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Assessing the Speciation Pattern of Lead and Zinc in Surface Water Collected from Abegede Creek, Ijora and Lagos

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A two-stage sequential extraction procedure for the speciation of zinc and lead has been applied to surface water randomly collected from three sites in Abegede Creek, Ijora and Lagos. The determination of the labile and non-labile metals species was carried out by flame atomic absorption spectrophotometry (FAAS). The mean values of non-labile zinc and lead concentrations from the three sites, A, B and C are 0.54 ± 0.25 mg/l; 0.55 ± 0.26 mg/l; 1.13 + 0.76 mg/l, respectively for zinc and 0.13 ± 0.09; mg/l, 0.17 ± 0.07 mg/l; 0.42 ± 0.23 mg/l respectively for lead. These are higher than for the labile species in the three sites; 0.14 ± 0.07 mg/l; 0.21± 0.22 mg/l; 0.73 ± 0.82 mg/l, respectively for zinc and ND; 0.02 ± 0.04 mg/l; 0.16 ± 0.22 mg/l, respectively for lead. The statistical analysis of variance of the distribution of zinc and lead in the three sites were estimated at 95% confidence level. The values of metals obtained were compared with Nigeria's background values for some rivers and the World Health Organization limits for drinking water respectively and found to be generally higher especially for lead levels. The probable sources of zinc and lead in the Creek are from natural and point sources, although there could be non-point source contributions from urban run-offs and vehicular exhaust.

Key words: Speciation, Heavy metals, Labile, Non-labile, Flame atomic absorption spectrophotometry.

Introduction

In natural aquatic ecosystems, metals occur in low concentrations, however, the occurrence of heavy metals in excess of natural loads is of concern (Botkin and Keller 1997; Fatoki and Awofolu 2003; James and Okolo 2003). This situation has arisen as a result of increasing urbanization and industrialization, and laxity in enforcing environmental regulations especially in most developing economies (UNEP 1986; Biney *et al* 1994; Appleton *et al* 2001; Yusuf 2003).

The accumulation of metals in an aquatic environment has direct consequences on man and the ecosystem (Fergusson 1990; Holm *et al* 1995; Vincent *et al* 2001; Almeida *et al* 2001).

The bio-availability of water-bound metals is of importance from an ecotoxicological viewpoint (Deverey *et al* 1993; Botkin and Keller 1997; Calace *et al* 2000).

Legislation governing the maximum permissible levels of a polluting metal in an environmental medium such as water refers to total concentration rather than the chemical form of that metal (Ure and Davidson 1995). Most of the previous works have been limited to the determination of total concentration of the metals only. However, the determination of total concentration of the metals does not give adequate information about the bio-availability of potentially toxic metals. Fractionation (operationally defined as speciation) is now acknowledged to be a necessary tool to acquire this information (Pardor *et al* 1989; Deverey *et al* 1993; Calace *et al* 2000, He *et al* 2000, Tokalioglu *et al* 2000; Tokalioglu *et al* 2003).

The objective of this study was to determine the concentration of the labile and non-labile forms of lead and zinc in the water samples collected from the Abegede Creek, Ijora and Lagos. This is with a view to ascertain the potential bio-availability of these metals. The Creek is an important natural fresh reservoir for fishing and other recreational activities. It is adjoined upstream by some major refined petroleum oil marketing companies which discharges waste-waters into the Creek.

Materials and Methods

Water samples were collected randomly from the Abegede Creek between the months of October and November, 2001 from three different sites A, B and C indicated in Fig 1.

A – Beside Lagos State Water Corporation Headquarters, Ijora.
B – National Arts Theatre, Water Front, Iganmu.
C – A pool of water adjacent to the National Arts Theatre Iganmu Water Front off the main course of Abegede Creek.

From the samples 100 ml aliquot were acidified with 5 ml 0.01 M HNO_3 for preservation and stored in polyethylene bottles in a refrigerator before analysis (Holm *et al* 1995; APHA 1998)

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Nature of sites. An auto-mechanic workshop is located around site A, there is also a road adjoining the site, which carries a high volume of pedestrian and vehicular traffic. There is a continual discharge of effluent of petroleum products (petrol, diesel and lubricating oil) into the Creek particularly by the petroleum marketing companies. Virtually all the major petroleum marketing companies - African Petroleum, National Oil, Total and Mobil have their oil installations and storage tanks adjacent to site A. Traces of human waste (defecation) are also found in the site A. For site B, there is heavy vehicular traffic on the bridge (Eko Bridge) transversing this site. School children and others use site C as a swimming pool. There is also a road from Orile Iganmu transversing this site. This pool of water has the best aesthetic value compared to sites A and B.

