Hindawi

Research Article

Chemical Speciation and Potential Mobility of Heavy Metals in Organic Matter Amended Soil

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Organic matter (OM) degradation from amendments used in the remediation of metal-contaminated soils leads to modifications in soil chemical properties immediately after addition, which can also affect the soil metal distribution. Therefore, the speciation and potential mobility of heavy metals e.g., lead (Pb) and cadmium (Cd) were evaluated in three soils amended with OM. Soils, both spiked (with lead nitrate and cadmium nitrate solution) and unspiked, were treated with OM at a rate of 5 tons/ha in a moist condition. The samples were in incubation for 30 days in 30% moist condition. A chemical fractionation procedure was applied to determine the distribution of Pb and Cd in soils. The potential mobility of metals was also determined. Metals transformed from mobile to immobile fractions in both spiked and unspiked soils (not treated with organic matter), but OM increased the mobile fraction of Pb in unspiked soil and decreased it in spiked soil. In contrast, the mobile fraction of Cd decreased in soils (not treated with OM), but the OM increased the mobile fractions in spiked and unspiked soils. The mobile fraction (as a percentage of total) of Cd was higher than the mobile fraction of Pb indicating the greater mobility of Cd compared to Pb. However, the three soils showed a more or less similar pattern in transforming Pb and Cd in soils since their characteristics were almost the same.

1. Introduction

Nowadays, contamination of soil with heavy metals is a widespread and crucial problem worldwide for human health and environmental standards. Uncontrolled industrialization, intensive agricultural activities, and industrial and urban sewage waste discharge have created heavy metal contamination in developing countries like Bangladesh. Properties like non-biodegradability, toxicity, ecological risk, bioaccumulation, persistence, ubiquity, biogeochemical recycling, and abundance make heavy metals a fascinating research arena [1–4]. Soil and sediments contaminated with heavy metals are often hazardous [5]. These heavy metals can deposit in the human body through the food chain and are very harmful agents for humans due to the lack of an efficient excretion mechanism in the human body [6, 7]. It causes lung cancer, proliferative lesions of the prostate, bone fractures, dysfunction of the liver and kidney, nerve tissue damage, and hypertension in humans [6, 8] by getting mixed up in the food chain [9, 10].

In case of contamination of soil by heavy metals, it is necessary to identify the available and unavailable forms of heavy metals so that the soil is managed in such a way as to prevent unavailable forms from becoming available. The total concentration of trace metals in the soil provides limited information about their toxic effects [11]. However, the forms of trace metals present in the soil determine their relative mobility and bioavailability. The availability of heavy metals in soils is closely related to their distribution and transformation in soils [12, 13]. Heavy metals are associated with soil components in different ways, and these associations indicate their mobility and bioavailability [14]. Bioavailability and metal mobility are also related. A higher concentration of mobile toxic metals (Cu, Pb, Cd, and Al) in

the soil increases the potentiality of the plant uptake and animal/human consumption [15, 16]. The bioavailability of heavy metals is associated with several factors, among which soil pH and soil organic matter (SOM) content are critical [17].

OM is a vital soil constituent influencing soils' physical, chemical, physicochemical, and biological properties. OM plays a significant role in forming complexes and retaining heavy metals in an exchangeable form [18]. Increasing the OM in the soil helps to minimize the absorption of heavy metals by plants. A land rich in OM actively retains metallic elements. OM can immobilize heavy metals or work as a factor that causes their release. These two properties affect each heavy metal differently [18]. For example, Cu is bound and rendered unavailable chiefly through the formation of complexes [19], while Cd is retained in an exchangeable form and is more readily available [20].

The decomposition of OM releases humic acids, which have a significant impact on the availability of metals. High molecular weight humic acids strongly bind metals and render the metals unavailable within the soil solution. Contrarily, low molecular weight humic acids enhance the availability of metals by forming chelates and preventing their adsorption onto solid surfaces [21]. The retention of cations by humic acid due to dissociation of functional groups is controlled by pH. At pH 6–8, humic acids develop a greater surface area and heavy metal retention peaks [21]. According to McBride [22], the sequence of affinity of divalent metal ions for OM is as follows: Cu > Ni > Pb > Co > Ca > Zn > Mn > Mg. Generally, more electronegative metal ions form a stronger bond with OM. Heavy Metal desorption from OM requires considerable activation energy to overcome [22].

OM content in soil has been shown to increase the uptake of lead (Pb) by roots [18], determine the nutritional status of the soil, keep heavy metals in an exchangeable form and chelate with heavy metals to increase metal bioavailability [23]. Some authors have pointed out that the Pb fixation by SOM is more critical than the fixation by hydrous oxides [24]. Basta et al. [25] described that Pb shows a strong affinity for SOM and forms innersphere metal surface complexes. Therefore, SOM should be considered as an essential sink of Pb in polluted soils. Again, low-molecular-weight OM fractions bound more Cd than higher-weight fractions, whose effects increased the Cd mobility [26].

OM reacts strongly with metals in soils; however, its transformation with time could modify its impact on metal behaviour in soils. Shortly after adding organic materials to soil, the effects on soil properties depend on the degradation process of such materials, which could affect heavy metal solubility. Martınez et al. [27] found a paralleled behaviour between dissolved organic C and total soluble metal concentrations in OM-rich soils, increasing with incubation time. Thus, the addition of OM can affect the transformation of heavy metals into the soil and affect their availability to plants.

In the case of plants, free metal ions in the soil solution may be more toxic than metals in the complex states [28].

Accordingly, only the labile metal species (soluble, exchangeable, and chelated) are available to plants. Thus, the detection of total concentrations must be complemented by evaluating available fractions of metals [29].

The information about the movement of heavy metals in the soil is essential for assessing the possible risks of metal contamination and the feasibility of its remediation in the soil. It's thus crucial for agriculturists to identify the heavy metals in the soil in both the available and unavailable forms, and this study will guide them in managing the soil in such a way as to prevent plant toxicity.

However, information regarding the effect of applied OM on the redistribution of metals in Bangladesh soils with exogenous metal contamination in the literature is scarce. The specific objective of this work was to determine the mobility and bioavailability of heavy metals (Pb and Cd) through the application of the geochemical fractionation technique and to assess the efficiency of organic amendments as alternative techniques to redistribute Pb and Cd in contaminated soils with time.

