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Extrapolative study on the Distribution, Bioavailability and Health Risks Assessment of Trace Metals of Ishiet River using Sediment

Emmanuel U. Dan*, Anietie E. Edet, Kokoette Raymond, Ubongete M. Akpabio

Department of Chemistry, University of Uyo, Uyo, Akwa Ibom State, Nigeria
*corresponding author's email: danmarble2003@gmail.com

Abstract Seasonal studies on the distribution and species of some trace metals in sediments obtained from Ishiet River and Control were carried out using standard analytical procedures. Total trace metal concentrations in the studied sediment indicated marked variations between seasons and sampling points. Concentrations of trace metals were lower than their respective acceptable limits except for Fe, with the studied sediment recording higher concentrations of the metals than the Control. Zn, Cu and Fe in the studied sediment were associated mostly in residual fractions, Pb and Cd in reducible and acid extractable fractions for sediments obtained during both seasons. Generally, bioavailability factors of trace metals in the sediment revealed higher value in Cd and least in Cu for dry and wet seasons. Results for trace metal fluxes indicated highest flux by Fe and least by Pb for both seasons. Pollution status of the studied sediment was assessed by calculating contamination and enrichment factors, degree of contamination, geo-accumulation and pollution load indexes and values obtained were compared with existing models. Carcinogenic and non-carcinogenic health risks associated with human exposure (children and adult) to the studied sediment have also been reported.

Keywords sediments, trace metals, speciation, Ishiet River, health risk

Introduction

The universal importance of water in all part of the environment cannot be overemphasized. Because of its uniqueness, the substance is critical in the sustenance of life and human existence. River water supports many life forms including washing, fishing, farming and other purposes. Since the onset of industrial revolution, the river has become one of the most recipients of toxic wastes from domestic, industrial, and agricultural run-offs. These toxic wastes including pesticides and trace metals, apart from contaminating the surface water are also being trap by the sediments. Sediments have a large capacity to retain trace metals, and can immobilize them within the stream sediments by some processes such as adsorption, flocculation and co-precipitation [1]. Therefore, sediments in aquatic environment usually serve as a pool that can retain trace metals or release same to the surface water by remobilization under favorable conditions [2, 3].

The interaction of river sediment with surface water can lead to several reactions which can play a vital role in the mobilization and fluxes of trace metals. Numerous studies have demonstrated that the concentrations of trace metals in sediments can be sensitive indicators of contaminants in aquatic system like river. This is because when wastes are being discharged into the river, the final point of accumulation (storage) is the sediment. Although, there are no much benefits of sediment to humans in terms of its direct usage as in the case of water, it is a home for some sedentary organisms like periwinkles, crabs commonly consumed by man. Also, Sediments conserve important environmental information and magnitude of suspended loads of rivers which has many practical applications ranging from geomorphologic studies of denudation rates and patterns of landform development to problem of upstream soil loss and downstream channel and reservoir sedimentation [4].

According to Loizidou [5] contamination of sediments with trace metals is a serious environmental problem as aquatic organisms may accumulate these metals in their organs to toxic levels and transfer same into human body through consumption, causing serious health hazards.

The release of heavy metals from sediment into the water body and consequently to aquatic organism will depend on the chemical fractionation, metal fluxes and other factors [6]. However, in sediments, heavy metals can be present in various chemical forms and generally exhibit different physical and chemical behavior in terms of chemical interaction, mobility, bioavailability and potential toxicity. With no reports available on the pollution status of Ishiet river and its sediment, the present study was undertaken to assess the quality of Ishiet river by ascertaining the health risk hazards and pollution status of the sediment. This was done by determining the total concentration of some trace metals; species (speciation), trace metal fluxes, bioavailability and hazardous potentials of trace metals in the sediment. Therefore, this research work is a deductive study on the current health risk hazard and pollution status of Ishiet river using the sediment.

Materials and Methods

Description of Study area

Ishiet River is found in Uruan Local Government Area in Akwa Ibom State, Southern Nigeria. It has geographical coordinates of 4^0 57’ 0’’ North, 8^0 1’ 0’’ East. The river is a tributary to Cross River which empties into the Atlantic Ocean at Bight of Bonny; and tidal flux by tidal wave from the Atlantic Ocean do flow to many upstream zones along its courses example Nwaniba and Ikpa Uruan. This area is within a typical tropical rainforest zone that is characterized by distinct dry and wet seasons. The wet season usually begins in March and is often accompanied by heavy storms though usually for a short duration. The annual average rainfall is about 2168 mm. The dry season which normally lasts between three to four months from November to March is often influenced by the hot north – easterly wind blowing from sahara desert. Figure 1 shows the location of sampling sites on the map of Uruan Local Government Area.

Sample collection

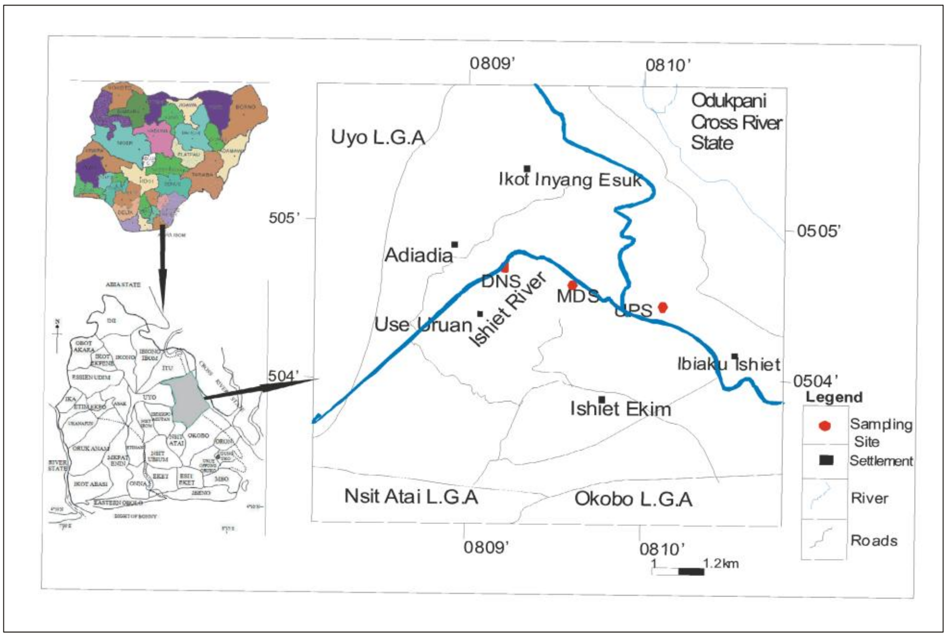

Figure 1: the location of sampling sites on the map of Uruan

Sediment samples were collected from Ishiet River in December 2017, January and February 2018 representing dry season, and April – June 2018 representing the wet season. At each sampling points (UPS – upstream, MDS – midstream, DNS – downstream), three (3) sub-samples and one (1) composite sample were collected for one month. Thus, eighteen (18) sub-samples and six (6) composite samples were obtained for the six months. Sediment from Ntak Inyang was also collected and used as control since there has been no report of intense human activities around that area in addition to it being more than 30 kilometers away from the studied river. Sediment sample cores were taken using Van Veen sediment grab sampler into black calico bag, labeled and transported to the laboratory for analysis.

