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Concentration and speciation patterns of some heavy metals in streams sediments in an urban city in Nigeria

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ABSTRACT

Concentration and distribution patterns of some heavy metals in stream sediments in Ibadan, a typical urban city in Nigeria were investigated. Stream sediments were collected from seven streams at 30 sampling sites within Ibadan metropolis and analysed for their total metal concentrating and speciation. The sediments were totally decomposed with hydrofluoric acid and Aqua regia for total metal concentration and subjected to sequential extraction for their speciation Pb, Zn, Ni, Co, Cd, and Cr were determined in this study using Atomic Absorption Spectrophotometer. The overall mean concentrations (ug/g dry weight of sample) and ranges were Pb(136.95±95.2,15.6-44.40), Zn(102±69, nd-240), Ni 137.0±11.50,4.17-14.20),Co(25.20±7.9,11.50-62.50), Cu(45.90±28.3,6.89-134),Cd(2.57±0.37,1.4-3.8) and Cr 54.20±20.4,14.40-12.70) giving an order of Pb>Zn>Cu>Ni>Co>Cd. The mean concentrations of Pb and Zn were very high especially in areas with high population and traffic densities. Speciation studies revealed largely anthropogenic heavy metal enrichment for Pb, Zn, Cu and Cd and implicated refuse dumping and urban run-off water, transporting metals from land derived wastes as the source of the enrichment of the streams. Ni, Co and Cr were identified as being of geometrical origin. There were no significant difference among Ni, Co, Cd and Cr mean concentrations between the streams, indicating that they may be from the same source. Many of the metals showed significant correlation at P>0.05 levels.

Keywords: Heavy metals, metal concentration and speciations, contamination of stream sediments.

INTRODUCTION

Heavy metals are natural components of the environment. However, its presence is a serious problem as they pollute the soil, water and air (Unurea and Omanwa 2005). In recent times however, the occurrence of metal contaminants especially the heavy metals in excess of natural loads has become a problem of increasing concern. This situation has risen as a result of rapid growth of poplation, urbanization, industrialization as well as lack of environmental regulations (Asiagwu, Okoye, Eboatu 2006).

Water is probably the most common chemical known to man and it is also the only inorganic substance which occurs in all the states of matter on this planet (Frank 1985). The provision of water for domestic and other uses in rural and urban centers is one of the unatractable problems in Nigeria today. (Egboka, Cherry and Farwldon 1982) Due to this inadequate municipal water supply many inhabitants of Ibadan depends on boreholes and other surfaces water sources for their needs.

A wide variety of metals in various forms can be found in water, some concentration occur naturally (background level), their presence being influenced by the soil or rock mineralogy, while others can be introduced through man's activities. (Laws 1985). Many heavy metals such as Fe, Mn, Ni, Zn, Co, Cd and Pb occurs in nature in ore deposits (Ezigbo 1989). These metals are released through leaching and weathering into the aquatic environment. Thus area characterized by metal bearing formation are expected to have elevated levels of metals in water and sediment (Forstner and William 1983). (Frason and Chester 1996).

Water sediments and the biota are generally metal reservoirs in aquatic environment. Metal concentrations in these reservoirs have been determined for a variety of environments. Research works have shown that nearly all the metal contents in aquatic environment reside in water sediment, while the other fractions in biota are small (Bower 1979). The concentrations of harmful and toxic substances are of many orders of magnitude higher in water sediments and biological tissues than in water itself. (Madri and Aston 1983). Therefore the concentrations detected in water sediments may reflect the degree of pollution. (John and John 1986). Sediment analysis is thus an important tool to trace man-induced pollution of water (Bower 1979).

Studies of various environmental media in Ibadan, Nigeria have highlighted the growing hazards of heavy metal- related pollution load (Oninwa 2001, Oninwa and Fakayode 2000, Oninwa and Adoghe (1997, Umurea and Oninwa 2005). This present study aims at further assessing the level of heavy metal loads in streams, sediments, enhanced by human activities and growing population and to identify the other major anthropogenic sources of these heavy metals in the environment.

