Assessment of Bioavailable Trace Metal Levels in Bed Sediment of River Water System

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Authors' contributions

This work was carried out in collaboration between all authors. Author TBW designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches. Authors GSA and KBC managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The study was carried out to assess contamination and seasonal variations in bioavailable forms of trace metal (Cd, Cr, Cu, Fe, Pb, Ni, Zn, Mn) concentrations in bed sediment. Sediment samples were collected from five sampling points during dry and rainy seasons along Mada River, Nasarawa state, Nigeria. The samples were extracted using HCl/HNO$_3$ (3:1v/v) and Ethylenediaminetetraacetic acid (EDTA). Trace metal levels in the extracts were quantified using atomic absorption spectrometer (AAS). Enrichment factors (EF) and Geochemical index (IGeo) were also determined. Acid leachable metal concentrations in bed sediment were higher than the EDTA extractable trace metal levels during the rainy season. Sediments were enriched with Fe and Mn. Igeo index revealed class 0 – uncontaminated for the sediments during both seasons. Acid leachable Cu, Pb and Zn concentrations correlated positively and strongly for both periods of analysis; indicating same source and mechanism. Analysis of variance (ANOVA) indicated significant differences ($P<.05$) between acid leachable and EDTA trace metal concentrations. Metal concentrations, though higher during the rainy season, were below the Consensus-Based Sediment Quality Guidelines (CBSQG), the threshold and probable effect concentrations.

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The moderately to strongly contaminated nature of surface sediment could be as a result of anthropogenic source of metals entering the coastal zone through river inputs. Further study on the impact of trace metal contents in bed sediment on the quality of the overlying water column of the river is recommended.

Keywords: Sediment; acid leachable; EDTA, extraction; bioavailable; contamination; trace metals.

1. INTRODUCTION

Bed sediments in water system are repositories for various metals, acting both as sinks and sources of supply for the elements to overlying water column [1-3], because of anthropogenic wastes discharged into water bodies [4,5].

The determination of total heavy metal content of sediment samples is not sufficient to evaluate the possible mobility and, consequently, the bioavailability of toxic metals to living organism [6-8]. Bioavailable metal may be defined as the ecologically significant ambient metal in a habitat, given its potential for ecotoxicological effects [9]. The behaviours of elements in the environment depend on their forms [6,8,10].

Quantification of bioavailable trace metals in sediments is typically done using chemical solutions of varying, but specific strengths and reactivities, to release metals; as single or sequential extraction [5,11-13]. Single extractants may broadly be divided into weak replacement of ion salts ($MgCl_2$, $CaCl_2$, NH_4NO_3), dilute solutions of either weak acids (CH_3COOH) or strong acids (HCl, HNO_3), and chelating agents (DTPA, EDTA).The first type of extractants are able to release into solution metals which are associated with the exchange sites on the sediment solid-phase and hence can be considered as bioavailable [5]. The chelating agents, such as DTPA, EDTA and NH_4AOC, form complexes with free metal ions in solution and thus reduce the activities of the free metal ions in solution [14]. For soil or sediment, extraction method is usually use for isolating functionally defined matter, for example, plant available form, exchangeable cations or labile forms, which are not narrow to individual chemical forms but may embrace a number of chemical substances that share a common function and are all available to plants or organisms [15].

The extractable trace element amount depends on the nature of the extractant, sediment/extractant ratio, extraction time and methodology [15]. Extraction can be used to assess potential environmental effects, and to signal possible remedies [16]. However, in several countries, extraction data are being included to classify sediments within contaminated or non contaminated group, or to establish the maximum allowable concentrations [12].

Sample digestion is often a necessary step before determining metal concentrations in solid samples. Three commonly used digestion procedures include hot plate aqua regia, microwave aqua regia, and microwave aqua regia + HF. The aqua regia (3:1 v/v, HCl to HNO_3) digestion procedure is considered adequate for analyzing total recoverable trace metals in sediments and is used to estimate the maximum element availability to aquatic organisms [17,18]

Intensive irrigation farming takes place along the river bank, especially during dry season. Fertilizers, herbicides and pesticides used on crops grown, and other wastes are transported

into the river during rainy season, which eventually settle down as bed sediment, overtime. Trace metal accumulation and contamination of bed sediment has become a thing of concern worldwide, because accumulated metals can be remobilized into the water column under favorable conditions, therefore affecting the aquatic ecosystem. The objectives of this study is to asses seasonal variations in the levels of acid leachable and EDTA trace metal concentrations, and the contamination of the bed sediment of the river system by the trace metals.

