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LEVELS OF SOME HEAVY METALS IN SOKOTO-RIMA RIVER SYSTEM IN NORTH-WESTERN NIGERIA

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ABSTRACT

Levels of some heavy metals in Sokoto- Rima River system at the fishing site of Argungu International Fishing and Cultural Festival were analyzed. Water samples were collected monthly for 12 months and analyzed for the heavy metals. Statistical analyses of the data were based on months, wet and dry seasons and five sub-seasons (early rainy, flood, early dry, mid dry and late dry sub-seasons). Pb (2.50 ±0.78 Mg/L), Cr (0.22 ± 0.03 Mg/L), Cd (0.41 ±0.21Mg/L) and Mn (1.48 ± 0.27 Mg/L) ions were higher than the recommended water quality standards while Zn ion was within recommended standard for aquatic life. There was no seasonal influence on the concentrations of Cr, Zn and Mn ions. The level of Fe, Pb, Cr, Cd and Mn ions should therefore be corrected to recommended standards for aquatic life.

Keywords: Heavy metals; Sokoto- Rima River system

INTRODUCTION

Over the last few decades, fresh water contamination with the pollutants has been a matter of concern (Lenand *et al*., 1998). River and surface waters may be contaminated with the heavy metals. The awareness of the potential hazards due to the contamination of water bodies by toxic heavy metals release from natural and anthropogenic sources is on the high site.On the aquatic environment and the diversity of organisms therein, contamination with the heavy metals causes deleterious effects (Sreedevi *et al.*, 1992).

Depending on the concentration, heavy metals may have useful or harmful effects on life (Forstner and Wittmann, 1981). Trace heavy metals are ubiquitous, readily dissolved and are transported by water and can be taken up by aquatic organisms due to bioaccumulation and biomagnifications in the food chain (Erhabor*et al*., 2010). Lead (Pb) and Cadmium (Cd) being non-essential for biological system, are the most toxic and continuous exposure of aquatic organisms to their low concentration may result to bioaccumulation and subsequent transfer to man through food web (Heath, 1991).

The major sources of heavy metals in the water bodies include domestic, agricultural and industrial activities (Lioyd, 1992). The author noted that the concentrations of heavy metals vary from one water body to another due to different levels of agricultural and industrial activities close to these water bodies. The quality of natural water bodies may be affected by metals pollution resulting from socio-economic activities (Manson, 1992).

Several works evaluated heavy metals compositions of natural water bodies in different socio-ecological zones of Nigeria. These include those of the rivers of Zamfara State Reserve in Zamfara (Ipinjolu and Argungu, 1998), Kainji Lake (Mbagwu, 2000), Areba River in Olomoro, Niger Delta (Idodo-Umeh and Oronsaye, 2004), Kware Lake (Onaji *et al.*, 2005) and River Jama'are (Akinola and Madara, 2009). However, heavy metals in Sokoto-Rima River at the Fishing site for Argungu International Fishing and Cultural Festival being a major source of water for domestic uses, livestock watering, irrigation and fishing activities to the communities living around it is still not documented. It is in the contest of the foregoing that this study which assessed the levels of some heavy metals in this important river system in order to provide base line information for monitoring and control water quality was designed.

MATERIALS AND METHODS

Study Area

The study site along Sokoto-Rima River system was at Argungu within the fishing area for theArgungu International Fishing and Cultural Festival (AIFCF) in Kebbi State in North -Western Nigeria .The area is situated in Sudan Savanna Zone, on longitude 4^0 31^1 36^{11} E and latitude 12^0 45^1 26^{11} N. Five sampling points denoted as A, B, C, D and E were used. Sampling points B, C and D were in the main water area of AIFCF known in the local area as *matanfada,* while A and E were 500m each upstream and downstream the fishing area before and after the field area respectively.

Water Sampling

A total of 15 one litre capacity plastic containers were used, three containers for replicate samples at each point. Water samples were collected monthly for 12 months.The samples collected were analyzed in the Physical Laboratory of the Faculty of Agriculture, Usmanu Danfodiyo University, Sokoto, Nigeria for heavy metals compositions.