MATERIAL AND METHODS

Sediments of seven different streams spread across different areas of Ibadan metropolis were collected and investigated for their heavy metal contents and speciation. A total of 30 surface sediment samples were collected from all the seven streams. The number of sampling sites for each varied with the length of the stream as shown in Fig 1.

Sampling was carried out within the period of two weeks. Samples were collected using big plastic grab samples and put in black polythene bag for laboratory work. The samples were air-dried for four days at room temperature and large objects (sticks, stones etc) were removed. The samples were then sieved through 100 mesh screen to obtain a homogenous particle size of about 150mm. While the coarse samples were first crushed in motar before sieving.

2.00g of sieved sediment were oven-dried at 105^0C and 0,500g accurately weighed into a clean and dry Teflon beaker. A mixture of 5ml HF and 5ml aqua regia (1:3 HNO_3, HCLv/v) all (analar grade) were added and the acid-sediment mixtures digested in a water bath at 100^0C for 1 hour. Subsequently a 5ml HF and 5ml aqua regia were made and digested for another 1.5 hours for complete decomposition of the sediments (Okoye, Afolabi, Ajao 1991). After cooling at room temperature, 20ml saturated Boric acid was added to complex with residual hydrofluoric acid, which would otherwise attack glass wares. The digested samples were filtered into 500ml standard flasks using Whatmen No. 1 filter paper, made up to a mark after quantitatively transferring rinsates with deionized water. The filterates were subjected to metal analysis. The concentration of each metal in the sample solutions were measured against those of serially diluted mixed standard solutions of 1000ppm containing each metal with linear concentrations ranges using Buck 200 A model atomic absorption spectrophotometer with an air acetylene flame. Blank digestion was also carried out using a mixture of 10ml HF and 10ml aqua regia put into a Teflon beaker without the sample and heated in a water bath at 100^0c for 3 hours. 0.500g of CANMET stream sediment reference material STSD-2 was similarly disgested for 3 hours for complete decomposition. Boric acid was then added and the solution filtered. The filtrates were subjected to metal content analysis using buck 200A AAs.

For speciation studies, samples were prepared using the method adapted by (Tessier, Campbell and Buson 1979). 1.00g of sieved sediments samples were used for sequential extraction processes. A total of seven samples representing the seven streams were investigated. Between each successive extraction, separations were made by centrifuging at 10,000ppm for 30 minutes. The supernatants were filtered through Whatman No.1 filter paper into 25ml flask made up to the make with deionized water for analysis. Whereas, the residues were washed with 8.0ml of deionised water, after centrifugation for 30 minutes. Blanks for successive steps were also prepared. The residues were filtered into a 50ml standard flask and made up with deionized water after digestion. All the supernatant solutions and residual sample solution as well as the blanks were analyzed for their metal contents, using a Buck 200A model AAS.

RESULTS AND DISCUSSION

Mean and ranges of metal concentration of seven stream sediment drawn from 30 sampling sites in Ibadan metropolis is contained in Table 1. The total sites metal concentrations of the different sampling varied considerably with population and traffic densities which reflects the different levels of human activities in the study area.

As indicated in Fig 1 and Table I Aladoin (1), Oke-Ado, Pugbe, Alawo, Bede market, Popoyemoja and Alalubose streams (sampling sites) which are located and flows across an area of very high population and traffic densities characterized by refuse dumps in the streams and other human activities such as mechanic and welding workshops etc, show very high concentration values for Pb, Zn, Cr and Cu. Same trend was observed for other areas of relatively high population and traffic densities such as Agric (1), Osuoyemi Groangba , Mifutau, Lanihan, Babania, Koro, Agbongbon, Idiarer, Yejide, Kudeti and Aladoin (1) in which concentration values for Pb, Zn, Cr and Cu also relatively high (Umrea and Onionwa 2005).

