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Enhancing phytoextraction of potentially toxic elements in a polluted floodplain soil using sulfur-impregnated organoclay☆

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ABSTRACT:

Enhancing metals phytoextraction using gentile mobilizing agents might be an appropriate approach to increase the phytoextraction efficiency and to shorten the phytoremediation duration. The effect of sulfur-impregnated organoclay (SIOC) on the redistribution of potentially toxic elements (PTEs) among their geochemical fractions in soils and their plant uptake has not yet been studied. Therefore, our aim is to investigate the role of different SIOC application doses (1%, 3% and 5%) on operationally defined geochemical fractions (soluble + exchangeable; bound to carbonate; manganese oxide; organic matter; sulfide; poorly- and well-crystalline Fe oxide; and residual fraction) of Cd, Cr, Cu, Ni, Pb, and Zn, and their accumulation by pea (*Pisum sativum*) and corn (*Zea mays*) in a greenhouse pot experiment using a polluted floodplain soil. The SIOC caused a significant decrease in soil pH, and an increase in organic carbon and total sulfur content in the soil. The addition of SIOC increased significantly the soluble + exchangeable fraction and bioavailability of the metals. The SIOC leads to a transformation of the residual, organic, and Fe-Mn oxide fractions of Cd, Cu, Ni, and Zn to the soluble + exchangeable fraction. The SIOC addition increased the potential mobile (non-residual) fraction of Cr and Pb. The SIOC increased the sulfide fraction of Cr, Ni, and Zn, while it decreased the same fraction for Cd, Cu, and Pb. The effect of SIOC on the redistribution of metal fractions increased with enhancing application dosages. Pea accumulated more metals than corn with greater accumulation in the roots than shoots. Application of the higher dose of SIOC promoted the metals accumulation by roots and their translocation to shoots of pea and corn. Our results suggest the potential suitability of SIOC for enhancing the phytomanagement of PTEs polluted soils and reducing the environmental risk of these pollutants.

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1. Introduction

Floodplain soils are often polluted with potentially toxic elements (PTEs) because anthropogenic sources usually discharge wastes enriched with PTEs into rivers where these compounds are transported with particulate matter downstream and deposited on the floodplains (Rinklebe et al., 2019). Trace elements are distributed in soils among different geochemical fractions. These fractions are operationally defined and they comprise the soluble + exchangeable fraction, the fraction of metals bound to carbonates, to manganese oxides, to soil organic matter, to sulfide/sulfate, to poorly and well crystalline iron oxides, and the residual (silicate) faction (El-Naggar et al., 2018, 2019). Trace elements such as As, Cd, Cr, Cu, Ni, Pb, and Zn are potentially toxic to plants, animals and humans and may enter the food web, posing risks to the surrounding wildlife in riparian ecosystems and humankind (Antoniadis et al., 2019a,b). Therefore, a remediation of floodplain soils polluted with PTEs is necessary for mitigating their environmental and human health risk. Choosing a cost-effective remediation method, which can be adapted to the given soil physicochemical properties, pollutant levels, as well as to current land use is particularly important for mitigating the pollution risk and the reclamation of polluted sites (Bolan et al., 2014). The term "Green remediation" has been established during the past two decades to maximize the net environmental benefits of a cleanup trial (Wang et al., 2018).

Phytoremediation of PTE contaminated soils is a natural and environmental friendly technology (Antoniadis et al., 2017). Enhancing metals phytoextraction using a mobilizing agent might be an appropriate approach to increase the phytoextraction efficiency and to shorten the phytoremediation duration (Shaheen and Rinklebe, 2015). Sulfur-impregnated organoclay (SIOC) might be a promising mobilizing agent and can be used for enhancing metals phytoextraction in polluted soils.

We hypothesize that the addition of SIOC which is rich in total content of S, Al, Fe, and organic carbon to the PTE polluted soil should decrease the soil pH, which might affect the PTE redistribution among their geochemical fraction (in particular the mobile, oxide, organic, and sulfide fractions) and might therefore increase their mobilization and bioavailability. We assume that the SIOC-induced decrease of soil pH in the treated soil is the key driver for increasing the solubility and phytoextraction of Cd, Cr, Cu, Ni, Pb, and Zn. Soil pH, may also regulate other processes such as the acidic dissolution of Fe-Mn oxides, which can affect the Fe-Mn oxide fractions.

