



Geochemical interactions in the trace element–soil–clay system of treated contaminated soils by Fe-rich clays

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Abstract Clays have been widely applied in contaminated soils in order to reduce the mobility of potentially toxic elements (PTEs), such as Pb, Zn and Cu. In the present study, three Fe-rich clays from Greece were selected as amendments of three contaminated soils with distinct physicochemical and mineralogical characteristics. The amendments consisted of palygorskite-rich (PCM), Fe-smectite-rich (SCM) and natural palygorskite/Fe-smectite-rich (MCM) clays. The changes induced in the environment of the soil–PTE–clay system were assessed by examining the water-labile fraction of Pb, Zn and Cu, as well as the bioaccessibility of Pb, in the contaminated soils. The initial water-leachable concentrations of PTEs in soil were within the range 1826–6160 µg/kg Pb, 152–645 µg/kg Cu and 370–4052 µg/kg Zn. All three Fe-rich clays exhibited high retention efficiency toward PTEs, following the order Pb (55–70%) > Zn (45–55%) > Cu (0–45%). The high reactive surface area of the clay particles acted as a substrate for the deposition of Fe–Al oxides with a concomitant removal of PTEs that were transported

through the colloidal fraction. Furthermore, the decrease in relative bioaccessibility of Pb (5–10% compared to the control) suggests dissolution of primary clays followed by entrapment of the element in secondary Fe-rich precipitates. In conclusion, the use of Fe-rich clays as soil amendments may have a positive effect in reducing the environmentally significant PTE fraction in soils, especially when different clay phases coexist.

Keywords Retention · Soil leachate · Bioaccessibility · Alkaline soil · Acidic soil

Introduction

The study of soil contamination is commonly based upon the “source–pathway–receptor” model (Hodson 2010). Chemical interactions occurring in the soil/water interface play a key role in the transportation of contaminants from their source (e.g., soil) to receptors such as water and biota. In order to break the “source–pathway–receptor” chain, various soil and water remediation technologies have been applied, aiming in either treating the contaminated source, or controlling the transportation path to the final receptor.

In recent decades, emphasis has been given in sustainable remediation technologies that “eliminate and/or control unacceptable risks in a safe and timely manner, and which maximize the environmental,

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social and economic benefits of the remediation work” (Smith et al. 2009). The remediation methods that meet best the aforementioned criteria involve in situ soil containment and stabilization treatments (Chen et al. 2017). Moreover, the use of natural materials (geomaterials) as soil additives for stabilization is gaining attention because these amendments are cost-effective, versatile, sustainable and result in less secondary pollution (Hodson 2010; O’Day and Vlassopoulos 2010; Shen et al. 2018).

Geomaterials commonly applied for remediation purposes include carbonates, sulfates, phosphates, oxides, zeolites and clays (O’Day and Vlassopoulos 2010). Clays have exceptional physicochemical properties, and therefore, they have been widely used for the removal of potential toxic elements (PTEs) (such as Pb, Cu, Zn, Cr, Co, Cd, Hg and As) from wastewaters (e.g., Zhu et al. 2016; Burakov et al. 2018). Their small grain size, high surface area and layer charge are capable for stabilizing PTEs via different mechanisms such as: (a) the formation of ionic or covalent chemical bonds, (b) the exchange with other mobile ions present in their structure and (c) precipitation onto the surface by the formation of insoluble phases (O’Day and Vlassopoulos 2010).

Stabilization of PTEs in soils using clays has been studied through laboratory and field-scale trials (Abad-Valle et al. 2016; Liang et al. 2014; Sun et al. 2016). Some of them employed a more holistic approach in order to evaluate the stabilization process and determine the controlling factors by determining the residual, labile, phytoavailable and bioaccessible metal fractions in the treated soils. Palygorskite (Álvarez-Ayuso and García-Sánchez 2003; Liang et al. 2014; Zotiadis et al. 2012), sepiolite (Abad-Valle et al. 2016; Liang et al. 2014; Sun et al. 2016) and bentonite (Sun et al. 2016) exhibited high retention capacities toward Pb, Zn, Cu and Cd in mining and agricultural soils, in terms of their water-leachable and phytoavailable PTE fraction. Their retention efficiency was attributed to both the type of the applied amendment and the special characteristics of the contaminated soil. However, in some cases the addition of a mineral amendment has minor effect in leachability of the PTEs from soils (Houben et al. 2012), whereas it can even mobilize them from low energy sites, by altering the physicochemical conditions of the soil (Sanderson et al. 2015). In a similar manner, the type of the amendment controlled the

bioaccessibility of Pb in the respective treated soils, being more profound with treatments where Fe oxides were involved (Lee et al. 2009; Sanderson et al. 2015).

Clays have also been used in the treatment of leachates generated from waste landfills and contaminated soils. The application of smectite may reduce the leachate migration through the soil by forming a barrier to contaminants (Ruiz et al. 2012). Bentonite composites proved also efficient in attenuating the PTE content in an acid mine drainage (AMD) through neutralization and co-precipitation of Fe–Al phases (Falayi and Ntuli 2014; Masindi et al. 2015). It is therefore deduced that in both soil and soil leachates (including AMD), the mobility of PTEs is controlled by various factors, such as the presence of organic matter and Fe–Al oxides, the soil pH, the metal speciation and the presence of anionic species (carbonates, sulfate, chloride).

The use of Greek clays as amendments of contaminated soil and water has also been investigated. Bourliva et al. (2015) studied the potential of wastewater treatment with bentonite clay from Milos Island (SW Aegean, Greece) and showed a decrease in PTE content up to 74%. Systematic empirical studies regarding the use of Greek palygorskite-rich clay proved its efficiency in removing Pb and Cu from aqueous solutions (Kypridou and Argyraki 2018; Pyrgaki et al. 2018). The palygorskite-rich clay showed also high efficiency in stabilizing Pb, Zn, Ni, Cu, Sb and Mn in a contaminated mining soil during both laboratory and in situ field-scale experiments, where an up to 60% decrease in the water-leachable PTE fraction has been demonstrated (Zotiadis et al. 2012).

The metal (Pb and Cu) sorption efficiency of the Fe-rich palygorskite and smectite clays of the present study, under static (batch) sorption conditions were studied by Kypridou and Argyraki (2018). The authors evaluated possible sorption mechanisms and concluded that both metals were retained mainly by surface complexation onto the palygorskite-rich samples, and by ion-exchange in smectite-rich samples. Precipitation of Pb-rich phases (oxides and carbonates) was also identified in all clay samples after the interaction with metal solutions. Although these experiments gave a first insight on the clay–metal interactions, they cannot fully describe the retention processes that occur in natural solution systems. Thus, the study of soil leachates and porewater before and

after the interaction of contamination soil with the amendments would provide much more realistic information on the geochemical processes taking place during the interaction.

The present study focuses on the interactions that occur in the PTE–soil–clay system of three clay-treated contaminated soils and soil leachates of distinct origin and characteristics. The soils were collected from mining and urban areas of Greece with variable contamination levels (regarding Pb, Zn and Cu) and have different mineralogy and physicochemical properties. The aim of the study is: (a) to assess the role of soil characteristics in the mobilization of PTEs, and (b) to evaluate the effectiveness of Fe-rich clays in reducing the environmental mobility of PTEs in soil in terms of their water-labile and bioaccessible fraction especially with respect to Pb.

Materials and methods

Clay amendments

The clay amendments employed in the current study include a palygorskite-rich clay (PCM), a Fe-smectite-rich clay (SCM) and a natural palygorskite/Fe-smectite mixture (MCM), originating from Northern Greece. The bulk samples were provided by the Geohellas S.A. mining company, which is responsible for the exploitation of the respective clay deposits. All three samples are the alteration products of ultramafic rocks and consist of palygorskite and Fe-smectite (mainly nontronite) in various proportions, as well as a number of auxiliary phases (quartz, serpentine, plagioclase, carbonates). The field samples were grinded in a laboratory ball mill to obtain a homogeneous particle size < 200 mesh, but no further purification was employed. A rigorous characterization of the clay samples regarding their mineralogy, structure, chemistry and physicochemical properties has been carried out by Kypridou and Argyraki (2018) and is summarized in Table 1.

Selection and preparation of the contaminated soil samples

The contaminated soil samples that were selected for the stabilization experiments had previously been collected from areas affected by different

Table 1 Summary of the main mineralogical, chemical and physical characteristic of the clay samples (Kypridou and Argyraki 2018)

	PCM	SCM	MCM
Palygorskite fraction	70%	0%	20%
Fe-smectite fraction	20%	70%	40%
Fe ₂ O ₃	5.9	9.3	9.9
MgO	12.2	18.9	27.5
PZC	~ 8.5	~ 9	~ 9
CEC (meq/100 g)	27	62	29
BET-N ₂ surface area (m ² /g)	193	123	182

contamination sources in Greece, i.e., from the historical mining area of Lavrion (Attica), from the active mining area of Stratoni (Chalkidiki) and from an urban park in the Municipality of Kessariani (Athens), previously used as a firing range. The soil samples were selected for their high concentration in PTEs, especially Pb.

The historical mining area of Lavrion (E. Attica) is famous for the Pb–Ag–Zn mixed sulfide deposits, which were exploited since ancient times and until 1978 producing large amounts of wastes and slags (Demetriades 2010; Skarpelis 2007; Skarpelis and Argyraki 2009). The sampling area serves nowadays for agricultural purposes and is in close proximity to abandoned mine waste piles making it a typical example of heavily contaminated site by a variety of PTEs. The maximum near-total PTE concentrations in surface cover of the wider area of Lavrion reach 1.6 wt% Pb, 5517 mg/kg Zn and 180 mg/kg Cu and are associated with nonferrous slag, sulfates and Fe oxides (Argyraki et al. 2018; Demetriades 2010).

