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Heavy Metals Pollution of Streams and River Sediments in Parts of Akpabuyo Local Government Area Nigeria and Its Implication for Agricultural Practices and Environmental Protection

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Abstract

This study was initiated to evaluate the spatial distribution of heavy metals in streams and river sediments in parts of Akpabuyo, Cross River State, Nigeria. Surfacial streams and river sediment samples were taken from ten sampling stations and analyzed for availability of Fe, Zn, Mn, Cr, Ni, Co, Cu, Cd, and Pb. The concentrations of the heavy metals were found to be in the ranges (mg/kg): Fe (144.45 - 564.76), Zn (19.56 - 44.36), Mn (11.93 - 30.06), Cr (9.75 - 27.68), Ni (6.56 - 18.04), Co (5.36 - 56.41), Cu (3.35 - 6.80), Cd (1.18 - 2.91), and Pb (1.34 - 4.41). The order of concentration in most of the streams and river sediments were found to be: Fe > Zn > Mn > Cr > Ni > Co > Cu > Pb > Cd. The sediment quality indexes used were Geo-accumulation index, contamination factor and pollution load index. The Geo-accumulation index values for Cadmium ranged between 1.4 and 2.7, indicating moderate to severe contamination and that of Cobalt in Ekpene Tete was 0.985, implying moderate contamination. The contamination factor value for Cobalt in Ekpene Tete was 2.969, indicating moderate contamination factor, while that of Cadmium in the entire sampling station ranged between 3.953 and 9.717, implying considerable to very high contamination factor. Also, the pollution load index values indicate that these metals ranged around background levels, with exception of Cadmium in all the sampling stations, indicating pollution. Furthermore, comparison of the heavy metals with other studies showed that the concentration of Cadmium in the study area was higher. The high concentration of Cadmium in the study area is possibly due to weathering of rocks and minerals in the nearby Oban Massif and Calabar Flank and farming activities in the area. The toxic level of Cadmium has negative implications for the environment and the food chain since the area is agrarian.

1. Introduction

Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of body of water (Davies and Abowei, 2009). River and stream sediments are vital and integral parts of any river ecosystem. They provide the substrate for living organisms and through interaction with overlying waters such as nutrient cycling play important roles in aquatic ecosystems (Charkhabi et al., 2008).Besides the natural processes, heavy metals such as iron, zinc, manganese, chromium, nickel, cobalt, copper, lead and cadmium may enter into the aquatic system due to anthropogenic factors such as mining operations, disposal of industrial wastes and applications of biocides for pest. The concentration in sediments depends not only on anthropogenic and lithogenic sources but also upon the textural characteristics, organic matter contents, mineralogical composition and depositional environment of the sediments (Trefry and Parsley, 1976). The composition of sediment sequences provides the best natural archives of recent environmental changes (Davies and Abowei, 2009). The occurrence of heavy metals in excess of natural background level in aquatic ecosystems has become a thing of public concern. However, contaminations of aquatic ecosystem in developing nations are mostly related to the consequences of population growth, urbanization, agricultural activities and development of new industrial zones (Olade, 1987 and Paul and Pillai, 1983). Heavy metals in environment may accumulate to toxic levels without visible signs.

Therefore, this study was carried out to evaluate the concentration of heavy metals in streams and River sediments in parts of Akpabuyo area and ascertain the possible sources of these heavy metals.

2. Study Area

The study area is part of Akpabuyo Local Government Area in Cross River state, Southeast Nigeria and lies between longitudes 8°22'30"E - 8°30'0"E and latitudes 4°52'30"N - 4°57'30"N, covering an area of 126.40 square km. (Fig. 1). The area is situated near Nigeria's boundary with Cameroon Republic and within a coastal plain characterized by undulating topography with the lowest and highest elevation of about 2.72m and 71.5m respectively. The surfacial geology is unconsolidated formation ranging from coarse to medium sands. These sands belong to the Benin Formation, the youngest sedimentary Formation in the Calabar Flank of the Southern Benue Trough of Nigeria. The Benin Formation is Tertiary in age and overlies the Nkporo Shale which is Maastritchtian - Campanian in age (Reyment, 1965).