Additionally, increasing total content of sulfur and soil organic carbon may influence the redistribution of the elements among their geochemical fractions, particularly the sulfide and organic fractions, and thus, may increase their potential mobilization. Therefore, to verify our hypotheses, we conducted a pot experiment using a multi-metal polluted floodplain soil treated with SIOC in different doses i.e., 0, 1, 3, and 5% (W/W), and cultivated the untreated and treated soil with pea, followed by corn. The application of SIOC to polluted soils for enhancing the PTEs phytoremediation is not yet reported. Also, the effect of SIOC on the redistribution of PTEs among their geochemical fractions in polluted floodplain soils and subsequent plant uptake has not yet been studied. Therefore, our objectives were: (1) to study the effect of SIOC dosages on the mobilization and the potential redistribution of Cd, Cr, Cu, Ni, Pb, and Zn among their geochemical fractions in the soil; (2) to assess the ability of SIOC for enhancing the phytoextraction of Cd, Cr, Cu, Ni, Pb, and Zn by the roots and their translocation into the shoots of pea and corn, and (3) to evaluate the potential of SIOC in managing the risk of PTEs in polluted floodplain soils.

2. Materials and methods

2.1. Sampling and characterization of the studied soil and organoclay

We collected a composite subsurface sample (26–40 cm depth) of a polluted floodplain soil located at the lower course of the Wupper River (51°4′0.48"N, 6°4′0.48"E) in the western part of Germany. The soil is classified as Eutric Fluvisols according to IUSS-FAO (2006). More details about the sampling site and soil characterization are given in the supporting information (Appendix A) and Shaheen and Rinklebe (2015).

The organoclay MRM was provided by the Colloid Environmental Technologies Company (CETCO), 2870 Forbs Avenue, Hoffman Estates, IL 60192, United States. As indicated the company homepage and the patient of Wang et al. (2008), the organoclay MRM is sulfur impregnated organophilic clay, and it is a proprietary granular adsorption media effective in removing oils, greases other non-aqueous phase liquids and other dissolved high molecular weight/low solubility organics. This Organoclay is specially formulated for use in the following applications; organophilic filtration media, bulk sediment capping and as a stabilization additive. The use of a sulfur-impregnated organoclay provides a PTE removal media having increased reactivity, stability, and PTE removal ability. The PTE removal media described herein is prepared by impregnating an organophilic clay with elemental (free state) sulfur. Alternatively, the clay can be made organophilic by onium ion reaction prior to or simultaneously with impregnating the organoclay with sulfur (Wang et al., 2008). More details about the spectroscopic characterization of organoclay MRM is provided in Wang et al. (2019).

The morphology and the chemical composition of the SIOC and the soil particles were characterized with an environmental scanning electron microscope (ESEM, Quanta 450 FEG, FEI, Hillsboro, OR, USA) with energy dispersive X-ray spectroscopy (EDX, Si-Li detector from EDAX/Ametek, Berwyn, PA, USA). In contrast to classic scanning electron microscopy, water vapor at $p = 1–2600$ Pa is present in the sample chamber of an ESEM (Rinklebe et al., 2016).

2.2. Greenhouse pot experiment

The impact of SIOC on PTEs accumulation by pea (*Pisum sativum*) and corn (*Zea mays*) was investigated in a greenhouse pot experiment between April and August 2017. About 3 kg of air-dried soil (<2 mm) were mixed with 0 (control), 30 (1%), 90 (3%), and 150 g (5%) of the SIOC and placed into plastic pots (diameter 0.25 m, height 0.30 m) in triplicate. A complete randomized block design was composed of four treatments (three treatments of SIOC plus one control) with three replicates each. The pots were irrigated with approximately 1 L deionized water to reach a moisture content of about 60% of the field capacity. Deionized water was used to adjust the moisture to about 60% of field capacity in all pots during the experiment. The SIOC amended soil was incubated at field capacity for 20 days prior to planting. About fifteen seeds of pea were sown directly into each pot in first of May 2017. One week after germination, plants were thinned to leave ten seedlings per pot. During the growing period, the gravimetric water content was kept constant (60%) by weighting the pots daily and adding deionized water. The pots were rotated in the greenhouse, so they were exposed to the same environmental conditions. The peas were maintained for 30 days in the greenhouse. Then, roots and shoots of the plants were harvested using ceramic knife/shear. After harvesting pea, corn was planted in second of June 2017. The procedure for corn was similar to pea. Corn was maintained for 63 days in the greenhouse; then, it was harvested in fifth of August 2017. After harvest, plants of corn were separated into roots and shoots, and thoroughly washed with 1 mM HCl, then with deionized water, and air-dried. The plants dry biomass was determined and the material subsequently ground with a stainless homogenizer. A composite rhizosphere soil sample from each pot was collected after the harvest of corn. All soils were air-dried, and passed through a 2-mm sieve.