Sample preparation and analysis

Sediment samples and Control were air-dried for 72 hours, disaggregated and sieved through a 2mm plastic sieve to remove large debris, gravels and other unwanted materials. The sieved samples were crushed and homogenized to uniform powdered samples. One gram each was weighed into digestion flask and digested with 4M HNO_3 and H_2O_2. The solution was left to digest under reflux for one hour and evaporated to near dryness at a temperature of 120^{o}C on a hot plate. The resulting solution was allowed to cool before it was leached with 5cm^3 6M HCl and filter into a volumetric flask and made up to the mark with deionised water. Concentrations of Pb, Cd, Zn, Ni, Cu and Fe were determined using atomic absorption spectrophotometer (Unicam model 939).

Optimised BCR sequential extraction procedures

Sequential extraction of trace metals in studied sediment and Control were carried out using optimized BCR procedures as described by Rauret [7] Procedures performed for each fraction are given below

Fractions	**Designations**	**Procedures**
1	Acid extractable (weak acid extractable, exchangeable and carbonate bound)	1 g of homogenized sediment sample, 40 ml of 0.11M acetic acid solution was added. The mixture shaken with a mechanical shaker for 16h and extract separated by centrifugation at 3000 rpm for 20 mins collected and stored in polyethylene bottles.
2	Reducible (Metal fraction bound to Fe-Mn oxides and Hydroxides)	40 ml of 0.50 M hydroxylammonium chloride ($NH_2OH.HCl$) solution was added to the residue from step 1 above, shaken for 16 h at room temperature and centrifuged as in step 1 to separate the supernatant from the residue
3	Oxidisable (Metal fraction bound to sulphide and organic matters)	Residue from step 2 was treated with 10 ml 8.8 M hydrogen peroxide (H_2O_2) and allowed to digest for 1 h. The mixture was evaporated to dryness and 50 ml of 11M ammonium acetate ($CHCOONH_4$) added, shaken for 16h at room temperature and centrifuged to separate the extract from residue
4	Residual (Metal fraction bound to crystalline silicates in soil)	To the residue from step 3, a mixture of 5ml Conc. trioxo-nitric acid (HNO_3) and 15ml Conc. hydrochloric acid (HCl) was added and placed on hot plate for 2h. The mixture was cooled and filtered through Whatman No. 50 filter paper into a volumetric flask for analysis.

Percentage recovery and bioavailability factor of trace metals were determined using equation 1 and 2 below

$$\%\ Recovery = \frac{\sum n\ Sequential\ extraction\ procedures}{Single\ extraction\ with\ strong\ acids} \quad (1)$$

$$Bioavailability\ factor = \frac{F1}{F1+F2+F3+F4} \times 100 \quad (2)$$

Where n = concentration of a particular metal and the single digestion with strong acids used for digestion of residual fraction F1 = acid extractable fraction, F2 = reducible fraction, F3 = oxidisable fraction and F4 = residual fraction in modified BCR speciation procedures

Flux determination

Trace metal fluxes in sediment were calculated using equation 3 described by Udosen [8].

$$F = R\,(1-\theta)\sigma C \qquad (3)$$

Where $F = flux$, $R = sedimentation\ rate$, $\theta = porosity$, $\sigma = dry\ density$, $C = metal\ concentration$

Pollution status of sediment

Pollution status of the studied sediment was assessed by calculating the following parameters: contamination and enrichment factors, degree of contamination, geo-accumulation and pollution load indexes. Contamination factor of trace metals was determined using equation (4) below

$$Contamination\ factor = \frac{Concentration\ \ of\ metal\ \ in\ studied\ \ soil}{Reference\ \ soil\ (control\ )} \qquad (4)$$

Degree of contamination (Cdeg) and enrichment factor (EF) were determined using equations 5 and 6 [9].

$$Cdeg = \sum MPI \qquad (5)$$

Where MPI = metal pollution indexes for all the studied trace metals

$$EF = \left(\frac{M}{Fe}\right)S \Big/ \left(\frac{M}{Fe}\right)C \qquad (6)$$

Where S = sediment, C = control

Geo-accumulation indexes of the metals and pollution loads were calculated using equation 7 and 8 below

$$Igeo\ \ = Log\ 2(Cn/1.5Bn) \qquad (7)$$

Cn = measured concentration of trace metal in studied sediment, Bn = Concentration of trace metal in Control sediment, Log 2 and 1.5 are constants described in Huu *et al* [10].

$$PLI\ = (MPIPb\ \times MPICd\ \times MPICu\ \times MPI\ Zn\ \times MPIFe\ \times MPINi)^{\frac{1}{6}} \qquad (8)$$

Health risk assessment

Cancer and non cancer potential of trace metals in the studied sediment were also evaluated. For non cancer, the following parameters were used; daily intake (DI), hazard quotient (HQ) and total chronic hazard index (THI), while for cancer; incremental lifetime cancer risk was used. Daily intake of trace metals was calculated using equation 9 given below

$$Daily\ intake = \frac{C \times lngR \times EF \times ED}{BW \times AT} \qquad (9)$$

Where C = mean metal concentration; IngR = sediment ingestion rate; EF = exposure frequency per day per year, ED = exposure period in a year; BW = body weight in kg and AT = average time for non-carcinogens [11, 12]. Values for each parameter have been reported by Ebong et *al.*,[13].

