
Seasonal Mean Levels of Heavy Metals in Water and Associated Sediments from Ajawere River in Oke-Osun Farm Settlement, Osogbo, Nigeria

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Abstract

The seasonal mean variations of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the water and sediments of Ajawere River in Oke-Osun Farm Settlement, Osogbo, Nigeria were evaluated. Samples collected were analyzed for their heavy metal levels using Graphite Furnace Atomic Absorption Spectrophotometer (GF-AAS). Seasonal mean ranges of heavy metals in the river sediments (mg/kg) were 3.39 ± 1.34 Cd to 43.24 ± 6.15 Cr in the rainy season and 4.56 ± 1.21 Ni to 55.35 ± 4.29 As in the dry season. Seasonal mean levels of heavy metals (mg/L) in the river water ranged between 3.02 ± 0.72 As and 179.49 ± 21.45 Fe in the rainy season while the dry season mean levels ranged from 3.09 ± 1.65 Co to 278.81 ± 51.59 Fe. Wide seasonal variations were observed for Cr, Cu, Mn, Ni, V and Zn in the sediments and for all the other metals apart from As, Ni and V in the water samples. The *I*-geo values obtained indicated that the sediments were moderately polluted with respect to Cr, Cu and Pb, and was either heavily polluted or very heavily polluted with respect to As and Cd. Metal levels in the river water, in many cases, were above the specified guideline limits for natural waters. The results obtained from this study indicated that the river sediment and water samples from Oke-Osun Farm Settlement were contaminated with heavy metals in varied degrees and gave cause for concern.

Keywords: Heavy metals, sediments, water, farm settlement, Ajawere River

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Introduction

The presence of heavy metals in the environment constitutes a major global source of concern to environmental scientists and engineers because heavy metals are not only harmful to humans and animals, but tend to bio-accumulate in the food chain (Yoon *et al*., 2006). According to WHO (1973; 1977), in a bid to improve their living conditions, human beings try to exploit the nature, manufacturing new products, establishing more industries, and improving on old ones. Fossil fuel combustion, agrochemical applications, metallurgical industrial activities and industrial wastes generation over the last century (Fitzgerald and Clarkson, 1991; Mason *et al*., 1994) have undoubtedly intensified the emission of various heavy metals and other pollutants into the environment thereby stressing the terrestrial, aquatic and atmospheric ecosystem beyond their natural recycling capability.

Environmental pollution from increased human activities, apart from being aesthetically offensive, can be a genuine health hazard to people as well as to plants and other biota (Onder and Dursun, 2006). The adverse effects of these pollutants on human health, agricultural productivity, natural ecosystem and total environment are significant (UNEP, 1978). It is on record that increase in heavy metal emissions has affected all environments: terrestrial (Godbold, 1994; Grigal *et al*., 1994), lacustrine (Cossa *et al*., 1994; Watras, 1994), and coastal ecosystem (Baeyens *et al*., 1998; Mason and Lawrence, 1999). Davies (1992) observed that awakening of the public conscience to environmental degradation started with events such as the observed effect of lake eutrophication following river pollution by phosphates and nitrates from detergents and fertilizers; the problems of combating photochemical smog; Minamata (methyl mercury poisoning) and *Itai-itai* (cadmium) diseases in Japan which helped to create a climate of thought in which it was acceptable to consider a role for heavy metals in human health.

By far, anthropogenic activities rather than natural geochemical activities are more responsible for the rapid chemical redistribution of free and combined lethal elements like As, Cd, Pb, Hg in the environment. Continuous exposure to heavy metal pollutants is being increasingly implicated in the etiology of a large number of ailments including cardiovascular diseases, reproductive failure, dermatitis, allergies and some cancers (Nriagu, 1979). Prasad and Oberleas (1976) maintained that a public health problem likely to remain unresolved for a long time is the fact that a large number of people are at risk of being poisoned by a persistent exposure to environmental doses of heavy metals.

