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Health Risk Assessment of Heavy Metals in Sediment of Tropical Freshwater Stream

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Abstract

An investigation of the heavy metals in the bed sediment of Asunle stream was carried out to assess how seriously the sediment is polluted using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The potential health risk assessment was calculated for a lifetime exposure (ingestion) based on the United State Environmental Protection Agency (USEPA) models to determine the carcinogenic and non-carcinogenic risks for children and adults. The range of values (mg/kg) of heavy metals in bed sediment were: Fe (2850 – 7260), Mn (58 – 209), Co (0.7 – 33), Ti (21.6 – 67), Ba (1.61 – 9.81), Zn (7.5 – 79), Cu (5.6 – 25), As (8 – 137), Al (273 – 2160), Y (24 – 49), and Sr (0.10 – 5.3). As and Sr, values were below the background values for typical soil. The health risk assessment of heavy metals in the bed sediments revealed that carcinogenic risk was almost insignificant while the non-carcinogenic risk was significant since their values were above the recommended minimal risk level. The results also revealed that children are more vulnerable to hazards than adults. The chronic hazard quotient index for exposure to these metals through ingestion exceeded the acceptable USEPA value of 1.0.

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1. Introduction

Over time pollution from both point and non-point sources have been a great challenge to water bodies [1] all over the world, and sediment has been the reservoir of these pollutants. The Obafemi Awolowo university dumpsite had been reported to be polluted with the heavy metals and non-metals, metalloids, actinides and rare earth metals at varying degrees [2]. Leaching of these elements into the adjoining stream is inevitable The distribution of metals in the sediment of a tropical stream adjoining a university dumpsite, and runs through human settlements with heavy agricultural activities can provide researchers with proof of the anthropogenic impact on the ecosystem, and thus aid in assessing the ecological risk to the aquatic habitats and toxic risks on terrestrial habitat. The build-up of heavy metals in sediment has significant environmental implications on water quality and local inhabitants [3]. The impact of open dumpsite on groundwater contamination with heavy metals was investigated by Coker et al. [4]; their results revealed contamination of groundwater as a result of leachate from the dumpsite.. Ogunfowokan et al. [5] earlier conducted an early wet speciation study of heavy metals in the water and sediment of

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the Asunle stream using atomic absorption spectroscopy (AAS). Contamination factors of the study area were not fully explored. This study is a follow-up monitoring of the perennial stream with a comprehensive seasonal study and the use of ICP-OES to further established the contamination levels of the adjoining stream to the Obafemi Awolowo University dumpsite. The study further fully explored the pollution status of the stream. Health risk assessment of the stream had not been conducted in the previous study. The objectives of this study was to investigate the metal concentrations of the bottom sediments using ICP-OES; their contamination factors and conduct the health risk assessment.

2. Materials and Methods

2.1. Study area

Asunle, an adjoining stream is a periodic stream that has its spring located about 100 m uphill from the Obafemi Awolowo University (OAU), Ile-Ife refuse dumpsite (Figure 1).The university dumpsite falls between Latitude 07° 32´N and Longitude 4° 31´E. Geologically, the study area falls within the basement complex of southwestern Nigeria. It forms part of African crystalline shield with which consists predominantly of dolerites, apitite, microgranite genesis, granite genesis, ultrasonic rocks, mica and banded genesis. The characteristic of wastes generated in this dumpsite had been reported by Olutona et al[6] The stream was about 100 m away from the major road that runs a stretch of more than 10 km, cutting across three human settlements [5]. It has the highest vegetation cover (about 90%) of all the sites. Noticeable human activities along the stream are rigorous farming activities where cash crops (such as palm trees, cola nut, and cocoa) and various food crops were planted. Oil palm processing took place in all the human settlements along this stream. Along the course of the stream, water from the stream is used by the inhabitants who are predominantly farmers for palm oil processing, irrigation of fruits and vegetables, mixing and dilution of agrochemicals used for spraying of both cash and food crops. Downstream, the water from the stream is utilized for household purposes [6-7].

2.2. Sample Collection and Analysis

Five sites were chosen for this study along the course of the stream. Sediment samples were collected on a monthly basis for the period of eight (8) months (4 months dry and 4 months wet). Sediment sampling protocol described by IAEA [8] was employed in this study. Sediment samples were collected from the upstream (source as control), point of discharge and downstream sampling points of receiving stream (Figure 1). Composite sediment samples (two samples) were randomly collected (10-20 m apart) at 0-3 cm depth each month from each location. Sediment samples were collected using stainless steel scoop facing upstream. Excess water was drained from the scoop. Black cellophane nylon beforehand cleaned with pure acetone was used to collect the sediment samples. The samples were air dried for about five days and further dried at 50 ºC in a vacuum oven to ensure that the samples were completely

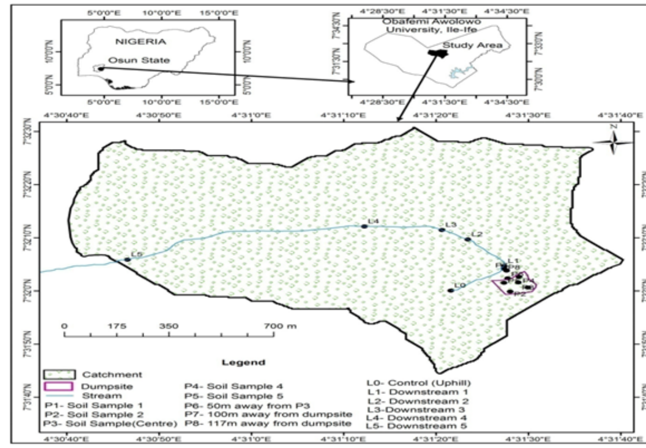

Figure 1. A Map of Asunle an adjoining stream to Obafemi Awolowo University dumpsite

dried. The dried samples were crushed, ground and sieved with 500-micron plastic sieve. The samples were stored in clean 250 mL capacity amber bottles kept in the refrigerator until further analysis was required. One (1 g) each of the samples was acid digest using nitric acid (5 mL) and perchloric acid (1 mL) acid. The digested samples were concentrated to a volume (< 2 mL) transferred into a volumetric flask (25 mL) and topped up with distilled water. The digested solutions were analysed using ICP-OES.

The Agilent, Varian 710 ICP-OES equipped with axially-viewed plasma available at the Department of Nano Science, University of the Western Cape, Cape Town, South Africa was used for metal analysis in this study. The axially-viewed plasma cover all-important wavelength in the visible region from 177-785 nm. The ICP-OES is equipped with CCD detector and optimized optical design that give excellent signal-to-noise performance, ensuring low detection limit. The CCD features the Clocked recombination System (CRS) for anti-blooming protection. To enhance the performance of the 710 series are the accessories such as VGA for mercury and hydride forming elements, the fast SPS auto sampler for unattended automation, the SVS switch valve for rinsing and improve productivity, the AGM for organic matrices and the USN for lower detection limit with environmental sample.

