Full Length Research Paper

Assessment of the redistribution extent of As, Cr and Cu during sequential extraction

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In this study, sequential extraction method was used to assess the metal speciation in a chromated copper arsenate contaminated soils. Total value of 47.75 mg arsenic kg^{-1} dry soil, 659.43 mg chromium kg^{-1} and 406.50 mg copper kg^{-1} were obtained in the soil sample. Sequential extraction was conducted for the chromated copper arsenate contaminated soil. The experimental results show that the specific reagents were effective for the extraction of metals from the different fractions of the contaminated soil. In this study, 12.85, 10.17, 7.57, 6.00 and 10.11 mg As kg^{-1}, 34.48, 132.80, 0.00, 223.96 and 241.69 mg Cr kg^{-1} and 7.00, 20.50, 22.50, 136.50 and 194.50 mg Cu kg^{-1} were obtained in the exchangeable, carbonate, Fe-Mn oxide, organic and residual fraction of the soil. The study revealed the release and redistribution of metals in the various soil fractions during the sequential extraction process, but knowledge about this behaviour and the extent of metal redistribution is ambiguous.

Key words: Sequential extraction, chromated copper arsenate (CCA), arsenic, chromium, copper.

INTRODUCTION

Soils are major sink for metal contaminants released into the environment. Human activities in the recent decades have increased soils polluted by heavy metals. These activities include mining, smelting, spillage of chemicals such as pesticides, wood preserving agents (Khodadoust et al., 2005). Heavy metals cannot be destroyed by biochemical processes; hence to evaluate the environmental impact of a contaminated soil, knowledge of the total concentration of metal is insufficient without considering their speciation (Lo and Yang, 1998; Kirpichtchikova, 2006; Asagba et al., 2007).

Total metal concentration is a good indicator of the degree and extent of contamination (Tessier et al., 1979). Its use in assessing the potential effect of soil contamination implies that all forms of a given metal have an equal impact in the environment (Jaradat, 2006).

Metals are distributed throughout soil components and are associated with them in various ways including ion exchange, adsorption, precipitation and complexation (Lo and Yang, 1998). Sequential extraction is used to assess heavy metal distribution and mobility in soils (Wasay et

al., 2001).

It is pertinent to note that the usefulness of any extraction scheme is dependent on the final use of the data acquired as several batch and sequential extraction schemes exist for assessing the various species of metals in soils (Tessier et al., 1979; Oviasogie and Ukpebor, 2003; Clevenger, 1990; Asagba et al., 2007). In the sequential extraction process, heavy metals are commonly partitioned into five operationally defined fractions. The most widely used sequential extraction method was provided by Tessier et al. (1979) and is based on the fact that different forms of heavy metals retained in soils can be extracted selectively by a series of extraction reagents.

In the use of sequential extraction method for the study of metal speciation, three possible limitations have been identified by earlier workers. They include the limited selectivity of extractants, redistribution of metals during the extraction process and the deficiency of reagent dose at high metal concentration (Ramos et al., 1994; Tu et al., 1994; Lo and Yang, 1998; Asagba et al., 2007).

Despite these limitations, these schemes are useful in examining the association of trace metals with various components of soils and in obtaining useful information on heavy metal distribution in soils.

