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Characteristics Levels of Predictions of Extractable Metals (Cd, Pb and Fe) in Sewage

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ABSTRACTS

Sewage is the part of wastewater that is contaminated with feces or urine but is often used to mean any wastewater. When this is done sewage refers to wastewater from sources including homes, industries, medical facilities, street runoff and business. It consists of nutrients and organic matters that can provide soil benefits and are widely used as soil amendments. In an attempt to investigate the partitioning of three metals: Cd, Pb and Fe in sewage, standard operationally defined procedures; sequential extraction was employed in the study. The effect of extractant concentrations was also studied and found to affect extractability across the various fractions (reducible. oxidizable and residual). The highest acid extractable fraction (1.78 ±0.01mg/kg)was recorded in Fe while the least (0.16±0.01mg/kg)was found in cadmium. The reducible fractions across the various concentration ranged from 0.03-0.23 mg/kg for Cd,0.01-0.43 mg/kg for Pb and 1.04-2.54 mg/kg for Fe. For the oxidizable fraction, the range was 0.15-0.24 mg/kg in Cd,0.006-0.23mg/kg in Pb and 0.556-2.08 mg/kg in Fe. The residual fraction across the three experimental design of variable pH and 0.79-1.07-0.21mg/kg for Cd,0.01-0.8 mg/ kg for Pb and 0.79-1.07mg/kg for Fe. The findings showed that the metal ions binding to the biotic surface such as sewage is pH dependent and that is an optimum pH for bioavailability of metals, also the pH changes during extraction was dependent on the composition of the sample. The sewage pH and organic matters influence was observed only on cadmium ($r = -0.970$ at $p < 0.05$) with displaying of negative correlation. The concept might be a valuable yardstick in predicting metal ion sorption quantitatively in a complex system and predict the relative change in availability due to environmental changes. The differences in the metal concentrations were most pronounced in B-H and G-H due to high total contents of heavy metals.

Key Words: Bioavailability, Sequential extraction, Heavy metals, sewage Sludge

INTRODUCTION

Sewage sludge (or domestic sewage, domestic wastewater, municipal wastewater) is a type of wastewater that is produced by a community of people in form of small liquid with suspensions of small solids. It is typically transported through a sewer system. It consists of nutrients and organic matters that can provide soil benefits and are widely used as soil amendments .They also however contain contaminants including metals, pathogens and organic pollutants.(Odetola and Awoniyi,2007).Sequential extraction to fractionate metals or other elements in the solid materials (soils, sediments, sludges solid waste etc) into several groups or different leachability is widely employed to determine the distributions of metal in different phases. Although, the procedures used are generally tedious and time consuming the results furnish detailed information about the origin, mode of occurrence, bioavailability, potential mobility and transport of the metals in natural environment (Ololade,2009). The technique is therefore widely used as a tool for the study of the origin and fate of metals in the environment. However, despite the fact that the development and use of extraction schemes started in early 1970s, uniformly in the procedures used is still lacking. In addition, problems of poor selectively redistributions during extraction and dependency of results on operating conditions have been frequently raised.(Hoodas *et al*.,1904)The most widely used sequential extraction schemes are probably those proposed by Tessier *et al*.,1979 and the community Bureau of reference(BCR)(Basta ,2000)These procedures have been demonstrated to give satisfactory results for the targeted phases owing to a careful selection of

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reagents and detailed condtions. However, many authors (Dudka *et al*.,1990), (Paola, *et al*.,.2008), (Vollprecht *et al*.,2020), have reported the problem of readsorption and the dependence of readsorption on the phase composition of the sample being analyzed. Paola, *et al*.,2008. discovered that the recovery of spiked metals (Pb, Zn, Cu. Ni) was less for model mixed phase sediments than for single phase materials, and questioned the selectivity of the sequential extraction procedure. (Maiz *et al.*,1997; Sahiquillo *et al*.,1999) found to affect extractability Paola, *et al.*,2008 in both the exchangeable and acid soluble metal extractions steps. Extraction temperature has also been found to affect the extraction efficiency for some metals (Filqueiras *et al.*, 2002) The effect of extraction time on metal extractability has been reported not to be crucial, probably due to the relatively long extraction time employed in most procedures. Among the numerous group of elements present in sewage sludge, heavy metal are undoubtly the most crucial and at the same time the most controversial ones responsible for pollution (Fuentes *et al*.,2004).