The choice of ICP-OES is due to its analytical advantage over other excitation sources originates from its capability for efficient and reproducible vaporization, atomization, excitation and ionization for a wide range of elements in various sample matrices. This is basically due to high temperature 6000-7000K, in the observation zones of the ICP which is much higher than the maximum temperature of flames or furnaces (3300K). This instrument also makes it capable of exciting refractory elements and renders it less prone to matrix interferences. Similarly, the choice of axial rather than radial view ICP-OES is due to the fact that the axial view provides better LODs than radial view. This may be attributed to longer viewing path available down the axis of the plasma, thus a better sensitivity of 5-10 fold improvement in the LOD can be achieved.

2.3. Calculation of Pollution Assessment Indices

In this study, geo-accumulation index, enrichment factor, contamination factor and pollution index have been applied to assess heavy metals distribution and contamination in the sediment samples from Asunle Stream.

2.3.1. Enrichment Factor (EF)

Enrichment factor (EF) analysis is a method used to differentiate between the metals originating from anthropogenic activities and those from natural sources and to assess the degree of anthropogenic influence [9]. The EF is defined as follows:

$$\mathrm{EF} = \frac{\left[\frac{\mathrm{Cx}}{\mathrm{CAl}}\right] sample}{\left[\frac{Cx}{CAl}\right] background} \tag{1}$$

Where, $[C_x/C_{Al}]$ sample is the ratio of metal $[C_x]$ to that of Al $[C_{Al}]$ in the soil /sediment sample and $[C_x/C_{Al}]$ background is the ratio of metal and Al concentration of the geochemical background. The geochemical background values of metals are not available. Thus, the geochemical average shale values given by Turekian and Wadepohl [10] were adopted. Seven contamination categories are recognized based on enrichment factor as follows [11]:

2.3.2. Geo-accumulation Index

The geo-accumulation index (I-geo) values were calculated for different metals as introduced by Muller[12] as follows:

$$\text{I-geo} = log_2\{\frac{Cn}{[1.5\ Bn]}\} \tag{2}$$

where C_n is the measured concentration of the heavy metal 'n' in the sample and B_n is the geochemical background value of element 'n' and 1.5 is the background matrix correction factor.

2.3.3. Contamination Index

The calculation of contamination index of metals in the sediment samples was done using the relationship:

$$\text{Contamination Index (CI)} = \frac{Metal\ concentration\ in\ the\ soil}{Background\ value\ of\ the\ metal} \tag{3}$$

2.3.4. Pollution Load Index

Each location was evaluated for the extent of metal pollution by employing the method based on the pollution load index (PLI) developed by Thomilson *et al.* [13] as follows:

$$\mathrm{PLI} = n\sqrt{CF_1} \times CF_2 \times CF_3 \times CF_4 \ldots\ldots CF_n \tag{4}$$

where n is the number of metals studied and CF is the contamination factor calculated as described in equation 3.

2.4. Health Risk Assessment

The basic formulas and values used for the calculation of ingestion and inhalation of soil as described by Grezetic *et al.* [14] are shown below.

Chronic Daily Intake (CDI) for carcinogenic risk (ingestion of soil):

$$\text{Carcinogenic CDI (mg/kg/day)} = CS\,xIFx\frac{\mathrm{EF}}{\mathrm{AT}} \tag{5}$$

$$\text{where IF} = \frac{\mathrm{IR_{Adult}} \times \mathrm{ED_{Adult}}}{\mathrm{BW_{Adult}}} + \frac{\mathrm{IR_{Child}} \times \mathrm{ED_{Child}}}{\mathrm{BW_{Child}}} \tag{6}$$

*l*Non-carcinogenic: CDI (mg/kg/day)

$$= CS \times IN \times EF \times \frac{\mathrm{ED}}{\mathrm{BW}} \times AT \tag{7}$$

3. Results and Discussion

3.1. Validity of Analytical Method Adopted for Heavy Metal Analysis

The linear calibration curve for each metal was plotted and each near unity. Blank and internal standard were also conducted to authenticate the results and to check for background contaminants. Table 1 presents the limits of detection (LOD) and quantification (LOQ) of the elements.

3.2. Heavy Metals in Asunle Stream Sediment

This section of the study presents the metal content in the Asunle stream bed sediment. Generally, the concentrations of metals in the bed sediment were significantly lower at $p < 0.05$ when compared with either those of the dumpsite soils or the lateral soil sampling towards the receiving stream. The data obtained (Table 2) were subjected to Duncan Multiple range test to establish possible differences in all the sampling periods. The statistical analysis showed that except for Fe, Mn, Ba, Cu, and Y, all other metals had significant difference in all the sampling periods.

Biologically, iron (Fe) plays a crucial role in the transport and storage of oxygen, and also in electron transport [15]. It is safe to say that, with only a few possible exceptions in the bacterial world, there would be no life without iron [16]. The monthly mean level of Fe ranged from 2850 ± 1600 mg/kg in August to 7260 ± 5400 mg/kg in February. These values were below the background value of 47,200 mg/kg in shales [10] and 26,000 mg/kg elemental concentration of typical soil [17].

Manganese is an indispensable element in human food with a normal nutritional intake considered to be nearly 2 –5 mg/day [18]. It is a constituent of certain enzymes and can also activate many enzymes [19]. Manganese monthly mean levels ranged from 58 ± 50 mg/kg in August to 210 ± 210 mg/kg in February. These values were below the background value of 850 mg/kg in shales [10] and 550 mg/kg elemental concentration of typical soil [17].

Cobalt means levels ranged from 0.73 ± 1.74 mg/kg in December to 33 ± 21 mg/kg in August. The values obtained in the

Table 1. Validation of analytical methods

	Fe	Mn	Cr	Ni	Co	Ti	Zr	Zn	Cu	Be
λ (nm)	238.2	257.6	267.7	221.6	238.89	336.12	343.82	213.86	324.75	313.04
%RSD	0.71	1.41	1.05	1.07	0.01	0.84	0.67	0.59	0.67	0.86
LOD	0.006	0.003	0.0009	0.03	0.018	0.0012	0.015	0.00	0.002	0.001
LOQ	0.06	0.03	0.009	0.3	0.18	0.012	0.15	0.00	0.02	0.01

dry season were low when compared to the background level of 19 mg/kg in shales [10] and 9.1 mg/kg elemental concentration of typical soil [17]. The monthly mean levels of Ti ranged from 21.6 ± 5.6 mg/kg in November to 67 ± 77 mg/kg in February. These values were below the background value of 4600 mg/kg in shales [10]. Barium monthly mean values ranged from 1.61 ± 3.94 mg/kg in July to 10 ± 16 mg/kg in February. These values obtained were below the background value of 580 mg/kg in shales [10].