Sediments in coastal systems have been found to be intense repositories of contaminants (Harvey and Luoma, 1985; Mason and Lawrence, 1999; Griscom *et al*., 2000). Direct and indirect aquatic environment contamination by toxic substances including heavy metals will affect humans as a final consumer because anthropogenic metals are either retained within the water bodies or may be taken up by organisms such as plankton, benthos or fish and finally transferred to humans (Ahmad *et al*., 2009). Unlike most organic pollutants such as organo-halides, heavy metals are non-biodegradable; heavy metals may only undergo relocation and species transformation across environmental compartments. Hence, the resident time of heavy metals in the environment is usually long. As a result, heavy metals have greater potential of constituting both short and long term serious health threat to man and other organisms as they remain persistent in the environment for years.

This paper determines the seasonal levels of heavy metals in water and associated sediments from Ajawere River in Oke-Osun Farm Settlement, Osogbo, Nigeria, to evaluate the pollution status of the aquatic environment.

Study area

Oke-Osun farm settlement is situated between longitudes 04.31 and 04.33^{o}E and latitudes 007.44 and 007.46^{o}N (Figure 1). It is located about 3.5 km South of Osun Grove in the outskirt of Osogbo metropolis. The location is a rural setting within an acquired 2,500 ha parcel of land (Oyekunle *et al.*, 2011). There is a perennial river (River Ajawere) that serves as the main drainage for the settlement and as a tributary to River Osun. River Ajawere has three existing fish ponds and a reservoir under construction across it during the period of this study. The reservoir is intended to serve as the source of potable water for people around the Osun State Government Secretariat at Abere in Osogbo.

About 90% of the total farm land consists mainly of cultivated plots allocated to farmers who plant food crops mainly while about 10% of the farm land is used for building houses by the settlers (Oyekunle *et al.*, 2011). Crops harvested from this settlement are sold to consumer intermediaries from Osogbo and its environs. The perennial nature of Ajawere River within the farm land encourages inland valley agricultural (fadama) practice, and as such, the planting of certain vegetables (e.g. *Amaranthus*) is done round the year. The farmers here actively apply agrochemicals from time to time to improve crop yields without a follow-up assessment of how much of the agrochemicals as fertilizer, herbicides and germicides affect the non-target components of the ecosystem. The choice of this river for the present study was informed primarily by the fact that it represents, to a large extent, an important aquatic habitat on the course of the only perennial river serving as the main drainage for the cultivated area. Hence, the study will give, in part, the heavy metal pollution assessment of the settlement.