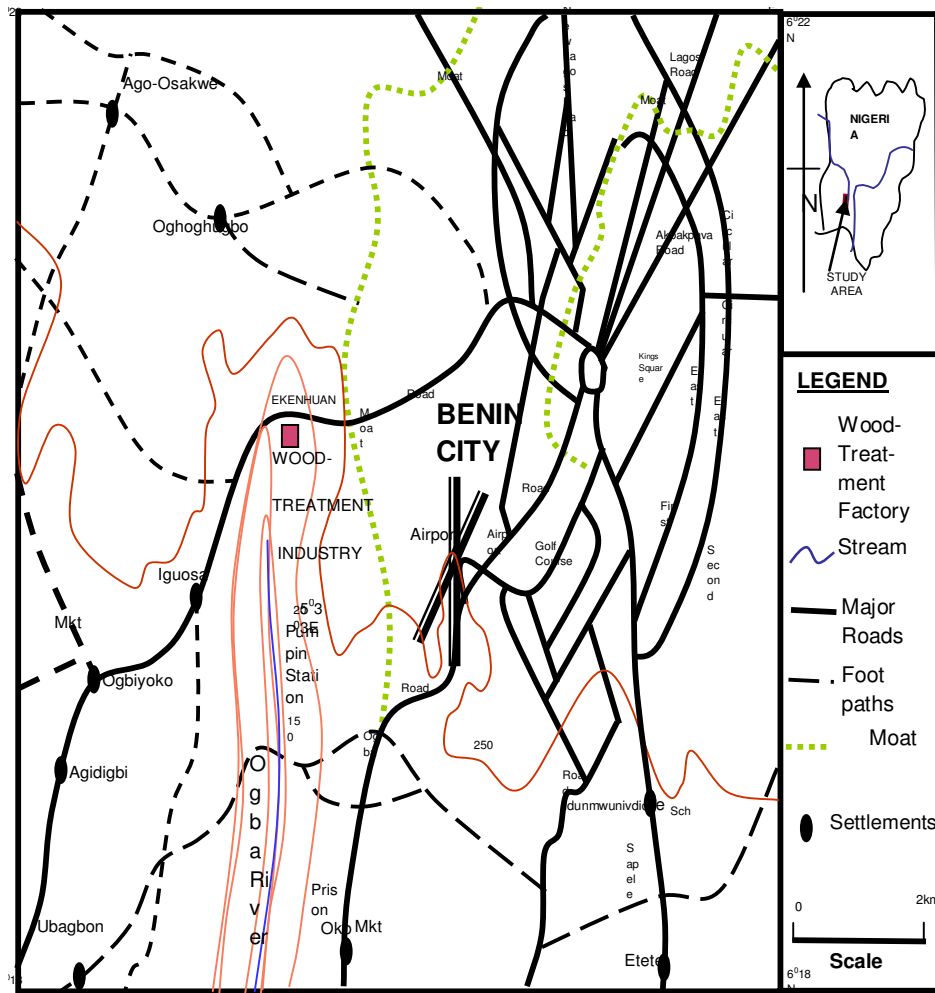*Corresponding author. E-mail: esohe_grc@yahoo.com.

Figure 1. Map of Benin City showing the study site.

The aim of this study was to determine the extraction efficiency and selectivity of the widely used sequential extractants for a chromated copper arsenate (CCA) contaminated soil and to assess the metal species and the phenomena of metals distribution during the sequential extraction process.

MATERIALS AND METHODS

Soil sampling, preparation and analysis

Ten grab samples were collected from ten different locations at the topsoil depth of 0 to 10 cm from the vicinity of a wood treatment factory in Benin City, Nigeria (Uwumarongie-Ilori and Okieimen, 2010) as shown in Figures 1 and 2 and the geographical positioning system (GPS) readings are as follows:

Site A: N 06° 19′ 641′′, E 005° 35 416′′
Site B: N 06° 19′ 642′′, E 005° 35 418′′
Site C: N 06° 19′ 635′′, E 005° 35 421′′
Site D: N 06° 19′ 647′′, E 005° 35 402′′
Site E: N 06° 19′ 667′′, E 005° 35 410′′
Site F: N 06° 19′ 651′′, E 005° 35 426′′

Site G: N 06° 19′ 642′′, E 005° 35′ 408′′
Site H: N 06° 19′ 652′′, E 005° 35′ 438′′
Site I: N 06° 19′ 645′′, E 005° 35′ 407′′
Site J: N 06° 19′ 646′′, E 005° 35′ 404′′

The study was performed on an aggregate sample prepared by mixing thoroughly equal amount of each of the 10 soil samples to make three replicate samples. The soil samples were air-dried at ambient temperature (28 to 31°C), crushed in a porcelain mortar and sieved through a 2 mm sieve.

Pseudo-total concentration of As, Cr and Cu in the contaminated soil was determined by digesting 1 g of sample, 5 ml of nitric and 1 ml of perchloric acids and diluted to 100 ml with distilled water. The resultant extract was then analysed using Buck scientific VGP 210 Atomic Absorption Spectrophotometer. The metal concentrations of the triplicate aggregate soil sample are given in Table 1 expressed as mean and standard deviation.