Zinc is an indispensable element essential for the life processes of several enzymes. Zn impedes at diverse levels in the endocrine system and lipids and carbohydrate metabolism [20]. At higher levels zinc may be carcinogenic [21]. The monthly mean values of Zn ranged from 7.53 ± 9.31 mg/kg in August to 79 ± 46 mg/kg in January. These values were below the background value of 95 mg/kg in shales [10] and 60 mg/kg elemental concentration in typical soil except values obtained in December and January that were above the elemental concentration in typical soil[17].

Copper is a vital metal to human life at modest levels operational as part of some enzymes e.g., tyrosine (necessary for the formation of melanin pigments), cytochrome oxidase, superoxid dismutase, and amine oxidases. It is essential for the utilization of iron in the formation of haemoglobin [22]. Cu monthly mean values ranged from 5.63 ± 7.16 mg/kg in July to 25 ± 43 mg/kg in February. The values were below 45 mg/kg background value in shales[7] and 25 mg/kg elemental concentration in atypical soil [17]. Arsenic is a metalloid, poisonous [23] classified as carcinogenic, and harmful to human healthiness. In addition to natural origin, it can also be predominant in the soil in an area where there are mining-related activities; municipal sewage, coal burning, agrochemicals, fertilizers, vehicular emissions and wood preservative chemicals and industrial effluents [24-26]. The monthly mean values of As ranged from 8.42 ± 21 mg/kg in December to 137 ± 100 mg/kg in August. Except for December, the values obtained were above the background value of 13 mg/kg in shales[7] and 7.2 mg/kg elemental concentration in atypical soil [17].

The monthly mean values of Al ranged from 273 ± 288 mg/kg in August to 2160 ± 610 mg/kg in January. The values were below 80,000 mg/kg background value in shales [10]. Yttrium was only above the detection limit in January and February and ranged between 24 ± 60 mg/kg and 49 ± 120 mg/kg. The values were above the background value of 26 mg/kg in shales[7]. Strontium ranged from 0.10 ± 0.17 mg/kg in June to 5.25 ± 2.45 mg/kg in January. The values were below the background value of 300 mg/kg in shales [10].

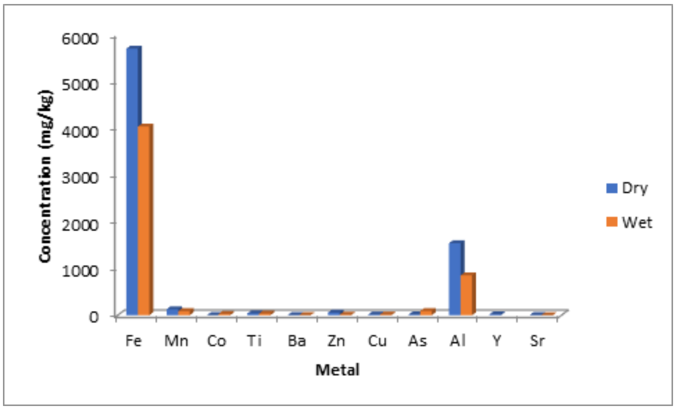

Figure 2. Seasonal levels of heavy metals in sediment of Asunle stream

3.3. Seasonal Levels of Heavy Metals of Asunle Stream Sediment

Seasonal variation of heavy metals of Asunle stream sediment is presented in Figure 2. The data obtained revealed that all the metals with exception of Co and As were generally higher in the dry season. Moreover, the concentrations of Fe and Al were exceptionally higher than all other metals in both seasons. Higher levels of these metals in dry season might be due to the slower movement of water in the stream during the dry season resulting in greater settlement chances of the metal-bound sediment particles. Also, the lower levels of the metals in the bed sediment during the wet season compared to the dry season might be due to dilution arising from high precipitation.

3.3.1. Principal Component Analysis of Heavy Metals in Sediment of Asunle Stream

The principal component analysis (PCA) of heavy metals in the bed sediment (Figure 3), the total variance for the two components was explained by 55.32%. The first component accounted for 39.23% of the explained variance in which Fe, Al, Ba and Mn recorded high positive loadings of 0.86, 0.79, 0.78 and 0.72, respectively. The second component accounted for 16.09% of the explained variance and only As had the highest loading 0.74. In terms of association, four groups can readily be identified. These are Zn, Sr, Cu and Al; Mn, Ba, Fe and Ti; As and Co; and Y. The metals that are associated probably have a common origin or source.

3.4. Pollution assessment indices

3.4.1. Geo-accumulation Index of Heavy Metals in Sediment of Asunle Stream

The geo-accumulation index of heavy metals in the bed sediment of Asunle Stream is presented in Table 3. The results ob-

Table 2. Monthly levels of heavy metals in sediment of Asunle stream

	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
Nov	3530^{a}	68^{a}	1.87a	21.6^{a}	BDL	49^{abc}	8.87^{a}	14^{bc}	1270^{d}	BDL	2.53^{ab}
	±1900	±45	±3.67	±5.6		±31	±11	±34	±650		±1.31
Dec	5130^{a}	110^{a}	0.7^{a}	32^{ab}	2.9^{a}	69^{bc}	18^{a}	8^{bc}	1650^{a}	BDL	3.9^{ab}
	±3100	±65	±1.7	±12	±7.0	±64	±32	±21	±770		±3.8
Jan	6850^{a}	124^{a}	2.9^{a}	31^{ab}	5.96^{a}	79^{c}	14^{a}	15^{c}	2160^{a}	24^{a}	5.3b
	±3600	±95	±5.3	±12	±12	±46	±25	±37	±610	±60	±2.5
Feb	7260^{a}	209^{a}	5.0^{a}	67^{b}	9.81^{a}	31^{ab}	25^{a}	33^{ab}	1070^{ab}	49^{a}	2.7^{ab}
	±5400	±210	±8.6	±77	±16	±49	±43	±46	±740	±120	±4.5
May	4970^{a}	96^{a}	25^{b}	59^{ab}	7.73^{a}	12^{a}	24^{a}	114^{bc}	1430^{bc}	BDL	0.44^{ab}
	±3900	±118	±14	±43	±19	±16	±36	±39	±1300		±1.10
Jun	4970^{a}	124^{a}	21^{b}	28^{ab}	3.1^{a}	16^{a}	13^{a}	46^{ab}	997^{ab}	BDL	0.10^{a}
	±3000	±150	±13	±15	±7.6	±16	±15	±86	±550		±0.17
Jul	3320^{a}	74^{a}	31^{b}	25^{ab}	1.6^{a}	8.6^{a}	5.6^{a}	62^{ab}	701^{abc}	BDL	BDL
	±2500	±68	±18	±17	±3.9	±9.5	±7.2	±95	±600		
Aug	2850^{a}	58^{a}	33^{b}	27.4^{ab}	BDL	7.5^{a}	13^{a}	137^{a}	273^{c}	BDL	3.2^{ab}
	±1600	±50	±21	±4.8		±9.3	±14	±100	±290		±8.1