2.3. *Chemical analyses of soils and plants*

All soil samples (experimental soil, control soil, and SIOC-treated soils) were analyzed for the geochemical fractions of the metal, pH, and soil organic carbon. The geochemical fractions of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S, and Zn in the soils were sequentially extracted using a modified eight-step procedure which has originally been developed by Zeien and Brümmer (1989) and modified by El-Naggar et al. (2018). These fractions are operationally defined and they comprise the soluble + exchangeable fraction (F1), the fraction of metals bound to carbonates (F2), to manganese (Mn) oxides (F3), to soil organic matter (SOM; F4), to poorly (F6) and well crystalline iron (Fe) oxides (F7), and metals in sulfidic and residual (silicate) forms (F5 and F8, respectively). Details on the extraction steps and conditions are provided by the supporting information (Appendix A; Table S1) and published in El-Naggar et al. (2018). We determined the pseudo-total contents of metals by digesting 0.6 g soil in a microwave system (Milestone MLS 1200 Mega, Sorisole, Italy) with 1 mL concentrated HCl (32%) and 3 mL concentrated HNO_3 (65%) (U.S.E.P.A., 2007). For the determination of metals in the plant samples, 0.5 g of plant material was dry-ashed in a muffle furnace at 450 °C for 5 h, and extracted with 20% HCl (Jones et al., 1991). The concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S, and Zn in the solutions of soil and plant samples were determined by inductively-coupled optical emission spectrometry (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany).

2.4. *Quality control and statistical analysis*

Soil reference materials (BRM No. 13 and BRM No. 10a) obtained from the Federal Institute for Materials Research and Testing (BAM) were extracted and analyzed for their total metal content. The recovery of metals ranged from 88 to 109%. Also, certified plant reference materials of the cabbage powder (BCR No. 679; made by European Commission-joint research Centre, Institute for Reference Materials and Measurements) was used for analytical quality control. In addition, the quality of data was routinely monitored by analyzing blanks and sample replicates. Analysis of variance (ANOVA) and Duncan's multiple range tests were performed to compare the means of the treatments at using the SPSS 22.0 package.

3. Results and discussion

3.1. *Chemical and spectroscopic characteristics of the studied soil and organoclay*

The soil under study is moderately acidic (pH 6.7), rich in silt and total carbon (C) (71 g kg^{-1}), and has a moderate cation exchange capacity (15.1 $cmol_{(+)}$ kg^{-1}) (Table 1). Oxalate-extractable Fe made up 71% of the Fe extracted by dithionite-citrate-bicarbonate (Table 1), which is a typical feature of soil subjected to periodical redox fluctuations that result in poorly crystalline and small Fe oxides, as recently reviewed by Rennert (2019). The soil showed high pseudo-total content (g kg^{-1}; Table 1) of Al (18.5), Fe (43.7), Mn (0.91), and S (0.99). The pseudo-total content (mg kg^{-1}; Table 1) of Cd (8), Cr (490), Cu (3044), Ni (81), Pb (412), and Zn (1324) exceeded the precautionary values of the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV 1999), and were higher than the upper limit of the trigger action values for PTEs in agricultural soils as reported by Kabata-Pendias (2011), implying a high potential environmental risk, which needs soil remediation. The high total contents of the PTEs in the floodplain soil at the lower course of the Wupper River are likely due to the anthropogenic activities (Shaheen et al., 2017a). The studied SIOC is moderately acidic (pH 6.7), contain high content of total sulfur (38.7 g kg^{-1}) and Al (11.9 g kg^{-1}), and rich in the total carbon content (14.5%) as showed in Table 1.

Table 1
Selected properties of the used soil and organoclay.

Properties	Unit	Soil	Organoclay
Total Al	[g kg^{-1}]	18.5	11.9
Total S		0.99	38.7
Total Fe		43.7	3.2
Fe_d		35.5	nd
Fe_o		25.2	nd
Total Mn		1.01	0.19
Mn_d		0.91	nd
Mn_o		0.86	nd
Silt	[%]	92	nd
Clay		2	nd
Total carbon		7	15
pH		6.71	6.7
CEC	[$cmol_{(+)}kg^{-1}$]	15.1	nd
Total metal content			
Cd	[mg kg^{-1}]	8	0.13
Cr		490	nd
Cu		3042	2.7
Ni		81	7.1
Pb		412	4.9
Zn		1324	36.9

Fe_d and Mn_d = Citrate-bicarbonate-dithionate extractable- Fe and Mn; Fe_o and Mn_o = Ammonium oxalate-oxalic acid extractable- Fe and Mn; nd: not determined; b.d.l.: below detection limits.

The SEM images of SIOC showed that it's contained Al, Si, O, Fe, S, C, and Ca, as indicated by their high fluorescence signals (Fig. 1 A). The appearance of S in the studied SIOC confirms its impregnation with sulfur. The presence of strong signal of Si and its similar distribution pattern with O could be linked to the montmorillonite, which contained abundant Si oxides. Fig. 1B shows soil particles and their elemental maps. The presence of these elements is caused by aggregation of common minerals such as quartz (Si), clay minerals such as kaolinite, saponite, chlorite, etc (Si, Al, K, Mg, Ca, potentially Fe), silicates (Si, Al, potentially Fe) and Fe oxides (Fe, potentially S) (Rinklebe et al., 2016). More details about the spectroscopic characterizations of the SIOC are provided in Wang et al. (2019).