Chemical Analysis

The concentration of heavy metals was determined using the procedure in AOAC (1990) as follows**.**

Lead (Pb) ion

10ml of water sample in cuvette, 1ml each of ammonium citrate, sodium hexametaphosphate and ammonia solutions were added. This was Cooled and added 1ml each of 10% potassium cyanide (KCN) and hydroxylamine hydrochloride. This was followed by addition of 0.5ml of dithizone working solution and shaked for one minute. Absorbance was measured at 520nm with LF.2000 Photometer.

$$Pb(mg/L) = \frac{Absorbance}{Aliquot\ (ml)} \qquad \text{(AOAC, 1990)}$$

Chromium (Cr) ion

10ml of water sample contained in cuvette was added into 0.2ml diphenylcarbazide reagent and 1ml of 5% sodium carbonate (Na_2CO_3). Absorbance at 370nm was measured using LF 2000 Photometre.

$$Cr(mg/L) = \frac{Absorbance}{Aliquot\ (ml)} \times 10 \qquad \text{(AOAC, 1990)}$$

Copper (Cu) ion

5ml of water sample was prepared and put in the cuvette, to this 2ml of 1% ammonium pyrolidinedithiocarbonate was added mixed and left for 2 minutes. 4ml of methyl pentane – 2 –1 was equally added and mixed properly. This was followed by shaking for 1 minute and allowed separation. With aid of LF 2000 Photometre at wavelength of 247nm, separated portion was read and the reading was obtained. From this, Cu was calculated by applying the relation:

$$Cu(mg/L) = \frac{Absorbance}{Aliquot\ (ml)} \times 1000 \qquad \text{(AOAC, 1990)}$$

Cadmium (Cd) ion

5ml of water sample was pipetted into cuvette, this was followed by addition of 0.1g of potassium hydrogensulphate, 0.2ml of hydroxylammoniumchloride and acidifying slightly with hydrochloric acid. Absorbance using LF 2000 Photometre at 229nm were measured.

$$Cd(mg/L) = \frac{Absorbance}{Aliquot\ (ml)} \qquad \text{(AOAC, 1990)}$$

Zinc (Zn) ion

5ml of water sample contained in a cuvette, 0.1ml of citric acid (0.5M) and 0.1ml ammonium hydroxide were mixed properly and added. This was followed by addition of 0.1ml each of HNO_3 and perchloric acid (60%).Using LF 2000 at 214 nm, reading was obtained and used in determining Zn as follows:

$$Zn(mg/L) = \frac{Absorbance}{Aliquot\ (ml)} \times 1000 \qquad \text{(AOAC, 1990)}$$

Manganese (Mn) ion

5ml of the sample was pipetted into the cuvette. To this, 1ml each of formaldoxine and $HClO_4$was mixed and added followed by rapid addition of 0.1ml of sodium hydroxide (NaOH) and cooling. Using LF 2000 Photometre at wavelength of 450nm a reading was obtained and was used in determining Mn as follows:

$$Mn\left(mg/L\right)=\frac{Absorbance}{Aliquot\ \left(ml\right)}\times 1000 \qquad \text{(AOAC, 1990)}$$

Statistical Analysis

The analyses were on monthly bases, two seasons and five sub-seasons namely early rainy (June and July), flood (August and September), early dry (October, November and December), mid-dry (January and February) and late dry (March, April and May) sub-seasons. Data generated were analyzed following analysis of variance (ANOVA) (Steel and Torrie,1980). The computer analysis was carried out using Statistical Package for Social Science (SPSS) software version 19. Mean separation was carried out following New Duncan Multiple Range Test and graphical presentations made.

RESULTS AND DISCUSSION

Concentrations in mg/L of heavy metals analyzed in this study are presented in Tables 1 and 2.

The results of the mean sub-seasonal analysis of lead ion showed lowest value (0.69 ± 0.64 mg/L) in the mid dry season at sampling point D in the AIFCF fishing site while highest (3.47 ± 0.16 mg/L) was obtained in early rainy sub-season at point E in the downstream (Table 1).The mean values for rainy and dry seasons were 3.11 ± 0.42 mg/L and 2.09 ± 0.69 mg/L, respectively, while an annual mean was 2.50 ± 0.78 mg/L (Table 2).