2. MATERIALS AND METHODS

2.1 Study Area

Mada river is located at latitude 8º4´N and longitude 8º30´E (Fig. 1), and flows centrally through Nasarawa state, almost bisecting it into two halves and joining the Benue River east of Loko [19].The water of the river is characterized by seasonal variations, and serves as the major source of portable water supply to some communities in the state, after treatment.

2.2 Sampling and Sample Preparation

Bed sediment samples were collected from five (5) points at distances between 5-10m from the river bank (Fig. 1) by scooping. The sediment samples were dried in an oven at 50ºC for two days [20], ground in a porcelain mortar using a pistil, and then sieved through 2mm mesh sieve. The sieved sediment samples were stored in acid washed polythene bottles with plastic screw caps, and preserved in a refrigerator for extraction.

2.3 Extraction of Bioavailable Forms of Metals

2.3.1 Acid leachable extraction

$28cm^3$ 37% HCl:70% HNO_3 (3:1 v/v) was added to 1.00g of the dried sieved (2mm) sediment sample and left to stand for 24hours. The mixture was then heated on a hot plate at 140ºC to near dryness. The residue was filtered through Whatman No. 41. The solution was then transferred into $50cm^3$ volumetric flask and made to mark with distilled water, and preserved for metal analysis.

2.3.2 EDTA extraction

$50cm^3$ of 0.05M EDTA was added to 10g (5:1) of the sieved sediment samples in $100cm^3$ conical flask. The mixture was shaken using an end to end shaker at 220rpm for 60 minutes and then filtered through Whatman No. 41 filter paper. The filtrate was preserved for metal analysis. Trace metal levels concentrations in sediments were quantified using Atomic Absorption Spectrometry (AAS) AA 600. Analyses were carried out in duplicates.
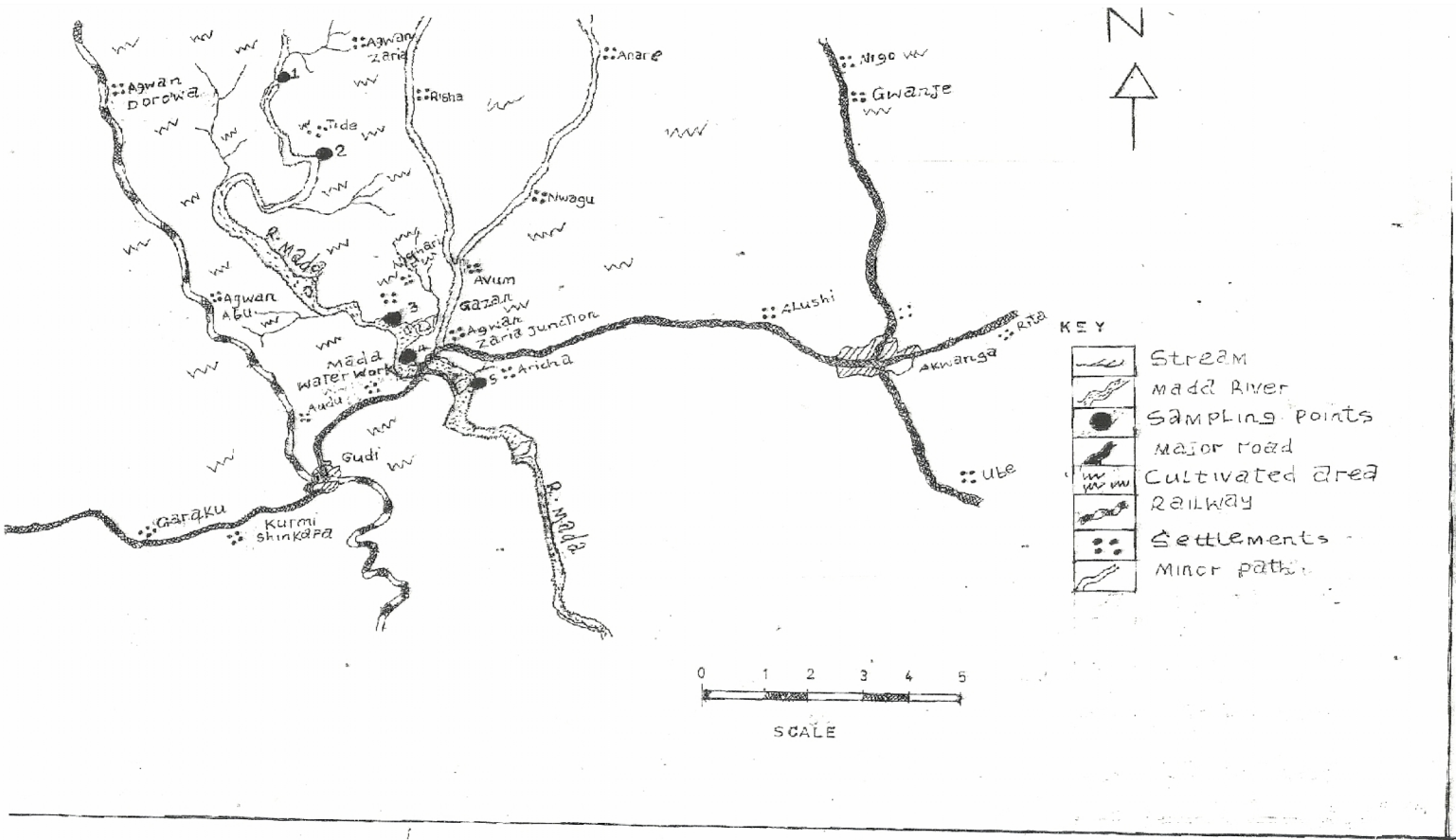
Fig. 1. Mada river showing sampling points