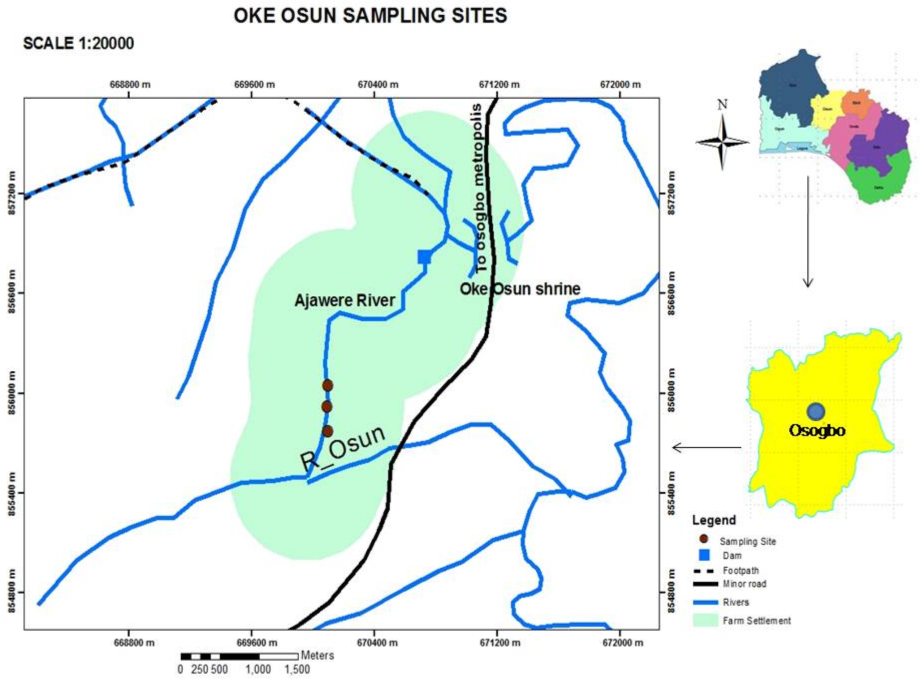

Figure 1: Map of the study area showing sampling sites

Materials and Methods

Polyethlene sample bottles and bags and Teflon beakers were washed with hot liquid detergent solution, soaked in 10% HNO_3 for 48 hours and later rinsed with triply distilled water prior to sample collection for heavy metals analysis (Ogunfowokan and Fakankun, 1998; Ogunfowokan *et al.*, 2008). The reagents used in this study were of spectra purity. They are: HNO_3 (AR) –

Riedel-deHaën, Germany; Trace metal standards (ppm) - Riedel-deHaën, Germany; HF (AR) - Rochelle Chemicals, SA; and Perchloric acid – MERCK, Germany.

Samples were collected on seasonal basis, comprising of four representative months (May, June, July and August of 2004) for the rainy season and four representative months (November and December of 2004 and January and February of 2005) for the dry season. Fine-grained surficial bed sediments were collected in polythene bags at a depth of 0 to 15cm at three sites along the river course using a hand held core sampler (Shelton and Capel, 1994). These samples were preserved in the refrigerator at about 4^oC before further analysis. The samples collected at a given site were later dried at ambient temperature and composited into a single representative sample. Final sample selection from the dried and pulverized bulk was done using coning and quartering method. Water samples from the river were collected from the same spots where sediment samples were collected using 100 mL pre-treated plastic bottles. The plastic bottles were rinsed first with the water samples at the site of collection before they were filled with the water samples to the brim and covered. Storage was done in a refrigerator at 4^0C prior to further analysis.

For the sediment samples, a modification of an earlier described method (Ogunfowokan *et al.*, 2008) was employed to secure the release of bound or free metals from the environmental matrix in their highest oxidation states. About 0.2 - 0.5 g of the selected sediment sample with particles ~ 0.5 mm in diameter was weighed into a Teflon beaker; 5mL of 70% HNO_3 was added and the beaker was covered with a watch glass. This was placed on a thermostatically controlled hot plate maintained at 120^oC for about 2 hours. Replenishing of the acid content was done at intervals to avoid bringing the content to total dryness. The beaker was allowed to cool and 5mL concentrated HNO_3 (e.g. 1.84), 2mL 60% $HClO_4$ and 5mL 40% HF were added. The beaker was replaced on the hot plate with a digestion temperature of 180 - 200^oC. When the solution became clear, the digestion was considered complete. The watch glass was now tilted sideways to volatilize most of the acid content at about 100^oC. The beaker was removed from the hot plate and cooled down after which 5mL of 6 M HNO_3 was added. Further boiling and gentle simmering for about 5 minutes was done. The watch glass was rinsed with triply distilled water into the beaker. The content of the beaker was quantitatively transferred into a 50mL volumetric flask and made up with triply distilled water to the mark. A blank determination was carried out to establish blank levels for the metals analysis.

The method of APHA et *al*. (1995) was used for water digestion. A 50mL aliquot of the collected water samples was measured and transferred into a 125mL Teflon beaker. 5mL of concentrated HNO_3 and some Hengar granules (anti bumping agents) were added. This was brought to a slow boiling on a hot plate. Evaporation was discontinued just before precipitation occurs. Replenishing of the content was done with 1:1 (v/v) HNO_3:$HClO_4$ mixture until complete digestion was ascertained i.e. when a light-coloured clear solution was shown. The digested sample was cooled down, quantitatively transferred into a 50mL volumetric flask and made up to the mark with triply distilled water. A blank determination was concurrently done.