The wider area of Stratoni (Chalkidiki) is an active mining site, known for the carbonate-hosted replacement Pb–Zn–Mn mineralization in the northeast and the porphyric Cu–Au deposit in the south of the Stratoni village (Siron et al. 2016). Stratoni village was developed as a residential area for miners and hosts the flotation plant that produces sphalerite and galena concentrates (Argyraki 2014). The soil in the wider Stratoni area is contaminated by PTEs having concentrations up to 1 wt% Pb, 24 wt% Mn, 14 wt% Fe, 6830 mg/kg Zn, 3690 mg/kg As and 694 mg/kg Cu (Kelepertsis et al. 2006).

Lastly, a soil from a highly contaminated urban site with PTEs within a public park in the Municipality of Kessariani, an eastern suburb of Athens (Attica, Greece) was used. The contamination in the park is not related to any industrial activity, but to former use of the area as a recreational shooting range. The topsoil has high concentrations of Pb, Sb and Ni originating from bullet cores and cartridges. A systematic study by Urrutia-Goyes et al. (2017a, b) on the topsoil of the park revealed an enrichment in Pb (mean 5560 mg/kg), associated with carbonate phases, as well as organic matter (Argyrazi et al. 2011).

Each soil sample was prepared by manual mixing of a number of sub-samples collected from each site, in order to obtain a homogenized composite sample representative of each contaminated area. All soil samples used in the experiments were air-dried and sieved to achieve grain sizes of < 2 mm, < 100 μm and $\leq 70 \mu\text{m}$ soil fractions.

Characterization of contaminated soil samples

An extensive characterization of the composite soil samples was carried out in order to associate their mineralogy and physicochemical properties to their PTE content. The soils were characterized regarding their mineralogy and physicochemical characteristics (pH, CEC, L.O.I, M.C.) in the Laboratory of Economic Geology and Geochemistry, (Dep. of Geology and Geoenvironment, NKUA). The mineralogical composition of the randomly oriented soil samples was determined by P-XRD (Siemens D5005 instrument, with Cu K α radiation operating at 40 kV and 40 mA) at 2-theta range from 3° to 65°, step 0.02°/s. Evaluation of the patterns was conducted using the DIFFRAC PLUS v2.2 software by Siemens. The pH of the soils was obtained by mixing 8 g of dry solid sample with 20 ml of deionized water (ASTM 1995). The mixtures were agitated for 15 min and left to settle for 30 min prior to measurement with a bench-top pH-meter (Jenway 3040 Ion Analyzer), calibrated with pH 4 and 7 buffer solutions (Carlo Erba Reagents S.A.S). Loss on ignition and moisture content was determined according to Storer (1984). The geotechnical properties of soil samples were determined in the Technical Laboratory of Edafomichaniki S.A., and included determination of grain size distribution by sieve analysis (ASTM D422-63 2007; ASTM C136 2014),

permeability tests (ASTM D2435 2011) and determination of Atterberg limits (ASTM D4318-84 2017).

The solid phases most probably related to PTE loads in the solid fraction were identified using SEM-EDS (Jeol JSM-5600 instrument operating at 25–30 kV), equipped with an Oxford ISIS 300 micro-analytical device and calibrated using cobalt. Electron-dispersive spectra (EDS) were obtained in carbon coated free surfaces of the examined solids, in backscatter electron mode (BSE).

The near-total elemental concentrations of the soil samples were determined by acid digestion following the US EPA Method 3050 (1996). Briefly, 0.5 g of the 100 μm dry soil fraction were weighted and digested by HNO₃–H₂O₂–HCl. The resultant solutions passed through a Whatman No. 41 filter, collected in a 100 ml volumetric flask and made to volume. All aqueous samples were stored in the refrigerator at 4 °C, prior to analysis by flame atomic absorption spectroscopy (F-AAS) (PerkinElmer 1100B instrument), in the Laboratory of Economic Geology and Geochemistry (Dep. of Geology and Geoenvironment, NKUA). The instrument was calibrated using a series of 0.5, 1, 2.5, 5 and 10 mg/l multi-elemental standard solutions prepared in the laboratory, by the appropriate dilution of mono-elemental standards (Sigma-Aldrich). Double-deionized water (Millipore Milli-Q Gradient A10) containing 2%v/v HNO₃ was used as a dilution agent. For quality control purposes, five sub-samples were analyzed for each soil in order to assess the precision of the analytical method. The analytical precision was very good (< 10%) to acceptable (< 30%) for all analyzed elements. A soil certified reference material (NIST SRM2710) was also analyzed along with the samples to test the analytical bias. The recovery rates were good for most of the elements analyzed (> 70%).

Preparation and treatment of contaminated soil leachates

The water-leachable PTEs fraction of the soils was determined following the EN 12457-4 protocol (2002). Each soil sample was mixed with deionized water to a 10 L/kg ratio, in polyethylene 1L bottles and placed in an end-over-end rotary shaker (10 rpm) for 24 h. The leachates were separated by centrifugation and subsequent filtration using 0.45 μm cellulose filters. The pH of the leachates was determined immediately after filtration. Then, the leachates were

acidified to pH 3.6 using HNO₃ (65%) and used as influents to the subsequent column experiments. Acidification of leachates served to maintain PTE mobility in order to simulate an acid mine drainage (AMD) solution.

The treatment of the acidified soil leachates was studied under dynamic flow conditions using an experimental setup of small-scale columns containing the Fe-rich clays. The columns were constructed using 15 ml PVC (diameter 1.2 mm) syringes. Due to the presence of smectite in the samples, all clays were diluted with quartz sand (particle size 10–30 µm). Quartz sand was selected as a dilution agent to improve the hydraulic properties of the sorbents. Moreover, quartz is considered an inert material regarding sorption. The optimum dilution ratio selected was 1:7 (clay/sand), based on previous laboratory trials (data not shown). Therefore, the resulted solid material was composed of 12% clay (0.5 g) and 88% quartz sand (3.5 g). The as-prepared solids were mechanically homogenized by mixing in a rotary shaker for 30 min. The hydraulic conductivity of the mixtures was determined by the ASTM (2011) protocol and ranged between $1.32\text{--}9.78 \times 10^{-6}$ cm/s, showing the high dependence of permeability on the smectite content of the samples. The mixtures were packed in the syringe and pressed manually using the syringe piston to attain a uniform bed height. The bed was supported on the bottom and top of the column by glass wool. Two columns were prepared for each clay–quartz mixture to test the repeatability of the results. Columns containing only quartz sand were also prepared as controls, to examine the influence of the dilution agent in the retention of PTEs.

The prepared columns were adjusted to three-channel micro-flow variable-speed peristaltic pumps (BQ80S, LeadFluid Co. Ltd) via silicon pipes, enabling the upward feed of the solutions. Upward flow was selected to inhibit clogging within the column. The effluents were collected from the top of the columns. Two pumps were used, enabling the simultaneous operation of 6 columns. The columns were saturated with double-deionized water with an upward flow of 0.07 ml/min (0.5 rpm) for 48 h to stabilize porosity. The pH of the effluents at equilibrium was recorded to be about 8. Previous laboratory experiments using mono-elemental solutions (unpublished data) showed that the selected experimental parameters (i.e., quartz/clay ratio, flow rate, saturation

time) enabled the study of dynamic sorption in relatively short running times (up to ~ 24 h).

After column saturation, the acidified leachates passed through the columns in an upward mode (0.63 ml/min) for 24 h. The pH of the effluents was recorded frequently to trace the progress of the experiment. Two effluents were collected for chemical analysis from each column, based on the recorded pH values. The first effluent was collected at pH within the range for natural waters ($\sim 7 \pm 1$) (t_1), to investigate the neutralization efficiency of the clays. The second effluent was collected at the end of the experiment (t_2 , 24 h). Since the glass wool filtered the effluents that exited the columns, and the solutions came out clear, no further filtration was applied. The initial and treated leachates were analyzed for major and trace elements using ICP-MS in a certified laboratory, after acidification with HNO₃ (65%). The analytical repeatability was assessed in terms of relative percent difference (RPD, %) between the duplicate columns and varied among the elements, being poor (30–40%) for the PTEs mostly due to the very low concentrations, close to the detection limit of the method (< 1 µg/l). Better repeatability was achieved for major elements including Ca, Mg, K and Na ranging from 4 to 14%.

Treatment of contaminated soils in pots

The stabilization efficiency of clays regarding the three contaminated soils was tested by means of a laboratory pot experimental setup. Two treatments were prepared for each clay sample in small Plexiglas pots by mixing appropriate quantity of clays with 250 g of each contaminated soil (< 2 mm) to obtain 2% and 10 wt% clay mixtures. The mixtures were mechanically homogenized using a rotary mixer for 30 min, filled the pots and saturated with deionized water. Two pots were prepared for each treatment to estimate the repeatability of the experimental results. Pots containing only contaminated soil (0% of clay) served as controls.

The pots were watered with deionized water on a weekly basis for 2 months, to maintain saturation state and compensate for evaporation losses. Until the end of the experiment, up to 200 ml of H₂O was added in each pot. The porewater was extracted at the end of the stabilization period via centrifugation at 3000 rpm, and the supernatant (10–20 ml) was collected and filtered through a 0.22 µm syringe filter. The

porewater pH was measured, and the water samples were acidified with HNO_3 (65%) and stored in the refrigerator at 4 °C prior to analysis using ICP-MS. The pH of the wet-treated soils was also measured. The experimental precision was good (RPD < 30%) for the major cations, but poor (RPD > 60%) for the trace elements, probably due to low elemental concentrations and the heterogeneous distribution of the elements in parent soils.