3.2. *Impact of SIOC on soil properties and plant biomass*

The addition of the SIOC decreased significantly the soil pH from 6.7 in the control to 5.3 in the treated soil (highest rate; 5%) (Appendix A; Table S2). This acidification might be caused by the enhanced production of sulfuric acid through bacteria-mediated sulfur oxidation; owing to the increase of sulfur content in the SIOC-treated soils (Kayser et al., 2000; Cui et al., 2004; Shaheen et al., 2019a). Also, the application of the SIOC increased significantly the soil total organic carbon content from 7.6% in the control to 8.1 in the treated soil (highest rate; 5%) (Appendix A; Table S2).

The highest rate of SIOC increased the total content of Fe, Mn, and S by 10, 11, and 133% and increased significantly the soluble + exchangeable fraction (F1) of Fe, Mn, and S by 23%, 746%

(8.5 fold), and 4296% (44 fold) as compared to the control soil (values have been calculated from data in Table S2). The addition of SIOC leads to a transformation of the residual fraction (F8) to the non-residual fractions (PMF) of Fe, Mn, and S by 15, 13, and 140% as compared to the control soil, respectively. The distribution of Al fractions was less affected by the addition of SIOC as compared to S, Mn, and Fe (Appendix A; Fig. S1).

The application of SIOC at doses of 3% and 5% decreased significantly the dry biomass yield of corn as compared to plants grown in the control soil (Appendix A; Fig. S2). This decrease is very likely linked to the significant pH decrease with added SIOC, which may have triggered PTEs phytotoxicity, a phenomenon observed particularly under the highest SIOC application dose. The low biomass yield under acidic conditions in sulfur-treated soils was also found by others (e.g., Cui et al., 2004; Shaheen et al., 2019a).

3.3. Impact of SIOC on the geochemical fractions and mobilization of PTEs in the soil

The distribution of Cd, Cr, Cu, Ni, Pb, and Zn among their fractions is presented as percentage of the total content in Fig. 2, and provided as mg/kg in in the supporting information (Appendix A; Fig. S3). The less strongly bound non-residual fractions of PTEs can be termed potential mobile fraction (PMF = $\sum$F1-F7) since this fraction constitute the contaminant fraction that has the potential to enter into the mobile aqueous phase in response to changing environmental conditions, such as pH, redox potential (E_H), and temperature (Shaheen and Rinklebe, 2014; Shaheen et al., 2018; 2019b). The PMF is often considered as the potential hazardous fraction to organisms because this fractions bond much less strongly with soil phases than residual does (Ma and Rao, 1997; Zhong et al., 2011; Rinklebe and Shaheen, 2014).

In the control soil, the Cd, Cr, Cu, Ni, Pb, and Zn were distributed mostly in the non-residual fraction (potential mobile fraction; PMF = $\sum$F1-F7), with a percent (% of the metal summation) ranged from 71% for Ni to 95% for Cd and Cu (Fig. 2). Among the PMF, Cd was dominant in F1, Cr in F6, Cu in F4, Ni in F6, Pb in F6, and Zn in F6. Cadmium showed the highest solubility (F1 = 19%), followed by Cu (8%), while the other elements showed negligible concentrations in this fraction. Chromium, Ni, Pb and Zn were dominantly associated with poorly crystalline Fe oxides, while Cu was with SOM, which may indicate that oxyhydroxide minerals are the predominant sorbents for Ni, Pb, and Zn, along with soil organic matter is the predominant sorbents for Cu in this soil (Rinklebe et al., 2016; Rinklebe and Shaheen, 2017).

The addition of the SIOC altered the distribution of Cd, Cr, Cu, Ni, Pb, and Zn among their different geochemical fractions and affected their potential mobile fractions (PMF = $\sum$F1-F7) (Fig. 2). For example, application of 5% SIOC increased significantly the soluble + exchangeable fraction of Cd, Cu, Ni, and Zn by 62, 40, 211, and 92% (Table 2), as compared to the control soil, respectively; while the soluble + exchangeable fraction of Cr and Pb was negligible in both the treated and untreated soil (Fig. 2). The SIOC transformed the residual and potential mobile fractions (in particular F4 and F3) of Cd, Ni, and Zn to the mobile fraction (F1) (Fig. 2). The addition of SIOC leads to a transformation of the crystalline Fe oxide (F7), Mn oxide fraction (F3), and the organic fraction (F4) of Cu to the soluble + exchangeable fraction (F1). The SIOC leads to a decrease in the residual fraction and an increase in the PMF of Cr and Pb. The SIOC 5% caused a decrease in the organic fraction of Cd (45%), Cr (15%), Cu (21%), Ni (22%), Pb (12%), and Zn (28%) as compared to the control (Table 2). The addition of SIOC 5% leads to an increase in the sulfide fraction of Cr (44%), Ni (7%), and Zn (12%), while it decreased the same fraction for Cd (13%), Cu (7%), and Pb (100%), as compared to the control (Table 2). The impact of the lower doses of SIOC (1 and 3%) on the redistribution of PTEs among their fractions was less than the higher dose (5%) as shown in (Fig. 3) and Table 2.