2. Materials and Methods

2.1. Experimental Setup. Composite soil samples were collected from the agricultural fields along the Karnatali and Dhaleshwari rivers exposed to different degrees of environmental pollution from nearly industrial effluents and wastes in Bangladesh. In Karnatali sampling area, two soil samples were collected from two different sampling points and one soil sample was collected from the Dhaleshwari sampling area and both areas were irrigated with river water. The locations are presented on a map with ArcGIS 9.3.1 (Figure 1). At every sampling point, samples were collected from the surface (depth up to 15 cm) using an augar. Each of the collected soil samples was air-dried and passed through a 2 mm stainless steel sieve for the incubation experiment. A portion of the soil sample (2 mm sieved) was further ground and passed through a 0.5 mm sieve for chemical analysis. Measurements of the soils' selected physical and chemical properties were carried out in triplicate according to conventional methods.

Leafy vegetables (spinach and red amaranth) were chosen as a source of OM because these vegetables are hugely grown in the sampling area and they will need less time for decomposition. The vegetables were collected from uncontaminated agricultural fields and carefully brought to the laboratory. The collected vegetables were washed with tap water, chopped into smaller pieces, and kept in a polythene bag for decomposition. After 15 days, the decomposed vegetables were spread on separate sheets of thick coarse brown paper and dried in air. The air-dried sample was oven-dried and ground with mortar and pestle. The ground sample was passed through a 0.5 mm sieve. The sieved samples were mixed thoroughly for making composite samples and preserved. Selected physical and chemical properties of OM were measured in triplicate according to the conventional methods.

Soil classification and essential properties of the soils and OM used are presented in Table 1.
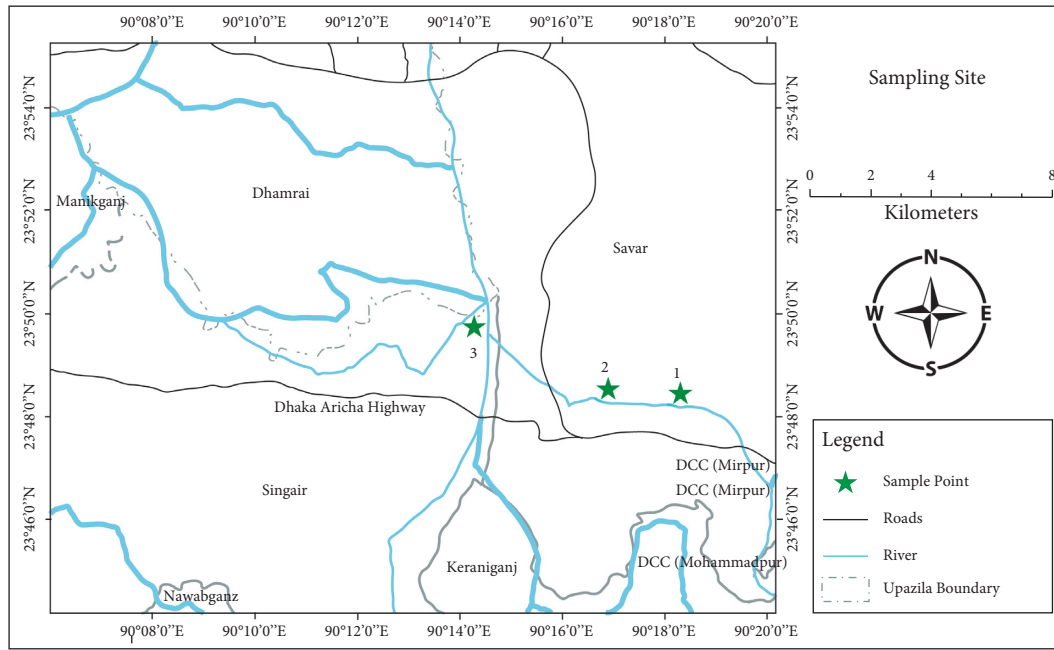
Figure 1: Location of sampling site.

Table 1: Characteristics of the soils and OM used in the experiment.

Parameter	Sampling point 1	Sampling point 2	Sampling point 3	OM
Moisture (%)	19.70	34.78	36.72	—
Texture	Silt loam	Silty clay loam	Silty clay	—
Sand%	3.17	7.69	1.23	—
Silt%	70.69	58.35	57.11	—
Clay%	26.14	33.96	41.66	—
pH	6.55	7.53	8.01	8.84
Organic carbon (%)	0.79	1.02	0.86	16.3
OM (%)	1.36	1.76	1.50	28.04
Total nitrogen (%)	0.08	0.10	0.09	1.60
C/N ratio	9.88	10.2	9.56	14.7
CEC (meq/100 g soil)	5.61	12.16	17.77	—
Total phosphorus (%)	0.05	0.04	0.04	0.79
Free carbonate (%)	2.31	2.59	2.72	—
Total Pb (mg/kg)	20.75	25.40	26.38	1
Total Cd (mg/kg)	0.28	0.21	0.38	BDL

BDL = below detection limit.

Before the experiment, an incubation study at a temperature of $24°C \pm 2°C$ was carried out in the laboratory. Fifteen grams of soil was taken in a 50 ml beaker. The initial concentration of Pb and Cd was 20.75 and 0.28 mg/kg in silt loam soil, 25.40 and 0.21 mg/kg in silty clay loam soil, and 26.38 mg/kg and 0.38 mg/kg in silty clay soil, respectively. The air-dried soils (<2 mm) were spiked with lead nitrate and cadmium nitrate solution so that the concentration of these metals in each soil sample became 100 mg/kg. The measured metal concentration in soils after spiking was about 90 mg/kg. Moist OM (15% moist) was mixed with the soil on an oven-dry weight basis at the rate of 5 tons/ha. 30% moist condition was maintained by periodic addition of deionized water throughout the experiment. A control treatment was done. Beakers were covered by parafilm to maintain moisture condition. Soil samples after 1 day, 3 days, and 30 days of incubation were placed in centrifuge tubes. These soils were analyzed for fractionation of metals following the sequential extraction method of Salbu et al. [30] modified from that of Tessier et al. [31].

2.2. Analyses. Particle size analysis of the soil samples was done by the hydrometer method as described by Gee and Bauder [32]. Textural classes were determined by Marshall's triangular coordinate system. Soil pH was measured (field condition) electrochemically using a glass electrode pH meter, and the ratio of soil to water was 1 : 2.5 as described by Jackson [33]. Cation exchange capacity (CEC) of soils was determined using a neutral (pH 7) 1 N NH_4OAc solution described by Schollenberger and Simon [34]. The organic carbon of the soil samples was determined by the wet-

oxidation method as outlined by Walkley and Black [35]. Soil OM was calculated by multiplying the percent value of organic carbon by the conversion factor of 1.724. Total nitrogen was determined by micro-Kjeldahl's method as described by Jackson [33].