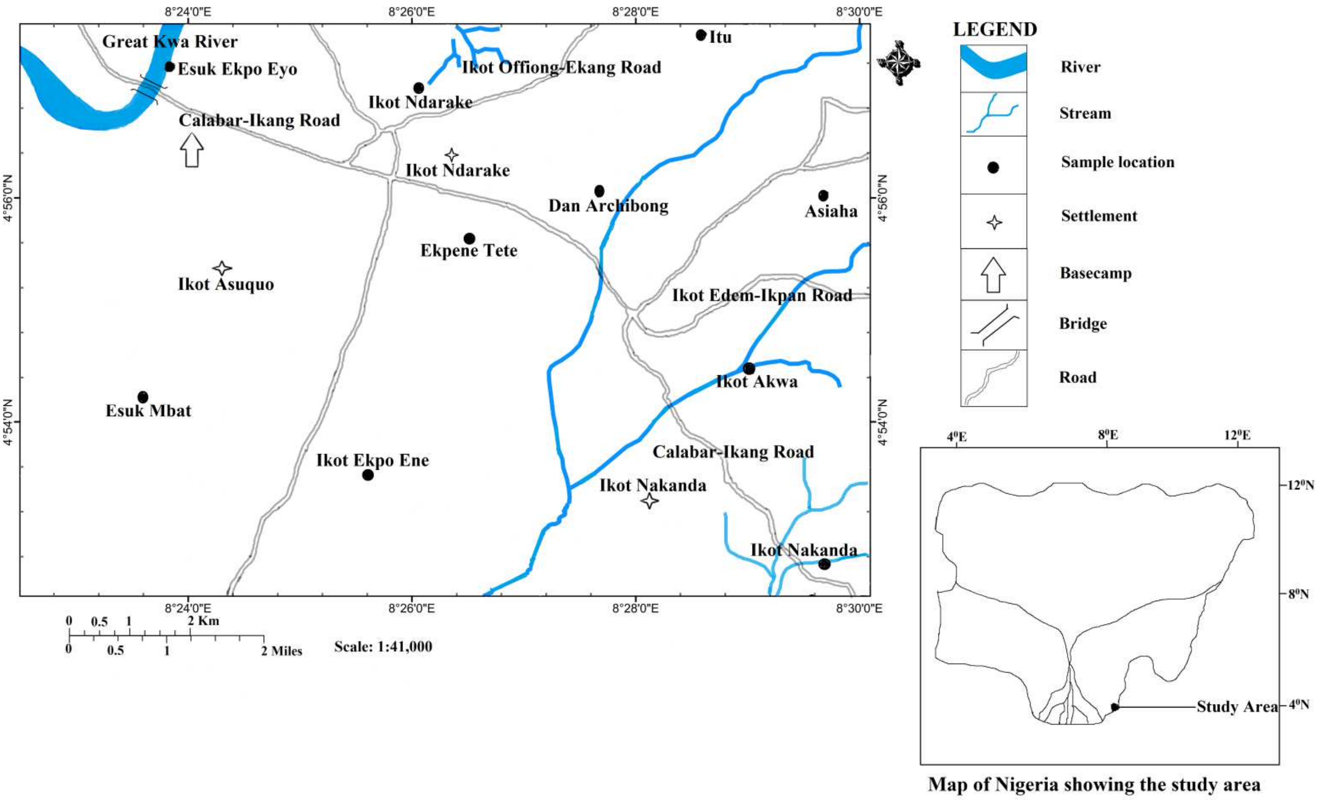

***Figure 1**. Sample Location Map of parts of Akpabuyo Local Government of Cross River State, Nigeria.*

3. Method of Study

Sediment samples were collected along active River and Channelized streams in parts of Akpabuyo area (Fig. 1). Samples for the study were collected at ten different locations, of which nine of the locations were streams and one river as shown in the map (Fig. 1). Sampling points were located using GPS and sediment samples were taken from active streams and river banks (left and right banks) and the centre in order to have a composite sample. These sediments were collected during a field work in May - June, 2014. The samples were collected with the aid of a trowel and stored in well labeled polythene bags. The trowel was washed before each use to minimize contamination. Sediments were later air-dried and the collected samples were transported to the laboratory for analysis. The samples were split into two parts. One part was passed through 2mm sieve whilst the bulk samples were ground to powder and later digested for chemical analysis. These samples were digested with perchloric acid ($HClO_4$), and nitric acid (HNO_3). The digested samples were analysed using Unicam 939 atomic absorption spectrophotometer (AAS) at Aluminium Smelter Company of Nigeria (ALSCON) in Ikot Abasi Local Government Area in Akwa Ibom State, Nigeria.