The bioaccessible metal fraction of the control and clay-treated soils was determined using the simplified bioaccessibility extraction test (SBET) (Method 1340, EPA 2017). Following the extraction of porewater, each solid sample was disaggregated and homogenized. Prior to extraction, a portion of the sample was oven-dried for 24 h at 105 °C to determine the moisture content of the solids. Depending on the moisture content, about 0.3–0.25 g of each solid sample were weighted to obtain the equivalent ~ 0.25 g of dry mass. The solids were dispersed in 25 ml glycine solution (0.4 M), adjusted to pH 1.5 with conc. HCl and preheated at 37 °C. The suspensions were agitated for 1 h within a thermostatic chamber maintaining the temperature at 37 °C. The supernatants were collected via centrifuging, filtered through 0.22 μm syringe filters and stored in the refrigerator at 4 °C prior to analysis for measuring concentrations of Pb, Zn, Cu, Fe and Mg by F-AAS (NKUA). Each sample was analyzed in duplicate to assess the analytical precision, which was acceptable (RPD < 20%) for all the studied elements.

Speciation calculations and geochemical modeling

PHREEQC geochemical code (Parkhurst and Appelo 1999) and minteq.v4 database (Allison et al. 1991) were employed in order to determine the relative abundance of the aqueous species and saturation indices (SI) of selected phases that may be present in the various solutions and leachates. The soil pH, the concentrations of Pb, Cu, Zn, Fe and Al and the accompanying anions (Cl^- , SO_4^{2-} , PO_4^{3-}) served as the input parameters for speciation calculations. The solutions were also equilibrated with atmospheric CO_2 ($P_{\text{CO}_2} = 10^{-3}$ atm), to simulate the influence of atmospheric CO_2 . For simplicity, the influence of organic carbon and of primary carbonates was not considered.

Results

Characteristics of contaminated soils

The physicochemical properties of the composite contaminated soils are given in Table 2. According to grain size analysis, the soil samples consist mainly of sandy grains (~ 49–63%) and silt (~ 32–46%). The soils liquefy at 24–32% water content, exhibit no plasticity and have low water permeabilities (~ $2\text{--}9 \times 10^{-5}$ cm/s). Based on the USCS soil classification (ASTM D2487-17 2017), the three soil samples were characterized as non-plastic, well-graded silty sands (SM).

The qualitative mineralogy of all three bulk soil samples consists mainly of quartz, plagioclase, muscovite and chlorite, which is related to the metamorphic basement in all three areas. The soils lack significant amount of clay phases, and therefore their CEC values are low (~ 17 meq/100 g) (Table 2). Kessariani and Lavrion soils have also a significant amount of carbonates (calcite, dolomite and/or ankerite), reflected in the alkaline soil pH (7.9), contrary to Straton soil, which has no carbonate phases and therefore is mildly acidic (5.8) (Table 2).

The descriptive statistics of near-total elemental concentrations (mean, median, standard deviation, %RSD minimum and maximum values) for each soil sample are given in Table 3. Among the three contaminated areas, Lavrion soil exhibited the highest near-total PTE concentrations. Lead concentrations followed the order Lavrion > Kessariani > Straton, whereas Cu and Zn concentrations increased as Lavrion > Straton > Kessariani. The Lavrion near-total soil concentrations are 4800 mg/kg Pb, 69 mg/kg Cu and 1590 mg/kg Zn (Table 3).

The relation between the PTEs and the soil components was assessed by examining the $\leq 70 \mu\text{m}$ soil fraction using SEM-EDS analysis (Fig. 1). According to SEM-EDS, these metals are found as disseminated grains of very fine size (~ 10 μm) within the Al-Si soil components (Fig. 1a, b). The grains contain up to 80% Pb, and 2% Cu and Zn, and are closely related to Fe oxides. The mean Kessariani soil concentrations are 1690 mg/kg Pb, 118 mg/kg Zn and 30 mg/kg Cu, respectively (Table 3). The soil samples contain grains with > 50 wt% Pb, accompanied usually by Cu (< 3 wt%) and Zn (< 2 wt%) (Fig. 1c, d). The metals are mainly found as

Table 2 Physicochemical properties of the contaminated soil samples

Grain size analysis	Soil		
	Lavrion	Stratoni	Kessariani
Fine gravel (%)	0.1	0.2	1.1
Coarse sand (%)	22.4	12.2	19.9
Medium sand (%)	17.9	17.2	13
Fine sand (%)	23.3	33.4	16.4
Silt (%)	31.7	34.6	45.7
Clay (%)	4.6	2.4	3.9
Atterberg limits			
LL (%)	23.8	27.2	31.9
PL (%)	Non-plastic	Non-plastic	Non-plastic
Hydraulic cond. (cm/s)	8.59×10^{-6}	7.07×10^{-5}	1.68×10^{-5}
Physical properties			
Moisture content (%)	0.82	1.25	0.75
pH	7.9	5.8	7.9
OM (%)	3.58	4.49	3.85
CEC (meq/100 g)	16	17	17

disseminated grains < 10 μm in size associated with Al–Si phases and Ca (Fig. 1c). Larger grains (~ 20 μm) containing up to ~ 80 wt% Pb were also observed (Fig. 1d), being most probably lead carbonates. The Stratoni soil has the lowest PTE concentrations of the three soils (432 mg/kg Pb, 85 mg/kg Cu, 324 mg/kg Zn) (Table 3). Lead, Zn and Cu were found in association with Fe–Mn phases and phosphorous. The Ti–P phases contain up to 23 wt% Pb, 1 wt% Cu and Zn, 2 wt% Ti and 6 wt% P (Fig. 1e). Cu-rich grains (80 wt% Cu) associated with Zn were also found (Fig. 1f).

Characterization and treatment of soil leachates under dynamic conditions

The water-leachable elemental concentrations of the soils are summarized in Table 4. The pH of the Lavrion and Kessariani leachates was alkaline, whereas the Stratoni leachate was mildly acidic, likewise the pH of the respective soils (Table 2). The alkaline leachates had also high Ca probably due to the dissolution of carbonate minerals. The leachable Pb, Zn and Cu concentrations were much lower than their bulk counterpart (Tables 3), following the order Kessariani > Lavrion > Stratoni. Furthermore, all leachates were characterized by a yellowish-brown color, even after filtration indicating a high content of

Al–Fe colloids. Lavrion and Stratoni leachates exhibited the highest Al and Fe concentrations (18.2–21.5 mg/kg Al, 8.2–15.2 mg/kg Fe) (Table 3). Moreover, all three leachates consisted of 50–200 mg/kg sulfur, whereas Stratoni and Kessariani had significant phosphorus (150–470 μg/kg).

The contaminated soil leachates were treated by small-scale columns containing 0% (control) and 12% Fe-rich clays, under dynamic flow conditions. The first outflow sampling occurred at t_1 , when the effluents were neutralized (pH ~ 7), and exhibited a clear color. The results showed 75–100 wt% retention of Pb by the clay columns, whereas significant retention was also observed by the controls (40–90 wt%). Zinc was highly retained (60–100 wt%) from all clay columns in comparison with the control (0–60 wt%). The retention of Cu was also significant, reaching 40–90 wt% in the clay columns and 0–50 wt% in the controls. Generally, the control columns could highly retain the PTE content of Lavrion leachates, compared to the respective Kessariani leachates. Finally, a significant retention of the soil leachable Fe and Al was also observed by all clay columns, being 70–100 wt%. The respective retention in the controls was 70–100 wt% for Fe and 20–100% for Al, respectively (Figure S1).

The second sampling was performed after 24 h of flushing (t_2). The collected effluents had a yellowish

Table 3 Descriptive statistics of pseudo-total elemental concentrations of the contaminated soils (mg/kg dry weight) and comparison with the respective literature data ($n = 5$)

	Pb	Cu	Zn	Mn	Fe
Soils of the current study					
Kessariani					
Mean	1690	30	118	507	21,500
Median	1658	30	108	513	21,565
Std	56	2	17	16	1168
%RSD	3	6	14	3	5
Min	1638	28	102	481	19,776
Max	1777	32	138	521	22,668
Lavrion					
Mean	4800	69	1590	1690	40,500
Median	4714	70	1597	1705	43,322
Std	285	1	79	29	6117
%RSD	6	2	5	2	15
Min	4412	68	1478	1652	29,647
Max	5151	70	1677	1723	44,047
Stratoni					
Mean	432	95	324	944	35,300
Median	436	94	323	10.7	8839
Std	10	2	13	1.1	25
%RSD	2	2	4	930	23,177
Min	419	92	310	956	44,320
Max	443	98	343	944	35,343
Soil reference data					
Athens urban soils ^a	45	39	98	554	24,000
Lavrion topsoils ^b	77	149	6500		
Lavrion overburden ^c	7305	186	6668	2189	44,771
Stratoni top soils ^d	895	150	654	3037	61,160
Stratoni garden topsoils ^e	1090	184	878	4470	45,700
European soils ^f	33	17	68	524	

Bold values denote that they exceed the respected limits for soils

^aAthens (Greece) urban topsoil geochemistry (AR) (Argyraki and Kelepertzis 2014)

^bLavrion topsoil data (Kalyvas et al. 2018)

^cPTE concentrations from the Lavrion overburden (unconsolidated material overlying the bedrock) (Demetriades 2010)

^dTopsoil concentrations in the wider Stratoni area (four acid digestion) (Kelepertzis et al. 2006)

^eGardening soil concentrations from Stratoni village (four acid digestion) (Argyraki 2014)

^fEuropean topsoil mean concentrations (AR) (Salminen et al. 2005)

color, and their pH was 4–5.5, whereas all the beds had been colored brown. The retention percentage decreased as higher leachate volumes passed through the columns. The clay-containing beds retained 57–68 wt% Pb, 31–44 wt% of Cu and 29–60 wt% of Zn in Lavrion. Additionally, ~ 40 wt% of Pb, 25–40 wt% of Cu and 30–40 wt% of Zn were retained for Stratoni leachates. Quartz removed ~ 20 wt% of each metal in these treatments. For Kessariani leachate, 50–60 wt% of Pb and 35–55 wt% of Zn were retained in the clay-containing beds, whereas 30% remained in quartz. However, Cu was only retained by MCM-Qz bed (30 wt%). Iron and Al were also retained by all columns, being 70–90 wt% in Lavrion, ~ 60 wt% in Stratoni and 70–80 wt% in

Kessariani leachates. The elemental concentrations in the effluents are provided in Tables S1 and S2, and the relative retention percentages in the different columns are shown in Figure S1 of the Online Resource file.