It is pertinent to note that there was also high levels of Ni and Cr in Aleshinloyen (1) Bode market, Aladonin (II) Popoyemoja, Kono and

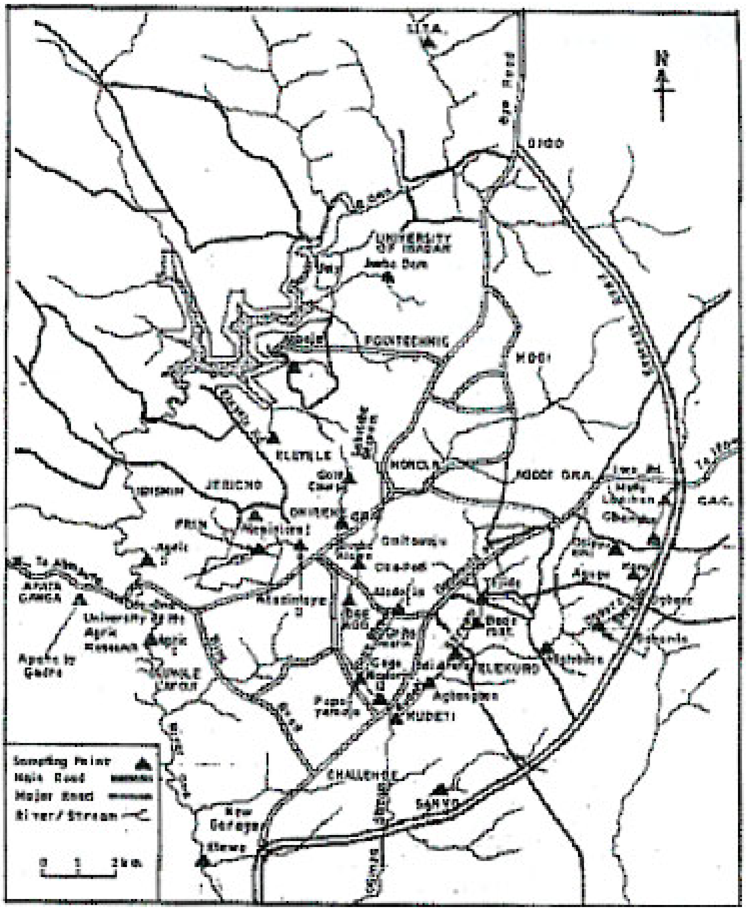

Fig. 1: Map of Ibadan Metropolis showing Areas and Sampling Points of Rivers/Streams

Alalubosa generally at low levels at many of the sampling sites except at Aladorin (1), where relatively high metal loads were obtained. Some other area like Golf course and GRA characterized by low population and traffic densities and in which the stream Onireke 0 Labelebe runs across have very low concentrations of all the metals determined (Nriagu 1990, Onionwa 2001).

The zonal distribution of metal is shown in Table 2. Pb, Zn, Cd and Cu have highest concentrations in the non-residual fraction suggesting that their enrichment in the environment was likely to be from anthropogenic activities. Lead level were much higher in the non-residual fractions than in the residual fraction, suggesting very strongly anthropogenic input as the major source to the environment. The major source of Lead to the aquatic eco-system could be from automobile exhausts (Gibbs 1973). Zinc has its highest concentration in the non-residual fractions, attributed to zine something and mining operations going on in the metropolis. Others source could be from the nature of zinc roofing sheets, and dumping activities of zinc-coated materials in the aquatic ecosystem. Ni and Co levels in the sediments samples were from natural source (geochemical reactions). Same trend was also observed for Cr. About 80% of sediment samples of Ni, Co and Cr were found in their residual fractions confirming that mining and smelting operations for these metals, including industries that uses these metal were not within the metropolis. Similarly, Cu and Cd present no definite pattern as to whether their sources to the aquatic ecosystem was from anthropogenic activities or geochemical reactions.

The findings were further subjected to analysis of variance (ANOVA) (Table 2) to known whether the metals in the groups of streams were from common source and the type of association between each metals using Pearson multiple correlation (Table 4).