MATERIALS AND METHODS

Study Area and sampling

This investigation was carried out within Boys, Girls and private Hostels of Ekiti State College of health sciences and technology Ijero Ekiti, Ekiti state South-Western part of Nigeria.

The collection of sewage samples were carried out in three different places from College of health science and Technology Ijero Ekiti, Ekiti Staste Nigeria namely Boys Hostel, Girls Hostel and one collected from private Hostel very closed to the main campus of the college. Sludge samples were taken from each location from heaps using an auger. After 3 - 6 individual samples were taken from each of the location, they were all mixed together and one average sample was composed for analysis.

Materials preparation

The samples were preserved inside a polyethylene bags that were previously soaked in 10% HNO_3 for 24 hr and then allowed to drain to dryness outside the chemistry laboratory environment of the college. The collected material was prepared by drying, ground to pass through a 1.0 mm stainless steel sieve and stored at 4°C for further analysis. The sewage sludge was analyzed for basic physico-chemical properties using standard procedures: pH – was measured with a glass electrode in 1 mol • L-1 KC1 (1:2.5 ratios) and Organic carbon - by wet dichromate oxidation with sulphuric acid.

Analytical determination of parameters for the sequential extraction

Acid-extractable (AE): 40 ml of 0.11 M HOAc was added to a 1-g aliquot, and then shaken for 16 h at 22 ± 5^0 C; extract was separated from the solid residue by centrifugation at 3000 Xg for 20 minutes (Ololade, 2009)

Reducible (RD): 40 ml of 0.5 M $NH_2OH.HCl$ from 1-1 solution containing 25 ml of 2 MHNO_3 (pH 1.5) was added to step 1 residue and shaken for 16hr at 22± 5^0C, then centrifuged at3000Xg for 20 minutes (Ololade ,2009).

Oxidizable (OX): To step 2 residue,10 ml of H_2O_2(pH 2-3) for 1 hr at room temperature was added and heated to 85± 2^0C for 1hr; a further 10 ml of H_2O_2 was added and heated 85± 2^0C for 1hr; 50 ml of 1 M NH_4OAc(pH 20) was also added and shaken for 16hr at 22± 5^0C;The solution was centrifuged at 3000Xg for 20 minutes(Ololade ,2009).

Residual (RS): To step 3 residue, 3 ml of distilled H_2O, 7.5 ml of 6 M HCl and 2.5 ml of 14 M HNO_3 was added and left overnight at 20^0C. The final solution was later boiled under reflux for 2 h, cooled and filtered. (Hussein *et al*., 2012)

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Determination of heavy metals in sewage by sequential extraction

The sequential extraction method applied in this study followed literature guidance (Tessier *et al.*, 1979; Rauret *et al*., 1999; Ross and Filip, 2003). The heavy metals were partitions into four operationally defined fractions, these include: acid extractable, oxidizable, reducible and residual fraction. The extraction was carried out in polypropylene centrifuge tubes of 50ml capacity with an intial mass of 2.5g oven dried (105^0C) fine fraction(<1mm) of the samples. The scheme below in 2.4 summarizes the procedure employed for the sequential extraction of metals in the sewage sample. In addition to the scheme below 2.5, little modifications were made on the reducible because, reducible fractions of heavy metals constitutes potential risk to living, especially, because of solubility, in aquatic environment (Boughriet *et al.*, 1992). The three different concentrations: 1.5 M,2.0 M and 3.0 M of HNO_3 were used during this study. This was to evaluate the impact of pH on the bioavailability of metals in sewage. After each successive extraction, the supernatant was collected after centrifuging at r/mins for 20 minutes, filtered through a 0.45 m membrane filter, and diluted to volume. The residue was washed with 10 ml of de-ionized water by shaking and diluted to volume. The residue was washed with 10 ml of de-ionized water by shaking and centrifugation without loss of solids. The total content from a separate sample was analyzed to evaluate the performance of sequential extraction by digesting it with HF and $HClO_4$ (5:1). Heavy metal concentrations of all extracts were determined by flame atomic absorption spectrophotometry (Alpha AAS, chemical Tech. Analytical Euro). All extractions were performed in triplicates and the mean values are presented with standard deviation. The obtained data were subjected to statistical analysis to evaluate the correlation coefficient® at two levels of significance (*$p< 0.01$ and $p< 0.0$)*

Quality Assurance

(QA)/control (QC) protocol prescribed by the U.S Environment Protection Agency (EPA) for metals analysis was used. In this study, analytical precision through replicate runs and the use of certified standard reference material PACS-2 (heavily contaminated marine sediment available from the natural Research council, Canada) was employed. The results indicated that the percentage recoveries are quite reasonable with 84 % being the least.