The alphabet in each column denotes mean that are significantly different ($p < 0.05$)
BDL = Below detection Limit

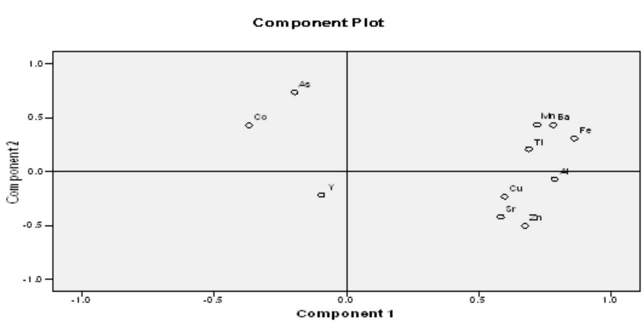

Figure 3. PCA of heavy metals in sediment of Asunle stream

tained revealed that the sediments were practically unpolluted with the metals during both seasons. Arsenic, however, demonstrated a moderate to heavily pollution status of the sediments during the dry season.

3.4.2. Enrichment Factor/Index of Heavy Metals in Sediment of Asunle Stream

The Enrichment Factor (EF) for the heavy metals in the bed sediments is presented in Table 4. These values were obtained using the geochemical background values in average shale [10]. The enrichment status of the soil based on Taylor [11] proposition revealed that the sediment was not enriched with Ti, Ba and Sr. On the other hand the enrichment of the sediment with Fe, Mn during the two seasons and Co in dry season were moderately severe. Enrichment of Zn in wet season and Cu in dry season were severe. Similarly, enrichment of the sediment with Zn and Y in dry season and Cu in wet season were very severe while those of Co in wet season and As in both seasons were extremely severe.

3.4.3. Contamination Factor with Respect to Temporal Variation of Heavy Metals in Sediments of Asunle Stream

The monthly and seasonal contamination factors (CFs) for each metal were calculated according to Equation 3. and presented in Table 5. Four groups of classification of CF were described by Nase et al. [27]; and Mmolawa *et al.*,[28]. These are: CF < 1 (low contamination); 1≤ CF < 3 (moderate contamination); 3 ≤ CF < 6 (considerable contamination), and CF > 6 (very high contamination).

The results of contamination factor of temporal variation of metals in bed sediment of Asunle river revealed that the mean value varied between 0.0007(Ti) and 0.60 (Zn) in wet and 0.003(Sr) and 6.9(As) in dry. These results indicated that the contamination due to Fe, Mn, Ti, Ba, Zn, Cu, Al, Sr in both seasons and Co in the dry season were low. The sediment was moderately contaminated with Co in the wet season and As in the dry season while the contamination of the sediment with respect to As in the wet season stood between considerable contamination and high contamination. The contamination status of the sediments with respect to the metals in decreasing order in dry season was: As > Y > Zn > Cu > Mn > Co > Al > Sr > Ba > Ti while in wet season, the order was: As > Co > Cu > Zn> Mn > Fe > Al > Ti > Ba > Sr.

3.4.4. Contamination Factor with Respect to Temporal Variation of Heavy Metals in Sediments of Asunle Stream

The monthly and seasonal contamination factors (CFs) for each metal were calculated according to Equation 3. and presented in Table 5. Four groups of classification of CF were described by Nase et al. [27]; and Mmolawa *et al.*,[28]. These are: CF < 1 (low contamination); 1≤ CF < 3 (moderate contamination); 3 ≤ CF < 6 (considerable contamination), and CF > 6 (very high contamination).

The results of contamination factor of temporal variation of metals in bed sediment of Asunle river revealed that the

Table 3. Geo accumulation index of heavy metals in the sediment of Asunle stream

	C_n			I-geo		Class		Pollution Intensity	
	Dry	Wet	B_n	Dry	Wet	Dry	Wet	Dry	Wet
Fe	5690	4030	47200	-3.64	-4.14	0	0	PU	PU
Mn	128	87.9	850	-3.32	-3.86	0	0	PU	PU
Co	2.64	27.7	19	-3.43	-0.04	0	0	PU	PU
Ti	38	34.8	4600	-7.50	-7.63	0	0	PU	PU
Zn	57.2	11.2	95	-1.40	-2.10	0	0	PU	PU
Cu	16.6	13.9	45	-2.03	-2.28	0	0	PU	PU
Ba	4.66	3.11	580	-2.27	-8.13	0	0	PU	PU
Al	1540	850	80000	-6.29	-7.14	0	0	PU	PU
As	17.8	89.8	13	-0.13	2.20	0	3	PU	MP-HP
Sr	3.58	0.97	300	-6.97	-8.86	0	0	PU	PU
Y	18.32	-	26	-1.09	-	0	0	PU	-

Key

PU= Practically Unpolluted, MP-HP = moderately to Heavy Polluted

Table 4. Enrichment factor of heavy metals in sediment of Asunle stream

	C_n			Enrichment Factor	
	Dry	Wet	B_n	Dry	Wet
Fe	5690	4030	47200	6.27	8.03
Mn	128	87.9	850	7.83	9.74
Co	2.64	27.7	19	7.22	137
Ti	38	34.8	4600	0.43	0.71
Ba	4.66	3.11	580	0.42	0.50
Zn	57.2	11.2	95	31.3	11.1
Cu	16.6	13.9	45	19.1	29
As	17.8	89.8	13	71	650
Y	18.3	-	26	36.6	ND
Sr	3.58	0.97	300	0.62	0.30

Key

Enrichment status: < 1 = No Enrichment, 1-3 = Minor, 3-5 Moderate, 5-10 = Moderately severe, 10-25= Severe, 25-30 = Very severe, and > 50 = Extremely Severe.

mean value varied between 0.0007(Ti) and 0.60 (Zn) in wet and 0.003(Sr) and 6.9(As) in dry. These results indicated that the contamination due to Fe, Mn, Ti, Ba, Zn, Cu, Al, Sr in both seasons and Co in the dry season were low. The sediment was moderately contaminated with Co in the wet season and As in the dry season while the contamination of the sediment with respect to As in the wet season stood between considerable contamination and high contamination. The contamination status of the sediments with respect to the metals in decreasing order in dry season was: As > Y > Zn > Cu > Mn > Co > Al > Sr > Ba > Ti while in wet season, the order was: As > Co > Cu > Zn> Mn > Fe > Al > Ti > Ba > Sr.

3.5. Spatial Variation of Heavy Metals in Sediment of Asunle Stream

The spatial variation of metals in bed sediments of the Asunle stream is presented in Table 6. The results obtained when subjected to ANOVA showed that all the metals in all locations were significantly different ($p < 0.05$) from one another with respect to Co, Ti, As, and Sr. This clearly indicated the non-uniformity in the levels of the metals found in the bed sediment. This could be due to uneven anthropogenic inputs of these metals, differential distribution by the flowing stream, the unequal sequestering influence of sediment components to precipitate the metals along the watercourse, etc. Similarly, the data were also subjected to Duncan Multiple range tests to establish possible differences in the mean values of metals in each location. The statistical analysis showed that except for Co, As and Sr, virtually all the metals had significant differences in all the locations investigated.