Increasing the soluble + exchangeable fraction and the PMF of the elements, in particular Cd, Ni, Cu, and Zn in the SIOC-treated soil as compared to the control might be explained by the following hypotheses: Firstly, the significant decrease in soil pH induced by

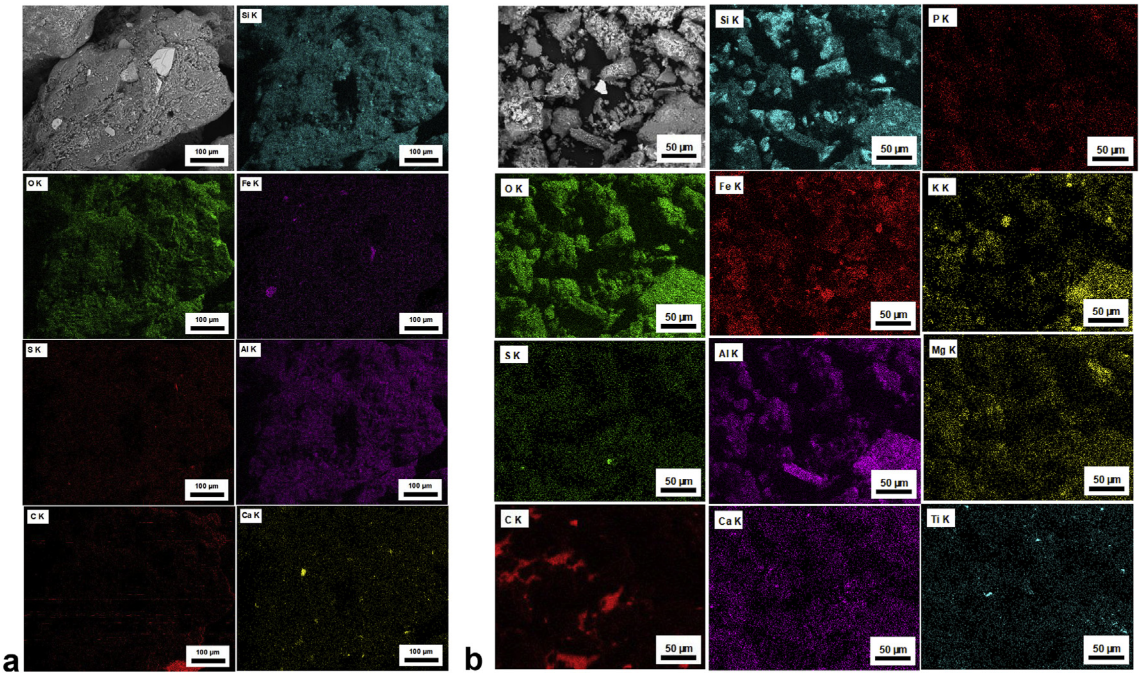

Fig. 1. Elemental mapping for the sulfur-impregnated organoclay (A) and in the soil (B) using environmental scanning electron microscopy with energy dispersive X-ray spectroscopy.

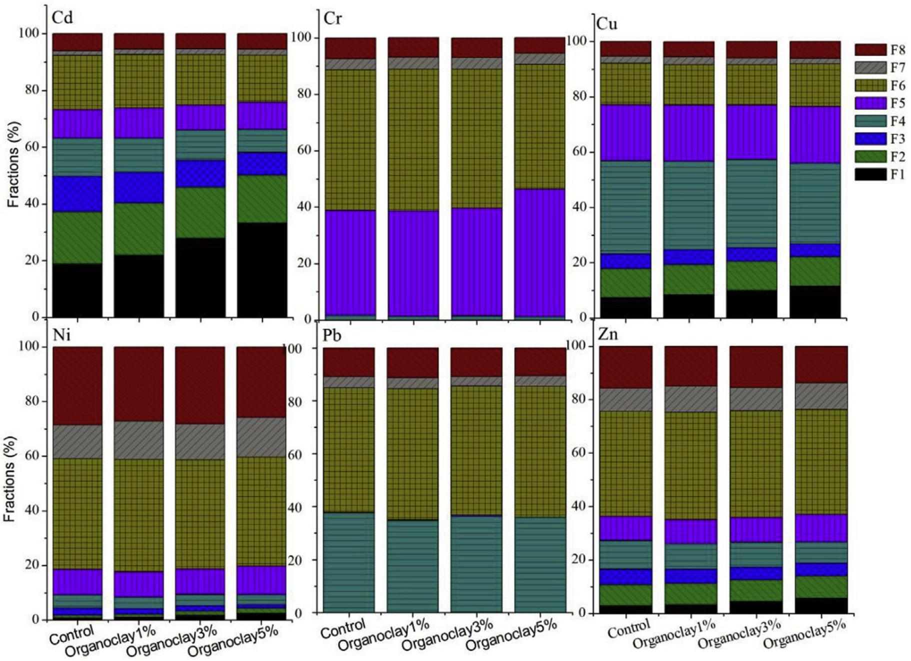

Fig. 2. Impact of the sulfur-impregnated organoclay on the distribution of Cd, Cr, Cu, Ni, Pb, and Zn among their geochemical fraction as percent of the total content.