Soil samples were digested with HNO_3 - $HClO_4$ (2 : 1) mixture as described by Piper [36] for the determination of total P. Total phosphorus was determined by the Vanado-molybdate yellow color method using UV-visible spectrometer (Model: Analytik Jena Specord 205) as described by Jackson [33]. Total Pb and Cd in the soils were determined using an atomic absorption spectrometer after digestion with aqua regia as described by Jackson [33].

The sequential extraction method of Salbu et al. [30] modified from that of Tessier et al. [31] was used for this study. The chemical fractions of the metals are operationally defined as follows:

Water soluble (F1): moist soil (equivalent to 2 g oven-dry) extracted with 20 mL deionized water in Teflon centrifuge tubes, reaction time was 1 h in 20°C on a rolling table.

Exchangeable (F2): residues from the F1 fraction, extracted with 20 mL of pH 7, 1 M NH_4OAc in Teflon centrifuge tubes, reaction time was 2 h at 20°C on a rolling table.

Carbonate bound (F3): residues from F2 fraction, extracted with 20 mL of pH 5, 1 M NH_4OAc in Teflon centrifuge tubes, reaction time was 2 h at 20°C on a rolling table.

Oxide bound (F4): residues from F3 fraction, extracted with 20 mL of 0.04 M hydroxylamine hydrochloride (NH_2OH HCl) in 25% acetic acid (v/v) at pH 3, reaction time was 6 h in a water bath at 80°C with occasional shaking.

Organic bound (F5): residues from F4 fraction, extracted with 15 mL of 30% H_2O_2 (adj. pH 2), reaction time was 5.5 h in a water bath at 80^0 C with occasional shaking. A second 5 mL 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added, and the sample was shaken on a rolling table for 0.5 h at 20°C.

Residual (F6): the residue from the F5 fraction, extracted with 7 M HNO_3 reaction time was 6 h in a water bath at 80°C with occasional shaking.

Following each extraction or wash, the mixtures were centrifuged at 10,000 rpm for 0.5 h. Before starting the next extraction step, the residues were shaken with 10 ml H_2O for 2 min by hand, centrifuged, and the wash solution was discarded. All reagents used for analysis were of analytical grade. All equipment and containers were soaked in 10% HCl and rinsed thoroughly in deionized water before use. Cadmium and lead concentrations in all extracts were measured by an atomic absorption spectrometer (AA-7000, Shimadzu, Japan). All the experiments were done in triplicates.

Pearson's correlation was performed to obtain the correlation between the changes in soil pH and the heavy metal speciation during incubation experiments. Statistical analyses were performed with the Minitab, version 17 package.

2.3. Quality Control and Quality Assurance (QC/QA). The quality control and quality assurance (QC/QA) of analysis were ensured by using a reference sample and a spiked

sample for every ten analyses. Operating parameters and recovery percentages of Atomic Absorption Spectrometer (AAS) for working elements are given in Table 2.

3. Results and Discussion

3.1. Effect of Applied Treatments on Soil pH. The pH of the soil was measured after 1day, 3 days, and 30 days of the incubation to assess whether the applied treatments have any effect on the pH of the soil or not, as pH is one of the main factors determining the forms of metals in soil. Although initially there was an increase in pH of soils, no significant changes in pH occurred in post-incubation soils with time after the application of the treatment and that of the control. The initial increase in pH might be due to organic matter addition since organic matter causes short-term increase in pH [37, 38].

3.2. Speciation of Lead and Cadmium in Soil. Speciation of metals in different soil components is discussed in relation to OM addition and soil types (Figures 2 and 3).

Sequential extraction methods are frequently used to characterize and predict the potential mobility and bioavailability of lead and cadmium in soils. Bioavailability of metals decreases in the order: water soluble (F1) > exchangeable (F2) > carbonate bound (F3) > oxide bound (F4) > organic bound (F5) > residual (F6) [39]. The early fractions, water soluble, exchangeable, and carbonate (F1 + F2 + F3) are regarded as the most reactive, most mobile, and most potentially available/bioavailable fractions. The metals in these fractions consist of those that can be accessed by man through ingestion and are usually considered as being of anthropogenic origin [40]. The metals in these phases are weakly or loosely bound to soil components and therefore, considered as mobile fractions (MF). On the other hand, the rest of the fractions (F4 + F5 + F6) are strongly bound to soil components and referred to as immobile fractions (IMF).

The results on metal content and distribution are expressed on an oven-dry weight basis. Recovery of Pb and Cd was calculated as the ratio of the sum of the fractions to the total content expressed in percent. The average recovery percentage of Pb was 84.16%, 89.86%, and 83.54% in silt loam, silty clay loam, and silty clay soils, respectively. On the other hand, the average recovery percentage of Cd was 90.74%, 92.50%, and 90.29% in silt loam, silty clay loam, and silty clay soils, respectively.