Sequential extraction and analysis

Sequential extraction was performed based on the method suggested by Tessier et al. (1979). The extraction was conducted using a mechanical shaker (Heldoph) and water bath. The mechanical shaker was kept at 2000 rpm and the temperature of

Table 1. Operation conditions of sequential extraction (for 1 g sample).

Soil components	Corresponding reagent	Temperature (℃)	Contact time
Exchangeable (F1)	$MgCl_2$ (pH 7.0)	Room	1 h
Carbonate (F2)	NaOAc/HOAc (pH 5.0)	Room	5h
Fe/Mn oxides (F3)	$NH_2OH.HCl$ (in 25% HOAc)	96 ± 3	6 h
Organic (F4)	30% H_2O_2 (pH 2) with HNO_3	85 ± 2	5 h
Residual (F5)	$HCl-HNO_3-HClO_4$		
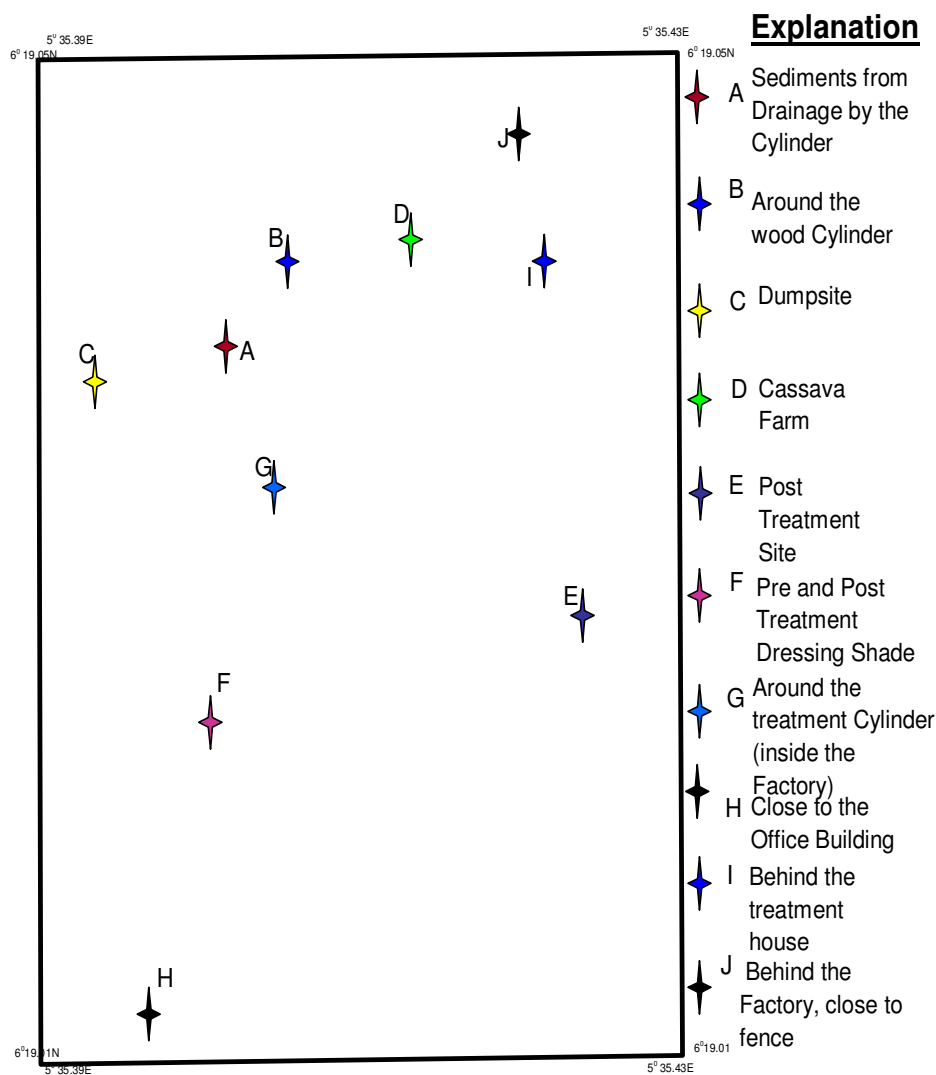
Figure 2. Wood-treatment industry site.

the water bath was controlled at a desired range as given in Table 1. The CCA contaminated soil underwent an extraction process using the specific reagents to investigate the completeness of metal removal from the soil fraction. For instance, the reagent $MgCl_2$ was used to extract the metal bound to the exchangeable fraction of the soil.