the addition of SIOC may enhance the solubility of the elements. In this respect, Shaheen et al. (2019a) found that application of elemental sulfur and sulfur-based materials decreased soil pH by about 3 units and thus increased the solubility of metals in the soil. Also, Kayser et al. (2000) and Cui et al. (2004) found that the mobile fraction of Cd and Zn increased significantly when soil pH decreased by about 0.3 units as a result of sulfur addition. At low pH, dissolved metal concentrations in soil water extracts might be dominated by free ionic forms followed by ion pairs (Kabata-Pendias, 2011). Secondly, increasing sulfur content in the treated soil may enhance the potential formation of metal sulfide under certain anaerobic conditions; then, these metals (in particular Cd and Cu) might be released again in soluble forms when sulfides are oxidized to sulfates under aerobic conditions (El-Naggar et al., 2018; Karimian et al., 2018). Moreover, the use of sulfur has been adopted for soil acidification which increases the solubility of metals in polluted soils (Kaplan et al., 2005). Thirdly, increasing soil organic carbon content in the SIOC treated soil as compared to the control may affect positively the metals solubility; metals (particularly Cu) behavior is dependent on the formation of soluble Cu-organic compounds; thus the observed Cu mobility increase in these soils as compared to the control (Kunhikrishnan et al., 2012). The role of soil organic carbon in Cu solubility is well-documented, as it affects Cu biogeochemistry and mobility (Kunhikrishnan et al., 2012). Fourthly, the associated metals with the Fe-Mn oxides (F3, F6, and F7) might be released under low pH, in particular in the 5% SIOC treatment as a result of the potential dissolution of these oxides under acidic and/or anaerobic conditions (Rinklebe et al., 2016). The inorganic and organic functional groups as indicated by diffuse reflectance infrared Fourier transform in the SIOC are likely to be involved in transformation of PTEs in the SIOC treated soil (Wang et al., 2019). In conclusion, the application of SIOC promoted the soluble + exchangeable fraction and the PMF of the studied elements, especially at higher doses of application, which might affect the plant uptake of these elements by the roots and shoots of pea and corn.

Table 2
Impact of SIOC dosages on the changes (%) of the metal fractions in the treated soil compared to the control.

Metal Fractions	SIOC Dosages (%)	Cd	Cr	Cu	Ni	Pb	Zn
F1	1	15	0	9	23	0	16
	3	39	0	25	117	0	55
	5	62	0	39	211	0	92
F2	1	−2	0	2	8	0	3
	3	−9	0	−4	41	0	0
	5	−16	0	−7	67	0	4
F3	1	−14	0	−2	−16	0	−10
	3	−28	0	−17	−23	0	−19
	5	−42	0	−24	−55	0	−20
F4	1	−12	−18	−8	−14	−11	−9
	3	−25	−8	−10	−11	−6	−15
	5	−44	−15	−21	−22	−13	−28
F5	1	4	4	−2	−1	80	1
	3	−19	6	−9	−1	216	1
	5	−13	45	−7	7	−100	12
F6	1	−3	4	−6	3	1	4
	3	−13	3	−8	−1	1	0
	5	−21	3	−7	−4	−3	−3
F7	1	10	9	9	13	−7	16
	3	19	7	−8	6	−19	−1
	5	19	16	−29	13	−13	12
F8	1	−10	−3	1	−4	0	−4
	3	−17	−2	4	−1	−1	−3
	5	−16	−15	3	−12	−11	−15

Increasing/decreasing percentage = treatment - control/control*100 (data calculated from Fig. 2).
(+): increasing; (−): decreasing.
F1: soluble + exchangeable fraction; F2: bound to carbonate fraction; F3: manganese oxide fraction; F4: organic matter fraction; F5: sulfide fraction; F6: poorly-crystalline Fe oxide fraction; F7: Well-crystalline Fe oxide fraction; and F8: residual fractions.
SIOC: Sulfur-impregnated organoclay.