4. Results

The result of the heavy metal analysis is presented in Table 1.

Table 1. *Heavy metal concentrations in streams and river sediments from parts of Akpabuyo area.*

Sample Locations.	Fe mg/kg	Zn mg/kg	Mn mg/kg	Cr mg/kg	Ni mg/kg	Co mg/kg	Cu mg/kg	Cd mg/kg	Pd mg/kg
Esuk Mbat	551.544	23.82	14.06	10.86	7.683	5.885	4.017	1.868	3.732
Esuk Ekpo Eyo	564.766	33.49	19.22	16.17	12.03	9.862	6.028	2.736	4.418
Ikot Akwa	302.036	35.10	21.37	18.48	14.16	11.34	6.014	2.709	3.832
Dan Archibong	328.300	19.65	12.58	9.748	6.743	5.308	3.352	1.186	2.576
Itu	144.450	20.81	11.93	9.835	6.562	5.601	3.513	1.204	2.609
Ikot Ndarake	302.036	38.15	22.57	20.53	16.79	12.36	6.233	2.841	2.636
Asiaha	472.752	44.36	30.06	27.68	18.04	12.95	6.801	2.915	2.685
Ikot Ekpo Ene	315.165	36.58	23.17	19.16	16.48	11.65	6.035	2.808	2.574
Ekpene Tete	170.716	21.54	12.52	9.862	10.72	56.41	3.388	1.488	1.382
Ikot Nakande	210.112	25.39	15.49	11.05	7.883	6.448	3.546	1.504	1.382