The entire sequential extraction procedure is schematically shown in Figure 3. One gram of soil was used and the sequential extractions were conducted in a polypropylene bottle to minimize any losses of solid materials. After extraction, solid/liquid separation was effected by filtering using Whatman No. 1 filter paper. Supernatant was analyzed for As, Cr and Cu concentrations. The solid phase was washed with 10 ml of distilled water and added to the filtrate. Triplicates of each experimental test were conducted and the results showed no significant differences between determinations.

Metal analyses were conducted with Atomic Absorption Spectrophotometer (Buck Scientific, VGP 210 model) involving
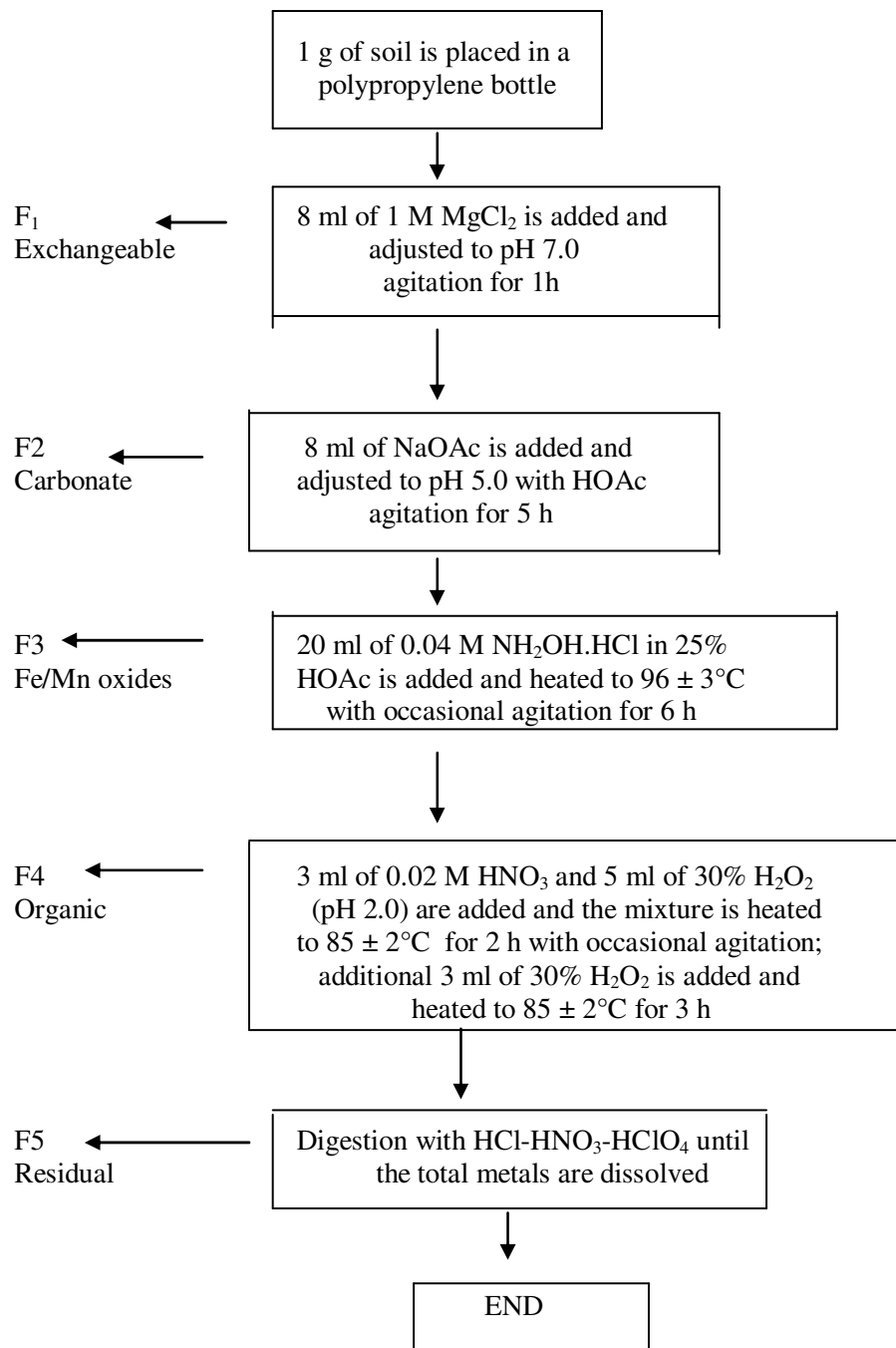
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                    ┌─────────────────────┐
                    │ 1 g of soil is placed in a │
                    │  polypropylene bottle │
                    └─────────────────────┘
                              │
                              ▼
  F₁        ◄──────  ┌─────────────────────┐
  Exchangeable       │ 8 ml of 1 M MgCl₂ is added and │
                     │   adjusted to pH 7.0 │
                     │    agitation for 1h  │
                     └─────────────────────┘
                              │
                              ▼
  F2        ◄──────  ┌─────────────────────┐
  Carbonate          │  8 ml of NaOAc is added and │
                     │ adjusted to pH 5.0 with HOAc │
                     │    agitation for 5 h │
                     └─────────────────────┘
                              │
                              ▼
  F3        ◄──────  ┌─────────────────────┐
  Fe/Mn oxides       │ 20 ml of 0.04 M NH₂OH.HCl in 25% │
                     │ HOAc is added and heated to 96 ± 3°C │
                     │  with occasional agitation for 6 h │
                     └─────────────────────┘
                              │
                              ▼
  F4        ◄──────  ┌─────────────────────┐
  Organic            │ 3 ml of 0.02 M HNO₃ and 5 ml of 30% H₂O₂ │
                     │  (pH 2.0) are added and the mixture is heated │
                     │ to 85 ± 2°C for 2 h with occasional agitation; │
                     │  additional 3 ml of 30% H₂O₂ is added and │
                     │     heated to 85 ± 2°C for 3 h │
                     └─────────────────────┘
                              │
                              ▼
  F5        ◄──────  ┌─────────────────────┐
  Residual           │ Digestion with HCl-HNO₃-HClO₄ until │
                     │  the total metals are dissolved │
                     └─────────────────────┘
                              │
                              ▼
                     ┌─────────────────────┐
                     │         END          │
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Figure 3. Sequential extraction scheme.