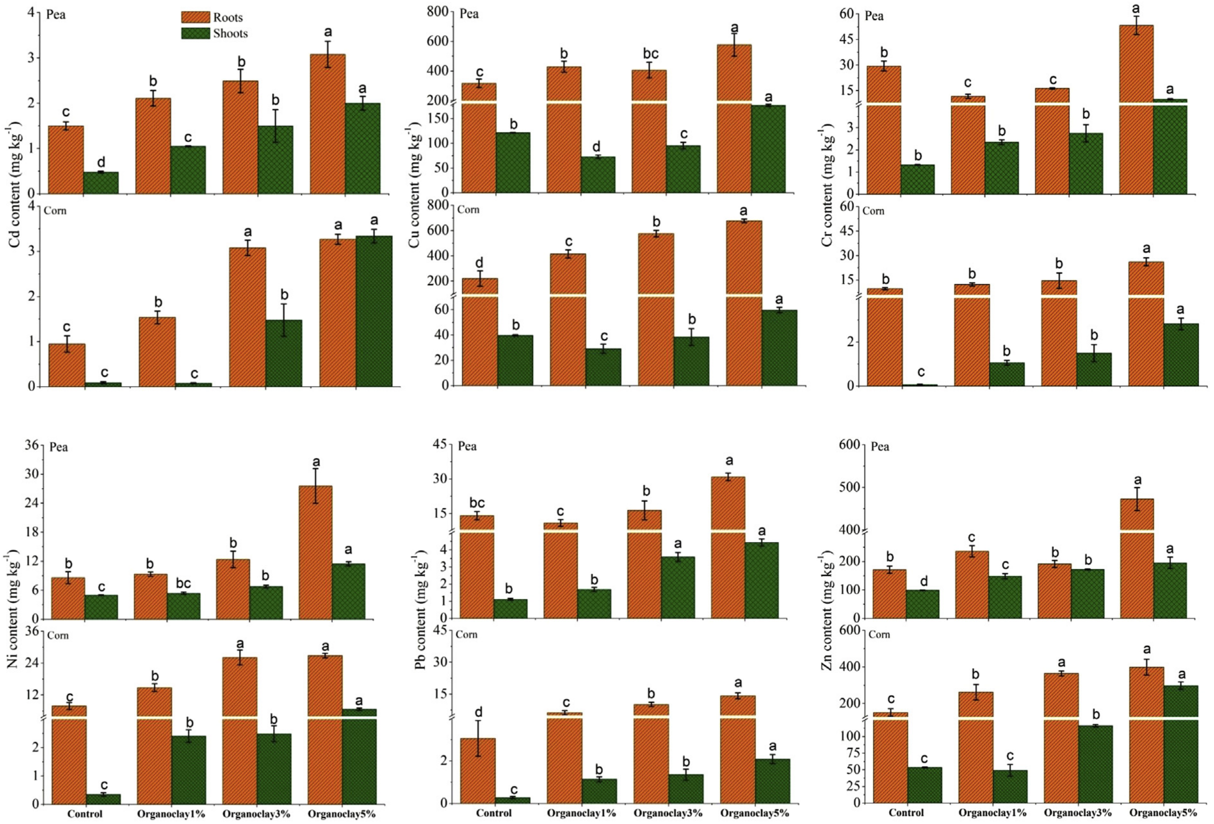

Fig. 3. Impact of the sulfur-impregnated organoclay on the Cd, Cr, Cu, Ni, Pb, and Zn contents in roots and shoots of pea and corn. Bars denote standard deviation from the mean ($n = 3$). The different lower case letters indicates significant differences between the control and organoclay treatments for root and shoot ($P < 0.05$).

Table 3
Impact of SIOC application rates on the changes (%) of the metal content in the roots and shoots of pea and corn in the treated soil compared to the control.

Metals	Roots			Shoots		
	SIOC 1%	SIOC 3%	SIOC 5%	SIOC 1%	SIOC 3%	SIOC 5%
Pea						
Cd	41	67	105	117	211	314
Cr	−60	−45	81	77	106	647
Cu	35	28	82	−40	−22	45
Ni	9	44	220	8	36	130
Pb	−22	16	119	52	220	296
Zn	37	12	175	50	73	97
Fe	−29	−37	162	−36	−14	251
Mn	29	109	434	152	344	678
Al	−50	−44	38	−8	8	474
S	296	293	327	297	457	379
Corn						
Cd	61	223	243	−13	1497	3497
Cr	25	49	166	1464	2115	4089
Cu	88	160	206	−27	−3.2	50
Ni	88	231	241	594	618	1831
Pb	106	232	364	308	386	648
Zn	73	140	163	−8	116	456
Fe	13	60	113	5.	19	68
Mn	102	348	542	27	192	326
Al	4	20	74	47	174	223
S	344	929	959	72	257	397

SIOC: Sulfur-impregnated organoclay.
Increasing/decreasing percentage = treatment - control/control*100 (data calculated from Fig. 3).
(+): increasing; (−): decreasing.

3.4. Impact of SIOC on PTEs uptake

Pea and corn differed in their abilities to uptake Cd, Cr, Cu, Ni, Pb, and Zn (Fig. 3). Pea plants absorbed higher concentrations of all elements (except for Ni and Zn in the roots of SIOC1% and SIOC3%) than corn plants. The roots of both pea and corn accumulated the elements under all treatments higher than the shoots, indicating a limited translocation of these elements in both plants.