The lowest sub-seasonal mean Cr level of 0.15 ± 0.08 mg/L was obtained in mid dry sub-season while the highest value of 0.24 ±0.01 mg/L was recorded in the flood sub-season (Table 1) The mean values in the rainy and dry seasons were 0.23 ± 0.01 mg/L and 0.20 ± 0.03 mg/L, respectively, with an annual mean of 0.22 ± 0.03 (Table 2).

Sub-seasonal means analysis of copper (Cu) revealed that lowest value of 0.70 ± 0.37 mg/L occurred in the mid-dry sub-season and highest value of 1.87 ± 0.74 mg/L in the upstream (Table 1).1.32 ± 0.34 mg/L and 1.11 ± 0.33 mg/L were the mean values for rainy and dry seasons, respectively, with annual mean of 1.19 ± 0.34 mg/L (Table 2).

The sub-seasonal mean for cadmium ranged from 0.12 ± 0.10 mg/L in mid-dry season to 0.91 ± 0.04 mg/L in late dry-season (Table 1).The mean rainy season value was 0.42 ± 0.17 mg/L and dry season was 0.41 ±0.23 mg/L while the annual mean was 0.41± 0.23 mg/L (Table 2). Zinc has lowest sub-seasonalvalue of 0.13 ±0.01mg/L) in late dry-season and highest sub-seasonal mean value of 0.18 ± 0.02 mg/L in early dry-season(Table 1). The mean values for rainy and dry seasons were 0.16 ±0.01 mg/L and 0.16 ± 0.02 mg/L, respectively, and the annual mean was 0.16 ± 0.01 mg/L (Table 2)

Mean sub-seasonal analysis of manganese revealed lowest of value of 1.16 ± 0.22 mg/L in the late dry-seasonand highest sub-seasonal mean of 1.90 ± 0.20 mg/L in the the flood season(Table 1). The seasonal mean values for rainy and dry seasons were 1.74 ± 0.13 mg/L and 1.29 ± 0.17 mg/L, respectively, with an overall mean of 1.48 ± 0.27 mg/L (Table 2).

The highest (3.47 ± 0.16 mg/L) Pb concentration was probably due to runoff and domestic waste water into this water body (Raphael, 2008). Both lowest and highest sub-seasonal values as well as seasonal and annual means were high than the water quality standards (0.03 mg/L) for aquatic life (FEPA, 1991). They were also higher than the concentrations of 0.94mg/L recorded for Kainji Lake (Mbagwu, 2000), 0.090 ± 0.028Mg/L in River Jamaare in Bauchi State Nigeria (Akinola and Madara, 2009) but were less than 4.04 mg/L recorded in Lugu dam and 4.05 mg/L obtained in Goronyo reservoir in north western Nigeria (Wapdiyel, 2002).

The low levels of chromium in this river could be attributed to lack of chromium sources such as mining operations, electroplating and galvanization (Cotton and Wilkinson, 1972) close to this water body. However, the seasonal and annual mean were higher than the standard (0.005 mg/L) for aquatic life (SON, 2007). The sub-seasonal means, seasonal and the annual means were higher than 0.0001 to 0.009 mg/l as the monthly range values in Areba River, Olomoro, Niger Delta, Nigeria (Idodo-Umeh and Oronsaye, 2004) and 0.02Mg/L between September and December and 0.46 ± 0.088Mg/L in June, with an overall mean of 0.09 ± 0.01Mg/L, in Kware Lake in north-western Nigeria (Onaji *et al.*, 2005).

The results shown by copper may be due to low water level, agricultural and domestic activities within the catchment area of this water body. The sub-seasonal means of copper are higher than the value of 0.21 ± 0.07mg/L recorded for stream/river in Zamfara Reserve in Zamfara State of Nigeria (Ipinjolu and Argungu, 1998), 1.11mg/l in Kainji Lake, Nigeria (Mbagwu, 2000) and 0.27 ± 0.02mg/l and 0.09 ± 0.11mg/l for rivers Oadaji and Katou, respectively, in Keffi, Nigeria (Gyar and Joseph, 2009).