2.4 Enrichment Factor (EF)

Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure; and to assess the degree of anthropogenic influence [19,21]. As the EF values increase, the contributions of the anthropogenic origins also increase [22].To determine an anthropogenic influence on fresh water ecosystem, the environmental factor (EF) for each metal was calculated as:

$$EF = (C_n/Fe) / (C_n/B_n)$$
C_n = measured content of elements

B_n = element's content in shale (Pb: 20, Cr: 90, Cu: 45, Cd: 0.20, Zn: 95, Fe: 95, Fe: 4700, Mn: 850, Ni: 68) [23].

2.5 Geochemical Index (Igeo)

Possible sediment enrichment of metal was also calculated in terms of Igeo index [21,24]. Igeo were calculated using the formula:

$$Igeo = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

C_n = measured content of element *n*
B_n = element's content in average shale. The factor 1.5 is introduced to minimize the effect of the possible variation in the background or control value [25]

2.6 Statistical Analysis

Pearson correlation matrix was used to establish the strength of the relationships for acid leachable metal concentration, while ANOVA was adopted to determine any significance differences in seasonal EDTA and acid leachable metal levels in sediment.

3. RESULTS AND DISCUSSION

Variations in the levels of acid leachable metal in sediment during the rainy season are shown in Fig. 2. Fe concentration was the highest in all the sites, attaining the maximum concentration at site 5 and lowest at site 3. Cd concentration was below detectable limit. Pb, Mn and Fe levels were relatively high. Trace metal concentrations generally increased from site 1 to 5, except for Pb, Fe and Mn at site 3.

During the dry season (Fig. 3), Fe concentration remained the highest in all sampling sites, with the highest concentration at site 5. Mn and Zn concentrations were relatively high. Cd and Cr concentrations were below detectable limits, except for Cr at sites 4 and 5. Concentrations of trace metals increased downstream, except at site 3, which recorded the lowest metal levels.
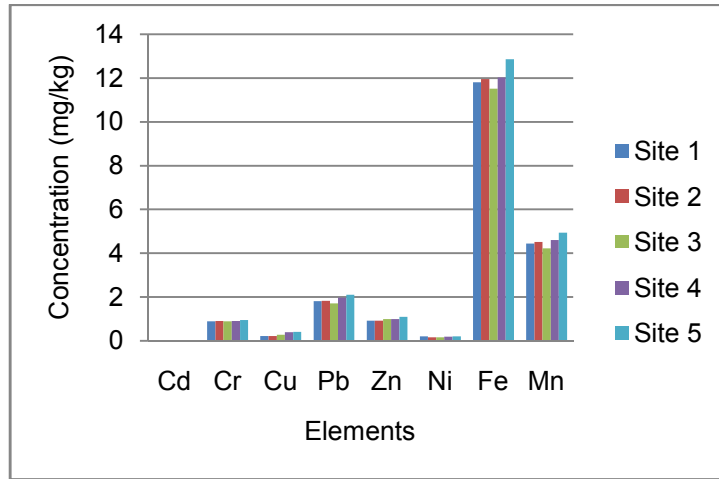
Fig. 2. Acid leachable trace metal concentrations (mg/kg) in sediment during rainy season
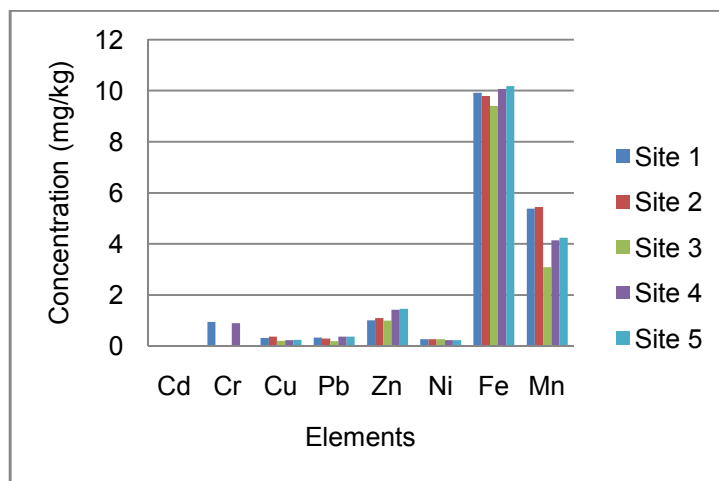