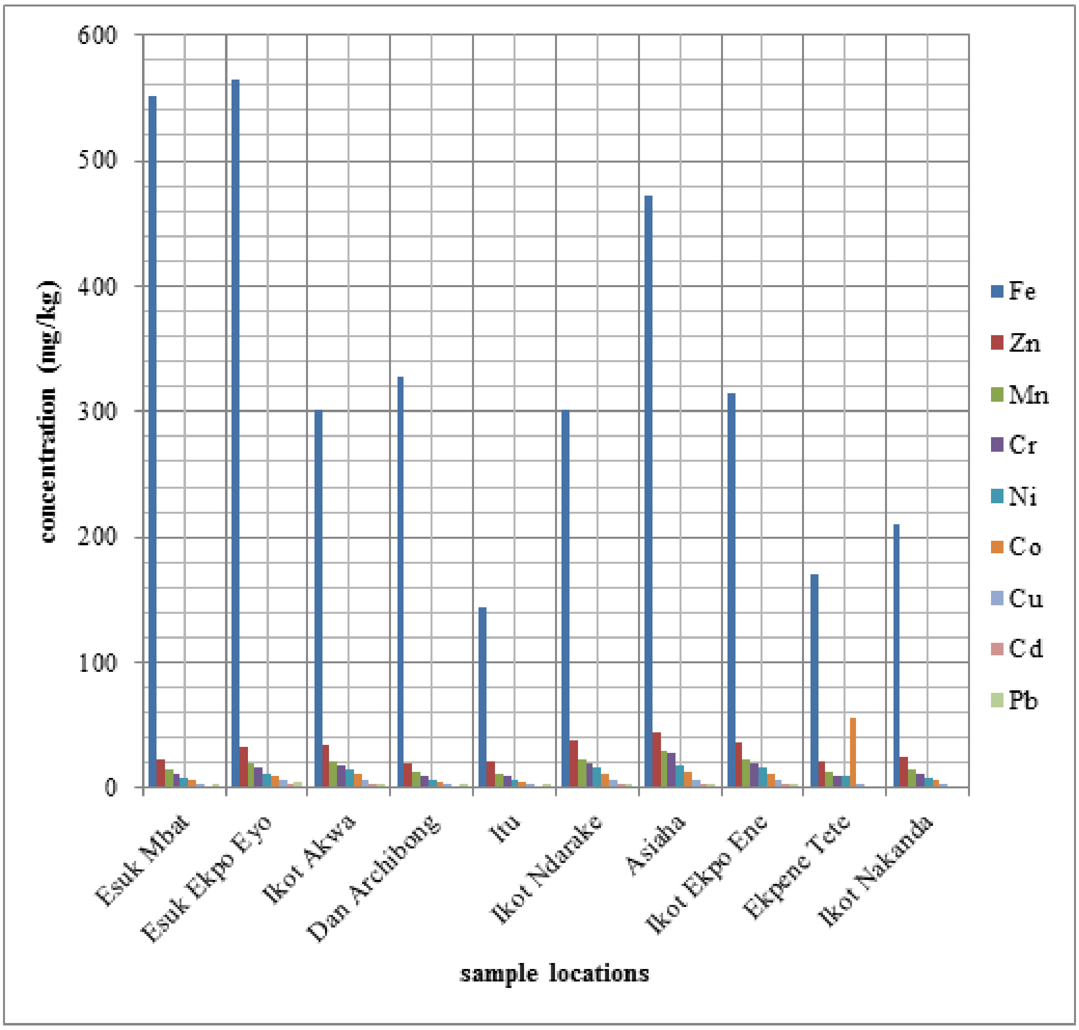

Figure 2. *Bar chart showing the distribution of heavy metals in streams and river sediments from parts of Akpabuyo area.*

The mean values of the concentrations for all samples amounted to: Fe-323.1877mg/kg, Zn-29.853mg/kg, Mn-18.297mg/kg, Cr-15.3375mg/kg, Ni-11.7091mg/kg, Co-13.7874mg/kg, Cu-4.8927mg/kg, Cd-2.1259mg/kg, Pb-2.7185mg/kg.

The concentrations of heavy metals in the sediments were found to be in the ranges (mg/kg): Fe (144.450 - 564.766), Zn (19.56 - 44.36), Mn (11.93 - 30.06), Cr (9.748 - 27.68), Ni (6.562 - 18.04), Co (5.368 - 56.41), Cu (3.352 - 6.801), Cd (1.186 - 2.915), and Pb (1.341 - 4.418). The order of concentration of the studied metals in most of the stream sediments were found to be Fe > Zn > Mn > Cr > Ni > Co > Cu > Pb > Cd. Asiaha area has the highest concentration of six of the nine heavy metals studied: Zn, Mn, Cr, Ni, Cu, and Cd while Dan Archibong has the lowest concentration for five of the nine heavy metals: Zn, Cr, Co, Cu, and Cd, and Itu for three metals: Fe, Mn, and Ni. Ekpene Tete has the highest concentration for Co (56.41mg/Kg) and the lowest for Pb (1.341mg/Kg). Esuk Ekpo Eyo has the highest concentration for Fe (564.766mg/Kg) alone.

A bar chart (Fig. 2) has also been used to show the concentrations of heavy metals at each sampling location.

5. Discussion

The level of contamination of sediment by a metal can be expressed in terms of Geo-accumulation Index (I_{geo}), contamination factor and pollution load index (PLI).

The Geo-accumulation Index (I_{geo}) was proposed by Muller (1969). It is expressed as:

$$\text{I-geo} = \log_2 (C_n / 1.5B_n)$$

Where, C_n is the measured concentration of element ‘n’ in the sediment and B_n (reference value) is the World geochemical background value in average shale (Turekian and Wedepohl, 1961). The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect.

Generally, the I-geo consists of 7 grades or classes as shown in (Table 2) below.

Table 2. *I-geo values with their corresponding classes and designation of sediment quality.*

I-geo Value	I-geo Class	Designation of sediment quality
>5	6	Extremely contaminated
4 – 5	5	Strongly to extremely contaminated
3 – 4	4	Strongly contaminated
2 – 3	3	Moderately to strongly contaminated
1 – 2	2	Moderately contaminated
0 – 1	1	Uncontaminated to moderately contaminated
< 0	0	Uncontaminated

Contamination factor proposed by Hakanson (1980) is expressed as:

$$Cf = M_c / B_c$$

Where M_c is measured concentration of the metal and B_c (reference value) is the World geochemical background value in average shale (Turekian and Wedepohl, 1961).