The seasonal and the overall means for cadmium were higher than the recommended water quality standard (0.1mg/L) for aquatic life (Roberts, 1978). The sub-seasonal, seasonal and annual means levels were higher than the value of 0.003 to 0.098 mg/L as the monthly range in River Areba in the Niger Delta Nigeria (Idodo-Umeh and Oronsaye, 2004) and 0.109 ± 0.044mg/L in River Jamaare in Bauchi State Nigeria (Akinola and Madara, 2009). They were close to the 0.33 mg/L reported for Kainji Lake (Mbagwru, 2000) and 0.34 mg/L in Ravi River in Pakistan (Tariq *et al*., 1994).

Based on the requirement of aquatic life, zinc recorded high values. This could be due to low water level (Goldman and Horne, 1983). The sub-seasonal, seasonal and the overall means were above the recommendation (0.05 mg/L) for aquatic life (Roberts, 1978) and were lower than the value of 10.14 ± 0.11mg/L in April during dry season in stream/rivers in Zamfara Reserve in Zamfara State in Nigeria (Ipinjolu and Argungu, 1998) but they were in line with value of 0.21 ± 0.02 mg/L obtained in Lugu dam (Wapdiyel, 2002).

The highest value of manganese recorded in flood sub-season could be attributed to weathering of rock, erosion of the soils and drainage from the agricultural lands (Tait, 1981). These sub-seasonal values, seasonal and overall means were higher than 0.15mg/l and 0.09mg/l for rivers and dams of Zamfara Reserve in Zamfara State, Nigeria (Ipinjolu and Argungu, 1998).

Table 1: Sub-seasonal means (mg/L) of some heavy metals in Sokoto- Rima River at the AIFCF fishing area