direct aspirations of the aqueous sample into an air-acetylene flame. Procedural blank samples were subjected to similar extraction method using the same amounts of reagents. Blank determinations of the elements were below the detection limits of the Atomic Absorption spectrophotometer. The concentration of As, Cr and Cu were determined in the standard stock solutions of 1000 ppm, prepared by Buck Scientific according to standard methods. A calibration curve was prepared at a minimum of six concentrations levels ranging from 0.00 to 5.00 ppm for the metals. The pH meter was calibrated with standard pH 4.00 and 7.00 buffer solutions.

RESULTS AND DISCUSSION

The pseudo-metal amount of metals in the CCA contaminated soil is given in Table 2. The amount of Cr (659.43 mgkg^{-1}) was highest, while the amount of arsenic (47.75 mgkg^{-1}) was the lowest of the metals studied.

The extraction results are given in Table 3. Metals associated with the exchangeable fraction of soils are exchangeable ions which occur either as free hydrated

Table 2. Total heavy metal content of aggregate soil sample collected from the CCA contaminated site (dry weight).

Metals	Amount (mgkg^{-1})
Copper	406.50 ± 2.12
Chromium	659.43 ± 1.48
Arsenic	47.75 ± 0.21

Table 3. Concentration of various forms of the heavy metals (mgkg^{-1}).

	As	Cr	Cu
F1	12.85 ± 0.14	34.48 ± 3.55	7.00 ± 1.41
F2	10.17 ± 0.08	132.80 ± 3.01	20.50 ± 1.41
F3	7.57 ± 0.10	0.00 ± 0.00	22.50 ± 0.71
F4	6.00 ± 0.00	223.96 ± 9.67	136.50 ± 3.54
F5	10.11 ± 0.74	241.69 ± 2.11	194.50 ± 1.41
Sum	46.70	632.93	381.00

ions or as various complexes with organic or inorganic ligands (Sparks, 2003). This fraction extracts elements which are affected by sorption-desorption processes caused by changes in water ionic composition (Hlavay et al., 2004).