The data presented in Figures 2 and 3 indicated that in all the three soils, the transformation of Pb and Cd occurred with time, although there were variations in the extent and pattern of transformation between spiked and unspiked soils. These variations might be due to the variations of treatment and soil properties, and the nature of the cations. Since the three soils investigated were almost similar in characteristics, there were not many differences in the transformation behaviour of Pb and Cd among the soils; however, remarkable differences were found between spiked and unspiked soils (both treated and not treated with OM).
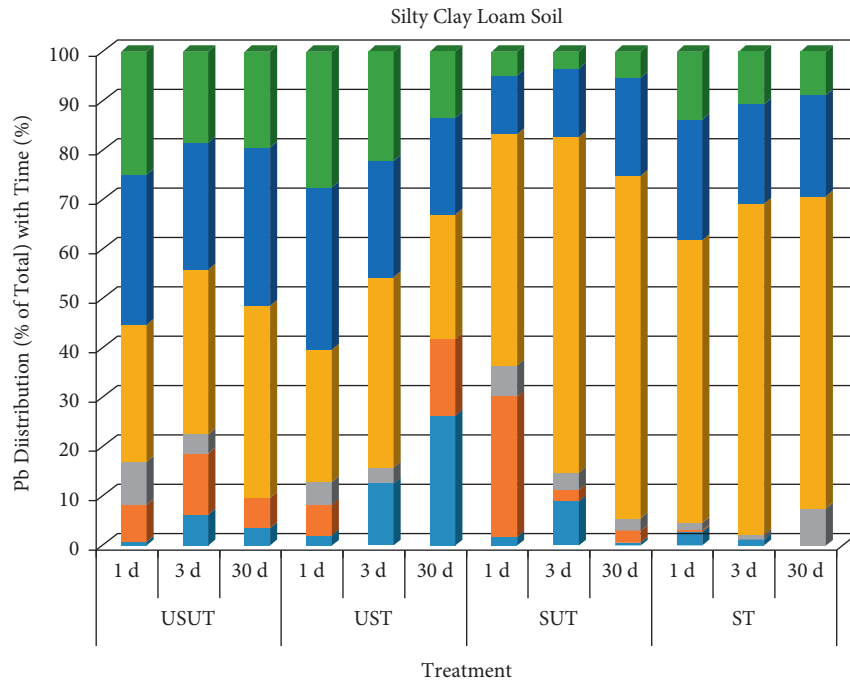
TABLE 2: Operating parameters and recovery percentages of atomic absorption spectrometer (AAS) for working elements.

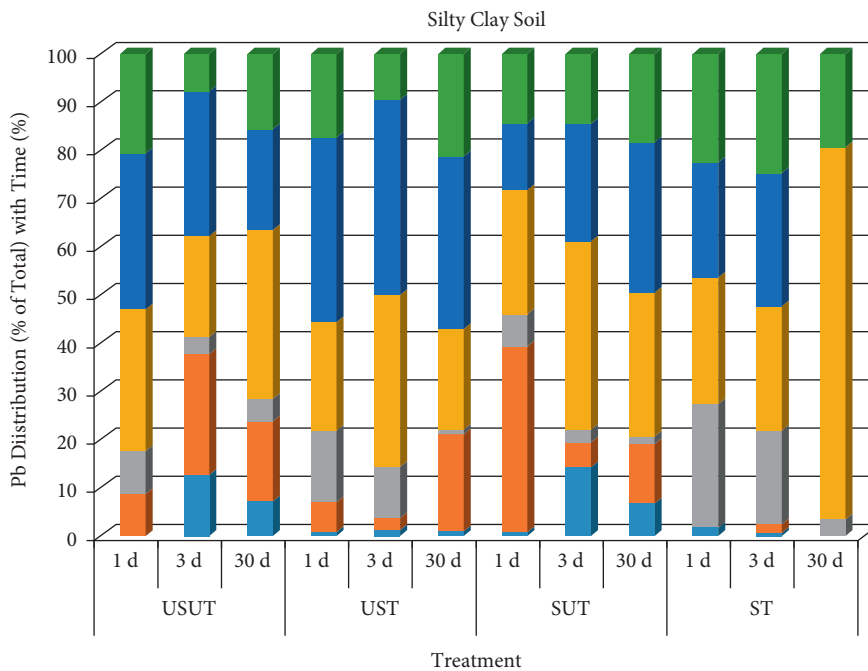| Heavy metals	Wave length (nm)	Lamp intensity (mA)	Slit intensity (nm)	Recovery percentage (%)
Pb	217.3	10	1	109
Cd	228.8	4	0.5	98
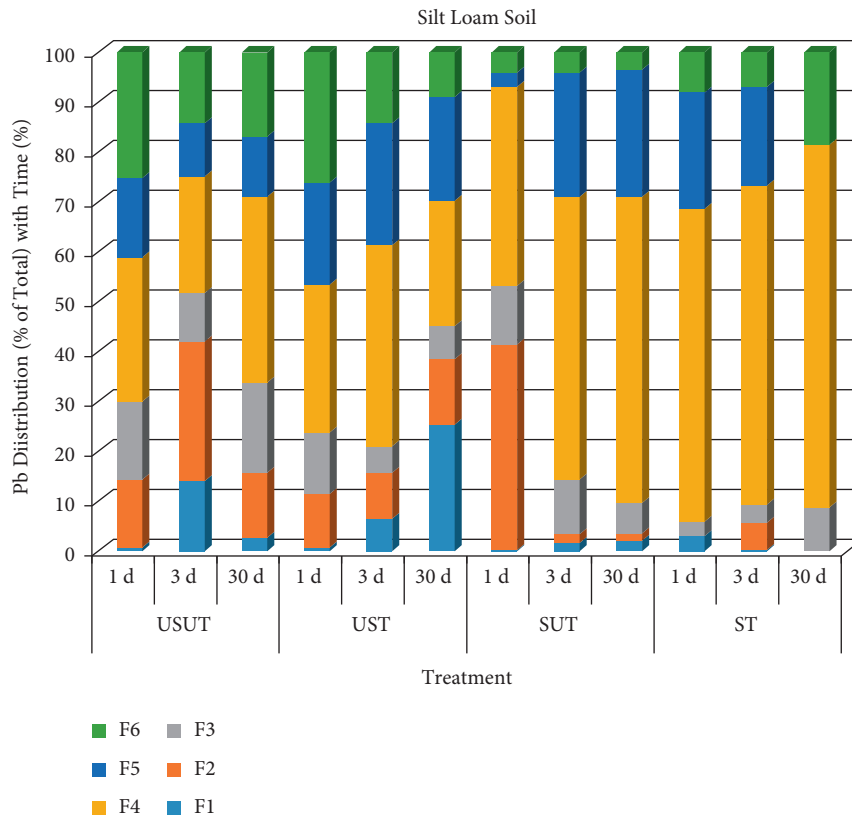
(a)

FIGURE 2: Continued.