Parameter	Location	Sub-season				
		Early Rainy	Flood	Early Dry	Mid Dry	Late Dry
Pb	A	3.37 ± 0.15[a]	3.35 ± 0.08 [a]	2.07 ± 1.30	1.76 ± 1.80	3.21 ± 0.13 [a]
	B	2.25 ±0.90 [b]	3.23 ± 0.15[a]	2.18± 0.85	1.69 ± 1.73	2.91 ± 0.59 [ab]
	C	3.45 ± 0.18 [a]	2.43 ± 0.34 [b]	1.90 ± 0.51	1.62 ± 1.66	2.16 ± 1.52 [b]
	D	3.22 ± 0.57[a]	3.17 ± 0.15 [a]	2.42 ± 1.08	0.69 ± 0.64	3.33 ± 0.14 [a]
	E	3.47 ± 0.16[a]	3.15 ± 0.79 [a]	1.52 ± 1.56	1.69 ± 1.73	2.18 ± 1.54 [b]
Cr	A	0.23 ± 0.01	0.24 ± 0.00	0.17[a] ± 0.10	0.19 ± 0.05 [ab]	0.23 ± 0.01
	B	0.23 ± 0.01	0.24 ± 0.01	0.20 ± 0.05	0.22 ± 0.02 [a]	0.23 ± 0.08
	C	0.23 ± 0.01	0.22 ± 0.02	0.18 ± 0.06	0.23 ± 0.01 [a]	0.23 ± 0.01
	D	0.23 ± 0.02	0.23 ± 0.02	0.19 ± 0.05	0.22 ± 0.01 [a]	0.23 ± 0.01
	E	0.23 ± 0.02	0.23 ± 0.02	0.17 ± 0.07	0.15 ± 0.08 [b]	0.23 ± 0.01
Cu	A	1.87 ± 0.74	1.17 ± 0.19 [ab]	0.97 ± 0.39	0.82 ± 0.40	1.94 ± 0.94 [a]
	B	1.73 ± 0.86	1.18 ± 0.18 [ab]	0.88 ± 0.33	0.70 ± 0.37	1.10 ± 0.23 [b]
	C	1.58 ± 0.84	0.90 ± 0.26 [c]	1.30 ± 0.67	0.88 ± 0.57	1.16 ± 0.51 [b]
	D	1.05 ± 0.08	1.20± 0.09 [a]	1.38 ± 0.65	0.78 ± 0.46	1.56 ± 0.22 [ab]
	E	1.55 ± 0.57	0.97 ± 0.12[bc]	0.91 ± 0.51	1.02 ± 0.92	1.23 ± 0.78 [b]
Cd	A	0.70 ± 0.24 [a]	0.40 ± 0.07 [ab]	0.26 ± 0.17	0.23 ± 0.22	0.91 ± 0.04 [a]
	B	0.57 ± 0.39 [ab]	0.42 ± 0.11 [a]	0.24 ± 0.09	0.18 ± 0.16	0.50 ± 0.32 [c]
	C	0.65 ± 0.30 [ab]	0.27 ±0.02 [c]	0.36 ± 0.29	0.33 ± 0.34	0.59 ± 0.13[bc]
	D	0.32 ± 0.09 [b]	0.37 ± 0.07 [ab]	0.45 ± 0.35	0.12 ± 0.10	0.74 ± 0.08 [ab]
	E	0.59 ± 0.18 [ab]	0.32 ± 0.06[bc]	0.22 ± 0.23	0.35 ± 0.36	0.69 ± 0.27[bc]
Zn	A	0.17 ± 0.02	0.16 ± 0.03	0.16 ± 0.04[bc]	0.16[ab] ± 0.01	0.15 ± 0.02 [ab]
	B	0.16 ± 0.02	0.16 ± 0.02	0.16 ± 0.02[abc]	0.18 ± 0.01 [a]	0.13 ± 0.01 [b]
	C	0.17 ± 0.02	0.16 ± 0.01	0.17± 0.02 [ab]	0.16 ± 0.02 [ab]	0.13 ± 0.02 [b]
	D	0.16 ± 0.03	0.16 ± 0.02	0.18 ± 0.02 [ab]	0.14 ± 0.01 [b]	0.17 ± 0.02 [a]
	E	0.15 ± 0.03	0.16 ± 0.02	0.15 ± 0.02 [c]	0.14 ± 0.06 [b]	0.14 ± 0.03 [b]
Mn	A	1.78 ± 0.10 [ab]	1.73 ± 0.12 [ab]	1.33 ± 0.55	1.24 ± 0.63	1.39 ± 0.23 [ab]
	B	1.48 ± 0.08 [c]	1.85 ± 0.05 [ab]	1.37 ± 0.29	1.13 ± 0.51	1.36 ± 0.10 [a]
	C	1.82 ± 0.13 [a]	1.68 ± 0.08 [b]	1.49 ± 0.25	0.94 ± 0.41	1.34 ± 0.28 [ab]
	D	1.60 ± 0.25[bc]	1.88 ± 0.18 [a]	1.40 ± 0.33	1.07 ± 0.59	1.50 ± 0.23 [a]
	E	1.77 ± 0.15 [ab]	1.90 ± 0.20 [a]	1.21 ± 0.40	1.25 ± 0.64	1.16 ± 0.22 [b]

*Values are mean ± standard deviation Means in a column of parameter with the same letters are not significantly different ($P<0.05$). A = Upstream; B, C and D are sampling locations in Argungu International Fishing and Cultural Festival AIFCF); and D = Downstream

Table 2: Mean values (mg/L) of some heavy metals in Sokoto-Rima River at the AIFCF fishing site