The total metal burden at the control point (Location 0) was generally low compared to other locations. This could be since this location is situated upstream some distance away from the dumpsite. The source of metal pollution at Location 0 might be traced to natural sources, agro-allied chemicals used by the farmers and deposition of metal containing fly ash coming from incineration of solid waste. Location 1 is the closest point on the stream bank from the dumpsite. It is at a lower gradient with respect to the dumpsite. This could explain why the potentially

Table 5. Contaminant factor of heavy metals in sediment

	Season	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
Nov	**Dry**	0.07	0.08	0.10	0.005	-	0.52	0.20	1.08	0.02	-	0.008
Dec		0.11	0.13	0.04	0.007	0.005	0.73	0.41	0.65	0.02	-	0.01
Jan		0.15	0.15	0.15	0.007	0.01	0.83	0.32	1.18	0.03	0.94	0.02
Feb		0.15	0.25	0.27	0.01	0.02	0.33	0.55	2.57	0.01	1.88	0.009
Mean		**0.12**	**0.15**	**0.14**	**0.007**	**0.009**	**0.60**	**0.37**	**1.37**	**0.02**	**0.71**	**0.01**
May	**Wet**	0.11	0.11	1.34	0.01	0.01	0.13	0.53	8.78	0.02	-	0.001
Jun		0.11	0.15	1.09	0.006	0.005	0.17	0.29	3.53	0.01	-	0.0003
Jul		0.07	0.09	1.64	0.005	0.003	0.09	0.13	4.77	0.009	-	-
Aug		0.06	0.07	1.76	0.006	ND	0.08	0.28	10.52	0.003	-	0.01
Mean		**0.09**	**0.11**	**1.46**	**0.007**	**0.005**	**0.12**	**0.31**	**6.9**	**0.01**	**-**	**0.003**

toxic metals burden of this location had generally higher values than other locations. From Location 1, there was a general decrease in concentrations of the metals downward the stream with exception of Location 4 which had a higher metal concentration than Location 1. This occurrence might be due to the flat topography of Location 4 which could encourage better and more effective sedimentation of metal containing particulates.

The Fe concentrations having a range of 1620 ± 630 mg/kg at Location 0 to 8310 ± 2700 mg/kg at Location 4 were below the background value of 47200 mg/kg in shales [10], and 26000 mg/kg elemental concentration of a typical soil[17]. Manganese is a vital nutrient and naturally occurring element, useful in steelmaking, fireworks, fertilizers, chemicals, glass, and dry-cell batteries production, textile and leather industries. Its presence in soil results in vegetable and animal foods reliably containing varying amounts of the mineral [29]. Manganese mean concentration ranged from 18 ± 18 mg/kg at Location 0 to 244 ± 110 mg/kg at Location 4. The values obtained were below the background value of 850 mg/kg in shales [10], and 550 mg/kg elemental concentration in a typical soil[17].

Cobalt in sediment could be of natural and anthropogenic origins. The anthropogenic sources could be as a result of phosphate-based fertilizer application, smelting, sewage sludge, alloys, and mining. In water, cobalt is basically settled in the bottom sediment while some may be adsorbed by suspended solids in the water column [29]. Cobalt ranged from 10 ± 11 mg/kg at Location 3 to 23 ± 22 mg/kg at Location 2. These values were very low with exception of Location 1 and 2 compared to 19 mg/kg in shales [10]. The mean concentrations of Co in all the locations were above 9.1 mg/kg elemental concentration of a typical soil [17].

The mean range value of Ti was between 18.3 ± 7.1 mg/kg at Location 5 and 59 ± 67 mg/kg at Location 2. These values were below the 4600 mg/kg background value in shales [10]. Barium levels ranged from 0.65 ± 1.9 mg/kg at Location 5 to 16 ± 17 mg/kg at Location 4. These values were below the background value of 580 mg/kg in shales [10].

Zinc is abundant in the environment, instituting 20–200 ppm (by weight) of the Earth's crust [29]. The mean concentration of Zn ranged from 13 ± 16 mg/kg at Location 0 to 84 ± 69 mg/kg at Location 1; the values were below the background value of 95 mg/kg in shales [10], and 60 mg/kg elemental concentration of a typical soil [17] with exception of Location 1.

Copper found their way into water bodies by natural weathering of soil and rocks or anthropogenic sources [29]. Copper mean concentrations ranged from 5.9 ± 4.3 mg/kg at Location 3 to 17 ± 30 mg/kg at location 0. The values of Cu at all locations were lower except at Location 1 when compared with the background value of 45 mg/kg in shales[10], and 25 mg/kg elemental concentration in a typical soil[17].The levels of As in the bed sediment ranged from 9 ± 26 mg/kg at Location 2 to 83 ± 80 mg/kg at Location 4. The mean values of As were higher than the background value of 13 mg/kg in shales[10] except at Location 2 where the value was higher.

The mean concentrations of Al ranged from 667 ± 400 mg/kg at Location 3 to 1590 ± 970 mg/kg at Location 1. The mean values of Al were low compared with the background value of 80,000 mg/kg in shales[10]. Yttrium was only above the detection limit at Location 0 and the value was above the background value of 26 mg/kg in shales [10] Strontium in bed sediment ranged from 0.8 ± 1.3 mg/kg at Location 0 to 4.4 ± 4.9 mg/kg at Location 1. The mean values of Sr obtained in this study were far below the background value of 300 mg/kg in shales[10].

Generally, the metals contamination levels in the bed sediment were wide-ranging significant among the stream site sampling locations. Potential toxic metals in bed sediments are either lithogenic or anthropogenic. The total metal burden at the control point was generally low compared to other locations. However, this could not be totally attributed to the lithogenic effect since there was the possibility of atmospheric distribution as a result of incineration of dumped solid waste. The total metal burden in the bed sediments of Locations 1 to 5 showed the influence of anthropogenic inputs because of the leaching of these metals from the dumpsite into the receiving stream. Since bed sediment acts as both carrier and source of contamination in the aquatic environment. High contaminations of the bed sediment with metals may have adverse effects on aquatic habitats; hence, remediation of the bed sediment is highly required.