Fig. 3. Acid leachable trace metal concentrations (mg/kg) in sediment during dry season

Rainy season results for the variations in sediment EDTA trace metal concentrations (Fig. 4) showed that concentration of Cd was below detectable limit. Trace metal concentrations were low in all the sites, except for Fe and Mn. The highest concentration of Fe, amongst metals, was recorded at site 2. Mn concentration increased downstream, except at site 4. EDTA results (Fig. 5) for trace metals during the dry season indicated spatial variations. Concentrations of Cd, Cr and Ni were below detectable limits, except for Ni at site 3. Cu and Pb concentrations were relatively high at site 2, but low for Zn. Concentration of Fe was highest in all the sites, attaining the lowest concentration at site 3. Mn concentration decreased downstream, except at site 2, where its concentration was relatively higher than at site 3.
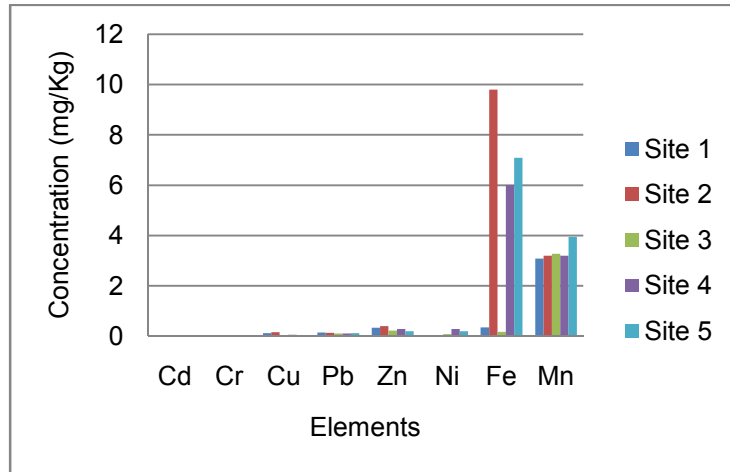
Fig. 4. EDTA extractable trace metal concentrations (mg/kg) in sediment during rainy season
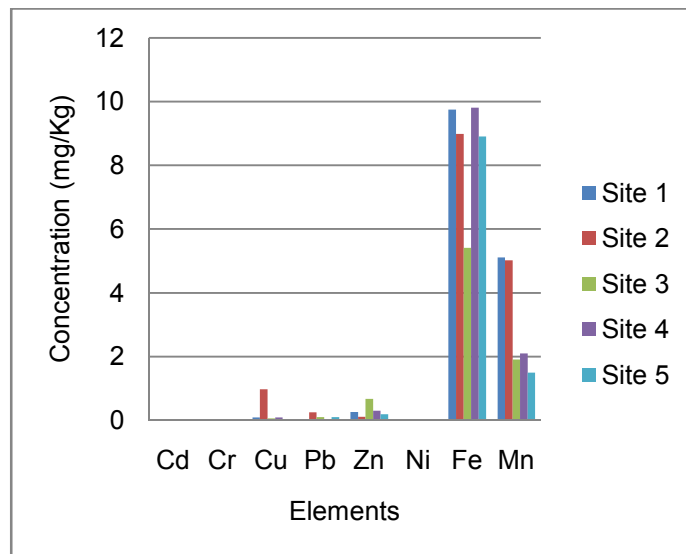