(b)

(c)

FIGURE 2: Speciation of lead into different fractions of three soils (a, b, c) in relation to time and different treatments; USUT- unspiked untreated, UST- unspiked treated with OM, SUT- spiked untreated with OM, ST- spiked treated with OM.
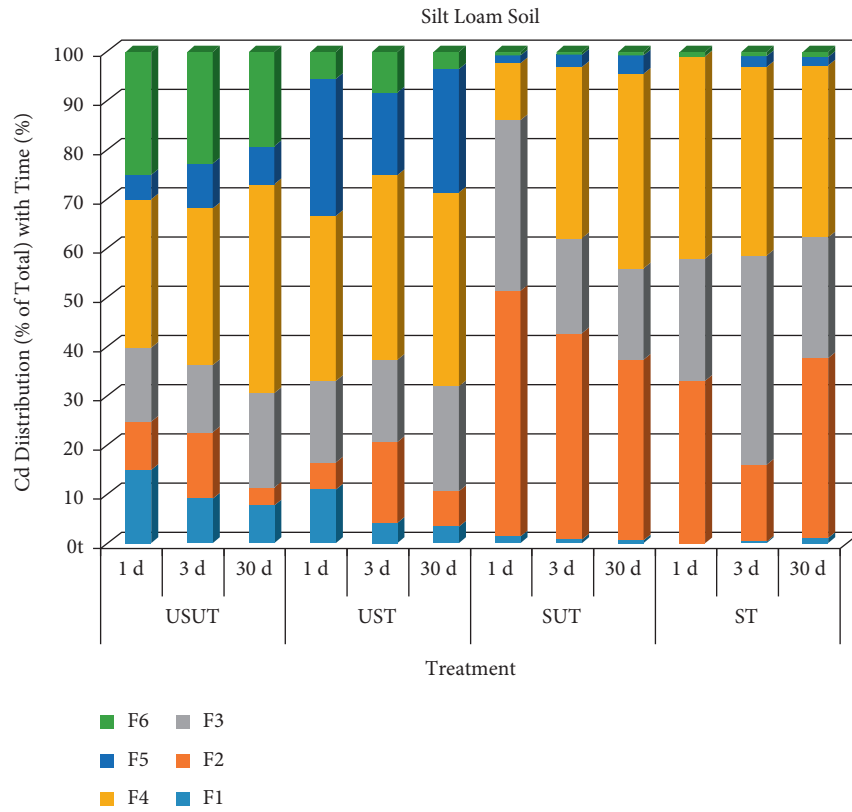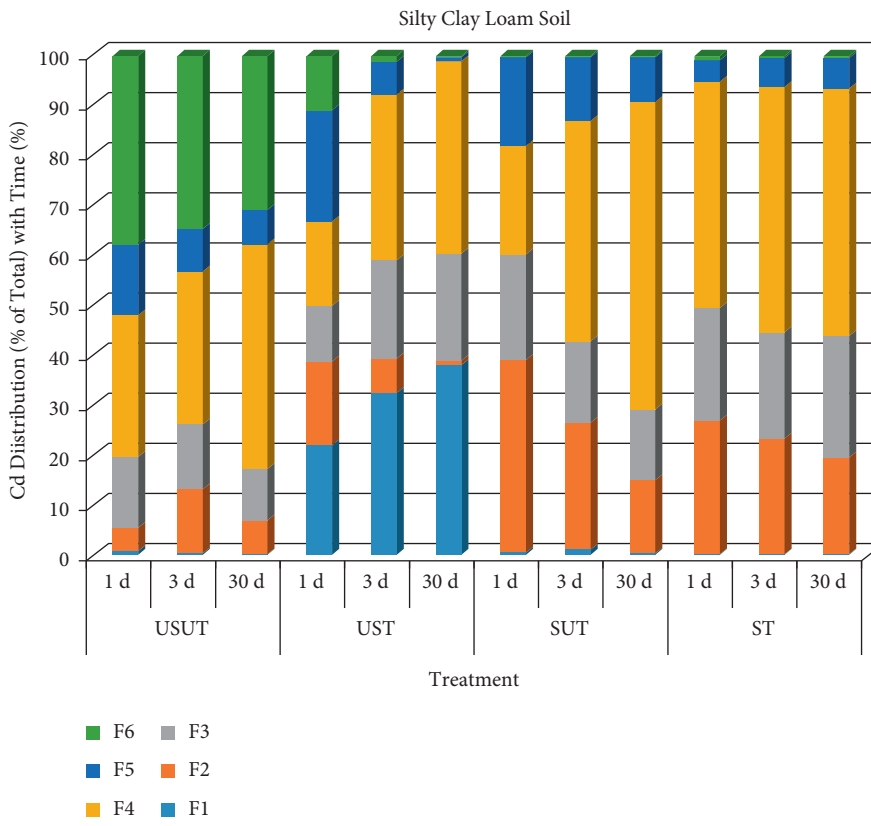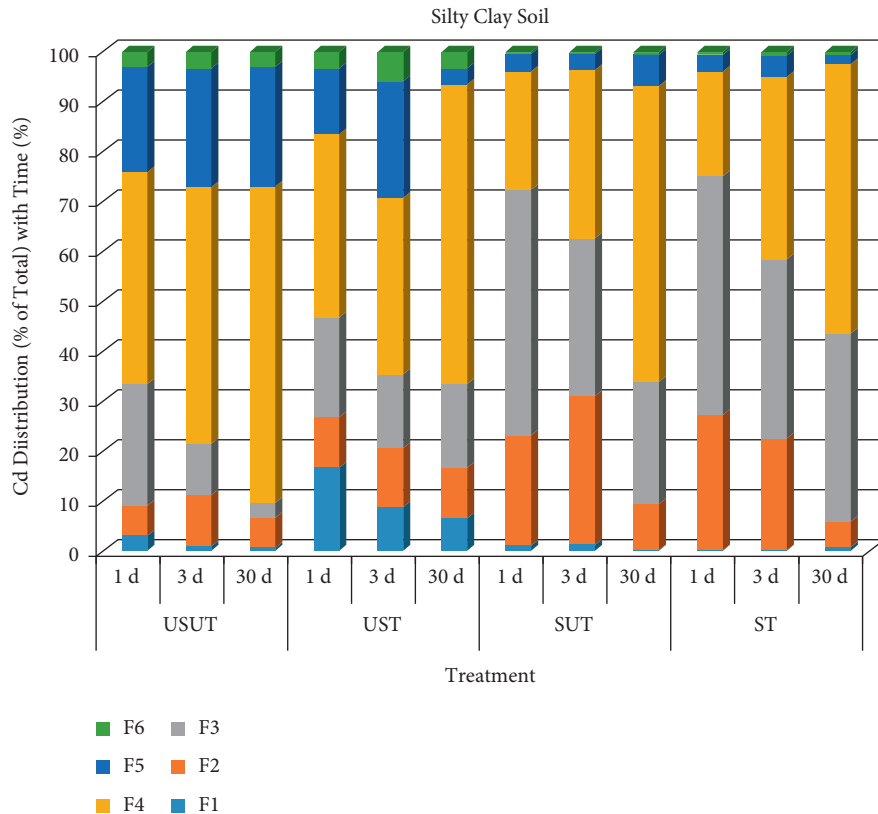
(a)

(b)

Figure 3: Continued.