In this study, the metals in the exchangeable fraction of the aggregated CCA contaminated soil were extracted using 1 M MgCl$_2$ (pH 7.0) solution. The amount of arsenic (27%) extracted from this fraction was the highest (Table 4). However, chromium and copper extraction were low, 6 and 2% respectively. This indicates that the use of 1 M MgCl$_2$ (pH 7.0) solution for extraction of metals from the exchangeable fraction of the CCA contaminated soil was best for arsenic of the three metals studied.

Metals associated with carbonate are usually in the form of carbonate precipitate or co-precipitate. These compounds have been implicated as immobilizing most heavy metals by providing an adsorbing or nucleating surface and by buffering soil pH (Asagba et al., 2007). Metals can be removed from this fraction by the application of an acidic solution (Tessier et al., 1979). A solution of 1 M NaOAc/HOAc (pH 5.0) have been found to be sufficiently efficient in dissolving calcite and dolomite and releasing metals bound to carbonate (Yong and Cloutier, 1993).

In this study, the amount of As extracted from the contaminated soil using 1 M NaOAc/HOAc (pH 5.0) was still the highest as 22% As was extracted by the solution. This was followed by the amount extracted by Cr (21%). Copper extraction was still relatively low, approximately 5%. The acidic NaOAc/HOAc solution may have dissolved metals bound to other soil components. Lo and Yang (1998) have reported the dissolution of non-corresponding phases by the same solution (Lo and Yang, 1998; Asagba et al., 2007). The dissolution of non Target phases is one of the drawbacks of sequential

schemes (Asagba et al., 2007).

Iron and manganese oxides have been implicated in the sequestration of heavy metals in the environment (Nacghtegaal and Sparks, 2004; Asagba et al., 2007). In our study, a reductive solution of 0.04 M NH$_2$OH.HCl (in 25% HOAc) was used to extract metals from the CCA contaminated Fe/Mn oxide fraction of the aggregate soil. From Table 4, we found that the reductive solution did not extract Cr from the soil. Copper (22%) was extracted most by the solution. Several types of association are formed between heavy metals and Fe/Mn oxides. These includes: exchangeable forms via surface complexation, moderately fixed via precipitation and co-precipitation and relatively strong chemical bounding (Yong and Cloutier, 1993). 0.04 M NH$_4$OH.HCl have been found to be suitable for extraction of these three metals from Fe/Mn oxides (Lo, and Yang, 1998).

The organic fraction of soils contains functional groups such as carboxyl, carbonyl and phenylhydroxyl. These complexing ligands can combine with heavy metals. They form covalent bonds with complexing ligands divalent cations such as Cu^{2+}. The release of heavy metals from this fraction of the soil can be assessed by oxidizing the organic matter to destroy its structure. A reagent of 30% H$_2$O$_2$ with HNO$_3$ suggested by Tessier was used for the extraction of metals from the CCA contaminated organic fraction. The result given in Table 4 shows that 36% Cu was extracted by the reagent, while a slightly less amount 35% (Cr) was extracted by the solution. The amount of As extracted by this solution was the least of the three metals.

In this study, the residual fraction of the CCA contaminated soil was assessed by digesting the residue with HCl, HNO$_3$ and HClO$_4$. Arsenic, chromium and copper contained in the contaminated residual fraction of the CCA soil were all removed after digestion. The triple

acids used are strong enough to destroy the structure of clay mineral present in the fraction of the soil. The amount of Cu (51%) extracted by the acids from this fraction is the highest. This was followed by the amount of Cr (38%) extracted. The amount of arsenic (22%) extracted by the acids was the least. It was observed in this study that the sum of fractions were not equal to the amount of pseudo-total analyzed.

Conclusion

The study revealed that the CCA contaminated soil contained As, Cr and Cu in various chemical forms. In the use of sequential extraction, the specific extracting reagents could extract As, Cr and Cu from the CCA contaminated soil. But, the influence of non-corresponding reagents on other soil components cannot be ignored during the whole extraction procedure. Thus the sequential extraction method provided by Tessier is not accurate for quantitative analysis because of the metals' mobility and redistribution in soils. Hence more research on how to minimize the impact of the extracting reagents on other soil components through modification of the current extraction procedures and finding suitable reagents with less impact is necessary.

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