Fig. 5. EDTA extractable trace metal concentrations (mg/kg) in sediment during dry season

Seasonal mean variations in acid leachable and EDTA metal concentrations results are presented in Table 1. Acid leachable metal concentrations varied in increasing order of Fe Zn > Mn > Cr > Pb > Cu > Ni > Cd in dry season and Fe > Mn > Pb > Zn > Cr > Cu > Ni > Cd during the rainy season. Metal levels were relatively higher during the rainy season, except for Zn (0.976±0.17mg/kg) and Ni (0.176±0.018mg/kg). Variations in EDTA metal levels were Fe > Mn > Zn > Cu > Pb > Ni > Cr ≈ Cd and Fe > Mn > Zn > Pb > Cd > Cr during dry and rainy seasons respectively. EDTA metal levels increased during the rainy season except for Cu, Zn and Fe.

The distribution of trace metals in sediment can provide evidence of anthropogenic inputs on aquatic ecosystem. Trace metal associated with the easily exchangeable EDTA extracts fraction in the sediment phase are the most mobile and bioavailabe [8]. The high levels of Fe, Mn, Zn, and Pb in both the aqua-regia (total) and EDTA extractable fractions might be due to disposal of domestic and agricultural wastes into the river, containing high levels of the metals [26].

The general increase in metal levels during the rainy season might be attributed to increase in waste discharge into the river due to rainfall and storm runoff, and subsequent settlement of these wastes as bed sediment. Trace metal concentrations increased downstream except at site 3 where concentration was lowest for most metals. The results for this study are comparable with those reported by [26-27]. A comparison of the acid leachable metal concentration with average shale values revealed that bed sediment samples from the river were not polluted.

During the rainy season (Table 2), EFs values were relatively high for Mn (86.54), Zn (9.30) and Cr (9.02). Trace metal EFs values increased during rainy season, except for Ni, Fe and Mn. Elements with EF values less than unity implies depletion in some of the phases relative to crustal abundance in the study areas. Higher values for Mn, Zn and Cr for both seasons suggests the presence of contaminated sediment derived from multiferrous source like domestic sewage, major storm events [26]. In general, as enrichment values increase, contributions from anthropogenic origin also increase [21,28]. The moderately to strongly contaminated nature of surface sediment could be as a result of anthropogenic source of metals entering the coastal zone through river inputs [29,30].

Sediment Igeo values varied according to metal and were negative (Table 3). Igeo values were higher during the rainy season, except for Cd (-1.56), Pb (-2.60), and Zn (-2.03). Negative values showed that sediment was unpolluted. Igeo values were generally higher in dry season, except for Cd, Pb, and Zn. Mada river sediment is classified under 0 Igeo class, indicating that the sediment is uncontaminated [31].

Correlation analyses for trace metal concentrations during rainy and dry seasons are presented in Tables 4 and 5 respectively. During the rainy season (Table 4), Cd and Ni correlated weakly with other metals, while correlations among other metals were significantly high, while correlations for Cr and Fe with other metals were weak, but significantly strong among other metals during the dry season (Table 5). Strong correlations between metals imply same source and pollution mechanism.

Variations in seasonal analysis of variance (ANOVA) for acid leachable and EDTA trace metal concentrations are presented in Table 6. During the dry season, total Cd, Zn, and Fe concentrations were significantly different from other trace metal concentrations. Zn and Fe total concentrations were significantly different ($P<.05$). Dry season EDTA Cd and Cr; Cu, Pb and Ni; Zn and Fe, and Mn concentrations were significantly different.

Table 1. Seasonal mean variations in acid leachable and EDTA extractable trace metal concentrations (mg/kg) in sediment

Extraction	Elements							
	Cd	**Cr**	**Cu**	**Pb**	**Zn**	**Ni**	**Fe**	**Mn**
ALd	0.0069±0.002	0.372±0.498	0.260±0.073	0.320±0.073	1.927±0.229	0.253±0.023	9.875±0.301	4.457±0.982
EDTAd	0.0035±0.002	0.004±0.003	0.254±0.406	0.102±0.091	0.309±0.219	0.009±0.012	8.574±0.1.817	3.129±0.178
ALr	0.007±0.003	0.902±0.024	0.296±0.349	1.879±0.153	0.976±0.017	0.176±0.018	12.030±0.504	5.00±0.262
EDTAr	0.0038±0.002	0.027±0.005	0.076±0.054	0.122±0.018	0.284±0.074	0.123±0.111	4.683±0.4267	3.338±0.342