To further assess the sorption efficiency of the clay components of each column in respect to the three soil leachates, the sorbed metal amount (q , $\mu\text{g/g}$) onto the clay fraction at t_1 and t_2 was estimated by subtracting the amount retained in quartz columns from the total retained amount. The total elemental amount retained by each column (M_{tot} , μg) was calculated from the elemental concentration (C_{tot} , $\mu\text{g/l}$) and the cumulative effluent volume (V , L) that flew through the columns, as:

$$M_{\text{tot}} = C_{\text{tot}} * V \quad (1)$$

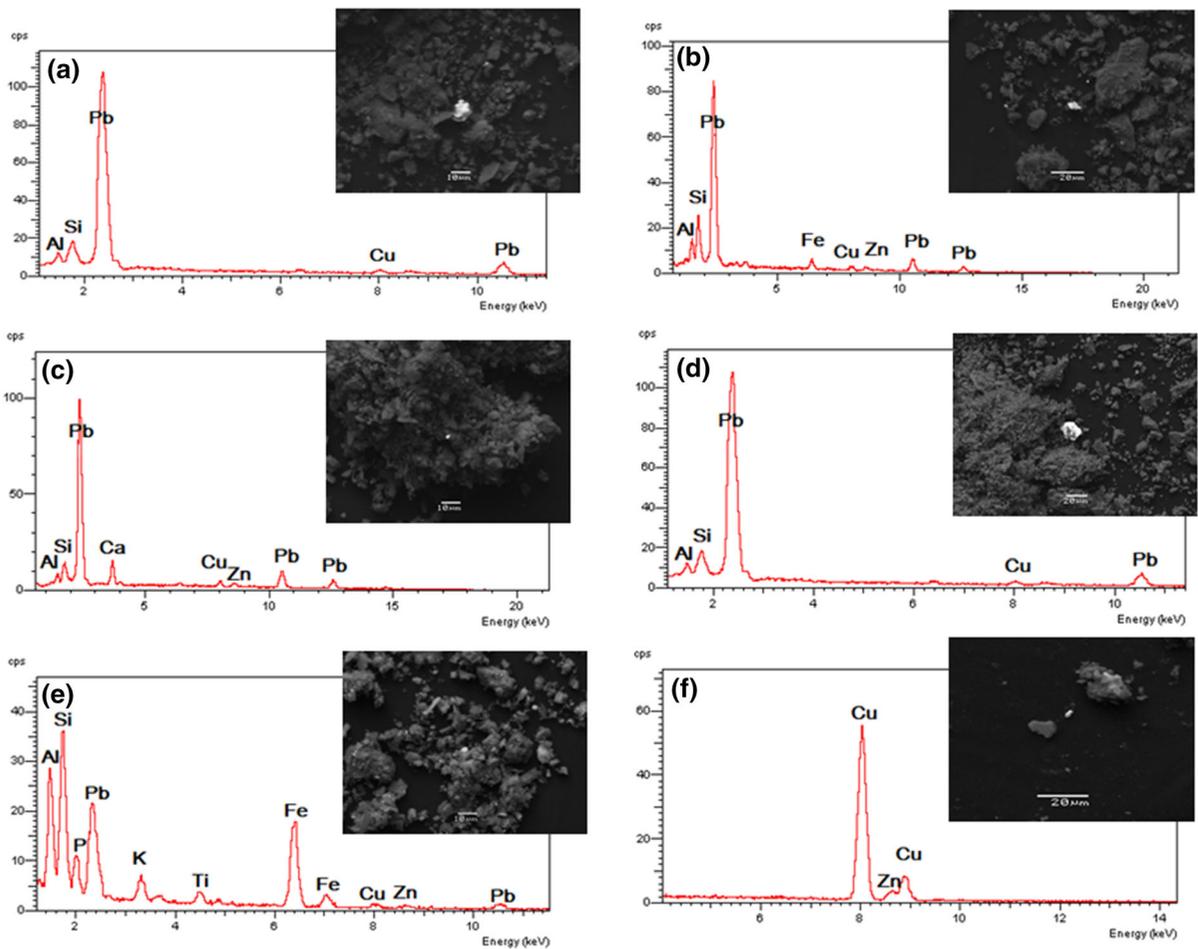


Fig. 1 SEM-EDS analysis of the Lavrion (a, b), Kessariani (c, d) and Stratoni (e, f) soil samples in BSE mode. The EDS spectra refer to the composition of bright grains, located in the center of

each image (The scale bars in all SEM images are 10 µm for a, c, e and 20 µm for b, d and f, respectively)

The sorbed metal concentration retained by quartz in sand columns is $q = M_{\text{qz}}/m_{\text{qz}}$, where m_{qz} is 4 g of quartz sand. The respective clay-containing columns contained 3.5 g of quartz therefore the metal fraction retained was $0.88 \cdot M_{\text{qz}}$. By subtracting this amount from the total retained in these columns, the fraction remaining upon the clay mass was estimated as:

$$q = \frac{M_{\text{cl}}}{m_{\text{cl}}} = \frac{M_{\text{tot}} - 0.88M_{\text{qz}}}{m_{\text{cl}}} \quad (2)$$

where m_{cl} is the clay mass (0.5 g) in the bed.

The respective q (µg/g) values for Pb, Zn and Cu for the three soil leachates are presented in Fig. 2. Kessariani leachate had higher initial Pb concentrations than Lavrion and Stratoni, and therefore all clays

sorbed higher Pb amounts. At t_1 (pH ~ 7), all clays sorbed 70–80 µg/g Pb from Kessariani leachates. SCM and MCM clays sorbed up to 40 µg/g Pb from Stratoni leachate, whereas only PCM managed to remove minor Pb from Lavrion leachate (~ 20 µg/g) (Fig. 2a). At t_2 (~ 24 h), the sorbed Pb content was ~ 300–350 µg/g for Kessariani, ~ 150–250 µg/g for Lavrion and ~ 50–100 µg/g for Stratoni leachates (Fig. 2b). In contrast, the Stratoni leachate had higher initial Cu concentration compared to the other leachates, therefore, up to ~ 16 µg/g of Cu were sorbed by the clays at t_1 (Fig. 3c) and ~ 25 µg/g at t_2 (Fig. 3d). The sorbed Cu content from Lavrion leachate at t_2 was < 10 µg/g by all clays, whereas ~ 5 µg/g from Kessariani leachate could remain sorbed by MCM (Fig. 3d). Finally,

Table 4 Chemical analysis of the soil leachates (mean \pm %RPD) and comparison with the maximum acceptable limits for waste characterization according to Directive 33/2003 (EU Council 2003)

Parameter	Soil samples			EC 33/2003		
	Lavrion ($n = 2$)	Stratoni ($n = 2$)	Kessariani ($n = 2$)	Inert wastes	Non-hazardous wastes	Hazardous wastes
pH	7.70 \pm 1.5	5.38 \pm 5.9	7.99 \pm 1.7			
Major ions (mg/kg)						
Ca	318 \pm 0	67 \pm 2	404 \pm 1			
Mg	24 \pm 5	15 \pm 6	32 \pm 2			
K	63 \pm 2	101 \pm 1	48 \pm 1			
Na	30 \pm 6	309 \pm 1	563 \pm 2			
Trace elements ($\mu\text{g}/\text{kg}$)						
Pb	2295 \pm 4	1826 \pm 0	6160 \pm 2	500	10,000	50,000
Cu	141 \pm 1	645 \pm 3	152 \pm 0	2000	50,000	100,000
Zn	2399 \pm 6	4052 \pm 4	370 \pm 16	4000	50,000	200,000
Mn	1817 \pm 3	17,902 \pm 0	2026 \pm 3			
Fe	8200 \pm 17	16,155 \pm 4	5505 \pm 12			
Al	18,165 \pm 15	21,465 \pm 0	8700 \pm 9			

Bold values denote that they exceed the respected limits for soils and wastes according to EU legislation

Stratoni leachate was enriched in Zn (Table 3); therefore, the sorbed metal amount reached $\sim 140 \mu\text{g}/\text{g}$ at alkaline pH (t_1) (Fig. 3e) and $\sim 280 \mu\text{g}/\text{g}$ at acidic pH (t_2) (Fig. 3f). The respective sorbed Zn amounts for Lavrion leachates ranged from 120 to 180 $\mu\text{g}/\text{g}$. The sorption selectivity of PTEs at t_2 follows the order $\text{Pb} > \text{Zn} > \text{Cu}$ for Kessariani leachates, whereas for Stratoni and Lavrion is $\text{Zn} > \text{Pb} > \text{Cu}$, regardless the composition of the clay bed (i.e., palygorskite or Fe-smectite-rich).