Hazard quotient and total chronic hazard index were calculated using equations 10 and 11 respectively

$$Hazard\ quotient = \frac{Daily\ \ intake\ \ of\ each\ metal}{Chronic\ \ reference\ \ dose\ \ of\ each\ metal} \qquad (10)$$

The Rfd mgkg^{-1}day^{-1} for metals studied are as follows: Pb (0.0035), Cd (0.001), Zn (0.3), Cu (0.04), Ni (0.02), and Fe (0.07).

$$THI = \sum HQ = HQPb + HQCd + HQZn + HQNi + HQCu + HQFe \qquad (11)$$

Where HQ is individual hazard quotient of trace metals in the sediment

Incremental lifetime cancer risk (ILCR) of trace metals in the sediment was determined using equation 12 given below

$$ILCR = DI\ \times CSF \qquad (12)$$

Where DI = daily intake of trace metals measured in mgkg^{-1}BWday^{-1}, CSF = cancer slope factors

CSF for Pb, Cd and Ni are 0.085, 6.3 and 1.7 respectively.

Results and Discussion

Total trace metal concentrations in Sediment

Table 1: Mean concentration (mgkg^{-1}) of trace metals in sediment and Control during dry season

Location	Pb	Cd	Zn	Ni	Cu	Fe
DNS	2.42	3.39	32.93	5.89	6.70	418.00
MDS	1.90	3.80	34.84	6.32	6.75	427.16
UPS	1.96	3.65	41.82	5.52	6.63	541.70
Min	1.96	3.39	32.93	5.52	6.63	418.00
Max	2.42	3.80	41.82	6.32	6.75	541.70
Mean	2.09	3.61	36.53	5.91	6.69	462.29
SD	0.28	0.20	2.68	0.40	0.06	36.55
% CV	15.80	10.70	12.50	11.50	8.80	14.10
Control	0.52	1.07	12.13	2.65	2.81	280.52

* Each value represents mean of three determinations analyzed individually in triplicate; DNS -downstream; MDS – midstream; UPS – upstream; SD – standard deviation, CV – coefficient of variance

Table 2: Mean concentration (mgkg^{-1}) of trace metals in sediment and Control during wet season

Location	Pb	Cd	Zn	Ni	Cu	Fe
DNS	2.33	3.93	32.25	9.17	6.57	677.98
MDS	1.92	3.75	36.08	9.29	6.79	666.09
UPS	2.12	4.29	38.66	9.89	7.06	717.90
Min	1.92	3.75	32.25	9.17	6.57	666.09
Max	2.33	4.29	38.66	9.89	7.06	717.90
Mean	2.12	3.99	35.66	9.45	6.81	687.32
SD	0.21	0.27	3.22	0.38	0.25	27.13
% CV	18.90	8.80	11.80	4.60	9.10	33.40
Control	0.40	0.69	7.81	3.66	2.91	324.04

* Each value represents mean of three determinations analyzed individually in triplicate; DNS –downstream; MDS – midstream; UPS – upstream; SD – standard deviation, CV – coefficient of variance

Results for trace metals in sediments from Ishiet River and Control during dry and wet seasons are presented in Table 1 and 2. The results indicated varied concentrations of trace metals between the sediment sample and the Control for both seasons. Also, from the results, each of the reference points (DNS, MDS, and UPS) recorded varied concentrations for each of the trace metals studied for both season. The results revealed a trend of DNS > UPS > MDS for Ishiet River sediment during both seasons. For dry season, Pb indicated a range of 1.96 – 2.42 mg/kg with mean of 2.09 mgkg^{-1}, while for wet season, the range for Pb was 1.92 – 2.33 mgkg^{-1} and mean of 2.12 mgkg^{-1}. The results obtained shows that mean concentrations of Pb in dry season was lower when compared to the mean concentration of Pb in wet season. The disparity in the mean concentration of Pb in Ishiet River sediment between dry and wet seasons can be explained as a result of mineral weathering and possible run –off from industrial, agricultural and residential land uses into the river which can easily settles onto the sediment during wet season. Mean concentrations of Pb obtained in this study for both seasons are lower than 7.00 mg/kg and 4.85 mg/kg reported by Iwegbue *et al.*, [14] and Udosen *et al.*, [15] for sediment from Ase River, Delta State, Southern Nigeria and Imo River estuary, Eastern Nigeria respectively. However, the mean concentrations obtained for Pb are lower than 0.07 mg/kg previously reported by Ideriah *et al.*, [16] for sediments from Abonnema Shoreline, Nigeria. From the results, the concentrations of Pb in sediment from Ishiet River and Control for dry and wet seasons were within the permissible limits of 40 mg/kg stipulated by World Health Organization [17] for sediment. For both seasons, % CV indicated values of 15.80 and 18.90 which are close to each other and show that the measured concentrations of Pb in the sediments are close to the mean.

Results for Cd in sediments from Ishiet River and Control for dry and wet seasons are presented in Table 1 and 2. The results indicated varied concentrations of Cd in sediments from Ishiet River and Control during dry and wet seasons. For sediments obtained from Ishiet River during dry season, the order of abundance of Cd was MDS > UPS > DNS, while for wet season, the order of abundance was UPS > DNS > MDS. Mean concentrations of Cd for dry and wet seasons were 3.61 mg/kg and 3.99 mg/kg respectively, with ranges of 3.39 – 3.80 mg/kg and 3.75 – 4.29 mg/kg. However, mean concentrations of Cd were higher in Ishiet River sediments obtained during wet season than dry seasons. The presence of Cd in the sediments maybe due to incidences of local spillage of petroleum products, spent oil run-off from roads and motor parks into the river. Higher concentration of Cd in sediments during wet season maybe traceable to the activities of erosions leading to leaching of cadmium containing wastes into the river which later settles in the sediment. Results for mean concentration of Cd obtained in this study for both dry and wet seasons are lower than 12.62 mg/kg and 6.39 mg/kg previously reported by Egbenni *et al.*, [18] and Okoye [19] for sediments from Lagos lagoon and Ebute – Meta Rivers, Nigeria but higher than 0.84 mg/kg reported by Maitera *et al.*, [20] for sediment from River Gongola, Adamawa State, Nigeria. The results also indicated that the mean concentration of Cd obtained in this study for sediments are lower than 6.00 mg/kg stipulated by WHO [17] for sediments. However, higher concentration of cadmium is extremely toxic to fish and other sedentary population such as perewinkles, crabs etc. Its effects on the growth rate have been observed even for concentrations between 0.005 and 0.01 mg/kg [21].