There was no significant difference between the streams for Ni, Co, Cd and Cr, suggesting their presence in the stream sediment to be from a common source, likely from nature. There was however significant difference that exists for Pb, Cu and Zn, between the stream sediments,

Table 1: Mean Concentrations (ug/g. dry weight) Standard Deviation (SD), Range of Total Heavy Metals Conents in Stream sediments in Ibadan city

Stream	Pb		Zn		Ni		Co		Cu		Cd		Cr	
	Mean ± SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range
Odo-Ona	121±140	21.9-434	661±60.1	nd-200	37.2±17.7	18.8-64.6	38.5±11.7	17.7-55.0	27.2±24.2	13.3±87.8	2.8±0.7	2.0-3.8	45.0±35.4	14.8-12.6
Ogbere	92.5±27.7	46.9-121.9	85.4±25.3	42.0-106.2	43.7±16.5	27.1-66.9	46.2±12.2	31.3-62.5	40.8±21.3	25.0-76.0	2.9±0.6	2.20-3.80	74.3±60.0	37.5-17.7
Ogunpa	309±166	46.9±444	160.9±88.8	7.74-227	33.3±20.8	12.5-58.3	38.1±12.2	28.1-55.2	84.5±49.3	10.56-134	2.5±0.7	1.40-3.40	66.0±40.8	16.4-127
Alalugbosa	49.0±17.8	34.4-68.8	359±39.2	Nd-777	58.4±72.5	12.5-142	21.9±9.5	11.5-30.2	24.1±5.1	20.6-30.0	2.5±0.5	2.0-3.0	43.8±42.7	17.2-93.0
Kudeti	165.0±28.8	125-188	180.0±48.9	122-240	31.2±10.9	22.9-45.8	38.0±4.6	34.3-43.8	61.8±5.5	56.7-69.4	2.8±0.5	2.20-3.40	54.5±9.6	46.9-68.0
Gege	184.0±35.4	159-209	172.5±67.2	125-220	33.3±41.2	4.17-62.5	35.4±4.6	20.8-50.0	78.2±56.4	38.3118.0	2.7±1.6	1.60-3.80	72.6±62.9	28.1-117
Onirekere labelabe	28.1±17.8	15.6-40.6	9.96±14.07	nd-19.9	18,8-25.0	18.8-25.0	28.2±13.2	18.8-37.5	11.4±3.5	8.89-13.9	1.8±0.6	1.40-2.20	16.5±3.3	14.1-18.8
Total	135.5±95.2	15.6-444	102±69	Nd-240	37.0±11.5	4.17-142	35.2±7.9	11.5-52.5	46.9±28.3	8.89-134	2.57±0.37	1.40-3.8	54.2±20.4	14.1-127

nd-not detected

Table 2: concentrations of Heavy metals species in streams, sediments of Ibadan metropolis expressed by µg/g dry weight of sample