Parameter	Location	Rainy season	Dry season	Annual mean
Pb	A	3.36 ± 0.01	3.3 ± 0.78	2.75 ± 0.78
	B	2.74 ± 0.69	2.26 ± 0.61	2.45 ± 0.61
	C	2.94 ± 0.72	1.89 ±0.27	2.31 ± 0.70
	D	3.19 ± 0.04	2.14 ± 1.34	2.57 ± 1.11
	E	3.31 ± 0.22	1.80 ± 0.34	2.40 ± 0.87
	Mean	3.11 ± 0.42	2.09 ± 0.69	2.50 ±0.78
Cr	A	023 ± 0.01	0.20 ± 0.03	0.21 ± 0.03
	B	0.24 ± 0.01	0.22 ± 0.02	0.22 ± 0.02
	C	0.23 ± 0.01	0.21 ± 0.03	0.22 ± 0.022
	D	0.23 ± 0.00	0.21 ± 0.02	0.22 ± 0.017
	E	0.23 ± 0.00	0.18 ± 0.04	0.20 ± 0.04
	Mean	0.023 ± 0.01	0.20 ± 0.03	0.22 ± 0.03
Cu	A	1.52 ± 0.49	1.24 ± 0.61	1.35 ± 0.52
	B	1.45 ± 0.39	0.89 ± 0.20	1.12 ± 0.40
	C	1.24 ± 0.48	1.11 ± 0.21	1.16 ± 0.29
	D	1.13 ± 011	1.25 ± 0.41	1.19 ± 0.30
	E	1.26 ± 0.41	1.05 ± 0.16	1.14 ± 0.26
	Mean	1.32 ± 0.34	1.11 ± 0.33	1.19 ± 0.34
Cd	A	0.55 ± 0.21	0.47 ± 0.38	0.50 ± 0.30
	B	0.50 ± 0.11	0.31 ± 0.17	0.38 ± 0.17
	C	0.46 ± 0.27	0.43 ±0.14	0.44 ± 0.17
	D	0.35 ± 0.04	0.44 ± 0.31	040 ± 0.23
	E	0.25 ± 0.02	0.42 ± 0.24	0.35 ± 0.20
	Mean	0.42 ± 0.17	0.41 ± 0.23	0.41 ±0.21
Zn	A	0.17 ± 0.01	0.16 ± 0.01.	0.16 ±0.00
	B	0.16 ± 0.00	0.16 ± 0.03	0.16 ± 0.18
	C	0.17 ± 0.01	0.15 ± 0.02	0.16 ± 0.02
	D	0.16 ± 0.00	0.16 ± 0.02	0.16 ± 0.01
	E	0.16 ± 0.01	0.14 ± 0.01	0.15 ± 0.01
	Mean	0.16 ± 0.01	0.15 ± 0.02	0.16 ± 0.01
Mn	A	1.76 ± 0.04	1.39 ± 0.16	1.54 ± 0.23
	B	1.67 ± 0.26	1.29 ± 0.14	1.44 ± 0.26
	C	1.75 ± 0.10	1.26 ± 0.28	1.45 ± 0.34
	D	1.74 ± 0.20	1.32 ± 0.23	1.49 ± 0.30
	E	1.83 ± 0.10	1.21 ± 0.05	1.46 ± 0.35
	Mean	1.74 ± 0.13	1.29 ± 0.17	1.48 ± 0.27

*Values are mean ± standard deviation Means in a column of parameter with the same letters are not significantly different ($P<0.05$). A = Upstream; B, C and D are sampling locations in Argungu International Fishing and Cultural Festival AIFCF); and D = Downstream