Geochemistry of soil porewater in clay-treated soils

The clay treatments had no significant effect in the soil pH and chemical composition of porewater compared to the control samples. Significant changes were observed only for the Stratoni soil and included the increase in soil pH from 5.10 to 6.67 and the reduction in Zn from 1500 $\mu\text{g}/\text{l}$ (control) to 95–500 $\mu\text{g}/\text{l}$. However, there was no systematic trend between the 2% and the 10% clay treatments. The respective porewater data are available in Table S1 (Online Resource) and were used as input to PHREEQC, in order to estimate the aqueous species and saturation indices of selected phases that control the mobility of PTEs in the porewater of soils.

The speciation of PTEs in porewater as predicted by PHREEQC is presented in Table 5. The saturation indices of selected solid phases are provided in Table S3 (Online Resource). Due to the elevated pH (> 7), and the presence of carbonates, Pb in the porewater of Kessariani soil is predicted to form mainly aqueous PbCO_3 (65–78%) complexes, whereas a small percentage maybe present in the form of PbOH^+ ($\sim 10\%$) and Pb^{2+} ($< 10\%$) (Table 5). Furthermore, the data showed that the solutions are oversaturated in respect to hydro/cerussite ($\text{SI} \sim 0-1$) and $\text{Pb}_3(\text{PO}_4)_2$ ($0 < \text{SI} < 1.5$), and in equilibrium with $\text{Pb}(\text{OH})_2$ ($\text{SI} = 0$) (Table S3). Copper is mainly mobilized as aqueous CuCO_3 (77–85%), whereas CuOH^+ and Cu^{2+} consist $< 10\%$ of dissolved phases. Additionally, Zn is predicted to be present as Zn^{2+} (70–82%) and aqueous ZnCO_3 (10–20%) (Table 5). However, no secondary Cu and Zn solid phases (i.e., anglesite, smithsonite, malachite, etc.) are expected to form ($\text{SI} < -1$). The solutions are also oversaturated in respect to Fe-oxyhydroxides (e.g., goethite, ferrihydrite, lepidocrocite) ($3 < \text{SI} < 5$), in equilibrium with Al-oxyhydroxides ($0 < \text{SI} < 1$) (e.g., gibbsite, boehmite) and undersaturated in respect to amorphous $\text{Al}(\text{OH})_3$ (Table S3).

The pH of Lavrion soils was also alkaline ($\text{pH} > 7$). The respective PHREEQC speciation calculations for

Fig. 2 Sorbed Pb, Cu and Zn concentrations ($\mu\text{g/g}$) (mean \pm RPD) by the clay and quartz sorbents obtained at the two sampling times (t_1 and t_2) in respect to the soil leachates

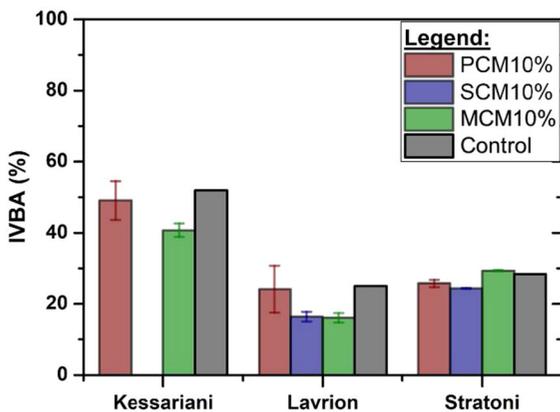
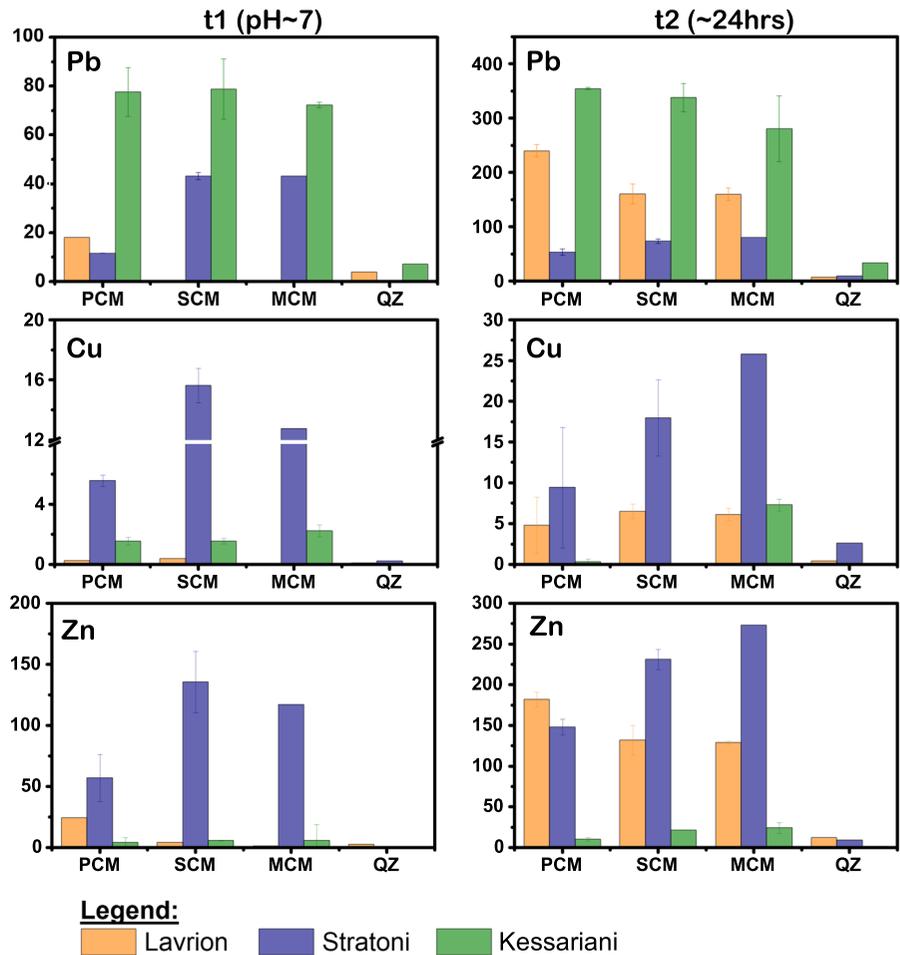


Fig. 3 Relative in vitro bioaccessibility (mean \pm RPD) in respect to Pb for each soil treatment (There are not available data for the 10%SCM Kessariani treatment)

Pb indicated that the uncharged $\text{PbCO}_3(\text{aq})$ complexes are the dominant aqueous species in all Lavrion porewater samples (67–77%) (Table 5); however, the solutions are undersaturated in respect to any Pb hydroxycarbonate phase ($\text{SI} < -0.5$) or phosphates ($\text{SI} = -3$) (Table S3). PbOH^+ and Pb^{2+} consist of the remaining 10–14% and 5–11% of the total Pb content, respectively (Table 5). $\text{PbSO}_4(\text{aq})$ complexes are predicted to be less than 1%, and most of the sulfates remain in the anionic form. Copper is present as $\text{CuCO}_3(\text{aq})$ (76–86%), whereas charged complexes, Cu^{2+} and CuOH^+ , account for up to 10% each (Table 5). The predominant Zn forms are Zn^{2+} (70–80%) and $\text{ZnCO}_3(\text{aq})$ (< 20%), whereas ZnOH^+ and $\text{ZnSO}_4(\text{aq})$ are less than 10% (Table 5). The solutions are also undersaturated to any carbonates or sulfides of Cu and Zn (Table S3). However, the

Table 5 Relative concentration of Pb aqueous species in soil porewaters (% to the total) of selected aqueous phases calculated with PHREEQC code (minteq.v4 database)

Element	Aqueous species	Kessariani (%)	Lavrion (%)	Stratoni (%)
Pb	Pb ²⁺	5–9	5–13	65–77
	PbOH ⁺	10–15	10–14	< 5
	PbCO ₃ (aq)	62–76	62–77	< 2
	PbHCO ₃ ⁺	< 5	< 5	< 2
	PbSO ₄ (aq)	< 2	< 5	20–30
	Pb(OH) ₂ (aq)	< 1	< 1	< 1
Cu	Cu ²⁺	< 5	3–8	72–88
	CuOH ⁺	7–11	7–11	< 5
	CuCO ₃ (aq)	77–85	76–86	< 5
	CuSO ₄ (aq)	< 1	< 1	10–16
Zn	Zn ²⁺	67–82	70–80	83–97
	ZnOH ⁺	< 5	< 5	< 1
	ZnCO ₃ (aq)	7–20	7–19	< 1
	ZnHCO ₃ ⁺	< 5	< 5	< 1
	ZnSO ₄ (aq)	< 10	< 10	3–16
	Zn(OH) ₂ (aq)	< 1	< 1	< 1

presence of Fe-oxyhydroxides ($1.9 < SI < 4.0$) and boehmite ($0 < SI < 1.2$) (Table S3) is slightly favored under these conditions.