Stream/site	Pb	Zn	Ni	Co	Cu	Cd	cr
Odo-Ona (Alalubosa)	**Nd**	**Nd**	**Nd**	**0.2.0±0.001**	**Nd**	**Nd**	**0.272+0.001**
Fraction 1 Exchangeable							
2. Bound of Carbonate	46.1±0.1	76.0±0.2	1.563±0.003	2.000+0.004	11.50±0.02	0.2083±0.0004	0.391+0.001
3. bound of Fe Mn Oxides	49.2_0.1	60.8+0.1	3.44+0.01	2.000+0.004	1.125+0.002	8.06+0.02	nd
4. bound of organic matter	1.95.3+0.4	28.0+0.1	0.625+0.001	nd	46.4+0.1	Nd	7.61+0.02
5. residual	65.6+0.1	64.8+0.1	35.0+0.1	32.0+0.1	17.00+0.03	319+0.001	94.8+0.2
2	6. 356.2+0.6	229.6+0.5	40.63+0.11	36.25+0.12	76.03+015	11.46+0.03	102.9+0.2
Alalubosa (Aleshinloye I)	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**0.543+0.001**
Fraction 1 Exchangeable							
2. Bound of Carbonate	10.16+0.02	40.4+0.1	Nd	0.500+0.001	1.125+0.002	Nd	0.391+0.001
3. bound of Fe Mn Oxides	13.28+0.03	44.1+0.4	2.50+0.001	3.25+0.04	Nd	Nd	Nd
4. bound of organic matter	11.72+0.02	Nd	Nd	Nd	2.125+0.004	Nd	Nd
5, residual	20.31+0.04	25.0+03	21.88+-.04	21.00+0.04	11.00+0.02	1.805+0.004	34.8+0.1
2 55.47+0.21	109.5+0.3	24.38+0.05	24.75+0.05	14.25+0.03	3.96+0.04	35.7+0.4	
Gege (Aladorin I)	**Nd**	**Nd**	**0.313+0.001**	**0.500+0.00**	**Nd**	**Nd**	**0.815+0.002**
Fraction 1 Exchangeable							
2. Bound of Carbonate	9.38+0.02	64.7+0.1	1.563+0.003	1.250+0.003	4.00+0.04	Nd	0.1943+0.0004
3. bound of Fe Mn Oxides	11.72+0.02	45.0+0.1	1.563+0.003	2.75+0.01	Nd	0.347+0.001	Nd
4. bound of organic matter	31.3+0.1	69/0+0.3	21.88+0.04	20.50+0.04	15.25+0.03	3.06+0.01	33.2+0.4
5. residual	136.0+0.3	195.50+0.33	25.63+0.05	25.00+0.05	39.25+0.08	3.62+0.01	38.8+0.1
Ogunpa (Dugbe Alawo)	**Nd**	**Nd**	**1.250+0.003**	**0.750+0.002**	**0.1250+0.0003**	**Nd**	**0.543+0.001**
Fraction 1 Exchangeable							
2. Bound of Carbonate	10.94+0.02	82.6+0.2	3.44+0.01	3.00+0.01	19.00+0.04	0.347+0.001	nd
3. bound of Fe Mn Oxides	14.84+0.03	70.9+0.1	3.75+0.01	3.00+0.04	2.38+0.01	1.250+0.003	Nd
4. bound of organic matter	53.1+0.1	18.20+0.04	Nd	Nd	28.8+0.1	Nd	1.067+0.002
5. residual	82.5+0.1	119.6+0.2	18.13+0.04	14.00+0.03	23.3+0.1	0.556+0.004	65.8+01
2 141.38+0.25	291+0.5	26.57+0.06	20.75+0.95	73.61+0.25	2.15+0.04	67.4+0.4	
Kudeti (Idiarere)	**Nd**	**Nd**	**Nd**	**0.250+0.001**	**Nd**	**0.556+0.001**	**Nd**
Fraction 1 Exchangeable							
2. Bound of Carbonate	2.34+0.01	70.4+8.1	2.188+0.004	2.25+0.01	4.00+0.01	0.278+0.001	nd
3 bound of Fe Mn Oxides	5.47+0.01	60.0+0.1	7.50+0.02	4.00+0.01	0.750+0.002	Nd	1.367+0.003
4. bound of organic matter	84.40.2	35.9+0.1	0.936+0.002	1.750+0.004	32.5+0.1	Nd	5.16+0.01
5. residual	43.8+0.1	62.9+0.1	16.88+0.03	13.50_0.03	19.25+0.04	0.972+0.002	31.5+0.1
2 136.01+0.32	229+0.4	27.51+0.06	21.75+0.00	56.50+0.35	1.806+0.004	38.2+03	
Ogbere (Mufutau Lanihun)	**Nd**	**Nd**	**Nd**	**0.500+0.001**	**Nd**	**Nd**	**0.543+0.001**
Fraction 1 Exchangeable							
2. Bound of Carbonate	11.74+0.02	22.29+0.004	0.625+0.001	0.250+0.001	1.750+0.004	Nd	0.1953+0.0004
6. bound of Fe Mn Oxides	25.0+0.1	17.59+0.04	1.250+0.003	1.000+0.002	0.250+0.001	0.694+0.001	Nd
7. bound of organic matter	32.8+0.1	11.62+0.2	0.938+0.002	Nd	11.25+0.02	Nd	5.16+0.01
8. residual	14.06+0.03	11.39+0.02	3.75+0.01	3.50+0.01	6.25+0.01	Nd	8.70+0.02
2 83.00+0.25	62.9+0.3	6.56+0.02	5.25+0.01	19.50+0.04	0.694+0.001	14.60+0.03	
Onilekere Labelabe**(onireke Gulf course)**	**Nd**	**Nd**	**Nd**	**0.750+0.002**	**Nd**	**Nd**	**0.543+0.001**
Fraction 1 Exchangeable							
2. Bound of Carbonate	Nd	11.56+0.02	0.625+0.001	0.750+0.002	0.375+0.001	Nd	Nd
3. bound of Fe Mn Oxides	4.68+0.02	9.68+0.02	1.250+0.003	0.500+0.001	nd	9,556+0.001	Nd
4. bound of organic matter	7.03+0.01	0.1106+0.002	Nd	Nd	5.75+0.01	Nd	5.43+0.004
5. residual	14.06+0.03	22.6+0.1	18.13+0.04	14.50+0.03	5.00+0.01	1.111+0.002	13.60+0.03
2 25.78+0.05	**43.95+0.14**	**20.00+0.04**	**16.50+0.04**	**11.13+2.02**	**1.667+0.002**	**19.57+0.64**	