Reagents. High purity chemicals and reagents (purchased from Merck and Aldrich Chemical Company), together with distilled-deionised water were used. Standards were prepared from analytical grade chemicals (Merck). Standard stock solutions were prepared from nitrate salts of Pb and Zn in 1% of HNO_3 in calibrated flasks. Diluted standard solutions were prepared from the stock standard solutions.

Resin preparation. Amberlite CG 120 cation exchange resin (100-200 mesh) sodium form was converted to the calcium form as reported earlier (Holm *et al* 1995). Sodium form resin 27.5 g was weighed and transferred into a glass column, rinsed several times with deionised-distilled water and shaken mechanically. The fine particles were decanted and the resin soaked in 1 M HNO_3 for 8 h in the glass column to remove traces of trace metals impurities. This was followed by the sequential addition of 1 M calcium acetate, 0.01 M calcium acetate and 0.01 M calcium nitrate respectively, followed by the addition of deionised/diluted water until effluent and influent pH were identical. The resin was then dried at 45°C in a Gallenhamp Oven model 300, for 3 days.

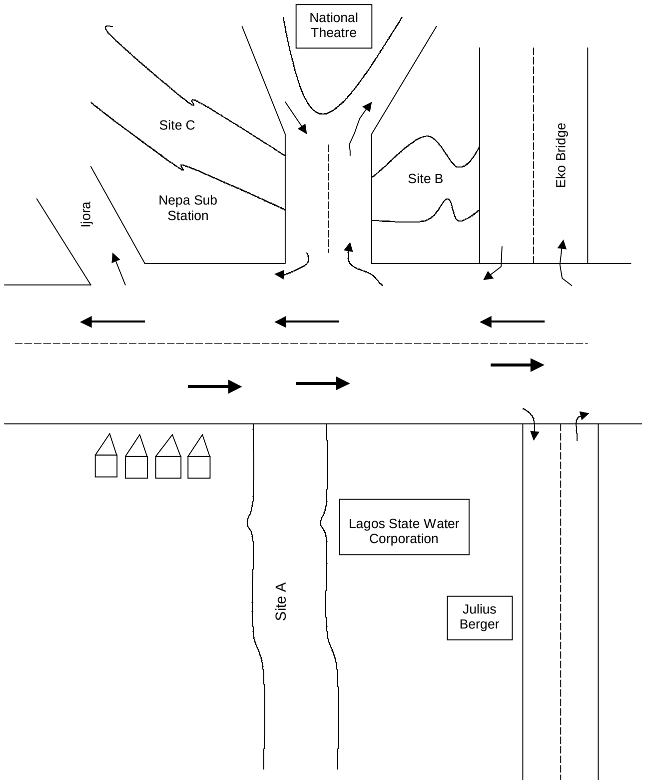


Fig 1. Sketch map of the sample sites.

Speciation procedure. A 25 ml aliquot of sample solution was added to about 400 mg of modified Amberlite resin in a bottle and shaken for 24 h in a mechanical shaker. The solution and resin were then separated by filtering under gravity. The resultant filterates were analysed for labile zinc and lead species using flame atomic absorption spectroscopy (FAAS). To the same resin was added 30 ml of 2 M HNO_3. The content was shaken vigorously for 5 min and immersed in a water bath (100°C) with intermittent mechanical shaking for 2 h (Fig 2). The resultant filterates were then analysed for non-labile zinc and lead fractions using FAAS. The total metal was estimated by the addition of the individual labile and non-labile metal species as indicated by Calace *et al* (2000).

Instrumentation. The metals were determined with the use of a Perkin Elmer Oak Brown model 2380, Atomic Absorption Spectrophotometer. An atomizer with air/acetylene burner was used for determining zinc and lead. All instrumental settings were those recommended in manufacturer's manual. The instrument was calibrated with analytical grade metal standard stock solution in replicate. The wavelengths (Pb, 283.3 nm; Zn, 213.0 nm) used for the determinations and other working parameters are listed in Table 1.

Statistical analysis. Analysis of variance was used to estimate statistically significant differences at 95% confidence level (Sokal and Rohlf 1995).