Unlike Cd and Pb, Zn plays a significant role in the life processes of all aquatic plants and animals although they are usually require in trace amounts. At elevated levels, it is usually toxic to most aquatic species and can lead to formation of different Zn complexes that are detrimental to aquatic animals [22]. Results for Zn in sediments from Ishiet River and Control for dry and wet seasons are presented in Table 1 and 2. From the results, sediments from Ishiet River at each point of reference for both dry and wet season recorded same order of abundance UPS > MDS > DNS. The mean and ranges for sediment from Ishiet River obtained during dry season were 36.53 mg/kg and 32.93 – 41.82 mg/kg, while for wet season were 35.66 mg/kg and 32.25 – 38.66 mg/kg. The mean concentrations for sediment from Control obtained during dry and wet season were 12.13 mg/kg and 7.81 mg/kg. From the results, Zn recorded higher concentrations in sediment obtained during dry season than in wet season for both Ishiet River and the Control. Ranges for Zn obtained in this study for dry and wet seasons are lower than 123.45 – 165.34 mg/kg and 200.59 – 200.67 reported by Akan *et al.*, [23] and Adebayo [24] for sediments from Lake Chad and Ureje Rivers respectively. Concentrations of Zn in the sediments obtained in this study were lower than recommended values by WHO [17] for sediment.

Results for Ni concentration in sediment from Ishiet River and Control for dry and wet seasons are presented in Table 1 and 2. Trend of abundance of Ni in sediment from Ishiet River for dry and wet seasons indicated different trends which were MDS > DNS > UPS for dry season, and UPS > MDS > DNS for wet season. For both samples, that is Ishiet River and Control sediments, mean concentrations of Ni were higher in samples obtained during wet season than in dry season. Mean and range for Ni in sediments obtained during dry season were 5.91 mg/kg and 5.52 – 6.32 mg/kg, while for wet season, the sample recorded mean Ni concentration of 9.45 mg/kg and range of 9.17 – 9.89 mg/kg. For sediment from the Control River, mean for Ni in sediment obtained during dry and wet season were 2.65 mg/kg and 3.66 mg/kg respectively. The presence of Ni in Ishiet river sediment is an indication of its presence in the water body. Nickel in rivers is linked mostly to anthropogenic activities than natural [25]. Activities such as the use of chemical fertilizers, pesticides, discharging of Nickel containing wastes on farmlands close to river are prime contributors. Ranges for Ni in sediments from Ishiet River obtained in this study are lower than 24.31 – 47.23 mg/kg reported by Akan *et al.*, [23] for sediments from Lake Chad River, but higher than 1.40 – 1.84 mg/kg previously reported by Olajire *et al.*, [26] for sediment from Ileja River, Osun State, Southern Nigeria. However, the mean concentration of Ni obtained for sediments used in this study are well below the permissible limit of 20.00 mg/kg stipulated for unpolluted sediments by WHO [17].

Aquatic organism required Cu for many purposes ranging from its use in the normal functioning of enzymes, formation of haemglobin and haemocyanin in bloods of vertebrates and shellfishes etc [27]. However, higher concentration of Cu in fresh water can also be detrimental to aquatic organism as it could lead to improper functioning of olfactory response, cardiovascular and nervous systems. These complications usually lead to reduction in the population of fishes, crabs in natural waters [27]. Results for Cu concentration in sediments from Ishiet River and Control for dry and wet seasons are presented in Table 1 and 2. Trend of abundance of Cu in sediments from Ishiet River for dry and wet seasons indicated same trend as in the case of Ni. For sediments from Ishiet River, the following trend was observed for samples obtained during dry season MDS > DNS > UPS, while for wet season, the trend was UPS > MDS > DNS. For both samples, that is Ishiet River and Control sediments, mean concentrations of Cu were higher in samples obtained during wet season than in dry season. Mean and range for Cu in sediments from Ishiet River obtained during dry season were 6.69 mg/kg and 6.63 – 6.75 mg/kg, while for wet season, the sample recorded mean Ni concentration of 6.81 mg/kg and a range of 6.57 – 7.06 mg/kg. For sediments from the Control River, mean Cu in sediment obtained during dry season were 2.81 mg/kg, and 3.91 mg/kg for wet season. Ranges for Cu in sediments from Ishiet River obtained in this study are lower than 2083.30 – 2264.43 mg/kg reported by Ololade [28] for Ondo Coastal sediments, but higher than 1.75 – 2.04 mg/kg previously reported by Uwah *et al.,* [29] for sediment from Qua Iboe River, Southern Nigeria. However, the mean concentration of Cu obtained for sediments used in this study are well below the permissible limit of 25.00 mg/kg stipulated for unpolluted sediments by WHO [17].

Concentrations of Fe in sediment from Ishiet River and Control for dry and wet seasons are presented in Tables 1 and 2. Trend of abundance of Fe in the study sediment revealed the following UPS > MDS > DNS for dry season, while for wet season, the trend was UPS > DNS > MDS. For both samples (Ishiet River and Control sediments), mean concentrations of Fe were higher in samples obtained during wet season than in dry season. Also, Ishiet River sediment recorded higher mean of Fe than in Control sediments for both dry and wet seasons. The higher concentration of Fe in Ishiet River when compared to the Control sediment indicates an additional source of Fe in Ishiet River. Human activities in and around the Ishiet river may have been responsible for the additional concentrations of Fe to the river. Mean and range for Fe in Ishiet River sediments obtained during dry season were 462.29 mg/kg and 418.00 – 541.70 mg/kg, while for wet season, the sample recorded mean Fe concentration of 687.32 mg/kg and range of 666.09 – 717.90 mg/kg. For sediments from the Control River, mean concentration of Fe were 280.52 mg/kg and 324.04 mg/kg for dry and wet season respectively. Ranges for Fe in the studied sediments obtained are lower than 1582.95 – 1910.34 mg/kg reported by Adekoya *et al.*, [30] for sediments from Lagos Rivers, but higher than 73.24 – 82.58 mg/kg previously reported by Ebong *et al.*, [31] for sediment from some Rivers in Niger Delta region of Nigeria. However, the mean concentration of Fe obtained for sediments used in this study are well above the permissible limit of 30.00 mg/kg stipulated for unpolluted sediments by WHO [17]. This means that the sediment is polluted with Fe although total trace metal determination is not enough to proof this assertion.