3.5.1. Contaminant Factor of Heavy Metals with Respect to their Spatial Variation in Sediment of Asunle Stream

Table 7 is presentation of monthly and seasonal contamination factors (CFs) for each heavy metal. The results revealed

Table 6. Spatial variation of heavy metals in sediment of Asunle stream

Site	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr	Total metal burden
0	1620^{a} ±630	18^{a} ±18	10^{a} ±14	40^{ab} ±19	BDL	13^{a} ±16	17^{a} ±30	41^{a} ±73	1280^{abc} ±730	55^{a} ±110	0.8^{a} ±1.3	3090
1	7440^{cd} ±3400	117^{bc} ±100	21^{a} ±24	59^{b} ±67	6.54^{a} ±13	84^{b} ±69	51^{b} ±32	61^{a} ±100	1590^{bc} ±970	BDL	4.4^{a} ±4.9	9430
2	3030^{ab} ±1700	43^{ab} ±300	23^{a} ±22	29^{ab} ±14	BDL	32^{a} ±26	8.50^{a} ±14	9.31^{a} ±26	896^{ab} ±580	BDL	3.4^{a} ±6.9	4070
3	4960^{bc} ±2900	172^{cd} ±130	10^{a} ±11	25^{ab} ±10	BDL	31^{a} ±39	5.9^{a} ±4.3	70^{a} ±77	667^{a} ±400	BDL	0.99^{a} ±1.18	5940
4	8310^{d} ±2700	244^{d} ±110	10^{a} ±14	47^{ab} ±36	16^{b} ±17	25^{a} ±20	6.63^{a} ±11	83^{a} ±80	2020^{c} ±960	BDL	2.00^{a} ±2.54	10800
5	3820^{ab} ±3100	54^{ab} ±52	17^{a} ±16	18.3^{a} ±7.1	0.7^{a} ±1.9	21^{a} ±29	2.1^{a} ±5.2	58^{a} ±75	722^{a} ±760	BDL	2.01^{a} ±2.9	4710

The alphabet in each column denotes a mean value that is significantly different at $p < 0.05$ from each other.

that the contamination of bed sediment with respect to Fe, Mn, Ti, Ba, Zn, Al, Sr, and Zn were low. Co at Locations 1 and 2 as well as Cu in Location 2 exhibited moderate contamination. Similarly, Y had moderate contamination. Arsenic contamination varied between considerable and high contaminations except Location 2 which exhibited low contamination.

3.5.2. Pollution Load Index (PLI) of the Sediments

PLI was employed to adequately compare whether all the locations suffer contamination or not. The PLI was intended at providing an extent of the degree of the total contamination of the sampling locations along the course of the stream. Table 8 shows the result of the PLI for the eleven metals studied at the various locations. Based on the results, the overall degree of contamination in all the locations was of the order: Location 1 > Location 4 > Location 3 > Location 0 > Location 5 > Location 2. Results of PLI indicated that no location was polluted with Fe, Mn, Ti, Ba, Zn, Al and Sr. However, Location 0 was polluted with As and Y; Location 1 with Co, Cu and As; Location 2 with Cu only; and Location 3, 4 and 5 with As only.

3.6. Correlation Analysis of Heavy Metals in Sediment of Asunle Stream

The determination of the correlation analysis is to quantify the strength of association observed between two variables. This association is likely to better illustrate the causal relationship between the variables. Two-tailed correlation analysis between various metals detected in the lateral sampling of sediment toward the receiving stream is presented in Table 9. The result obtained revealed that Fe was positively correlated with Mn, Ti, Ba, Zn, Cu, Al and Sr. Manganese positively correlated with Ti, Ba and As, Ti positively correlated with Ba, Cu, Al and Sr; Ba correlated positively with Al; Zn positively correlated with Cu and Al; Cu and Al and Sr are positively correlated, and Fe and Sr are positively correlated. However, Co negatively correlated with Zn and Al while Zn negatively correlated with As and As in turn negatively correlated with Sr. Correlation analysis obtained in this study was similar to the values obtained from the dumpsite soil [2]. The association between these metals could be attributed to a common source, hence, positive correlations among these metals were controlled by features such as, anthropogenic factors, properties and soil genesis [5]. The strong association among Fe, Ba, Zn, Al could be attributed to the degradation of e-waste materials in the dumpsite that was leached into the stream.

3.7. Health Risk Assessment of Heavy Metals in Sediment of Asunle Stream

The model used to calculate the exposure of humans to potentially toxic metals in the sediments is based on those developed by the United States Environmental Protection Agency. The chronic daily intake for carcinogenic risk (oral) in the bottom sediment of the Asunle stream is showed in Table 10. The chronic daily intake for Fe ranges from 0.31 – 3.87 mg/kg/day. There is no available MRL data for Fe.

Manganese is an essential component of steel. Inorganic-Mn is equally used in the manufacture of dry cells, fireworks, and glass various chemicals, leather and textile, and fertilizer. Manganese found their way into water bodies majorly via the erosion of rocks and soils, mining works, and leaching e-waste material dumped in landfills [29]. The chronic daily intake of Mn for carcinogenic (oral) in the sediment of the Asunle stream ranged from 0.006 – 0.1 mg/kg/day. Literature has no stipulated MRLs values for various stages of toxicity for oral exposure to Mn, though neurobehavioral disorder has been established in literature from intermediate- and chronic-duration oral exposure to excess inorganic-Mn, hence, an interim guidance value of 0.16 mg Mn/kg/day is recommended by ATSDR for community health assessments [30]. The level of Mn recorded in this study are below any alerting values.

Cobalt, is vital for beings with dietary allowance of 0.1 µg, and mean regular consumption from food is valued to be 5 – 40 µg/day [31]. The chronic daily intake for Co in the bed sediment ranged from 0.0002 – 0.004 Co mg/kg/day. The minimal risk level (0.01 mg Co/kg/day) has been stipulated for average

Table 7. Contaminant factor of heavy metals in spatial variation in sediment of Asunle stream

	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
0	0.03	0.02	0.54	0.009	ND	0.13	0.39	3.18	0.02	2.11	0.003
1	0.16	0.14	1.09	0.01	0.01	0.90	1.13	4.73	0.02	ND	0.01
2	0.06	0.05	1.20	0.006	ND	0.33	0.19	0.72	0.01	ND	0.01
3	0.11	0.20	0.53	0.006	ND	0.32	0.13	5.39	0.008	ND	0.003
4	0.18	0.29	0.54	0.01	0.03	0.27	0.15	6.35	0.02	ND	0.007
5	0.08	0.06	0.89	0.004	0.001	0.22	0.05	4.44	0.009	ND	0.007

Table 8. Pollution load index of heavy metals across the sampling locations

Sites	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
0	0.03	0.02	0.54	0.009	ND	0.13	0.39	3.18	0.02	2.11	0.003
1	0.16	0.14	1.09	0.010	0.01	0.90	1.13	4.73	0.02	ND	0.01
2	0.06	0.05	1.20	0.006	ND	0.33	0.19	0.72	0.01	ND	0.01
3	0.11	0.20	0.53	0.006	ND	0.32	0.13	5.39	0.008	ND	0.003
4	0.18	0.29	0.54	0.010	0.03	0.27	0.15	6.35	0.02	ND	0.007
5	0.08	0.06	0.89	0.004	0.001	0.22	0.05	4.44	0.009	ND	0.007
Mean	**0.10**	**0.13**	**0.80**	**0.008**	**0.007**	**0.36**	**0.34**	**4.14**	**0.015**	**0.35**	**0.007**

length oral contact to cobalt [29]. The CDI values obtained in this study is below the MRL value for Co, hence there is no cause for alarm. Barium, an alkaline earth metal, with a variability of usages such as getters in electronic tubes, rodenticide, colorant in paints, and x-ray contrast medium [30]. The minimal risk level (0.2 mg Ba/kg/day) has been stipulated for average length oral exposure to barium. With the CDI of Ba in bed sediment ranging from 0.0002 – 0.001 mg/kg/day, the CDI value obtained in this present study was several folds (200 – 1000) below the recommended MRL.