ALd: acid leachable in dry season; ALr: acid leachable in rainy season; EDTAd: dry season; EDTAr: rainy season

Table 2. Enrichment factors (EF) for trace metal concentrations in sediments

Element	Dry season	Rainy season
Cd	0.02	0.02
Cr	9.02	9.10
Cu	4.48	4.85
Pb	6.19	6.92
Zn	9.30	9.90
Ni	7.03	6.92
Fe	4.80	4.70
Mn	86.54	84.20

Table 3. Geochemical index (Igeo) for trace metal concentrations in sediments

Element	Dry season	Rainy season
Cd	-1.56	-5.00
Cr	-2.55	-2.17
Cu	-2.43	-2.40
Pb	-2.60	-2.77
Zn	-2.03	-3.70
Ni	-4.80	-2.41
Fe	-3.85	-1.21
Mn	-2.46	-2.17

Table 4. Rainy season correlation matrices for acid leachable trace metal concentrations in sediment

	Cd	Cr	Cu	Pb	Zn	Fe	Ni	Mn
Cd	1	0.486	0.302	0.442	0.471	0.247	0.049	0.058
Cr		1	0.861	0.996	0.982	0.803	0.352	0.877
Cu			1	0.890	0.926	0.752	0.161	0.816
Pb				1	0.985	0.805	0.349	0.896
Zn					1	0.823	0.274	0.852
Fe						1	0.418	0.788
Ni							1	0.429
Mn								1

Significant at P = .05

Table 5. Dry season correlation matrices for acid leachable metal concentrations in sediment

	Cd	Cr	Cu	Pb	Zn	Fe	Ni	Mn
Cd	1	0.154	0.645	0.833	0.858	0.340	0.702	0.076
Cr		1	0.467	0.400	0.218	0.197	0.406	0.373
Cu			1	0.814	0.754	0.492	0.909	0.654
Pb				1	0.945	0.355	0.895	0.356
Zn					1	0.268	0.882	0.295
Fe						1	0.42	0.514
Ni							1	0.436
Mn								1

Significant at P=.05

Results for acid leachable metal concentrations during rainy season showed that Cr, Pb and Zn were significantly different from that of Cd, Ni and Mn. For EDTA, Cr and Cu, Pb, Zn and Ni, concentrations were significantly different from that of Cd, Fe and Mn. Generally, significant differences existed between acid leachable and EDTA trace metal concentrations.

Table 6. Analysis of variance (ANOVA) for acid leachable and EDTA trace metal concentrations in sediment

	Dry season		Rainy season	
	Acid leachable	EDTA	Acid leachable	EDTA
Cd	0.007[a]	0.003[a]	0.007[a]	0.004[a]
Cr	0.210[b]	0.002[a]	0.902[b]	0.627[b]
Cu	0.271[b]	0.078[b]	0.296[c]	0.076[b]
Pb	0.310[b]	0.051[b]	0.879[b]	0.122[c]
Zn	1.193[c]	0.303[c]	0.976[b]	0.284[c]
Fe	9.876[d]	0.574[c]	12.03[d]	4.683[d]
Ni	0.253[b]	0.009[a]	0.178[e]	0.123[c]
Mn	4.457[e]	3.129[d]	4.450[f]	3.338[e]

Mean with different letters within the same row for each season are significantly different at P =.05

4. CONCLUSION

The lowest and highest extractable metal concentrations were recorded for Cd and Fe respectively, for both acid leachable and EDTA extractions. Acid leachable metal concentrations in bed sediment were higher than the EDTA extractable trace metal concentrations. Trace metal levels increased during the rainy season but were below the CBSQG sediment quality guidelines, the threshold and probable effect concentrations. EF values indicated that the sediments were enriched with Fe and Mn, however, unpolluted. Igeo index revealed class 0–uncontaminated for the sediment samples analyzed. The moderately to strongly contaminated nature of surface sediment could be as a result of anthropogenic source of metals entering the coastal zone through river inputs. Cu, Pb and Zn correlated positively and strongly for both periods of analysis, which suggests a common source and mechanism of occurrence. Significant differences (P=.05) existed between acid leachable and EDTA trace metal concentrations in the sediment.

COMPETING INTERESTS

Authors declare that there are no competing interests.

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