(c)

FIGURE 3: Speciation of cadmium into different fractions of three soils (a, b, c) in relation to time and different treatments; USUT- unspiked untreated, UST- unspiked treated with OM, SUT- spiked untreated with OM, ST- spiked treated with OM.

3.3. Changes in the Distribution of Lead between Mobile and Immobile Fractions.

The changes in the distribution of lead between mobile and immobile fractions with time as affected by treatment are presented in Figure 4. The data showed a preferential distribution of lead among fractions.

It is evident from Figure 2 that in unspiked soils after 1 day of incubation, the order of association of Pb with different fractions (as a percentage of total) was F4 (oxide bound) > F6 (residual) > F5 (organic bound) = F3 (carbonate bound) > F2 (exchangeable) > F1 (water soluble) in silt loam soil, F5 > F4 > F6 > F3 > F2 > F1 both in silty clay loam and silty clay soils. The dominance of organic-bound fractions in silty clay loam and silty clay soil might be due to their higher organic carbon content than silt loam soil since Pb has a higher affinity to form complexes with soil OM [41]. However, after 30 days, changes occurred in all Pb fractions. In general, mobile fractions decreased with time in all unspiked soils, although an initial increase from 1 day to 3 days was also noticed. After 30 days, the highest mobile fraction of Pb was found in silt loam soil (as shown in Figure 4). Low pH, low organic carbon, and clay percentage might be the reasons for its highest mobile fraction after 30 days compared to others.

There were variations for all Pb fractions with time in soils receiving different treatments. When the soils were spiked with soluble salt of Pb, it was observed that after 1 day

of incubation, Pb was most abundant in the exchangeable fraction (40%) both in silt loam and silty clay soils but in the oxide-bound fraction (43%) in silty clay loam soil. As the incubation period increased, the value of mean exchangeable and carbonate-bound Pb decreased, but the mean oxide-bound and organic-bound Pb increased in spiked soils. No significant differences in the residual fractions of spiked soil were observed from 1 day to 30 days. This means that after 30 days of incubation, the added metals were unlikely to enter the crystalline lattice in conformity with Lu et al. [42]. The dominance of oxide-bound Pb in contaminated soils has also been reported by other investigators [14, 43–45]. On an average, it appears that with increasing incubation periods, Pb transformed from exchangeable and carbonate-bound fractions to oxide-bound and organic-bound fractions in spiked soils—this is in conformity with the findings of Lu et al. [42] that metals bound to Fe–Mn oxides and OM increased consistently with the 8-week incubation. Such trends demonstrated a decrease in the availability of Pb with time. The decreasing trend can also be evident in Figure 4. Although after 30 days, mobile fractions decreased in all spiked soils, the highest mobile Pb was found in silty clay soil, which retained Pb in the exchangeable fraction even at 30 days. The greater CEC of this soil might be the reason.

OM treatment showed considerable effects on Pb transformation in soils. When the OM was applied in
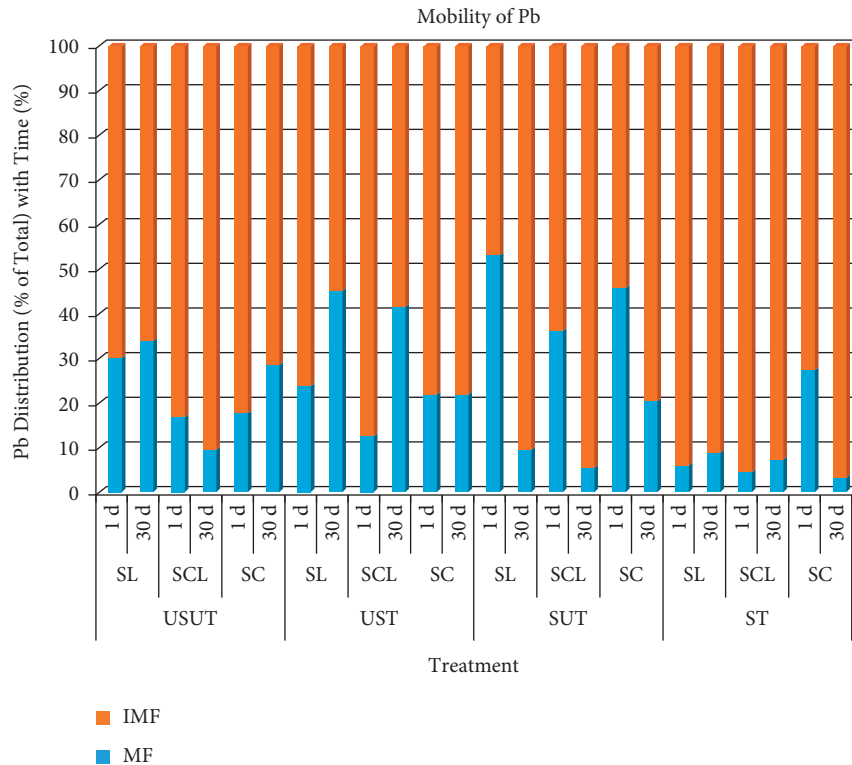
FIGURE 4: Changes in mobile and immobile fractions of lead in three soils with time; SL - silt loam soil, SCL - silty clay loam soil, SC - silty clay soil, USUT- unspiked untreated, UST- unspiked treated with OM, SUT- spiked untreated with OM, ST- spiked treated with OM, MF- mobile fractions, IMF- immobile fractions.

unspiked soil after 1 day, only slight changes occurred in Pb fractions compared to unspiked soils (not treated with OM). However, with time, Pb transformation occurred from carbonate-bound and residual fractions to the first two fractions in silt loam soil, from carbonate-bound, organic-bound, and residual fractions to other fractions in silty clay loam soil, whereas, from carbonate-bound to exchangeable and residual fractions in silty clay soil. OM treatment caused negligible changes in the exchangeable fraction of silt loam soil. Similar results were reported by Ghasemi-Fasaei and Shafigh [46]. The data suggested that with increasing incubation period, the transformation of Pb occurred from the less soluble form to a more soluble form upon the addition of OM. It is also evidenced from Figure 4 that in unspiked soils treated with OM, the transformation of Pb occurred from immobile fraction to mobile fraction with time. However, after 30 days, the highest amount of mobile Pb was observed in silt clay loam soil.