RESULTS AND DISCUSSION

Results

The result of sequential extraction of sewage sludge with variations in the pH of the residual fractions are presented in Table 3.1. The highest acid extractable fraction (1.78 ± 0.01 mg/kg) was recorded in Fe while the least (0.16 ± 0.01mg/kg) was found in cadmium. The reducible fraction across the various concentration ranged from 0.03 -0.17 mg/kg for Cd, 0.01-0.43 mg/kg for Pb and 1.04-2.54mg/kg for Fe. For oxidizable fraction, the range was 0.15-0.24 mg /kg in Cd,0.06-0.23mg/kg in Pb and 0.55-2.08mg/kg in Fe. The residual fraction across the three experimental design of variables pH ranged from 0.07-0.21mg/kg for Cd,0.01-0.08mg/kg for Pb and 0.79-1.07mg/kg for Fe. The result in Table 3.1 clearly demonstrated the impact of pH on metals bioavailability.

Table 3.1 mean concentration (±S>D) of heavy metals in various fraction of sewage

Location	Fraction	Cd (Conc/mg/kg)	Pb (Conc/mg/kg)	Fe (Conc/mg/kg)
B H	**Acid Extractable**	**0.16± 0.01**	**0.40 ±0.01**	**1.78±0.00**
	Reducible	**0.12± 0.01**	**0.22 ±0.01**	**1.04± 0.21**
	Oxidizable	**0.24 ±0.00**	**0.23 ±0.03**	**0.55 ±0.07**
	Residual	**0.07 ± 0.01**	**0.01 ± 0.00**	**1.91± 0.03**
G H				
	Acid Extractable	**0.16± 0.01**	**0.40 ±0.01**	**1.78±0.00**
	Reducible	**0.17± 0.03**	**0.43 ±0.03**	**1.23±0.11**
	Oxidizable	**0.15± 0.02**	**0.20 ±0.03**	**2.08± 0.13**
	Residual	**0.21 ±0.01**	**0.46 ±0.03**	**0.79 ±0.021**

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P H				
	Acid Extractable	**0.16± 0.01**	**0.40 ±0.01**	**1.78±0.00**
	Reducible	**0.03± 0.00**	**0.01 ±0.01**	**2.54±0.21**
	Oxidizable	**0.18± 0.11**	**0.06 ±0.01**	**1.71± 0.21**
	Residual	**0.11 ± 0.03**	**0.80 ± 0.11**	**1.07± 0.02**

B-H =Boys' Hostel, G-H= Girls' Hostel and P-H = Private Hostel

Sewage characteristics

Table3. 2. Total contents of carbon (mg/kg)

Location	pH	TOC (%)
B –H	7.4± 0.2	35.3 ± 2.2
G- H	7.6 ± 0.2	37± 2.3
P –H	7.2 ± 0.1	39± 2.5

Table 3.3 Correlation matrix of heavy metals (N=24)

	Cd	Pb	Fe
Cd	1	.665**	.379
Pb	.598**	1	.507**
Fe	.412*	.457*	1

Significant/r/*(p=<0.05); ** (p<0.001)

Hostels within the campus and private Hostel Pearson coefficients are shown above and below the diagonal line respectively=24 in each case (correlated values are in bold form).