Zinc, a vital metal has a recommended daily allowance between 5 mg (infant) to 15 mg for infants and adults, respectively [14]. Detrimental health effects of Zn range between 100 to 250 mg/day [32]. ATSDR [30] recommended minimal risk level of 0.3 mg/kg/day for both intermediate and chronic duration. The CDI for Zn in bed sediment ranged from 0.00008 to 0.009 mg/kg/day. The Zn level recorded in this study are far below the recommended limits, hence, not cause for immediate health concern.

Copper, an indispensable nutrient is vital in carbohydrate, and drug metabolism, haemoglobin formation, catecholamine biosynthesis, the cross-linking of collagen, elastin, and hair keratin, and the antioxidant defence mechanism[30]. Some of the evidence of Cu deficit are: anaemia, leukopenia, and osteoporosis. The recommended minimal risk level of both intermediate and chronic duration is 0.01 mg/kg/day. The value obtained in this study ranged from 0.0009 to 0.003 mg/kg/day which are far below the recommended value and pose no health threat to humans.

Arsenic is a metalloid, and very poison. Arsenic main route of exposure is via food and drinking water. Dietary exposures to arsenic in female ranges between 1.01, and 1,081 µg/day and mean (50.6 µg/day); male ranges between 0.21 and 1,276 µg/day, and mean (58.5 µg/day) [30]. The minimal risk level of 0.005 and 0.0003 mg As/kg/day has been resultant for acute and chronic duration oral exposure to inorganic arsenic. The CDI of As in bed sediment ranged from 0.004 to 0.01 mg/kg/day (Table 10). The values obtained in this study were above the recommended minimal risk level; hence, the risk of cancer is possible.

Aluminium, the third most abundant element of the earth's crust. There is appreciable amount of human data on the toxicity of Al because of oral exposure for instance, dialysis encephalopathy syndrome (a degenerative neurological syndrome), and Alzheimer's disease [30]. The minimal risk level for both intermediate and chronic duration is 1.0 mg/kg/day. The CDI of Al for carcinogenic (oral) in bed sediment ranged from 0.03 – 0.24 mg/kg/day. These values were below the minimum risk level; hence no health risk is implied. The levels of Strontium in fresh waters ranges between 0.5 and 1.5 mg/L. The daily exposure is estimated to be 3.3 mg/day (0.046 mg/kg/day): from inhalation (400 ng/day), drinking water (2 mg/day), and diet (1.3 mg/day) [30]. The minimal risk level of Sr in bed sediment ranged from 0.00001 to 0.0006 mg/kg/day. Thus, the values obtained in this study were also below the minimal risk level.

Table 11 presents the descriptive statistics of the cancer risk assessment of the heavy metals in bed sediment of Asunle stream. These values depicted non-hazard for both young and adult. The sequence of the total cancer risk of the studied metals are Fe > Al > Mn >As > Ti > Ba > Zn > Co > Y > Sr > Ba. Given the available toxicological profile of the studied metals, it is obvious that all the studied metals may not inevitably have any adverse effect on human. The levels obtained in this study are below the RAIS oral chronic reference dose (mg/kg/day).

The chronic daily intake for non-carcinogenic risk of both children and adult of metals in the bed sediment of Asunle stream are presented in Table 12 and 13. The level of human health risk caused by non-carcinogenic pollutants in children (x 10^6 mg/kg/day) (Table 12) ranged as follows: Fe (2910 - 51240), Mn (59.08 – 127.19), Co (0.75 – 34.19), Ti (22.05 – 60.23), Ba (1.65 – 7.90), Zn (7.69 – 80.66), Cu (5.75 – 24.59), Al (8.61 -139.83), As (279.40 – 8210), Y (25.02.A20), and Sr (0.10 – 5.37). Similarly, the level of human health risk caused

Table 9. Correlation analysis of metals in sediment of Asunle stream

	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
Fe	1.00										
Mn	0.875**	1.00									
Co	-0.266	-0.279	1.00								
Ti	0.481**	0.371**	-0.052	1.00							
Ba	0.719**	0.686**	-0.079	0.677**	1.00						
Zn	0.466**	0.226	-0.389**	0.274	0.225	1.00					
Cu	0.341*	0.175	-0.109	0.590**	0.284	0.535**	1.00				
As	0.040	0.083	0.365*	0.013	0.023	-0.307*	-0.108	1.00			
Al	0.646**	0.449**	-0.346*	0.444**	0.650**	0.544**	0.282	-0.224	1.00		
Y	-0.149	-0.145	-0.173	0.001	-0.076	-0.103	-0.064	-0.061	0.064	1.00	
Sr	0.345*	0.226	-0.066	0.292*	0.250	0.596**	0.485**	-0.335*	0.366*	-0.072	1.00

**** Significant at p < 0.01 level (two-tailed); * significant at p < 0.05 level n= 528**

Table 10. Chronic Daily Intake for Carcinogenic (oral) in Sediment of Asunle Stream

	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
Nov	3.87	0.007	0.0002	0.002	-	0.005	0.0009	0.002	0.14	-	0.0003
Dec	0.56	0.01	0.0008	0.004	0.0003	00.008	0.002	0.0009	0.18	-	0.0004
Jan	0.75	0.01	0.0003	0.003	0.0007	0.009	0.002	0.002	0.24	0.003	0.0006
Feb	0.80	0.02	0.0006	0.007	0.001	0.003	0.003	0.004	0.12	0.005	0.0003
May	0.55	0.01	0.003	0.006	0.0008	0.001	0.003	0.01	0.16	-	0.0005
Jun	0.55	0.01	0.003	0.003	0.0003	0.002	0.001	0.005	0.11	-	0.00001
July	0.36	0.008	0.003	0.003	0.0002	0.0009	0.0006	0.007	0.08	-	-
Aug	0.31	0.006	0.004	0.003	-	0.00008	0.001	0.01	0.03	-	0.0004