The worked-up samples from the outlined procedures above were analyzed for their heavy metal concentrations using Graphite Furnace – Atomic Absorption Spectrophotometry (GF-AAS) available at the Department of Chemistry, University of Botswana, Gaborone, Botswana. The GF-AAS was operated as per the manufacturer's manual. In this paper, the quality control measures adopted were blank determination, calibration of instruments, and use of standard soil reference materials, determinations of percentage recovery and determination of detection limits. The purpose of carrying out a blank determination was to ascertain the extent to which the materials and reagents used contribute impurities to the overall results obtained. This was done by running a separate determination under the same experimental conditions employed in the actual analysis of the sample, but excluding the sample. The values obtained from running blank determinations were subtracted from the analyte values as applicable.

The calibration of the GF-AAS used was done to evaluate the response of the analytical procedure with respect to known quantities of the standards of the heavy metals of interest so that the response to unknown quantities in the samples could be reliably estimated. For the GF-AAS 200, 180, 160, 140, 120, 100, 80, 60, 40 and 20 µg/L concentrations of each metal solution were prepared by serial dilution for the determination of metals in the digested water and sediment samples. These solutions were run to obtain the working calibration graph. GF-AAS (SHIMADZU AA-6800, Auto Sampler ASC-6100 and Atomizer GFA-Ex 7) was used to estimate the levels of heavy metals in the samples by automatic interpolation with respect to the calibration graph.

To ascertain the sensitivity and accuracy of the GF-AAS used, certified soil reference materials of known Cu and Ni contents were digested using the exact procedures employed for the determination of heavy metals in soil and sediment samples. The certified soil reference materials and their metal contents are GBW 07406 (Cu = 390.0 ± 6.0 µg/g; Ni = 53.0 ± 1.0 µg/g) and GBW 07407 (Cu = 97.0 ± 2.0 µg/g; Ni = 276.0 ± 6.0 µg/g).

Since no certified water reference materials were available to us during the course of this study, recovery analysis was performed in order to ascertain the efficiency of the analytical procedures using standard addition method. Two equal portions (50mL each) of the water sample were measured into separate Teflon beakers. One sample was spiked with 10µg/L of mixed metal solution while the other was left un-spiked. Both samples were digested as earlier outlined and their heavy metal concentrations were determined using GF-AAS. The percentage recoveries (%R) of metals were determined using the relationship:

$$\%R = (A' - A) / B * 100$$

where A′ is the concentration of the metal in the spiked sample; A is the concentration of the metal in the un-spiked sample; and B is the amount of the metal used for spiking.

The limits of detection were calculated based on the empirical definition by Miller and Miller (2000) who consider limit of detection as the analyte concentration that gives a signal equal to the blank signal plus three standard deviations of the blank. That is:

$$y_C = y_B + 3s_B$$

where y_C = analyte signal equivalent to detection limit; y_B = blank signal; and s_B = standard deviation of the blank. From the value of y_C, the analyte concentration corresponding to the detection limit was evaluated for GF-AAS determination of metals.

Results and Discussion

Validation of Analytical Procedures Adopted

The reproducibility and reliability of the analytical procedures adopted in this study was tested in terms of sensitivity, recovery, precision and accuracy. Table 1 shows the values for measuring conditions, calibration curve, percentage recovery (% R) and limit of detection (LOD) for the heavy metals. Under the experimental conditions used, the standard calibration curves obtained showed high linearity level with r^2 values between 0.9872 and 0.9998 for Cr and Mn respectively. Recoveries of heavy metals in water ranged from 85.73 ± 6.29% Mn to 99.44 ± 6.23% V. These values were high enough to be adjudged acceptable. The percentage relative standard deviation (%RSD) values for water ranged from 2.57 to 6.99 while the values lied between 2.29 and 9.74% for sediments. These values showed that precision was even better than the generally accepted 10% RSD level. The calculated LOD values were in good agreement with the values quoted by Harris (1999). Table 2 summarizes the reliability level of the GFAAS used to reproduce specified concentration values of heavy metals in certified reference standard soil samples (GBW07406 and GBW07407). The determined percentage concentrations of Cu and Ni were 98.62 ± 1.11 and 96.70 ± 2.15%, and 99.00 ±3.13 and 90.88 ± 2.95% respectively for the two certified reference soil samples and were in close agreement with those specified by the manufacturer. This further confirms the efficiency of the described procedure and the sensitivity of the GFAAS used for the heavy metals analysis.