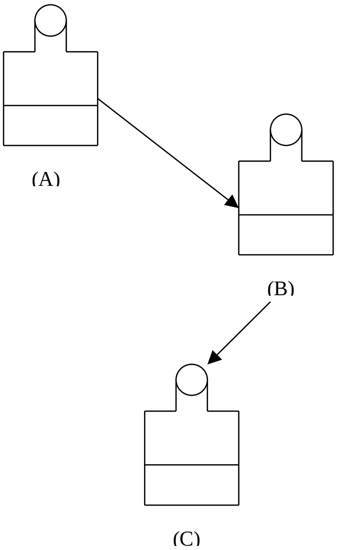
Table 1

Working parameters for the metal determination by FAAS

Element	Wavelength (nm)	Lamp current (mA)	Detection limit (ppm)	Calibration range (ppm)
Lead	283.30	1.50 - 4.00	0.05	0 - 2.00
Zinc	213.00	5.00 - 15.00	0.002	0 - 10.0

Results and Discussion

The detection limits of zinc and lead investigated and other working parameters for the FAAS are listed in Table 1. The mean concentration of the labile and non-labile zinc and lead have been determined. The results are presented in Table 2. As indicated, the mean values of the labile zinc concentration from the three sampled sites are 0.14 ± 0.07 mg/l, 0.21 ± 0.22 mg/l, and 0.73 ± 0.82 mg/l, respectively. Similarly, that of lead are ND, 0.02 ± 0.04 mg/l and 0.16 ± 0.22 mg/l respectively, for sites A, B and C. A similar trend has been observed before (Pardor *et al* 1989) in the speciation patterns of Valladolid waters. It should be noted however that some of the mean values are lower than the standard deviation. This is not uncommon for water sampled randomly over a period of time from surface and ground waters (Adeniyi and Huthman 2002; Fatoki and Awofolu 2003; James and Okolo 2003; Yusuf 2003).



(A) Stock water sample; (B) Labile (25 ml of water sample + 400 mg Amberlite resin, Stirred for 24 h); (C) Non-labile (25 ml of water sample + 2 M HNO_3 and 400 mg Amberlite resin on water bath for 2 h)

Fig 2. Experimental procedure for determination of lead and zinc in the water samples.

The non-labile zinc concentrations for the three sites are 0.54 ± 0.25 mg/l, 0.55 ± 0.26 mg/l and 1.13 ± 0.76 mg/l, respectively (Table 2 and Fig 3) Similar to labile species, non-labile levels of lead are 0.13 ± 0.09 mg/l, 0.17 ± 0.07 mg/l and 0.42 ± 0.23 mg/l, respectively for sites A, B and C (Table 2 and Fig 4). This is in agreement with earlier studies (Holm *et al* 1995). Lead has been found to occur in relatively smaller concentration than zinc in most natural water source (Pardor *et al* 1989; Garg *et al* 1992; Mathuthu *et al* 1993; Vazquez *et al* 1993; Biney *et al* 1994 ; Appleton *et al* 2001; James and Okolo 2003). This may not be unconnected with the fact that anthropogenic activities generating lead are now less widespread because of environmental pressure groups and increasing awareness of the deleterious effect of lead (Rain 1995; Botkin and Keller 1997; Tokalioglu *et al* 2000). Non-labile species are not expected to be bio-available (He *et al* 2000; Calace *et al* 2002). However, changes in certain physico-chemical conditions in the river system could result in the conversion of non-labile to labile species of metals and vice-versa (Ure and Davidson 1995; Tokalioglu *et al* 2000).

The statistical analysis of variance of the distribution of labile zinc and lead were not statistically significant at 95% confidence level. Similarly, the non-labile zinc was not significant whereas, the non-labile lead distribution was significant at 95% confidence level (Table 3).

The range of total concentrations found in the water samples are: 0.68 - 1.86 mg/l, Zn; 0.13 - 0.58 mg/l, lead. This showed that the heavy metals were present in considerable amounts in the Creek's water. Whereas, the total zinc level is lower than the World Health Organisation (WHO) (1996) limits of 0.5 mg/l for

Table 2

Levels of zinc and lead (mg/l) in fresh water samples from the Abegede Creek

Sampling sites	Metal	Labile species	Non-labile species	Total value	NBV (mg/l)	WHO (mg/l)
A	Zn	0.14±0.07	0.54±0.25	0.68±0.28	0.02 - 0.76	5.00
	Pb	ND	0.13±0.09	0.13±0.09	0.01 - 0.02	0.05
B	Zn	0.21±0.22	0.55±0.26	0.76±0.45	0.02 - 0.76	5.00
	Pb	0.02±0.04	0.17±0.07	0.19±0.06	0.01 - 0.02	0.05
C	Zn	0.73±0.82	1.13±0.76	1.86±0.97	0.02 - 0.76	5.00
	Pb	0.16±0.22	0.42±0.23	0.58±0.22	0.01 - 0.76	0.05

ND, Not detected; NBV, Nigeria's background values for some rivers; WHO, World Health Organisation limits for drinking water; Site A, Beside lagos state water corporation, Ijora; Site B, National arts theatre water front, Iganmu; Site C, Adjacent to the national arts theatre Iganmu water front off the main course of Abegede Creek.