Table 3. *Levels of contamination factor (Hakanson, 1980).*

Contamination Factor (Cf)	Contamination Level
Cf < 1	Low contamination factor
1≤ Cf < 3__	Moderate contamination factors
3≤ Cf < 6_	Considerable contamination factors
Cf ≥ 6	Very high contamination factor

Pollution load index (PLI) proposed by Tomlinson et al., (1980) can be used to evaluate the extent of pollution by heavy metals in the environment. The pollution load index (PLI) of heavy metal in a particular area is the n^{th} root of n number of that metal multiplied by the contamination factor (Cf) values.

$$\text{Pollution load index (PLI)} = (Cf1 \times Cf2 \times Cf3 \times \cdots \times Cf_n)^{1/n.}$$

The PLI values <1 indicates unpolluted whereas 1.0 indicates baseline level of pollutants present while values >1 are regarded as polluted (Tomlinson et al., 1980).

Table 4. *Summary of Geo-accumulation index (I-geo) of heavy metals in the study area.*

Heavy metals	Esuk Mbat	Esuk Ekpo Eyo	Ikot Akwa	Dan Archibong	Itu	Ikot Ndarake	Asiaha	Ikot Ekpo Ene	Ekpene Tete	Ikot Nakanda
Fe	-6.983	-6.947	-7.861	-7.733	-8.895	-7.861	-7.221	-7.795	-8.702	-8.380
Zn	-2.580	-2.102	-2.021	-2.864	-2.774	-1.906	-1.683	-1.961	-2.725	-2.488
Mn	-6.506	-6.049	-5.895	-6.658	-6.733	-5.820	-5.405	-5.779	-6.673	-6.368
Cr	-3.573	-3.061	-2.868	-3.791	-3.777	-2.716	-2.286	-2.817	-3.774	-3.610
Ni	-3.731	-3.084	-2.848	-3.919	-3.959	-2.602	-2.499	-2.629	-3.250	-3.693
Co	-2.275	-1.531	-1.329	-2.408	-2.347	-1.205	-1.138	-1.290	0.985	-2.144
Cu	-4.071	-3.485	-3.488	-4.330	-4.265	-3.437	-3.310	-3.483	-4.316	-4.251
Cd	2.053	2.604	2.589	1.398	1.419	2.658	2.695	2.641	1.725	1.740
Pb	-3.007	-2.763	-2.969	-3.541	-3.522	-3.508	-3.482	-3.542	-4.483	-4.439

The values in Table 4 above were presented in a bar chart form to easily delineate the heavy metals that constitute pollution in the various streams and river with reference to Table 2 above