The speciation calculations on all Stratoni porewaters showed that PTEs are mobilized as Pb²⁺ (65–77%), Cu²⁺ (72–88%) and Zn²⁺ (83–97%) (Table 5). The high sulfate content may also favor the formation of PbSO_{4(aq)} (20–27%), CuSO_{4(aq)} (10–16%) and ZnSO_{4(aq)} (3–16%) (Table 5), but the solutions are undersaturated in respect to anglesite ($SI < -3$), chalcantite ($SI < -7$) and zincosite ($SI < -13$). The presence of Al- and Fe-oxyhydroxides is ambiguous (Table S3).

Evaluation of bioaccessibility of PTEs in treated soils

The determination of the bioaccessible PTE fraction is crucial when assessing the risk to exposed populations, especially when considering health risks of Pb intake by children due to the hand-to-mouth habit. The released concentrations (mean \pm RPD%) of selected elements (Pb, Zn, Cu, Fe, Mg) after the SBET extraction are given in Table 6. The solid extracts of the 10% clay treatments exhibited a relative decrease in Pb, Cu, Zn and Fe compared to control samples. The respective Pb and Cu concentrations in the extracts of

the 2% clay treatments showed minor to no decrease, whereas Zn was even mobilized in Stratoni treatments (Table 6). The relative in vitro bioaccessibility (IVBA) was determined for Pb for the 10% treatments as follows:

$$IVBA (\%) = \frac{C_{\text{ext}}}{C_{\text{tot}}} \times 100 \quad (3)$$

where C_{ext} is extractable Pb concentration of SBET (mg/kg) and C_{tot} , the near-total Pb concentrations (mg/kg) presented in Tables 3. The IVBA values of Pb of clay-treated samples in respect to controls are presented in Fig. 3 and follow the order: Kessariani (52%) > Stratoni (28%) > Lavrion (25%). The application of 10% PCM amendment, did not alter the bioaccessible Pb fractions (4–8%) in all soil samples compared to the controls. Although the statistical significance of differences between the treatments could not be calculated, due to limited number of replications, the reduction percentages of each treatment are presented in Fig. 3, as an indication of their effectiveness. Specifically, the 10% SCM amendment reduced the Pb IVBA values by 34% and 13% in the Lavrion and Stratoni soils, respectively. Additionally, the 10% MCM amendment induced a 22% and 36% reduction in Pb IVBA values of the Kessariani and Lavrion soils, respectively.

Table 6 Elemental concentrations (per mg/kg of dry mass) of the solids extracted by SBET extraction test (mean ± RPD %)

Elements	Control	PCM 10% (%)	PCM 2% (%)	SCM 10% (%)	SCM 2% (%)	MCM 10% (%)	MCM 2% (%)
Kessariani							
Pb	874	827 ± 23	851 ± 0	n.d.	657 ± 5	686 ± 9	782 ± 20
Cu	12	8 ± 2	11 ± 18	9 ± 19	11 ± 17	9 ± 14	11 ± 5
Zn	63	30 ± 7	42 ± 23	26 ± 14	37 ± 19	29 ± 13	29 ± 24
Fe	364	258 ± 11	434 ± 70	284 ± 25	503 ± 62	346 ± 26	432 ± 3
Mg	3940	4570 ± 9	5780 ± 13	4560 ± 4	4110 ± 21	5930 ± 11	5170 ± 8
Lavrion							
Pb	1200	1160 ± 55	1010 ± 28	790 ± 17	1910 ± 31	770 ± 17	1060 ± 34
Cu	17	14 ± 0	16 ± 35	12 ± 21	16 ± 5	12 ± 26	20 ± 42
Zn	543	480 ± 19	572 ± 44	451 ± 16	596 ± 21	463 ± 23	536 ± 5
Fe	684	504 ± 27	640 ± 77	592 ± 39	637 ± 29	532 ± 15	904 ± 68
Mg	465	733 ± 0	565 ± 5	1290 ± 2	700 ± 11	1910 ± 0	800 ± 2
Stratoni							
Pb	122	111 ± 8	135 ± 21	105 ± 1	159 ± 60	127 ± 1	142 ± 15
Cu	27	19 ± 9	25 ± 22	19 ± 3	32 ± 72	21 ± 11	28 ± 32
Zn	57	83 ± 62	71 ± 19	112 ± 4	88 ± 52	113 ± 52	56 ± 21
Fe	687	537 ± 43	632 ± 2	447 ± 16	1980 ± 160	654 ± 18	1070 ± 71
Mg	239	417 ± 56	771 ± 122	944 ± 36	1210 ± 124	1040 ± 102	291 ± 33

n.d. not determined

Apart from Pb, Zn and Cu, significant changes in the concentrations of Mg and Fe were observed in the solid extracts of the clay treatments compared to control samples. The untreated soils (controls) released 240–3900 mg/kg Mg, whereas the clay-amended soils released systematically higher Mg concentrations (300–5900 mg/kg); the highest values were observed in the extracts of the 10% MCM treatments (Table 6). Additionally, the control soils released 360–690 mg/kg Fe, whereas the 2% treatments released 400–2000 mg/kg and the 10% treatments 260–650 mg/kg Fe, respectively (Table 6).

Two treated soil samples were selected and studied using SEM–EDS in order to identify possible changes in the morphology and chemistry of the solids after the interaction with the glycine extract (Fig. 4). The selected samples included the 10% MCM Kessariani treatment, and the 10% SCM Stratoni treatment, which showed the lowest relative bioaccessibility (i.e., the highest immobilization) of Pb. According to EDS spectra, Pb in the 10% MCM Kessariani treatments was associated with Ca and P in the treated soils (Fig. 4a, c). However, the SBET solid residue (Fig. 4b, d) was characterized by areas where soil

grains appear consolidated by an amorphous Fe-rich material which contained up to 62 wt% Fe and 2 wt% Pb. Similar consolidated soil masses were also observed to a lesser extent in the 10% SCM Stratoni treatment, which contained minor Pb (~ 2 wt%) (Fig. 4e, f).

Discussion

The studied soils are characterized by elevated near-total PTE concentrations (Table 3), being much higher compared to the respective mean values of European soils (33 mg/kg Pb, 17 mg/kg Cu, 68 mg/kg Zn) (Salminen et al. 2005). Lead concentrations in all three soils also exceed the Dutch intervention values (530 mg/kg Pb) (VROM 2013), whereas Lavrion soil has also elevated Zn concentrations according to the Dutch List (720 mg/kg Zn) (VROM 2013). The soils are classified as low-level contaminated wastes, according to South Australia EPA classification of solid wastes (SA EPA 2010).

While the total elemental concentrations in soil provide an estimation on their contamination, the

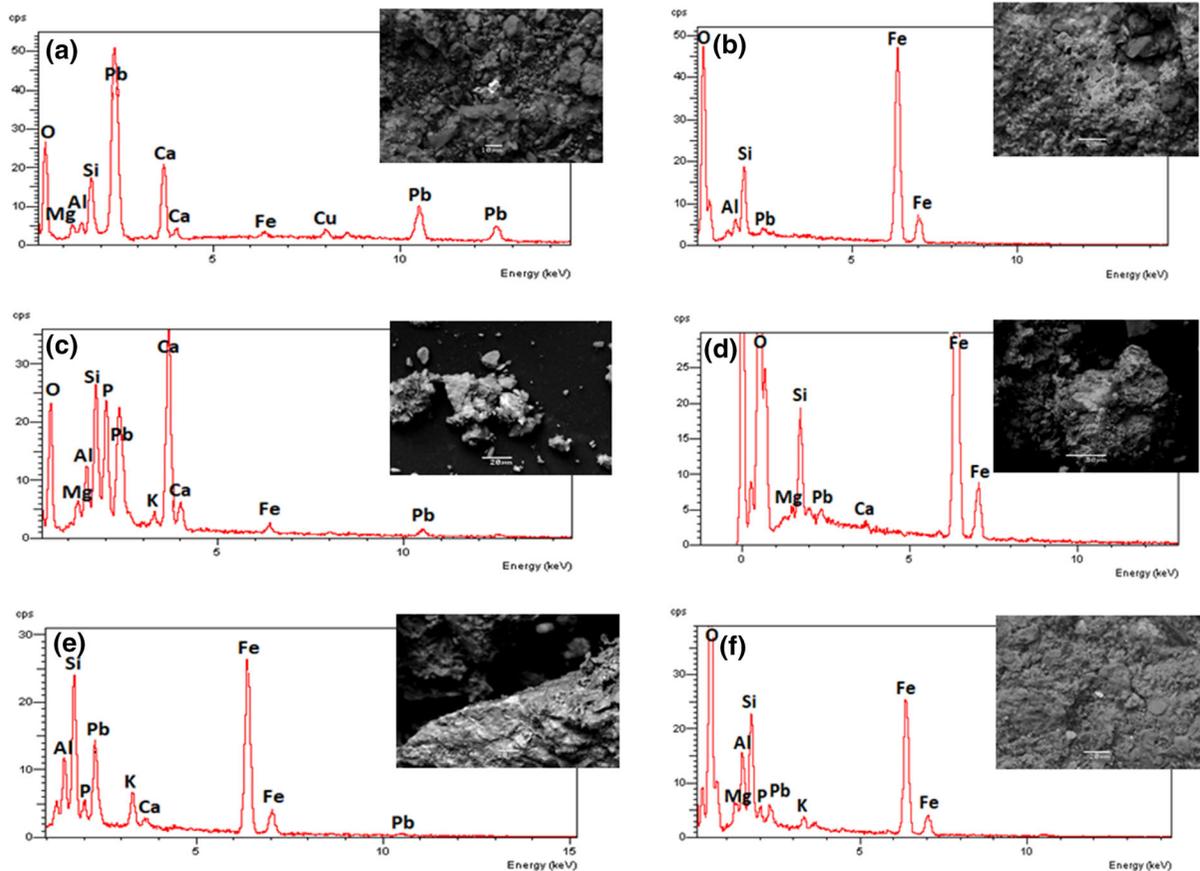


Fig. 4 SEM-EDS analysis of the 10% MCM Kessariani (a, c) and the 10% SCM Stratonii (e) soil treatments prior to SBET extraction, and the 10% MCM Kessariani (b, d) and the 10%