Application of OM in spiked soils yielded opposite results for unspiked soils. It was observed that when OM was applied in spiked soils, Pb decreased in water-soluble, exchangeable, and organic-bound fractions and increased in the remaining fractions in spiked silt loam soil during 1 day to 30 days. Similarly, in spiked silty clay loam soil, OM treatment increased the carbonate- and oxide-bound fractions, decreasing the first two fractions from 1 day to 30 days. Again, in spiked silty clay soil, OM treatment increased oxide-bound Pb at the expense of other fractions with time. The data suggested that in general, with an increasing

incubation period, the transformation of Pb occurred from a soluble form to a less soluble form in spiked soils when treated with OM, which is in conformity with Ghasemi-Fasaei and Shafigh [46]. It is also evidenced from Figure 4 that although a slight increase in the mobile fraction was observed in spiked silt loam and silty clay loam soil treated with OM, the value was less than the spiked soils (not treated with OM) after 30 days.

Overall, OM treatment transformed Pb from immobile to mobile fractions in unspiked soils, whereas, the very opposite trend was true in the spiked soils. This dissimilarity can be explained by the dual role of OM in metal mobility. OM treatment to soils can raise soil pH and add to the exchange capacity, both of which tend to decrease metal availability. However, these amendments also can add soluble organic ligands, which have the effect of increasing the mobility of metals [47]. Another reason might be the fast reaction of the added metal with soil components. As soluble lead (Pb) added to the soil quickly reacts with clays, phosphates, sulfates, carbonates, hydroxides, and OM, lead (Pb) might not be available to form a soluble complex with applied OM.

3.4. Changes in the Distribution of Cadmium between Mobile and Immobile Fractions.

The changes in the distribution of cadmium between mobile and immobile fractions with time as affected by treatment are presented in Figure 5. The data showed a preferential distribution of cadmium among different fractions.
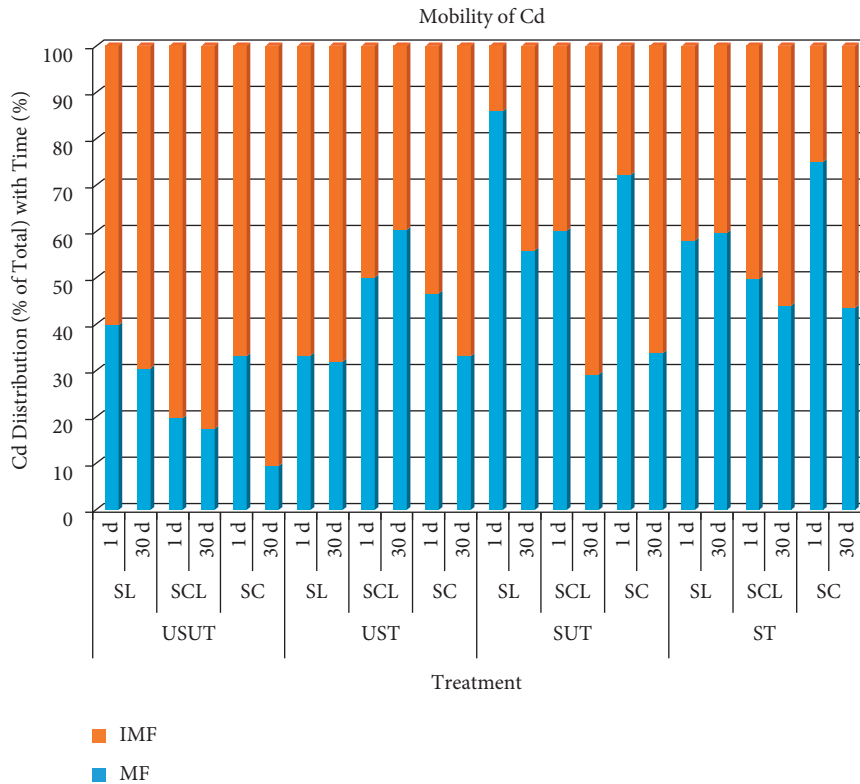
FIGURE 5: Changes in the mobile and immobile fraction of cadmium in three soils with time. SL - silt loam soil, SCL - silty clay loam soil, SC - silty clay soil, USUT- unspiked untreated, UST- unspiked treated with OM, SUT- spiked untreated with OM, ST- spiked treated with OM, MF- mobile fractions, IMF- immobile fractions.

The data presented in Figure 3 indicate that after 1 day, the amount of total Cd concentration associated with different fractions of unspiked soil was generally in the order: F4 (oxide bound) > F6 (residual) > F3 (carbonate bound) = F1 (water soluble) > F2 (exchangeable) > F5 (organic bound) in silt loam soil, F6 > F4 > F5= > F2 > F1 in silty clay loam soil while in silty clay soil the order was F4 > F3 > F5 > F2 > F6 = F1. It was observed that after 30 days of incubation, the distribution of Cd in different fractions was changed. In unspiked silt loam soil, Cd transformation occurred from water-soluble and exchangeable fractions to other fractions except for residual fractions. In unspiked silty clay loam soil, Cd transformed from other fractions to oxide-bound and exchangeable fractions, whereas, it transformed from water-soluble and carbonate-bound fractions to oxide-bound and organic-bound fractions in silty clay soil. The data presented in Figure 5 indicate that the transformation of Cd occurred from mobile fraction to immobile fraction in all unspiked soils after 30 days of incubation. However, after 30 days, the highest mobile fraction of Cd was found in silt loam soil.