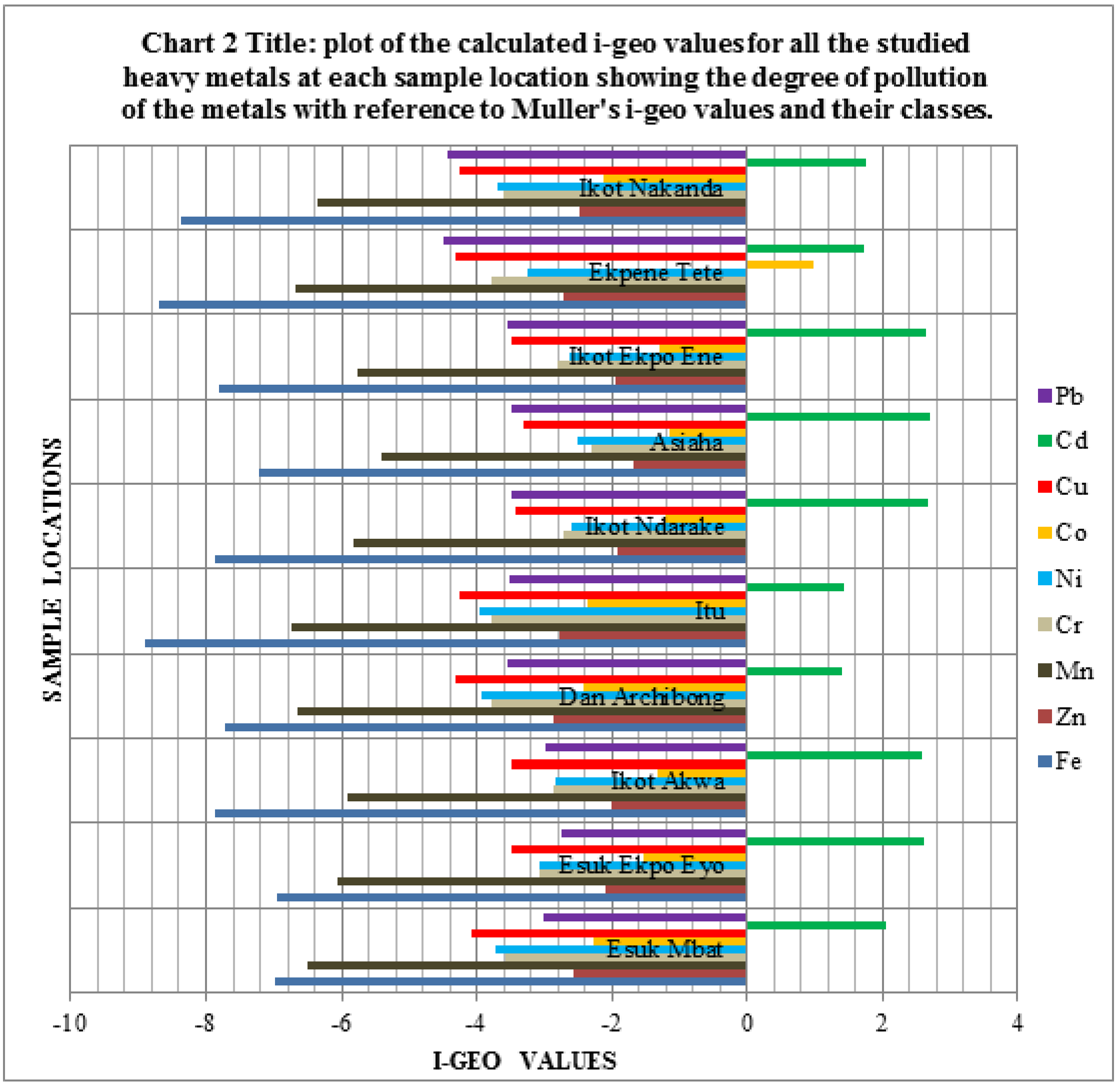

Figure 3. *Plot of the calculated I-geo values for all the studied heavy metals at each sample location showing the degree of pollution of the metals with reference to Muller's I-geo values and their classes.*

From the Figure 3 above, using the index of geo-accumulation, it is clear that the I-geo values for Fe, Zn, Mn, Cr, Ni, Co (except for Ekpene Tete), Cu and Pb are below zero (< 0 : class 0), which implies that the streams are uncontaminated by them. The I-geo values of Cadmium in all the locations are greater than zero as shown in Figure 3, ranging from 1.4 to 2.66 (the bars in green color), which is an indication of pollution. Dan Archibong, Itu, Ekpene Tete and Ikot Nakanda fall in class 2 (moderately contaminated), while Esuk Mbat, Esuk Ekpo Eyo, Ikot Akwa, Ikot Ndarake, Asiaha, and Ikot Ekpo Ene, fall in class 3 (moderately to highly contaminated) for Cadmium.

The I-geo value for Cobalt in Ekpene Tete was greater than zero as shown in Figure 3, fall in class 1 (uncontaminated to moderately contaminated), (see Table 2).

Table 5. *Summary of contamination factor values for the heavy metals in the study area.*

Sample Locations.	Fe	Zn	Mn	Cr	Ni	Co	Cu	Cd	Pd
Esuk Mbat	0.012	0.251	0.018	0.121	0.113	0.310	0.089	6.223	0.190
Esuk Ekpo Eyo	0.012	0.352	0.024	0.180	0.177	0.519	0.134	9.120	0.221
Ikot Akwa	0.006	0.370	0.027	0.205	0.208	0.597	0.134	9.03	0.192
Dan Archibong	0.007	0.207	0.016	0.108	0.075	0.279	0.074	3.953	0.129
Itu	0.003	0.220	0.015	0.109	0.097	0.295	0.078	4.013	0.130
Ikot Ndarake	0.006	0.402	0.029	0.228	0.247	0.651	0.137	9.470	0.132
Asiaha	0.011	0.467	0.038	0.308	0.265	0.682	0.151	9.717	0.134
Ikot Ekpo Ene	0.007	0.385	0.029	0.213	0.242	0.613	0.134	9.360	0.129
Ekpene Tete	0.004	0.227	0.016	0.109	0.158	2.969	0.075	4.96	0.069
Ikot Nakande	0.004	0.267	0.021	0.123	0.116	0.339	0.079	5.013	0.069