Table 11. Cancer Risk Assessment of Heavy Metals in Sediment of Asunle Stream

	Fe	Mn	Co	Ti	Ba	Zn	Cu	Al	As	Y	Sr
Min	0.62	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00
Max	7.74	0.04	0.01	0.01	0.00	0.02	0.01	0.02	0.48	0.01	0.01
Mean	1.94	0.02	0.004	0.008	0.0009	0.007	0.003	0.01	0.27	0.002	0.002
$\sum CDI_k SF_k$	15.5	0.148	0.024	0.062	0.007	0.059	0.027	2.12	0.082	0.016	0.012

by non-carcinogenic pollutants in adult (x10^6 mg/kg/day) (Table 13)ranged as follows: Fe (2480 – 6300), Mn (50.22 – 182.05), Co (0.63 – 215.30), Ti (18.75 – 53.09), Ba (1.39 – 8.52), Zn (6.54 – 68.56), Cu (4.89 – 21.43), Al (7.31 - 28.98), As (8.66 – 1880), Y (21.27 – 42.38), and Sr (0.00 – 4.56). The implication of these values is that the number of deaths that could be attributed to non-carcinogenic pollutant in each million is very high, hence the risk is of great concern. According to the United State Environmental Protection Agency (USEPA), the acceptable health risk level is $10^{-6} – 10^{-4}$ per year[13]. Besides, the CDI values for non-carcinogenic (oral) in children was slightly higher than the value obtained in adult. This also suggests that the children are more vulnerable to hazard than adults.

From each chronic non-carcinogenic exposure, the separate chronic hazard index (HI) was first calculated from the ratios of the chronic daily intake (CDI) to the chronic reference dose (RfD) for the individual metals and then the obtained results summed up as described in the equation:

Chronic Hazard Index = $\sum_{k=1}^{n} CDIk / RfDk$ [17]

where the hazard index is a unit less number that is expressed as the probability of an individual suffering an adverse effect. Table 14 presents the total chronic hazard quotient for both children and adults in the bed sediment. Generally, the hazardous index (HI) for ingestion of sediment by children is greater in comparison to that of adults. Consequently, the total chronic hazard quotient index of oral exposure to contamination in the bed sediment for adult and children are far above 1, great hazard for both young and old is depicted.

4. Conclusion

Along with several other metals, the determination of rare-earth metals and some other metals that have not been reported in earlier studies of the dumpsite was done. Values of metals present in the various matrices revealed that potentially toxic metal contamination had occurred to varying degrees that could cause health hazards. In some cases, the extent of contamination had reached the pollution levels that gave cause for concern. The geo-accumulation index, enrichment factor and contaminant factor revealed that the soil and sediment samples were heavily polluted with such contaminants as As, Cu and Be. The effective management of the water bodies and other aqueous

Table 12. CDI for Non-Carcinogenic (oral) for Children in Sediment of Asunle Stream (x10^6 mg/kg/day)

	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
Nov	3610	69.05	1.91	22.1	-	50.38	9.06	14.28	1290	-	2.59
Dec	51240	112	0.75	32.95	2.92	70.84	18.76	8.61	1690	-	3.93
Jan	7000	127	2.97	32.1	6.09	80.66	14.68	15.65	2210	25.02	5.37
Feb	7420	127	2.97	32.1	6.09	80.66	14.68	15.65	2210	25.02	0.28
May	5080	98.1	26.1	60.23	7.90	12.65	24.59	116.71	1460	-	0.45
Jun	5080	126	21.2	28.43	3.18	16.69	13.56	46.95	1020	-	0.10
July	3390	76.1	31.9	25.47	1.65	8.75	5.75	63.38	717	-	-
Aug	2910	59.1	34.2	27.96	-	7.69	12.86	139.83	279	-	3.30

Table 13. CDI for Non-carcinogenic risk (oral) for Adult in Sediment of Asunle Stream

	Fe	Mn	Co	Ti	Ba	Zn	Cu	As	Al	Y	Sr
Nov	3060	58.69	1.62	18.75	-	42.83	7.71	12.14	1100	-	2.19
Dec	4460	95.81	0.634	28.02	2.48	60.22	15.95	7.31	1430	-	3.34
Jan	5950	108.11	215.3	27.26	5.18	68.56	12.47	13.30	1880	21.27	4.56
Feb	6300	182.05	4.38	58.09	8.52	27.02	21.43	2898	930	42.38	2.35
May	4320	83.36	22.14	51.20	6.72	10.75	20.90	99.20	1240	-	0.38
Jun	4320	107.34	18.05	24.16	2.70	14.19	11.53	39.90	8.66	-	0.09
July	2880	64.67	27.09	21.65	1.39	7.44	4.89	53.88	609	-	-
Aug	2480	50.22	29.07	23.76	-	6.54	10.93	118.86	237	-	2.81

Table 14. Total Chronic Hazard Quotient Index (x 10^6) of the Heavy Metals in the Sediment of Asunle Stream

	Minimum Value		Maximum Value		Mean Value	
	Child	**Adult**	**Child**	**Adult**	**Child**	**Adult**
Mn	1284.35	1091.75	2765.00	3957.61	2161.96	2038.72
Co	37.30	3.70	1709.50	10766.00	762.16	1989.28
Ba	0.00	0.00	39.50	42.60	17.39	16.87
Zn	384.50	327.00	8345.00	3430.00	2990.81	1484.94
Cu	143.75	122.25	614.75	535.75	175441.70	330.66
As	28700.00	24366.67	466100.00	9660000.00	175441.70	1351079.00

matrices is vital to ensuring the safety of the receiving water bodies as well as public health. Regular monitoring of persistent organic pollutants is highly required. Future studies should be targeted on the assessment of these contaminants in the aquatic biota, crops, farmers and rural dwellers of the surrounding communities in this environment. Studies should be focused on the assessment of these contaminants in different biological samples, plant uptakes, farmers, and rural dwellers in this environment to ascertain the extent of bioaccumulation of these contaminants. Remediation of heavy metals in this water body is highly recommended.

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Appendix

Supplementary Data/Appendix

Variable	**Value used**
AT – averaging time for non-carcinogens	365 days/year/ ED *Child or adult*
AT – averaging time for carcinogens	565days/year/70 years
BW_{Adult} – body weight adult	70 kg
BW_{Child} –– body weight child	15 kg
CS – concentration in soil or sediment	chemical specific (mg/kg)
EF – exposure frequency	350 days/year
ET Indoor – Exposure time indoor	0.683
ET Outdooor- Exposure time outdoor	0.073
DF – dilution factor indoor	0.4
IN – inhalation rate	20 m^3/day
PEF – particulate emission factor, climate specific	m^3/kg
VF- volatilization factor, chemical specific	m^3/kg
IF – intake factor	-
IR *Adult* – ingestion rate adult	0.0001 kg/day
IR *Child* – ingestion rate child	0.0002 kg/day
ED *Child* – exposure duration childhood	6 years
ED *Adult* – exposure duration adulthood	24 years (for general case:30 years)