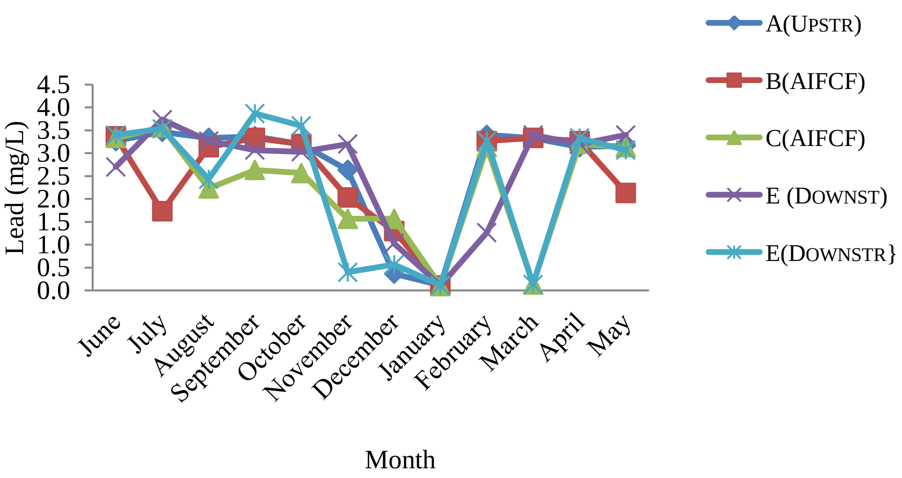

Figure 1: Mean monthly variation of lead at sampling points

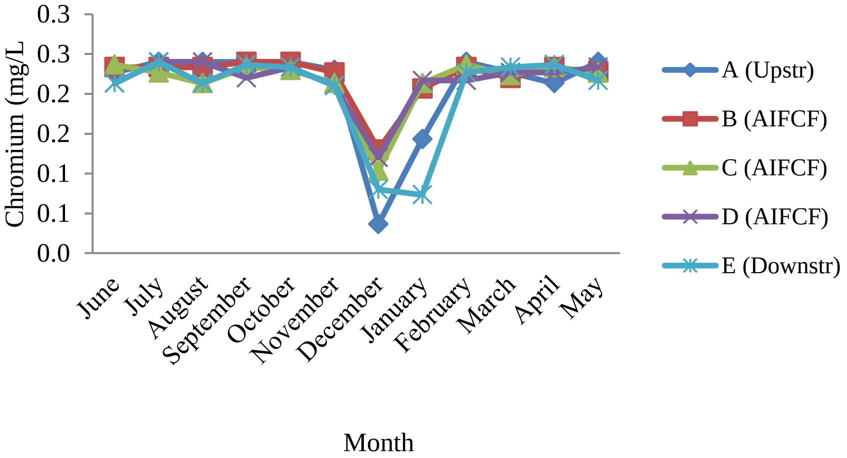

Figure 2: Mean monthly variation of chromium at the sampling points

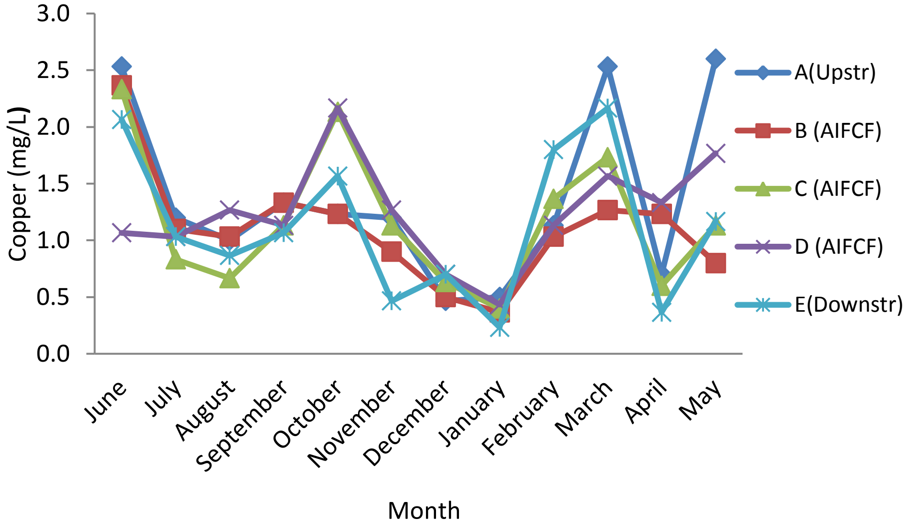

Figure 3: Mean monthly variation of copper at the sampling points

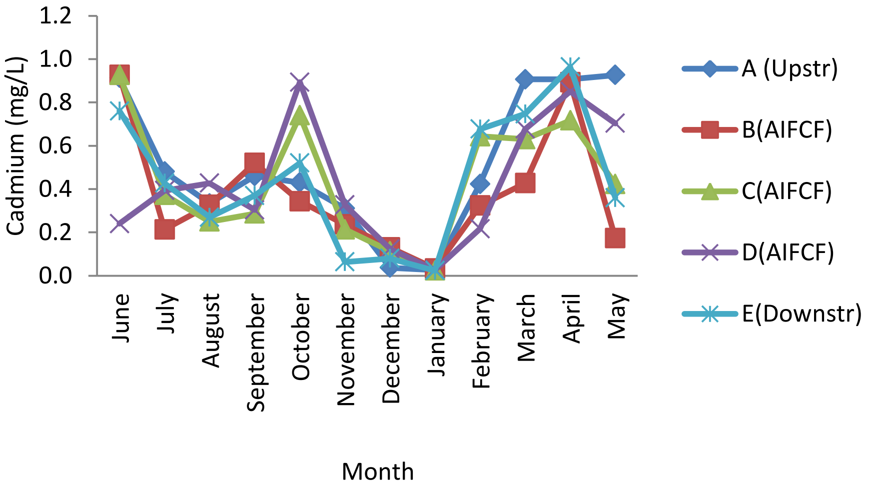

Figure 4: Mean Monthly variation of cadmium at the sampling points

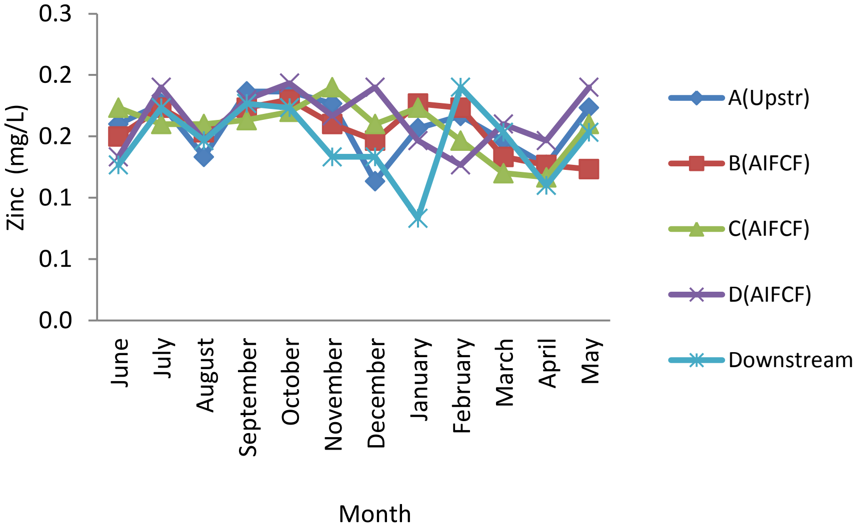

Figure 5: Mean monthly variation of zinc at sampling points