There were variations for all Cd fractions with time in soils receiving different treatments. When the soils were artificially spiked with soluble salt of Cd, it was observed that after 1 day of incubation, the highest amount of Cd was in the exchangeable fraction both in spiked silt loam and silty clay loam soils, whereas in spiked silty clay soil, Cd was mostly abundant in the carbonate-bound fraction followed

by an increase in exchangeable fraction. The mobile fraction of Cd in spiked soils was higher than that in unspiked soils. These results agreed with Kashem and Singh [48] and Chlopecka et al. [45]. However, as the incubation period increased, the values of mean water-soluble, exchangeable, and carbonate-bound Cd decreased, but the mean oxide-bound and organic-bound Cd increased in spiked soils except in spiked silty clay loam soil in which the organic-bound Cd decreased with time. After 30 days, Cd was mostly abundant in the oxide-bound fraction in all spiked soils. Lu et al. [42] also found that metals bound to Fe–Mn oxides and OM increased consistently in the 8-week incubation. It was observed that in spiked soils, exchangeable Cd first increased and then decreased with time. Similar results were found by Lu et al. [42]. Although in spiked soils, the mobile fraction of Cd was more compared to unspiked soil (as shown in Figure 5) with time the transformation of Cd occurred from mobile to immobile fraction. Such trends demonstrate a decrease in the availability of Cd with time. However, the highest mobile Cd found in silt loam soil might be due to its lower pH, lower content of clay, and lower organic carbon content than other soils. Mann and Richie [49] studied the transformation of added soluble Cd in Western Australian soils incubated at the field capacity regime under controlled conditions and reported that the Cd added transformed from soluble to less soluble fractions with time, depending upon soil type, soil pH, and rate of application.

When the OM was applied in unspiked soils after 1 day, it was found that Cd was mainly associated with oxide-bound fraction in silt loam and silty clay soils, whereas with organic-bound and water-soluble fractions in silty clay loam soil. These observations are similar to those in [13] who found that the addition of OM decreased Cd concentration in the water-soluble, exchangeable, and carbonate-bound fractions, whereas it increased Cd concentration in the next three fractions. However, it was observed that with increasing incubation period, the transformation of Cd occurred from water-soluble to other fractions in silt loam soil, exchangeable, organic, and residual fractions to other fractions in silty clay loam soil while from water-soluble, carbonate-bound, and organic-bound fractions to oxide-bound fraction in silty clay soil. Overall, OM addition in unspiked soils increased the mobile fraction of Cd in silt loam and silty clay loam soils and decreased it in silty clay soil, although the value was higher than unspiked soils not treated with OM, indicating greater mobility of Cd (as shown in Figure 5). The highest mobile fraction was found in silty clay loam soil after 30 days of incubation.

Again, when OM was applied in spiked soils, it was observed that after 1 day of incubation, Cd was dominantly associated with oxide-bound fraction both in spiked silt loam and silty clay loam soils while with carbonate-bound fraction in silty clay soil. However, it is evident from Figure 5 that with increasing incubation period, although no considerable changes in mobile fraction were observed in spiked silty clay loam soil, OM treatment slightly increased the mobile fraction in silt loam soil while considerably decreasing it in spiked silty clay soil. This suggests that OM treatment did not create any general pattern of Cd transformation when applied in spiked soils. Although the applied OM decreased mobile Cd in silty clay soil, the value was higher than in spiked soils not treated with OM. The highest mobile Cd was found in silt loam soil.

Overall, it can be observed from Figure 5 that the transformation of Cd occurred from mobile to immobile fraction both in unspiked and spiked soils. OM treatment increased the mobile fraction both in unspiked and spiked soils with time.

According to Jones and Jarvis [50], processes of metal mobilization-immobilization are affected by a variety of soil properties. To examine this influence, correlations between changes in soil pH during incubation and contents of Pb and Cd in the six chemical phases of the sequential extraction have been established for all soils. Fractions of Pb and Cd showed both significant (P-value <0.05) positive and negative correlation with soil pH changes during incubation. The exchangeable fraction of Pb in unspiked organic-matter-treated silt loam soil and the carbonate-bound fraction of Pb in spiked untreated silt loam soil showed a significant positive correlation with soil pH changes during incubation. Whereas the exchangeable fraction of Pb in unspiked organic matter treated silty clay loam soil and the organic bound fraction of Pb in spiked untreated silty clay loam soil showed a significant negative correlation with soil pH changes. In the case of Cd, the carbonate-bound fraction showed a significant positive and the organic-bound fraction showed a significant negative correlation in spiked untreated silt loam soil. But in spiked treated silt loam soil, the organic bound fraction of Cd showed a significant positive correlation with pH changes. In unspiked untreated silty clay loam soil, the oxide-bound fraction of Cd showed a significant negative and in spiked untreated silty clay soil, the water-soluble fraction of Cd showed a significant positive correlation with changes in soil pH during incubation.

4. Conclusion

The pattern of metal redistribution obtained in this study for lead and cadmium provides a basis for explaining the changes in the availability of these metals upon the addition of OM. In the spiked soils, the added metals were redistributed in different fractions depending on the nature of the metal.

The mobile fraction of Pb decreased with time in all unspiked soils. After 30 days, the highest mobile fraction of Pb was found in silt loam soil (32%) which might be due to its low pH, low organic carbon, and low clay percentage compared to others. In spiked soils, the mobile fraction of Pb decreased with time. Although, after 30 days, mobile fractions decreased in all spiked soils. the highest mobile Pb was found in silty clay soil (19%) which retained Pb in exchangeable fraction even at 30 days of incubation. The greater CEC of this soil is responsible for this retention. In unspiked soils treated with OM after 30 days of incubation, the highest mobile fraction of Pb was observed in silty clay loam soil (48%), whereas in spiked soils treated with OM, the highest mobile Pb was found in silt loam soil (8%).

Similarly, the transformation of Cd occurred from mobile to immobile fractions both in unspiked and spiked soils with the time of incubation. However, after 30 days of incubation, the highest mobile Cd was found in silt loam soil (29% in unspiked silt loam soil and 53% in spiked silt loam soil). Low pH, low organic carbon, and low clay percentage of this soil might be the reason for its highest mobile fraction of Cd. OM addition increased the mobile Cd in unspiked soils with time. In general, in both unspiked and spiked soils, the mobility of Cd increased with time upon the addition of OM. After 30 days of incubation, the highest mobile Cd was observed in unspiked silty clay loam soil (55%) and spiked silt loam soil (58%).

In conclusion, it can be said that OM treatment considerably influenced the speciation of lead and cadmium in soils with the time of incubation. OM increased the mobile fraction of Pb in unspiked soils and decreased it in spiked soils, whereas it increased the mobile fraction of Cd both in spiked and unspiked soils, indicating greater mobility of cadmium than lead.

However, spiked soils mimic true contaminated soils to a certain extent. Although our sequential procedure provided a reasonable degree of recovery and reproducibility, the similarity of the heavy metal distribution between natural and spiked soils and the consequent bioavailability is still in question. Further investigation is needed when such experiments are carried out with real contaminated soils. The

behavior of each heavy metal, including the bioavailability, cannot be compared with other metals. This fact must be taken into account in soil/plant studies.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

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