Trace metal speciation in Sediment

Trace metal speciation results for sediments from Ishiet River and Control for dry and wet seasons are presented in Table 3 and 4. This activity was carried out to assess the mobility and bioavailability of trace metals in river sediment.

Table 3: Results for speciation of trace metals in sediments from Ishiet River, percentage composition, recovery and bioavailability factor

	AEX F1	% Comp	RED F2	% Comp	OXI F3	% Comp	RES F4	% Comp	SoF	SoM	% Rec	BF
					Dry season							
Pb	1.04	17.78	2.23	38.12	1.12	19.14	1.46	24.96	5.81	6.28	94	18
Cd	3.61	36.07	1.76	17.58	1.84	18.38	2.80	27.97	10.01	10.84	93	36
Zn	21.08	19.93	26.34	24.90	16.18	15.30	42.17	39.87	105.77	109.59	97	20
Ni	2.92	17.50	2.41	14.44	7.04	42.18	4.32	25.88	16.69	17.73	94	18
Cu	2.08	10.68	2.67	13.71	5.40	27.72	9.33	47.89	19.48	20.08	97	11
Fe	369.40	29.35	234.08	18.59	201.10	15.98	454.16	36.08	1258.74	1386.86	91	29
						Wet season						
Pb	0.93	15.85	2.60	44.29	1.04	17.71	1.30	22.15	5.87	6.37	91	16
Cd	4.33	39.15	2.16	19.53	1.93	17.45	2.64	23.87	11.06	11.97	92	39
Zn	18.43	17.77	20.43	19.69	38.67	37.29	26.18	25.25	103.71	106.99	97	18
Ni	9.15	33.57	6.66	24.43	6.05	22.19	5.40	19.81	27.26	28.35	96	34
Cu	2.35	12.43	4.13	21.84	3.82	20.20	8.61	45.53	18.91	20.42	93	12
Fe	453.03	24.61	422.53	22.95	302.33	16.42	663.21	36.02	1841.1	2061.97	89	25

*AEX –Acid extraction fraction; RED – Reducible fraction; OXI – Oxidisable fraction; RES – Residual fraction; %Comp – percentage composition; %Rec – percentage recovery; SoF – Sum of fraction; SoM – Sum of metals; BF – Bioavailability factor

Table 4: Results for speciation of trace metals in sediments from Control River, percentage composition, recovery and bioavailability factor

	AEX F1	% Comp	RED F2	% Comp	OXI F3	% Comp	RES F4	% Comp	SoF	SoM	% Rec	BF
					Dry season							
Pb	0.31	21.68	0.73	51.05	0.21	14.69	0.18	12.58	1.43	1.55	93	22
Cd	1.42	50.33	0.63	20.86	0.40	13.25	0.47	15.56	3.02	3.20	94	49
Zn	14.08	40.22	3.73	10.66	7.15	20.43	10.04	28.69	35.00	36.38	96	40
Ni	1.43	20.52	1.29	18.51	2.58	37.02	1.67	23.95	6.97	7.96	88	21
Cu	1.63	20.19	0.94	11.65	3.46	42.86	2.04	25.28	8.07	8.44	96	20
Fe	143.51	19.09	102.43	13.62	189.77	25.24	316.16	42.05	751.87	841.57	89	19
					Wet season							
Pb	0.10	9.17	0.52	47.71	0.33	30.28	0.14	12.84	1.09	1.21	90	9
Cd	1.04	52.27	0.37	18.59	0.41	20.60	0.17	8.54	1.99	2.07	96	52
Zn	2.21	10.25	3.75	17.39	6.42	29.78	9.18	42.58	21.56	23.42	92	10
Ni	1.82	18.40	3.82	38.63	2.19	22.14	2.06	20.83	9.89	10.99	90	18
Cu	0.74	9.52	1.86	23.94	3.71	47.75	1.46	18.79	7.77	8.77	89	10
Fe	158.65	16.70	169.49	17.84	216.73	22.81	405.21	42.65	950.08	972.13	97	17

* AEX –Acid extraction fraction; RED – Reducible fraction; OXI – Oxidisable fraction; RES – Residual fraction; %Comp – percentage composition; %Rec – percentage recovery; SoF – Sum of fraction; SoM – Sum of metals; BF – Bioavailability factor

From the results, Pb in sediments from Ishiet River and Control were predominant in the reducible fractions than in any other fractions for both dry and wet seasons. The pattern of distribution of Pb in Ishiet River sediments followed RED > AEX > RES > OXI for dry season and RED > OXI > RES > AEX for wet season. For Control sediment, Pb pattern of distribution were RED > AEX > OXI > RES, and RED > OXI > AEX > RES for dry and wet season respectively. For sediment from Ishiet River, Pb was prevalent in the reducible phase constituting 38.12% and 44.29% of the total fractions of Pb for dry and wet season respectively. The reason for this could be attributed to the adsorption of Pb cations on the hydrous (armophic) oxides of Iron and Mn which is considered a reasonable universal fixation mechanism [32]. This finding of higher fraction of Pb in reducible phase than in other phases is in agreement with the report of Horsefall Jr *et al.,* [33] who also reported higher fractions of Pb in reducible phase for sediment collected from Okrika River, Southern Nigeria. Also, the results of Pb speciation in sediment from Ishiet River reveals that the concentration of Pb in Ishiet River needs to be examined since the mobilisable fractions recorded higher proportion (75.04%) than the immobile fraction (24.96%). It is possible that some concentrations of Pb from sediment can translocate or leach into the River thereby polluting it with the metal.

Cd was predominantly in the acid extractable (AEX) phases for both sediments from Ishiet and Control during dry and wet season. For Ishiet sediment, the order of association was AEX > RES > OXI > RED for sediment obtained during dry season, while AEX > RES > RED > OXI for wet season. For sediment from Control River, the order of association were AEX > RED > RES > OXI and AEX > OXI > RED > RES for dry and wet season respectively. Cd in the acid extractable fraction comprised 36.07% and 50.33% of the total fraction for Ishiet River and Control during dry season, while for wet season, acid extractable fraction comprised 39.15% and 52.27% of the total fraction for both sediments. The differences in the percentages of acid extractable fraction between the study sediment and Control with regards to season is due to the variation in the total Cd concentration of the sediments as indicated in Table 5 and 6. Cd speciation results obtained in this study agrees with the previous report of Osakwe *et al.,* [34], but in contrast with the report of Ahmed *et al.,* [35] who reported higher concentration of cadmium existed in oxidisable fraction in sediments from Idasa, Adamawa State, Nigeria.

