCZ sample which, was not the case as it is explained below. In the ZC sample, the adsorption rate of potassium is high enough to constantly adsorb potassium from solution. The continuous K^+ adsorption on zeolite (in the ZC sample) creates conditions of low mass effect, which facilitate potassium desorption from compost in the ZC sample. Thus, zeolite increases the desorption rate of potassium in the ZC sample compared to C and SC, while the maximum desorption of potassium is decreased (Fig. 1(b)). The increase in desorption rate is not observed in the SCZ sample because the number of easily accessible sites in the sample (due to the presence of zeolite) was not high enough to influence the kinetic reaction, as it was in the ZC sample (with a higher amount of zeolite). Thus, the presence of zeolite within the compost amended soil does not affect the rate of potassium release and potentially will not cause any rapid release of potassium in groundwater in field applications. In the case of the compost sample, the peculiar decrease in potassium desorption between the third and the ninth day (Fig. 1(a)) has also been observed by Nishanth and Biswas [47]. No specific mechanism was proposed for the decrease in potassium adsorption in the previous study; however, we believe that potassium and anions such as sulfate may create supersaturating conditions and thus potassium precipitation.

The total bioavailable potassium in the Am1 experiment shows that despite the presence of naturally hosted potassium in zeolite, its capacity to adsorb extra potassium is not impeded. The potassium bioavailability in the SC and SCZ kinetic experiment residues (Am1 experiment) shows that, zeolite addition resulted on average in an 18-fold increase in the bio-available potassium, which is mainly potassium in exchangeable form (Fig. 2(c) and (d)). This increase is due to (a) the naturally occurred exchangeable potassium in the zeolite ($12.2\ \mathrm{cmol\ kg^{-1}}$), and (b) the additional potassium adsorbed and “stored” in the zeolite channels ($2.9\ \mathrm{cmol\ kg^{-1}}$). Thus, the ammonium extraction in the kinetic residues (Am1 experiment) reveals the important process of the adsorption of potassium on zeolite, which is not discernible through the kinetic experiment in the SCZ sample. The increase in bioavailable potassium in the SCZ sample is facilitated due to the constant removal and “storage” of potassium in zeolite channels. Thus, the presence of naturally occurred potassium in zeolite prior to its mixing with compost is not a constraint to additionally adsorb potassium leached from the compost. Consequently, the zeolite addition in compost/soil mixtures restrains the most common cation (potassium) release in groundwater after compost application.

The pH-edge experiments show that the addition of zeolite has a significant effect on potassium adsorption for pH values >7 (Fig. 4(a)), related mainly to the H^+ stripping from the exchangeable sites and the subsequent potassium adsorption. It is obvious that the pH increase leads to the following effects (a) potassium release from the compost organic matter, (b) potassium adsorption on oxide (SOH-K) surfaces, and (c) zeolite potassium adsorption (Zeo-K). The content of potassium in the organic matter (ROH-K) is higher in the presence of H^+ rather than of OH^- (Fig. 4(b) and (c)). The release of potassium from the compost is related to the pH influence on the compost functional groups, such as the phenolic compounds which are dissociated at high pH [48]. Similar behavior was noticed in olive mill organic waste application in soil, where potassium was released from functional groups composed of polysaccharides, phenol polymers, and proteins [49]. The pH effect on zeolite adsorption has been described in various studies and the main characteristic is an adsorption increase with pH increase [50,51]. Similarly, in our case potassium adsorption increases in zeolite, revealing higher preference for zeolite (Zeo) than for oxide surfaces (SOH) (Fig. 4(a) and (c)). The previous findings are issues of great importance, since it is well known that arid agricultural areas, and sedimentary aquifers in fluvial environments in Europe, show pH values higher than seven [52]. Finally, the lower equilibrium constant (4.5) for the adsorption of K^+ on zeolite (Table 3) compared to other values appeared in literature [21], is related to the decrease in potassium selectivity. This differentiation is expected in nonhomoionic zeolite samples. For example, other naturally hosted cations in zeolite, such as Ca, would have influenced the exchange reaction and this is probably the case also in our study, since Ca has been described to occupy 40% of the exchangeable sites in the zeolite extracted from the same mining area [53]. Pabalan and Bertetti [54] showed that the Ca-K exchange is less thermodynamically favorable compared to other pair of exchange (e.g. Na-K) thus, the exchange of potassium for Ca rather for other cations would have decreased the equilibrium constant.

The potassium leaching results from the column tests follow the observations noted in the batch experiments. Thus, potassium leaching decreases in SCZ1 after the application of a 495 mm of rain simulating precipitation of one year. The SCZ2 results show that the use of zeolite in sticks limits potassium leaching (1.8-fold) compared to that of the SC, but not as much as in the case of SCZ1 (6-fold) (Fig. 5(b)). This is obviously related with the faster leaching of potassium in the SCZ2, due to preferential flow along the sides of the zeolite sticks. The leachate has less time to react with zeolite and the potassium diffusion through the zeolite stick is low. The higher potassium leaching in the second day in SCZ2 sample is attributed to preferential flow; however, in the following days potassium desorption is lower compared to SC (Fig. 5(a)). Finally, the column tests show that the extent of potassium release in the case of compost application without the use of zeolite in sandy soil and/or a sandy aquifer is larger compared after the addition of zeolite. A rough estimation which can apply in cases of compost application in soil at the same ratio which was used in the present study shows that about 1,152 t of potassium per hectare will be leached out without the zeolite use from the upper 15 cm of the soil profile (considering soil density of 1.3 t/m^3). With the application of zeolite, the potassium release is reduced in about 195 t per hectare (using the result from SCZ1 column). The previous results are significant in the estimation of the potential nutrient release toward groundwater, in semiarid areas in circumference Mediterranean countries.

5. Conclusions

The findings of the present study show that zeolite addition in soil treated with compost eliminates potassium leaching and stores potassium in bioavailable form. The significant conclusions are as follows:

(1) Zeolite addition in compost and compost/soil mixtures provides a significant capability to store potassium in a bioavailable form.
(2) Kinetic tests showed that potassium desorption rate is not changed with the use of zeolite, even the stored potassium in zeolite is increased.
(3) Regardless of the use of zeolite without pretreatment (without converting it to homoionic form), adsorption of potassium was still highly effective.
(4) Surface adsorption modeling shows that the potassium storage capability in bioavailable form would be enhanced in neutral and alkaline soils.

These results are of high significance in the case of compost application in remediation processes such as permeable reactive barriers, compost application in contaminated soils and compost application for soil quality enhancement for areas with sandy sediments. Further studies will reveal the balance between economically sustainable ZC mixing ratios for achieving nutrient retention and salinity reduction.

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