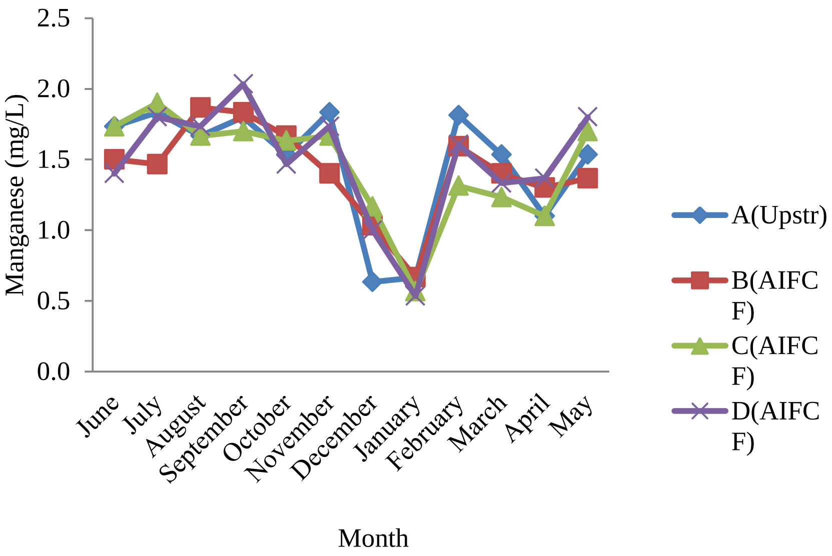

Figure 6: Mean monthly variation of mangannese at the sampling points

CONCLUSION

Lead, chromium, cadmium and manganese concentrations were higher than the water quality standard for aquatic life recommended by SON (2007), FEPA (1991) and Robberts(1978) and should therefore be brought to the recommended standard for aquatic life by regulating the entrance of these metals into this river system through monitoring of their sources.

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