Results for speciation of Ni in sediments from Ishiet River for dry and wet seasons indicated that the element was predominantly in the oxidisable and acid exchangeable phases respectively. For the Control, Ni was abundant in oxidisable and reducible phases for sediment obtained during dry and wet season respectively. Ni in oxidisable phase constituted 42.18% of the total fraction for sediment from Ishiet River during dry season, and acid extractable phase (33.57%) for wet season. The order of association for Ni in sediment from Ishiet River indicated the trend OXI > RES > AEX > RED for dry season, while the trend was AEX > RED > OXI > RES for wet season. Trend of Ni for sediment obtained from Control River were OXI > RES > AEX > RED and RED > OXI > RED > AEX for dry and wet season respectively. Results presented in Tables 3 and 4 also indicated that 74.12% of the total fractions of Ni in sediment from Ishiet River during dry season were non-lithogenous also called non-residual, while 25.88% were lithogenous or residual. For wet season, the result reveals that 80.19% of Ni is non-lithogenous fractions, while only 19.81% are lithogenous. This result means that greater percentages of Ni in Ishiet River sediment are labile or highly mobile and can move into the river body thereby polluting the River. It is possible that Ni when leached into the River body may change into different kinds of chemical substances depending on the physical and geochemical condition of the River [36]. Speciation results of Ni obtained in this study for Ishiet River sediments agrees with the report of Horsefall Jr *et al.,* [33], but disagrees with the reports of Fagbote *et al.,* [37] and Ebong *et al.,* [31] who reported higher fractions of Ni in acid exchangeable and residual fractions respectively in their respective studies.

Cu speciation results presented in Table 3 and 4 indicated that the metal was more abundance in the residual phase for Ishiet River sediment and oxidisable phase for Control sediment for the two season. Cu in the residual fraction comprised 47.89% for dry season and 45.53% for wet season of the total fraction for Ishiet River sediment. For Control sediment, Cu in the oxidisable fraction comprised 42.86% for dry season and 47.75% for wet season of the total fraction. Variation in the occurrences of higher concentrations of Cu in different phases between the study and Control sediments may be due to the physical and geochemical conditions of the Rivers. For the study sediment, the results indicate that the presence of Cu in the sediment may not be related to anthropogenic sources and as such is not readily available for aquatic organisms since they exist in residual form. Adebiyi *et al.,* [38] opined that metal associated with residual fraction usually forms part of the crystalline structure, not easily mobile and bioavailable. The finding of higher concentration of Cu in residual fraction in Ishiet River sediment is consistent with the report of Ebong *et al.,* [31], but in contrast with the report of Okoro *et al.,* [39] for Imo and Oyun River sediments respectively.

Like Cu, Fe concentrations in sediments from both the studied river and Control existed mainly in the residual fraction for both dry and wet seasons. This fraction constituted 36.08% and 36.02% in sediments from studied river for the two seasons, while for Control; it constituted 42.15% and 42.65% for dry and wet season respectively. Order of association for Fe indicated same trend of RES > AEX > RED > OXI for sediments from the studied river during dry and wet season. For Control, the trend were RES > OXI > AEX > RED and RES > OXI > RED > OXI for sediment obtained during dry and wet season respectively. The findings of higher fraction of Fe in residual phase obtained in this study for both studied river and Control agrees with the report of Olatunji *et al.,* [40] but disagrees with the report of Funtua *et al.,* [41] for Iwo and River Challawa sediments respectively. Higher concentration of Fe in residual phase in the studied river sediment indicates a non anthropogenic input of Fe into the river. Percentage recovery was used in this study as quality control measures. The result shows appreciable amounts of recovered metals ranging from 89 – 97% for both sediment and control (Table 3 and 4). These values are consistent with acceptable values recommended by Gaithersburg *et al.,* [42] for recoveries of metals

Bioavailability of trace metals in sediment

Results in Table 3 and 4 shows the bioavailability factors (BF) in percent of trace metals in sediments from studied river and Control for dry and wet seasons. From the results, BF of trace metals ranged from (11 - 39)% and (9 - 52)% for Ishiet River and Control sediments respectively. Cd and Fe in Ishiet River sediments exhibited highest bioavailability for samples obtained during dry season, while Cd and Ni recorded the highest bioavailability factor in same sediment for wet season. Cu recorded the lowest (11%) BF for sediment obtained from Ishiet River, while Pb had the lowest (9%) for sediment from the Control for both seasons. Higher BF factors recorded by Cd, Fe and Ni in sediments from Ishiet River during dry and wet season are traceable to the fact that more than 50% of the metals are in non residual forms. Lower BF recorded by Cu in Ishiet River sediments obtained during dry and wet seasons indicate its low availability in the studied sediments. Generally for Ishiet River sediment, order of BF were Cd > Fe > Zn > Pb = Ni > Cu for dry season, and Cd > Ni > Fe > Zn

> Pb > Cu for wet season. Generally, from the results of trace metals bioavailability in Ishiet river sediments obtained in this study, all the studied metals recorded moderate to high bioavailability potentials in the studied sediments except Cu for both dry and wet seasons. This means that the sediments have poor retention capacity of trace metals and as a result, the metals may be leached into the river body thereby causing the river to be polluted. Bioavailability factors of trace metals are directly proportional to the metal toxicity impact on its target system. That means that the higher the bioavailability factor of trace metals, the higher the impact of the metal on the environment they are found. Poor retention capacity (higher bioavailability factor) of trace metals of Ishiet River sediments may largely be due to several factors including age of the river, saturation and mineralogy [43].

Relationship of trace metals in sediment

Results presented in Table 5 shows the relationship between individual trace metal with another in Ishiet river sediments.

Table 5: Pearson correlation coefficient among trace metals in Ishiet river sediments

	Pb	Cd	Zn	Ni	Cu	Fe
Pb	1.000					
Cd	-0.412	1.000				
Zn	-0.087	0.012	1.000			
Ni	-0.338	-0.012	-0.218	1.000		
Cu	0.039	-0.223	-0.001	0.025	1.000	
Fe	0.856*	-0.368	-0.041	-0.002	0.236	1.00

*correlation significant at 0.01 level

Results obtained at 99% confidence limit revealed that there was no significant positive relationships existing between trace metals in Ishiet river sediments except for Fe/Pb pair (r value of 0.856). This means that increase in the concentration of one of the trace metal may not necessarily result in the increase in the concentration of the other one. Also, the results have shown that the presence of each of the trace metal studied in Ishiet river sediments comes from different sources. Strong positive relationships (adduce from r values in pearson correlation computation) between trace metals in any system usually reveals similar chemical properties and common source of the metal in that system [44].