From Table 5 above, it can be observed that the general concentration of heavy metals in the study area based on contamination factor indicates that Fe, Zn, Mn, Cr, Ni, Cu and Pb are found to have low contamination factors; i.e. below contamination level, while Cobalt also has a low contamination factor with exception of Ekpene Tete, which has a contamination factor value of 2.968, indicating moderate contamination factor. While the concentration of Cadmium from the study area shows that it has a high contamination factor value in all the locations ranging between 3.953 to 9.717, indicating moderate to very high contamination factor with reference to Table 3 above. Also, Table 6 above gives a summary of the pollution load index values (PLI) for all the metals in the study area. It can be observed that Fe, Zn, Mn, Cr, Ni, Co, Cu and Pb have pollution load index values of less than one indicating no pollution, while Cadmium has pollution load index value of greater than one indicating pollution.

Table 6. *The Pollution load index (PLI) for the heavy metals in the study area.*

Heavy metals	Pollution load index (PLI) values (mg/kg)	Interpretation
Fe	6.44×10^{-3}	Unpolluted
Zn	3.03×10^{-1}	Unpolluted
Mn	2.22×10^{-2}	Unpolluted
Cr	1.59×10^{-1}	Unpolluted
Ni	1.56×10^{-1}	Unpolluted
Co	5.4×10^{-1}	Unpolluted
Cu	1.04×10^{-1}	Unpolluted
Cd	6.67	Polluted
Pb	1.31×10^{-1}	Unpolluted

Table 7. *Comparson of the concentration of heavy metals in the study area with studies carried out in other areas as well as the world average shale values.*

Heavy metals	Mean concentrations from the study area.	Concentrations from Calabar River (after Ntekim et al., 1993).	Concentrations from Sangana River (NAOC, 2006).	World average shale values (Turekian and Wedepohl, 1961).
Fe	336.189mg/kg	80,752mg/kg	10,075mg/kg	46,700mg/kg
Zn	29.89mg/kg	164mg/kg	16.37mg/kg	95mg/kg
Cu	4.893mg/kg	64mg/kg	13.41mg/kg	45mg/kg
Cr	15.34mg/kg	65mg/kg	16.65mg/kg	90mg/kg
Ni	11.71mg/kg	67mg/kg	15.52mg/kg	68mg/kg
Pb	2.276mg/kg	20mg/kg	13.06mg/kg	20mg/kg
Cd	2.126mg/kg	0.03mg/kg	Not available	0.3mg/kg
Co	13.78mg/kg	15mg/kg	Not available	19mg/kg
Mn	18.30mg/kg	Not available	788mg/kg	790mg/kg

From Table 7 above, the concentration of Fe, Cu, Cr, Ni, Pb, Co and Mn from the study area are quite low in comparison with those reported from Calabar River, Sangana River and the world average shale values. Whereas, the concentration of Cd is high in comparison with those from other studies.

Ekwueme (1985), geochemically analyzed Limestones and Marls in nearby Calabar Flank and obtained Cadmium concentration of 0 to 8ppm. Ero and Ekwueme (2009), analyzed Pegmatites of the nearby Oban Massif and obtained Cadmium content of up to 11.1ppm. Weathering and erosion of these rocks could have enhanced the Cadmium content levels of streams and river sediments in parts of Akpabuyo Local Government Area. The enhanced concentration of the heavy metals in the streams and river sediments of the study area could also be due to anthropogenic pollution from farming activities (e.g, the application of fertilizers) because agriculture is the main occupation of the inhabitants in the study area and past agricultural practices resulting in erosion and deposition of sediments within stream channels have affected and may continue to influence stream sediment geochemistry in the study area. Other possible sources include: population increase and urbanization coupled with lack of proper waste disposal systems (ATSDR, 2012). These calls for mitigation before the heavy metals plough back into the food chains to cause serious health hazard in man.

6. Conclusion

The study has established that with the exception of Cadmium, heavy metal contamination is at present not significant in parts of Akpabuyo area. Frequent studies of these heavy metals should be carried out in order to ensure that the other metals that are found at harmless levels should remain at that level because the cumulative effect might be dangerous to both human health and ecosystem in the nearest future.

Therefore, in order to forestall the health implications of these heavy metals in the study area, there is need for establishment of proactive State Ministry of Environment, and sensitization of the populace on the needs for the proper disposal of wastes as well as control of the use of artificial fertilizers.

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