SCM Stratonii (f) residues after the SBET extraction (Scale bars in the presented captions include 10 μm (a), 20 μm (b, c, e, f) and 50 μm (d), respectively)

potential environmental hazard is preferably assessed by the mobile PTE fraction. The mobilization of PTEs in contaminated soil depends on their speciation, and the environmental changes that control (a) the stability of the hosting phases, (b) the kinetics of PTE release and (c) their transportation by the colloidal fraction (Berkowitz et al. 2008; Sparks 2005). Furthermore, under natural field conditions, PTEs are mobilized by percolating water, which is retained within the soil as porewater. Porewater is readily accessible by plants and microorganisms, and its chemistry is important in the evaluation of the potential hazard in an area (Liu et al. 2018; Song et al. 2017). For this reasons, international standards, such as the Directive EC 33/2003, were established based on the water-leachable PTE content of solid wastes, rather than their total amount. Based on Directive EC 33/2003, all three soils are characterized as “non-hazardous waste” due to high Pb concentrations, which

exceed the limit of “inert waste” (Table 4). The following discussion examines the mobilization of PTEs in each soil, based on their mineralogical and physico-chemical characteristics.

Mobilization of PTEs in the ex-firing range

Firing ranges and shooting sites are areas of high environmental concern, due to increased concentrations of Pb in the soils from the erosion of bullets and cartridges that are spread to the soil surface (Marjussen et al. 2017; Sanderson et al. 2012; Urrutia-Goyes et al. 2017a). The Kessariani soil was collected from an urban park which acted as a former recreational firing range (Argyraiki and Petrakaki 2010). Lead in this soil is concentrated in Pb-rich phases (> 50 wt%) (Fig. 1c, d), most probably lead carbonates. The presence of hydro/cerussite crystals, mainly

on the surface of bullet fragments, has been identified in shooting range soils (Mariussen et al. 2017; Sanderson et al. 2012). Previous research into the mobilization of Pb at this particular site has confirmed the rapid formation of Pb-carbonate phases on the surface of shots and their subsequent dissolution under surface soil conditions (Argyrazi et al. 2011). Moreover, despite Pb carbonates being rather resilient to weathering ($-13.3 < \log K_{sp} < -18.8$ for, *min-teq.v4* database), the abrasion of the solid grains during mixing (Hardison et al. 2004) could have also contributed to the high water-leachable Pb concentrations (Table 4 and Table S3). Water can readily oxidize the surface of the bullet fragments that are dispersed within the soil of shooting ranges (Argyrazi et al. 2011; Hardison et al. 2004; Ma et al. 2007). In contrast, Zn and Cu were found in association with Al–Si-rich grains (Fig. 1c, d), on which are retained through sorption, and therefore their release with water is expected to be limited (Table 4).

The high soil pH and the presence of carbonates supports the hypothesis that Pb and Cu are mobilized as aqueous carbonates ($\text{PbCO}_{3(\text{aq})}$ and $\text{CuCO}_{3(\text{aq})}$, $> 60\%$), whereas Zn is mostly present as Zn^{2+} ($> 67\%$) (Table 5). The presence of PTEs as uncharged aqueous species plays an important role in their interactions with the charged soil phases. Ostergren et al. (2000), who studied the Pb– CO_3 –goethite system, revealed that, at solution pH 4.5–6.5, sorption of Pb was enhanced by the formation of a ternary Pb-carbonate complex in the surface of goethite, whereas, at pH > 7 , the goethite–Pb interactions were hindered by the formation of $\text{PbCO}_{3(\text{aq})}$ species. Considering the above, the high mobility of Pb and Cu in Kessariani samples may be explained by the highly alkaline pH, which hinders the interaction of these metals with the clays and Fe–Al phases of the soil (Abad-Valle et al. 2016). Consequently, assuming that Pb and Cu are mobilized as $\text{PbCO}_{3(\text{aq})}$ and $\text{CuCO}_{3(\text{aq})}$ they would remain in the solution, unless oversaturation prompts precipitation of hydro/cerussite phases, such as those suggested by Kypridou and Argyrazi (2018). In contrast, Zn predominates as Zn^{2+} and can be more easily removed by the soil Fe–Al colloids and clays.

Mobilization of PTEs in the mining soils

The other two soil samples tested originate from a historical (Lavrión) and an active (Stratóni) sulfide mining area. In such areas, the speciation of released PTEs controls their solubility, mobility, bioavailability and toxicity. Acid mining drainage (AMD) is the major problem in sulfide mining areas, as the highly acidic environment (produced by the oxidation of sulfide ores) promotes the mobility of PTEs, and therefore their bioavailability in living organisms (Tabelin et al. 2018).

In the Lavrión soil samples, PTEs are mainly related to Fe oxides, sulfates, carbonates and slag (Argyrazi et al. 2018). Grains rich in Pb ($\sim 80 \text{ wt}\%$) are also probably hydro/cerussite, whereas the minor Cu and Zn ($\sim 2 \text{ wt}\%$) are related to the Al–Si soil matrix, as well as Fe oxides (Fig. 1a, b). Speciation calculations predict that Pb and Cu are mainly present as carbonates ($> 62 \text{ wt}\%$) due to the high soil pH (Table 5); however, the low concentrations would not prompt the formation of the respective precipitates, as in Kessariani soil (Table S4). Therefore, contrary to Kessariani soil, Pb and Cu would exhibit high mobility due to the absence of precipitates that would remove the elements from the solution. The effectiveness of palygorskite in stabilizing the contaminants present in Lavrión soils has previously been confirmed by laboratory and field-scale experiments, where the application of 10% palygorskite reduced the water-leachable fraction by up to 65 wt%, by increasing the soil pH from 6.5 to 8.2 (Zotiadis et al. 2012). However, the studied soil samples are alkaline; therefore, the presence of clays would not have significant effect in stabilization of PTEs through increasing the soil pH (Abad-Valle et al. 2016), as in Kessariani soils.

Stratóni is an active mining site, where the oxidation of sulfide minerals still occurs producing high sulfate concentrations (up to 240 mg/l in porewater) and mobilization of metal ions. Based on previous research (Argyrazi et al. 2007; Argyrazi 2014), Pb is mainly related to Fe–Mn oxides and phosphates. The Stratóni soil sample of the present study is mildly acidic (pH 5.7), without carbonate phases. Lead, Zn and Cu were found in association with Fe–Mn phases and phosphorous (Fig. 1e). Pyromorphite (a Pb-phosphate) has previously been reported in the garden soil of Stratóni village (Argyrazi, 2014). Lead phosphates are highly stable ($-23.8 < \log K_{sp} < -84.4$,

minteq.v4 database), justifying the lower water-leachable Pb concentrations (Table 4 and Table S3). Cu-rich grains (80 wt% Cu) associated with Zn (Fig. 1f) could originate from slag. Furthermore, the high sulfate concentrations (~ 6 mg/kg) in the soil leachates imply the oxidation of primary sulfides (galena and sphalerite) with concomitant release of Pb and Zn into the soil solution. Dissolved PTEs are mainly present as free cations (> 65 wt%) or aqueous sulfates (up to 30 wt%) (Table 5) and sorbed by Fe-oxyhydroxides through the formation of Fe-hydroxide/metal/SO₄ ternary complexes (Swedlund et al. 2003, 2009).

The interactions of Fe-rich clays with soil leachates

The retention efficiency of the selected Fe-rich clays regarding Pb and Cu has been extensively studied using laboratory mono-elemental aqueous solutions (Kypridou and Argyraki 2018). The results showed that sorption capacity for both Pb and Cu followed the order MCM $>$ SCM $>$ PCM, showing that sorption is primarily controlled by the mineralogical and physicochemical properties of the clay. Furthermore, that study emphasized the synergistic effect of the coexistence of palygorskite and Fe-smectite in MCM sample that resulted in its higher sorption capacity compared to the other Fe-rich clays (PCM and SCM).

However, in more complex systems, such as the soil solutions (leachates and porewater) of the present study, PTEs are not merely present in free cationic forms. Soil leachates contain a variety of additional phases, i.e., anionic species, organic matter and colloidal particles, upon which the PTEs are strongly bound and transported through the solid pores (colloid-facilitated transport) (Kretzschmar and Schäfer 2005; Sparks 2005). The studied soil leachates are characterized by a significant colloidal fraction (Table 3). The Fe and Al concentrations in the soil leachates followed the order Stratoni $>$ Lavrion $>$ Kessariani (Table 3). It is proposed that these Al-Fe colloids (mainly oxyhydroxides) are the main carriers of PTEs in the leachates, and a significant PTE amount is removed from the solutions through their entrapment by the colloids (Figure S1). Consequently, the removal of colloids from the aqueous phase would lead to a concomitant removal of PTEs.