Table 3

Statistical analysis of variance of the distribution of the labile, non- labile and total zinc and lead in the different sites

Nature of metals	$F_{cal.}$, 0.05	$F_{tab.}$, 0.05
Labile	1.23 (1.87)	3.68
Non-labile	2.44 (6.60*)	3.68
Total	3.82* (11.78*)	3.68

Values in parentheses are for lead, the rest are for zinc. *Significant difference at 95% confidence level.

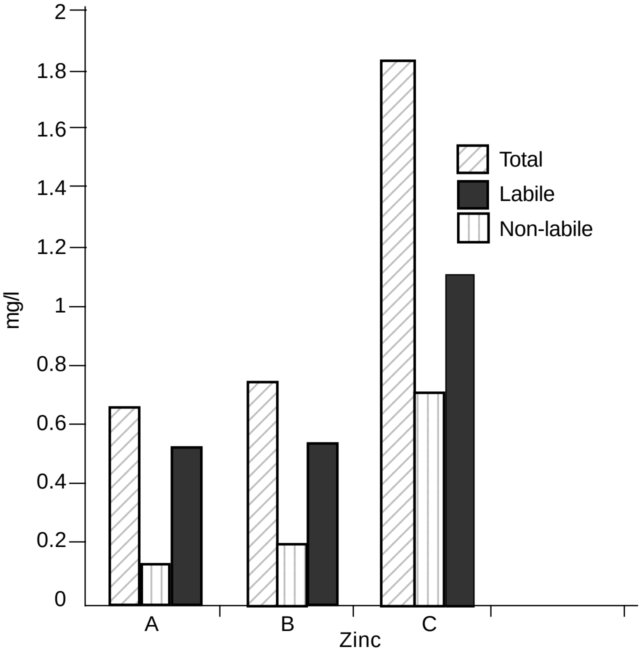


Fig 3. Concentration of zinc in three different sites A, B and C.

drinking water, it is higher than the Nigeria's background values of 0.02 -0.76 mg/l for some rivers. Zinc has low toxicity to man, but relatively high toxicity to fish (Fatoki and Awofolu 2003). In view of the fact that fishing is commonly practiced in this Creek, the levels of zinc is of great concern. Nevertheless, total lead in the water samples are generally higher than the Nigeria's background values (0.01- 0.02 mg/l) and the WHO limits for drinking water (0.5 mg/l). Undoubtedly, these relatively high values of lead are the result of acute pollution (Biney *et al* 1994; James and Okolo 2003; Yusuf 2003). This is equally of concern because of the many health problems associated with lead accumulation in the biological tissues (Needlemann *et al* 1990; Martinez-Tabche *et al* 1997; Tchernitchim *et al* 1998).

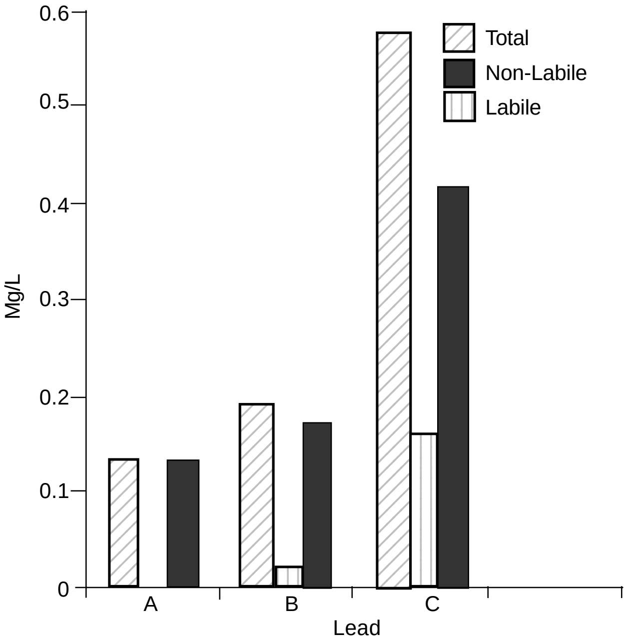


Fig 4. Concentration of lead in three different sites A, B and C.

The impact of oil marketing companies in the vicinity of the Abegede Creek cannot be overlooked as heavy metals are known to be associated with petroleum products and their effluents (Onianwa 1995; Martinez-Tabche *et al* 1997; Adeniyi and Oyedeji 2001; Adeniyi and Afolabi 2002; James and Okolo 2003). With continued activities of the oil marketing companies, heavy vehicular traffic around the Creek and urban runoffs, (Arienzo *et al* 2001; Hashmi and Khani 2003) it is expected that heavy metals contamination may become wide spread in the Creek in the coming years. There is the need to evolve a sustainable environmental remediation programme to arrest the level of contamination in the Abegede Creek.

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