DISCUSSION

The results of this study from table 3.2 revealed that investigated sewage sludge are characterized by varying chemical composition. Two major trends were observed; samples from B-H and G-H displayed the same trend with sample from P-H. from this point of view the content of organic carbon and pH are essential. pH values vary between 7.2 -7.6 with sludge B-G and G-H rendering higher values compared with sludges P-H. The levels of organic carbon varied considerably with highest and lowest value being 39 % and 35.3% respectively from B-H and P-H respectively. The value of organic content from G-H is 37 % is close to P-H, though slightly less than P-H. The increased level in G-H and P-H over B-G could be associated with the complexity of wastes emanating from the girls Hostel compared to those found within the private hostel. The higher percentage of organic carbon from the P-H demonstrates higher rate of biodegradation; an important tool for increased organic matter content.Organic matter and organic carbon play a vital role in soil amendments, the high level as recorded in this study coupled with neutral pH support the viewpoint that sewage sludge has high potential agricultural benefits for land application (Walter *et al.,* 1994; Fuentes *et al.,* 2004). The sewage pH and organic matters influence was observed only on cadmium (r= -0.970 at p< 0.05) with displaying of negative correlation. Several groups of elements are present in sewage sludge. Table 3.1 indicates that total content of Cd, Pb, and Fe showed significant differences between the investigated sludge samples. Two of the metals; Cd, and Pb are recorded at levels less than 1.0 kg/mg. The differences in the metal concentrations were most pronounced in B-H and G-H due to high total contents of heavy metals.

Sequential extraction

The analysis of sequential extraction conducted on metals showed that in spite of the significant effect of the nature of these elements on the rate and direction of the formation of chemical combinations, the similarly dominant quantity of Fe was found in both the organic combinations as well as residual fraction. The preference for this metal for organic matter is supported by the high stability constant of the metals complexes with organic matter (Gonzalez *et al.*, 1994).The metal levels in the oxidizable fraction which is associated with

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the organic matter are relatively high, particularly in Pb and Cd and they represent a large fraction of the average total metal concentrations in both B-H,G-H and P-H sewages. In this study, it is worthy to note that apart from Pb and Cd, the highest percentages of the extractable metals were recorded in the residual fractions from all the sewage sources and to a lesser extent in the exchangeable fractions in all the metals (Figures 3.2). Thus, the organic fractions in Fe, Mn and Cd account averagely for 022, 0.2, and 0.22 mg/kg respectively of the fractional sum of the metals without any significant difference ($p < 0.05$) between the various sample sources. In fact, regardless of the adjustment in the pH and sewage sludge sources, almost 70% of the concentrations occurred in the oxidizable and residual fractions (Figure 3.2).The results suggest that majority of the metals might be linked to organic substances or be co-precipitated with oxides, carbonates and phosphates in sewage sludge (Zhang et al.,2007).A relatively higher percentage in the amount associated with carbonate for Fe and lower percentage for Cd as compared with the oxide fraction was recorded. It is concluded that Cd pollutant may have been in both residual and oxidizable forms while Fe may probably be more in the residual and reducible forms. Among the various metals, the highest and least residual fractions were found in Fe and Cd respectively. This fraction of the metals represents the part that cannot be mobilized. In addition, the based on the data in Figures 3.2, greater percentage of Cd and Cu are released under the strong oxidizing condition. This is very significant because, this fraction constitutes an important source of potentially available trace metals (Ure and, Davidson, 1995). Significant positive correlation (= 0.01 and 0.05) were observed between some of the metals in samples from both the Campus hostels and Private Hostel (Table3.3). Cadmium was found to be positively correlated with Pb. Lead and Cd are two environmentally important heavy metals without any known biological function in plants, animals and humans. In this study, a very small proportion of Pb and Cd are found on exchangeable fraction while very high proportion lies within the oxidizable fraction. These findings is consistent with previous reports on the behavior of Pb in contaminated soils, for which there is little evidence of downward movement, with accumulation on the surface (Thornton, *1981*). In a study of Spanish soils, Ramos *et al.* (1994) also found that most Pb was associated with the oxide fraction, with only very little amount in the exchangeable fraction. Similar findings was reported by Olalade (2009). It thus shows that the oxide fraction in sewage sludge is capable of scavenging Pb.