Sedimentation rate, density, porosity and trace metal fluxes in sediment

Results of mean sedimentation rate, density and porosity and trace metal fluxes of Ishiet river sediments (dry and wet season) are presented in Table 6 and 7. Results in Table 8 were used to determined trace metal fluxes in the sediments

Table 6: Mean sedimentation rate, density and porosity of Ishiet river sediments (dry and wet season)

	Sedimentation rate (cms^{-1})	Density (cm^{-3})	Porosity
	Dry season		
Sampling sites			
DNS	0.0089	0.830	0.169
MDS	0.0096	0.750	0.184
UPS	0.0088	0.640	0.209
Mean	0.0090	0.740	0.190
SD	0.0004	0.095	0.020
	Wet season		
DNS	0.00067	0.802	0.191
MDS	0.0070	0.880	0.145
UPS	0.0073	0.731	0.131
Mean	0.0050	0.803	0.160
SD	0.0040	0.075	0.031

* Each value represents mean of three determinations analyzed individually in triplicate; DNS –downstream; MDS – midstream; UPS – upstream; SD – standard deviation,

Table 7: Trace metal fluxes ($mgcm^{-2}S^{-1}$) in Ishiet river sediments

Sites	Pb	Cd	Zn	Ni	Cu	Fe
DNS	0.0009	0.0017	0.0157	0.0039	0.0028	0.182
	(0.014)	(0.021)	(0.203)	(0.036)	(0.043)	(4.18)
MDS	0.0095	0.0195	0.168	0.048	0.035	2.322
	(0.012)	(0.023)	(0.22)	(0.04)	(0.04)	(4.189)
UPS	0.0099	0.0232	0.209	0.053	0.038	2.932
	(0.01)	(0.02)	(0.23)	(0.03)	(0.04)	(3.96)
Mean	0.007	0.015	0.131	0.035	0.025	1.782
	(0.01)	(0.02)	(0.22)	(0.04)	(0.04)	(4.11)

*values in () are for dry season; without () are for wet season; DNS –downstream; MDS – midstream; UPS – upstream.

Results in Table 7 reveal individual trace metal flux ($mgcm^{-2}S^{-1}$) for Ishiet river sediments obtained during dry and wet season on a site basis. The results indicated trace metal fluxes that varied between sampling point and metals for both dry and wet season. Ranges for metal fluxes were 0.007 – 1.782 for sediment samples obtained during wet season and 0.01 – 4.11 for sediment obtained during dry season. Generally for sediment obtained during dry and wet season, Fe recorded highest flux, while the least was recorded by Pb. For dry season, the order of association in metal fluxes was Fe > Zn > Ni = Cu > Cd > Pb, and was Fe > Zn > Ni > Cu > Cd > Pb for wet season. Higher flux shown by Fe may be due to unused boats (with some metallic components), metal pipes and broken boats abandoned at the bank of the river. Ranges of metal fluxes obtained for sediments in this study for both dry and wet seasons agree with 0.002 – 3.560 reported by Udosen *et al.*, [8] but at slight variance with 1.081 – 7.213 previously reported by Adekoya *et al.*, [30] in their respective studies. Variation in metal fluxes in Ishiet river sediment with the previously reported ones may be due to variation in concentration of the metal, sedimentation rate, porosity of the sediment. Positive metal fluxes recorded by the metals obtained in this study are an indication that the sediment acts as a sink for the studied metals [45]. Consequently, the implication is that these metals are likely going to be leached into the river body through surface runoffs and other agents.

Pollution status of sediments

Pollution status of a given environmental systems can be deduced using different empirical models. For this study, pollution status of Ishiet river sediments was assessed by calculating contamination and enrichment factors, degree of contamination, geo-accumulation and pollution load indexes. The obtained values were then compared with already existing classifications given by different models.

Table 8: Contamination and enrichment factors, geo-accumulation indexes, degree of contamination and pollution load indexes of trace metals in Ishiet river sediments

Parameters	Seasons	Pb	Cd	Zn	Ni	Cu	Fe	Cdeg	PLI
Contamination factor	Dry	4.02	3.37	3.01	2.23	2.38	1.65	16.62	2.66
	Wet	5.13	5.78	4.57	2.58	2.34	2.12	22.47	3.47
Enrichment factor	Dry	2.44	2.05	1.83	1.35	1.44	1.00	-	-
	Wet	2.50	2.73	2.15	1.22	1.10	1.00	-	-
Igeo	Dry	0.81	0.68	0.60	0.45	0.48	0.31	-	-
	Wet	1.06	1.16	0.92	0.52	0.47	0.43	-	-

*Igeo – Geo-accumulation index; Cdeg – Degree of contamination; PLI – Pollution load index

Results in Table 8 indicates that the contamination factors of the studied trace metals ranged between 1.65 – 4.02 for Ishiet river sediment obtained during dry season and 2.12 – 5.78 for wet season. Fe showed least contamination factors in Ishiet river sediments for both dry and wet season, while Pb in the case of dry season and Cd in the case of wet season were the highest. The results have also reveal that all the studied trace metals were in moderate to strongly polluted category except for Fe (dry season) based on Huu et al.,[10] classification.

This means that the studied metals have polluted the Ishiet river sediment and is expected to have impacts on the river, near-by soil and plants in the environment negatively.

Results for the degree of contamination (Cdeg) of Ishiet river sediments obtained during dry and wet season presented in Table 8 were 16.62 and 22.47 respectively. This means that the sediments were considerably contaminated (16 < Cdeg < 32) with the studied trace metals based on the model predicted by Hakanson [46]. Pollution load index (PLI) values recorded for Ishiet river were 2.66 and 3.47 for sediments obtained during dry and wet season respectively. This result further reveals that trace metals contamination of Ishiet river were higher during wet season than dry season as also confirmed by higher Cdeg.