Increasing the application dosages from 1% to 3% and 5% SIOC increased significantly the elements content in the roots and shoots of pea and corn as compared with the plants of the control soil. The regression analyses indicated that the metals content in the whole plants correlated significantly positive with the SIOC dosages (Appendix A; Fig. S4). The impact of SIOC 5% on the elements (except for Cu) uptake by the shoots was higher than the roots (Table 3). The 5% SIOC increased the elements content in the roots of pea and corn by between 81% with Cr to 220% with Ni in the pea plants and between 166% with Cr and 364% with Pb in the corn plants (Table 3).

Soil-to-plant transfer factor and roots to shoots translocation factor can be used to estimate the plants potential for phytoextraction of PTEs in soils and the translocation of these elements from the roots into the shoots (Wang et al., 2006; Shaheen and Tsadilias, 2009; Bolan et al., 2013; Antoniadis et al., 2018). The accumulation factor (AF, was calculated as follow: AF = mg element kg^{-1}plant/mg total-element kg^{-1}soil. We also calculated the translocation factor (TF) as follow: TF = mg element kg^{-1} shoots/mg element kg^{-1}roots (Appendix A; Table S3). The strong impact of SIOC doses on the elements uptake was in agreement with the AF values (Table S3). For example, the SIOC 5% increased the AF values of Cd, Cr, Cu, Ni, Pb, and Zn in the pea by 2.7, 1.6, 1.9, 2.9, 2.5, and 2.5 fold, respectively. The SIOC 5% increased the AF values of Cd, Cr, Cu, Ni, Pb, and Zn in the corn by 6.9, 2.0, 3.0, 4.2, 4.0, and 3.5 folds, respectively. The TF values indicated that addition of SIOC increased the translocation of the metals (in particular Cd) from roots to shoots as compared to the control plants (Table S3). The higher element uptake and accumulation by plants grown in the SIOC treated soils than the plants grown in the control soil can be explained by the significant increase of the solubility (F1) and potential mobility (PMF $= \sum$F1-F7) of all elements in the SIOC treated soils as discussed in section 3.3. The promotion of Cd, Cr, Cu, Ni, Pb and/or Zn accumulation by SIOC might be linked to the Fe/Mn/S accumulation by the plants (Appendix A; Fig. S5). Sulfur compounds may be able to facilitate the metal transport across the root plasma membrane, and their assimilation products in plant tissues play a critical role in the metal sequestration (Kabata Pendias, 2011; Shaheen et al., 2017b, 2019a). The presence of high sulfur content in the pea and corn plants induced by SIOC addition to soil compared to control indicates that sulfur is likely involved in metal uptake from soil. Also, sulfate was able to enhance the plant (e.g., *Lolium perenne*) uptake of Cu and Cd (Gunawardana et al., 2010) due to the formation of bioavailable $CdSO_4^0$ complexes (Kabata Pendias, 2011). Additionally, Fe transporters were reported to be able to facilitate Fe, Zn and Cd uptake (Grillet et al., 2018). Our SIOC-treated soils showed higher mobile Fe content relative to the non-treated soil; therefore it's possible that plants' iron transporters were more activelyinvolved in elements uptake. However, this hypothesis needs to be further elucidated. These results suggest that the application of higher dosages (3% and 5%) of SIOC promoted the accumulation of the studied elements by the roots and its translocation to shoots in the two plants. However, these higher doses, particularly the 5% dose decreased the plant growth, especially pea; therefore, more tolerant plants such as metal hyperaccumulators can be used to increase the efficiency of the phyto-management of the contaminated soils using this sulfur-modified organoclay.

4. Conclusions

The efficacy of sulfur-impregnated organoclay aiming to enhance the accumulation of Cd, Cr, Cu, Ni, Pb, and Zn by pea and corn in a polluted riparian soil has been investigated in this study. Our study provided results of using SIOC as a promising mobilizing agent for these elements and thus enhancing their phytoextraction by pea and corn. The potential redistribution of the elements from the residual fraction to the non-residual fraction (potential mobile fraction) and mobile fraction (soluble + exchangeable fraction) by the SIOC might be caused by the significant decrease of soil pH, increase of total carbon content, increase of total and mobile sulfur content, and/or by the associated changes in the chemistry of Fe-Mn oxides and the sulfide metal fractions. Application of the higher dosages (3 and 5%) of SIOC promoted the accumulation of the studied elements by the roots and their translocation to the shoots of pea and corn. Our results could be helpful for the phytoremediation of soils contaminated with toxic elements. To verify the collected results under various conditions, further work is necessary to enlighten the processes regarding metal mobilization by SIOC under dynamic redox conditions combined with spectroscopic techniques, as well as experiments under field conditions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.02.073.

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