nd=non-detectable

Table 3: ANOVA Table for 7 Heavy Metals from 30 sampling sites in 7 streams

Source of variation	Sum of Squares	Degree of Freedom	Mean Square	Fe_{23}calc	Fe23 Critical	Comment
Lead:”						
between Streams	212949.8	6	35491.635	2.97	2.53	Significant difference exists
“within samples”	274825.3	23	11948.926			
Total	487775.1	29				
Zinc”						
Between streams”	94630.504	6	15771.751	4.654	2.53	Significant difference exists
Within samples	77943.469	23	3388.846			
Nickel						
“Between streams”	2271.710	6	378.618	0.487	2.73	Significant difference exists
“Within samples”	17895.301	23	778.057			
Total	20167.011	29				
Cobalt:						
“Between streams”	1303.811	6	217.302	1.60	2.53	No significant difference exists
“within samples	3122.511	23	135.761			
Total	4426.322	29				
Copper”						
Between streams”	17629.133	6	2938.189	3.46	2.53	No Significant difference exists
“within samples”	19531.528	23	849.197			
Total	37160.661	29				
Cadmium :						
Between streams”	2.275	6	0.379	0.774	2.53	No Significant difference exists
“within samples”	11.260	23	0.490			
Total	13.535	29				
Chromium						
“Between streams”	7328.785	6	1221.464	0.722	2.53	No Significant difference exists
“within samples”	38901.085	23	1691.352			
Total	46229870	29				

signifying their presence in the environment were not from a common source of anthropogenic activities, thus confirming the findings in table 1 - 2. There was also significant correlation between most of the metals at 0.01 level and a few at 0.05 level.

The result showed significant correlation between most of the metals at 0.01 level and a few at 0.05 level.

Table 4: Multiple correlation of metal matrix

	Cd	**Cr**	**Co**	**Cu**	**Pb**	**Ni**	**Zn**
Cd	1.00	-	-	-	-	-	-
Cr	0.619**	1.00	-	-	-	-	-
Co	0.629**	0.639**	1.00	-	-	-	-
Cu	0.458*	0.637**	0.452	1.00	-	-	-
Pb	0.266	0.480**	0.321	0.773*	1.00	-	-
Ni	0.395*	0.657**	0.253	0.276	0.137	1.00	-
Zn	0.326	0.472**	0.336	0.841**	0.697**	0.117	1.00

** Correlation is significant at the 0.01 level
* correlation is significant at the 0.05 level

Conclusion

The average concentrations of Cr, Cd, Cu, Co and Ni in the stream sediment were within natural levels. Their major sources to the ecosystem studies are essentially of natural origin. Pb, Zn concentration were observed to be much higher than stated natural levels showing that their input to the environment (aquatic) were by anthropogenic activities. Generally, the ecosystem studied can be said to be not polluted with heavy metals except Pb and Zn, but are grossly polluted with human wastes and refuse dumps that contain mainly organic matters.

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