The presence of both clay and quartz particles in the column experiments plays a significant role in the retention of the Fe-Al colloids, by altering the pH of the passing-through leachates. The buffering capacity of the studied clays as described by their high PZC, (Table 1) and its role in the retention of Pb and Cu from mono-elemental aqueous solution was attributed to the protonation of the silanol (SiOH $<$) and/or aluminol (AlOH $<$) surface groups of palygorskite and Fe-smectite clay particles (Kypridou and Argyraki 2018). However, protonation reactions occur also in the silanol edges of quartz grains (Pokrovsky et al. 2006). As a result, the water-saturated columns had an alkaline porewater prior to flushing with the acidified soil leachates. When the leachates entered the columns, they were neutralized, leading to 100% retention of Fe and Al by all columns, regardless the solid or leachate composition (sampling time t_1) (Figure S1). Following this, the retention efficiency of Pb, Cu and Zn ranged between 40 wt% (in the control columns) and 100 wt% (in clay-containing columns). Speciation calculations using PHREEQC showed that, at alkaline pH (> 7), precipitation of ferrihydrite is favored (SI $\sim 1-3$), a Fe-oxyhydroxide that acts as sink of PTEs in natural environments by forming surface coatings on soil grains. The effluents were also undersaturated in respect to amorphous Al(OH)₃ (SI < -3) and in equilibrium with boehmite (SI ~ 0.5). Fe-coated quartz has shown high sorption efficiency toward PTEs (Lee et al. 2012). However, the high reactive surface of the clay particles may further enhance the retention of Fe-Al colloids (and subsequently the co-precipitation of PTEs), compared to quartz (Zhu et al. 2011). The prolonged flushing (for ~ 24 h) of the columns with the acidified influent (pH ~ 3.6) resulted in decreasing the pH in the column porewater, and in mobilizing the elements that were initially deposited upon the solid bed. Although a significant amount of Al and Fe remained sorbed by the quartz columns (control) at the second sampling (t_2 , 24 h) (> 50 wt% of both Fe and Al), the sorbed Pb, Zn and Cu amount was < 30 wt%. However, the clay-containing columns retained a significant amount of Pb, Zn and Cu (up to 50%). This difference indicates that the interaction of PTEs with the clay components of the beds hindered their mobilization and elution from the columns, compared to quartz sand. Sorption by clays could be achieved through the interaction of PTEs with the exposed clay structure (i.e., the part of

the clay surface that was not covered by the Fe–Al colloids) or by the sorption onto clay-hydroxide complexes. Such complexes are formed by the fixation of hydroxo-Al and hydroxo-Fe phases onto the clay surface, providing more active –OH surface groups for deprotonation and complexation of metals (Zhu et al. 2016). These complexes are found in acidic to mildly acidic soils and have higher affinity for PTEs than pure Al hydroxides (Carrillo-González et al. 2006). Moreover, metal solid phases such as carbonates (i.e., hydro/cerussite, smithsonite, etc.), sulfates (i.e., angle-site), chlorides and oxides were undersaturated in both sampling times.

The experiment with contaminated soil leachate demonstrated that the retention of PTEs by the clay beds is controlled by processes that differ from those occurring in the mono-elemental concentrated solutions. The interactions between the metals and the clay surfaces are primarily controlled by the speciation of PTEs in the initial aqueous system. The major factor controlling the sorption of PTEs is the presence of additional substances that can either block or compete for the sorption sites, depending on the environmental conditions (e.g., the pH). This is of high importance in acid mine drainage environments, where the presence of Fe colloids plays a major role in the speciation of PTEs (Jung et al. 2012).

Effect of Fe-rich clay treatments in bioaccessibility of Pb

The efficiency of the Fe-rich clay amendments in the stabilization of Pb was assessed by determining the bioaccessible Pb fraction which is primarily linked to health risks (Bolan et al. 2014). The reduction in the bioaccessibility of Pb in amended soils is depended upon the type of soil, the presence of soil colloidal phases and the organic matter that may enhance or inhibit the stabilization properties of the amendments (Sanderson et al. 2015).

The relative *in vitro* bioaccessibility (IVBA) of Pb in the control soils follows the order: Kessariani (52%) > Stratoni (28%) > Lavrion (25%) (Table 6). The respective near-total Pb concentrations follow the order: Lavrion (4800 mg/kg) > Kessariani (1700 mg/kg) > Stratoni (432 mg/kg) (Table 3). The high IVBA value of Kessariani soil is attributed to the Pb-carbonate phases, which are the major hosts of the element in the untreated soil sample and are readily

soluble under acidic conditions. High bioaccessibility of Pb in soils originating from shooting ranges has been reported by various authors and was correlated with their exchangeable and carbonate fraction (Kelebemang et al. 2017; Sanderson et al. 2012). Higher bioaccessibility is observed for Pb hydro/oxides, carbonates and chlorides compared to sulfates, chromates and phosphates (Walraven et al. 2015). Moreover, the erosion of Pb fragments by the acidic glycine solution during the SBET test could also increase the IVBA values in the respective soils. This agrees with the lower IVBA values observed in Lavrion and Stratoni samples, where Pb is mainly bound to Fe–Mn–Al oxides. The IVBA values of Stratoni is lower than those reported for the respective garden soil and house dust of the Stratoni village (~ 40%) (Argyraiki 2014).

The impact of the acidic solution (pH ~ 1.5) used in SBET on the clay amendments was evident by the relative changes in the Mg and Fe content of the soil residues after the extraction compared to the control. The increase in the concentration of Mg in the extracts of the treated soils, compared to control (Table 6), confirms the dissolution of the clay components present in the clay amendments (Bickmore et al. 2001; Gainey et al. 2014; Komadel and Madejová 2006). Among the clays, MCM is the most Fe–Mg-rich and therefore the high Mg release in MCM treatments is explained. Additionally, an increase in the leachable Fe concentrations was observed in the 2% clay treatments, whereas a relative decrease in Fe was exhibited in the 10% clay treatments, compared to the control (Table 6). This decrease was attributed to the Fe hydrolysis and oversaturation of the extracts (owing to the higher clay amount). Further analysis of the 10%-treatments using SEM–EDS (Fig. 4) confirmed the existence of an amorphous Fe-rich coating onto the solid grains. The absence of well-defined crystal morphology of these phases implies that they were formed due to mobilization of Fe from the dissolved components of the clay amendments, when compared to the control samples (Gainey et al. 2014). These changes were more profound in Kessariani soils, which are poor in primary Fe oxides. However, in the 2% treatments the mobilized Fe was not enough to prompt oversaturation, and therefore remained in solution, thus increasing the Fe concentration in the extracts (Table 6).

The observed Fe-rich coatings were also associated with minor amounts of Pb (Fig. 4). Although there is no systematic trend between the released Pb and Fe concentrations in the soil extracts (Table 6), the SEM–EDS observations indicate that the decrease in IVBA of the 10% MCM treatment of Kessariani soil could be attributed to the entrapment of Pb in the secondary Fe phases (Fig. 4b, d). The specific nature of these Fe-rich phases that may entrap PTEs in the acidic SBET solutions was could not be identified during examination by SEM–EDS (possibly due to overlapping spectral peaks of Pb $M\alpha$ and S $K\alpha$ at 2.28–2.35 keV region) (Newbury 2009). However, in acidic environments, such as in acid mine drainage (AMD), Fe can be present in the form of schwertmannite and jarosite, two common Fe-rich sulfates. Schwertmannite ($Fe_{16}^{3+}O_{16}(OH)_{12}(SO_4)_2$) maybe formed through abiotic precipitation and/or hydrolysis of Fe^{3+} at $pH > 1$, whereas jarosite ($KFe_3^{3+}(SO_4)_2(OH)_6$) is present at $pH < 2$ in an AMD environment. These phases are poorly crystallized (España 2007; Zhang et al. 2018), and their presence especially in Stratonis samples (which had high sulfur concentrations, Table 5) cannot be excluded. Considering the above, the role of Fe in reducing the bioaccessibility of PTEs in soils amended with Fe-rich clays needs further investigation.

Conclusions

The clay–soil–PTE ternary system is characterized by high complexity. The soil characteristics play the major role in the mobilization, transportation and interaction of PTEs with the soil components. In alkaline carbonate-rich soils, PTEs are mobilized and may precipitate as carbonates, or sorbed by the soil Fe–Al-oxyhydroxides. In acidic soils, where carbonates are absent, PTEs are mobilized in the form of free cations and aqueous sulfates. The increase in pH due to the clay amendments reduced PTE mobility and enabled the interaction of the metal with the clay surfaces.

The interaction of PTEs present in soil leachates with the Fe-rich clays showed that retention of PTEs is governed by changes in the overall physicochemical conditions of the system, primarily induced by the clays. The colloid-facilitated transport of PTEs in soil leachates inhibits direct interaction of PTEs with the

clay surface. The role of colloids in the retention of PTEs by the clay surfaces is ambiguous, since the colloidal coatings may prevent sorption, by blocking the pores of clay structure. However, the high buffering capacity of Fe-rich clays prompts the precipitation of the Fe–Al colloids, with concomitant removal of PTEs from the leachate. The noted effectiveness of Fe-rich clay amendments in reducing the relative bioaccessible Pb fraction was attributed to their Fe-rich nature. The entrapment of PTEs in secondary Fe-rich phases that were formed during the dissolution of the primary clay minerals showed the potential of Fe-rich clays as PTEs stabilizers. The presented research regarding the application of the clays as soil remediation agents demonstrated that stabilization of PTEs in soils is highly site-specific.

The current study provided an insight into the geochemical processes that occur at the clay/water interface of soil solutions (leachates and porewater). Some recommendations for further research aiming at understanding better the clay–water–PTE–system include the evaluation of the stabilization efficiency of the Fe-rich clays in respect to the extractability and phytoavailability of the contaminants in the amended soils.

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