To identify the source of trace metals into the sediments, enrichment factor was employed. Enrichment factors (EF) of trace metals in the studied sediments were calculated using the continental crust average model. Fe exhibited an EF value of 1.00 indicating that a greater proportion of Fe in the sediment may have emanated from natural processes [47]. EF values for Pb, Cd, Zn, Ni and Cu in the sediments were greater than 1.0 indicating that these trace metals were mostly from anthropogenic sources. Geo-accumulation index results reveals that Igeo for sediments obtained during dry season ranged from 0.33 – 0.81 and 0.43 – 1.16 for wet season. Pb recorded the highest (0.81) Igeo for sediments obtained during dry season, while Cd (1.16) was the highest for sediments obtained during wet season. The result reveals that the metals were in unpolluted to moderately polluted category (0 – 2) according to Huu *et al.,* [10] classification.

Health risk assessment

Human exposure to trace metals (via dermal, oral, ingestion) in a given environment usually leads to numerous health associated risk. In this study, health risk assessment of trace metals in Ishiet river sediments was evaluated by calculating daily intake (DI), hazard quotient (HQ) and total chronic hazard index (THI). The results are presented in Table 9 below.

Table 9: Non-carcinogenic risk for trace metals from Ishiet river sediment for children and adult

Parameters	Seasons	Pb	Cd	Zn	Ni	Cu	Fe	THI
Children								
Daily intake (DI)	Dry	0.0002	0.0003	0.003	0.0005	0.0005	0.04	-
	Wet	0.0002	0.0003	0.003	0.0008	0.0005	0.05	-
Hazard quotient (HQ)	Dry	0.06	0.30	0.01	0.03	0.01	0.58	0.99
	Wet	0.06	0.30	0.01	0.04	0.01	0.72	1.14
Adult								
Daily intake (DI)	Dry	0.00008	0.0001	0.001	0.0002	0.0003	0.02	-
	Wet	0.00008	0.0002	0.001	0.0004	0.0003	0.03	-
Hazard quotient (HQ)	Dry	0.03	0.10	0.003	0.01	0.008	0.23	0.38
	Wet	0.03	0.20	0.003	0.02	0.01	0.43	0.69

*THI – Total chronic hazard index

Results presented in Table 9 indicates that the seasonal daily intake rate of trace metals studied in Ishiet river sediment for children and adult were all below their recommended oral reference dose (RfDs) by United State Environmental Protection Agency [48]. Generally, DI of trace metals from Ishiet river sediments obtained during dry and wet season for children and adult were not significantly different except for Ni. The closeness in seasonal DI with regards to children and adult is as a result of the closeness in the mean concentrations of the metals in the sediments. Hazard quotient (HQ) results indicate that Pb, Cd, Zn, Cu recorded same HQ values for sediments obtained during dry and wet season for children. For adult, only Pb and Zn recorded same HQ values, while Cd, Ni, Cu and Fe were different. HQ values for Fe revealed higher value (0.72) in sediments obtained during wet season for children, than in the same season for adult (0.43). The difference in the seasonal HQ values of Fe in the case of children and adult is due to the difference in the DI values of the metal. Generally HQ values of trace metals indicated the following trends: Fe > Pb > Cd = Ni > Zn = Cu (dry season), Fe > Pb >Ni > Cd >Zn = Cu (wet season) for children; while Fe > Cd > Pb > Ni > Cu > Zn (dry season), Fe > Cd > Pb > Ni > Cu > Zn (wet season) for adult. Individual metal HQ values for all the metals studied for dry and wet season for both children and adult are less than 1.00. Thus; these metals may not pose any serious health risk in both children and adults. THI results presented in Table 9 indicated a higher value for sediments obtained during wet season in the case of children than others. For both children and adult, THI values for sediments obtained during dry and wet season were less than 1.00 except for that of the wet season (1.14) in the case of children. THI values less than 1.00 usually indicate that the studied metals may not cause any negative impacts on humans exposed to these metals [49]. However, routine assessment is encouraged to avoid bioaccumulation of trace metals and related health challenges associated with their presence in the ecosystem.

Table 10: Carcinogenic risk potential for trace metals from Ishiet river sediment for children and adult

Parameter	Seasons	Pb	Cd	Ni
		Children		
ILCR	Dry	1.7 E – 06	1.9 E – 03	8.6 E – 04
	Wet	1.7 E – 06	1.9 E – 03	1.4 E – 03
		Adult		
ILCR	Dry	6.9 E – 06	6.4 E – 04	3.4 E – 04
	Wet	6.9 E - 06	1.3 E – 03	6.9 E – 04

*ILCR – Incremental lifetime cancer risk

Potential cancer risk associated with trace metals studied in Ishiet river sediments (dry and wet season) was evaluated using incremental life time cancer risk (ILCR). For this study, the parameter was calculated only for Pd, Cd, and Ni and results obtained are presented in Table 10. ILCR values were same for Pb (1.7 E – 06) and Cd (1.9 E – 06) for children (dry and wet season), while wet sediments recorded 1.4 E – 03 Ni than dry (8.6 E – 04). For adult, ILCR for Cd and Ni were higher in wet than in dry, while Pb for both seasons were same (6.9 E – 06). Individual ILCR values (children and adult) for both dry and wet season indicated in Table 10 reveals that Pb, Cd, and Ni recorded values slightly higher than the USEPA permissible range of 1×10^{-6} to 1×10^{-4}. That is 1.7 E – 06 cancer risk for Pb (children and adult) means that if a million people are exposed, about two additional cancer cases would be expected and so on.

Conclusion

This study has revealed that seasonal concentrations of Pb, Cd, Zn, Ni, Cu and Fe in Ishiet river sediment vary significantly. Speciation results reveal that Zn, Cu and Fe were predominantly in residual phase, Pb in reducible, Cd in acid extractable and Ni in oxidisable phase for sediment samples obtained during dry season. For sediment samples obtained during wet season, Cu and Fe were predominantly in residual phase, Cd and Ni in acid extractable, Pb in reducible and Zn in oxidisable phase. Also, bioavailability factors for the metals were generally moderate with Cd and Fe recording highest bioavailability for sediment samples obtained during dry season, while Cd and Ni exhibited highest for sediment samples obtained during wet season. Trace metal fluxes varied significantly between sampling point and metals for both dry and wet season. Pollution status of the sediment using contamination and enrichment factors, degree of contamination, geo-accumulation and pollution load indexes has also been elucidated using empirical models. Seasonal daily intake rate of studied trace metals were all below recommended oral reference dose. Therefore, this study safely concludes that the studied sediment accumulates trace metals and can leach some of the concentrations of these metals to the surface water through interaction thereby causing pollution of Ishiet River.

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