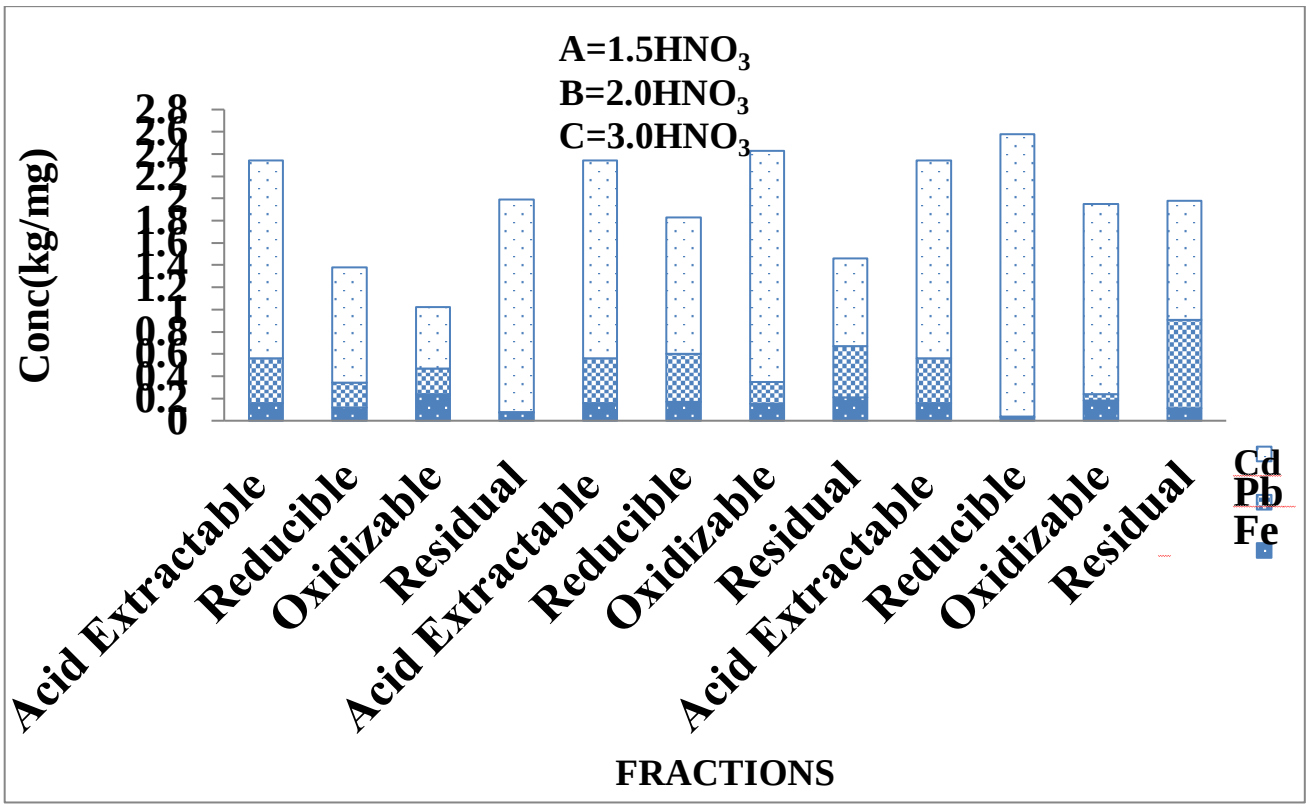

Figure 3. 1. The distribution pattern of metals across the various concentrations

The distribution pattern of the metals across the various concentrations is presented in fig 3.1. Signifcant variations were observed in the partitioning of the metals. The variability in concentrations of the reducible fractions i.e pH of the system displayed some trend in the concentrations of not only the reducible fractions but

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also the oxidizable and residual fraction. Iron demonstrated an increase in concentration with increased pH of the extractant (i.e. HNO_3). Both Cd and Pb shared similar pattern of initial increase in concentration which later falls drastically with further increase of pH from 0.30(2.0M HNO_3) to 0.48(3.0M HNO_3)

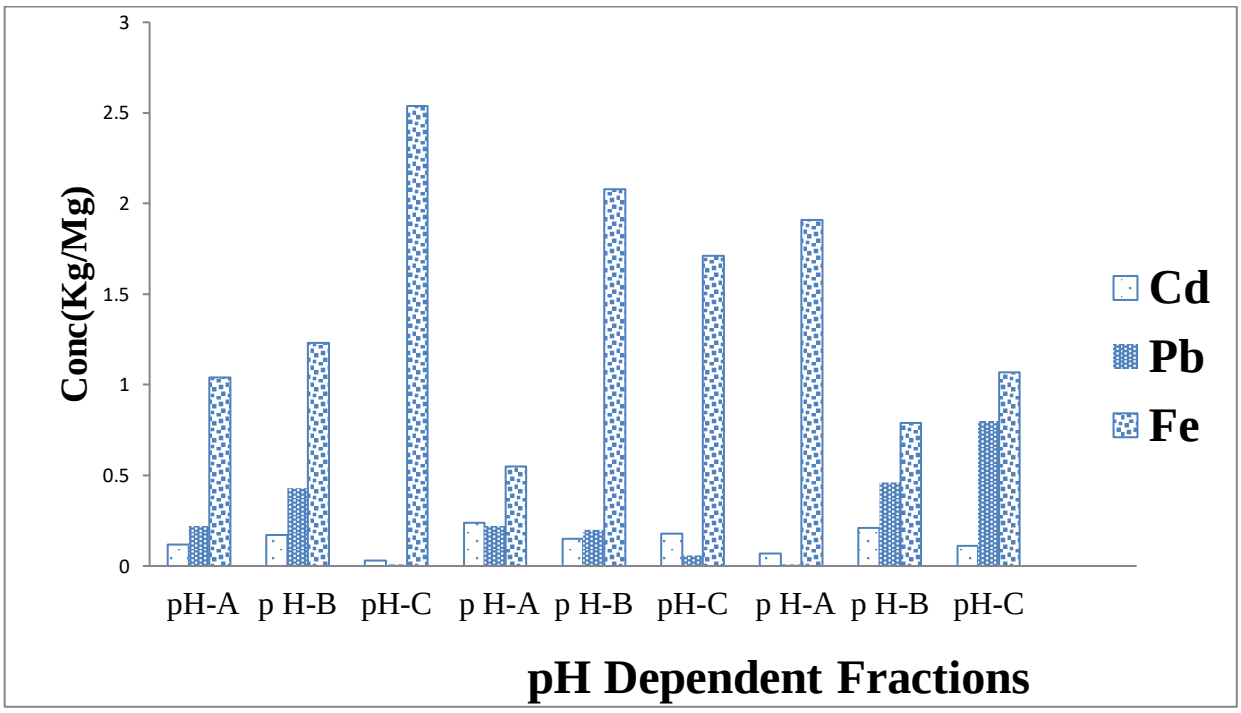

Figure 3. 2. pH Dependent concentrations of various Fractions

Fractions

A critical assessment of Fig 3.2 showed that certain trend were noticeable. In Pb, the oxidizable fractions were observed to decrease with increase in pH from 0.18 (1.5M HNO_3) to 0.48(3.0M HNO_3). However, the reversal is the case with the residual fraction which was observed to increase with increase in pH for Cd, highest concentration of metals were obtained at pH 0.30 (2.0 M HNO_3) for oxidizable and residual fractions. The observation particularly demonstrated that there is an Optimum pH for bioavailability of metals. For Fe, no pattern can be traced with pH values. The pattern displayed in Fig 3.2 shows that impact of pH is not only dependent upon the variation in the pH value but also on the nature of the metal involved. The non-regularity of the oxidizable and residual fractions with pH across the various metals is also indicative of partitioning nature of some metals in different chemical environment

CONCLUSION

Pollution of the environment by toxic metals has been on increase since industrialization began. The present work has revealed that total metal assessment may not necessarily reflect toxicity but through speciation analysis, mobile fraction of total metal present can be quantified. These fractions are bioavailable form which could lead to toxic on aquatic biota. The study clearly revealed that anthropogenic input of metals are mainly responsible for some metals such as Pb, Cd and Fe in the sewage. This may be said to have resulted from domestic activities since there is no other noticeable industrial source of these metals within the area. Though, Fe is considered in the study as nutritional metal, at high concentration especially in the bioavailable form, they can become toxic. Most importantly, two of the metals, Pb and Cd, are very toxic metals with no known biological function. Their levels (that is, Pb and Cd) in this study may be a sort of concern, because they may enter the food chain through plants or animals, contaminate surface and ground water and thus cause health hazards. This attempt of a pH-dependent approach, particularly in the reducible fraction has further expanded the scope of sequential extraction. Consequently, proper monitoring of the area is recommended. It must however be emphasized that sequential extraction procedure should be applied with full consideration of limitation. It is also hoped that more metals will be examined in the future.

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