Table 1: Measuring Conditions, Calibration Curve, % Recovery and Limits of Detection for Heavy Metals

Heavy Metal	**Current (mA)**	**Wavelength (nm)**	**Slit Width (nm)**	**Calibration Curve, r^2**	**%Recovery of Metals in Water[#]**	**Calculated LOD* (µg/L)**
As	12	193.7	0.5	0.9989	98.54 ±3.46	0.231(0.2)
Cd	8	228.8	0.5	0.9992	89.99±5.52	0.004(0.003)
Cr	10	357.9	0.5	0.9872	87.15±3.60	0.023(0.02)
Co	12	240.7	0.2	0.9983	97.42±4.12	0.021(0.01)
Cu	6	324.8	0.5	0.9994	99.22±5.06	0.033(0.02)
Fe	10	248.3	0.5	0.9981	97.50±2.69	0.024(0.02)
Mn	10	279.5	0.2	0.9998	85.73±6.29	0.013(0.01)
Ni	12	232.0	0.2	0.9993	97.20±7.61	0.031(NA)
Pb	10	283.3	0.5	0.9985	89.99±2.42	0.062(0.05)
V	10	318.4	0.5	0.9907	99.44±6.23	0.024(0.02)
Zn	8	213.9	0.5	0.9890	92.38±4.57	0.003(0.002)

[#] Values are mean of triplicate analysis ± % RSD; *Values in parenthesis are from Harris (1999); Lightening mode for all measurements was BGC-D_2; NA = not available

Table 2: Levels of Heavy Metals in Certified Reference Soil Materials.

Reference Material	GBW 07406	GBW 07407
Stated Cu content (µg/Kg)	390.0 ± 6.0	97.0 ± 2.0
Stated Ni content (µg/Kg)	53.0 ± 1.0	276.0 ± 6.0
Measured Cu content (µg/Kg)	384.63 ± 4.29	96.03 ± 3.01
Measured Ni content (µg/Kg)	51.25 ± 1.10	250.84 ± 7.39
% Measured Cu content	98.62 ± 1.11	99.00 ± 3.13
% Measured Ni content	96.70 ± 2.15	90.88 ± 2.95

Value = mean of triplicate analysis ± s.d.

Levels of Heavy Metals in Sediments

Levels of heavy metals in the river sediments from May 2004 to February 2005 are as presented in Tables 3 and 4. Arsenic monthly mean values for rainy season ranged from 11.22 ± 0.08 mg/kg in May to 14.53 ± 1.93 mg/kg in July while the values for dry season ranged from 15.79 ± 0.38 mg/kg in November to 71.45 ± 4.11 mg/kg in January. These values were much higher than the 0.32 mg/kg As mean level obtained for sediments of Ariake Bay, Japan by Tabata *et* al. (2009). The results of the dry season sediment samples compared well with the value (50 mg/kg) obtained for the estuarine sediment of the Patos Lagoon in Brazil (Mirlean *et al*., 2003). The rainy season mean of As (12.38 ± 1.59 mg/kg) was significantly lower ($p \leq 0.05$) than the dry season mean (55.35 ± 4.29 mg/kg). With background levels of As in unpolluted soils put at 5 mg/kg (Pais and Jones, 1997) it could be stated that the river sediment had suffered an increased contamination level as at the time of this study. This is probably as a result of the applications of arsenic containing herbicides in the past. Although As is a known toxin and carcinogen proven to cause human skin, lung, and bladder cancers, it is the magnitude of the dose (the amount and the route of administration) and the frequency of exposure that determines what health effects may occur. It is excreted in the urine, the sweat, and in the keratin of the skin, the hair, and the nails. Its disappearance rate from the blood is very rapid with a biological half-life of one hour and from the body into the urine with a biological half-life of four days. Because of its rapid elimination, arsenic dosages do not build up over time [Lamm, 2001]. Excessive and prolonged dependence on the water or bottom feeder fish from the river, however, may lead to arsenic related health problems.

The rainy season monthly mean levels of Cd ranged between 1.95 ± 0.58 mg/kg in July and 5.13 ± 0.86 mg/kg in May while the dry season mean levels ranged from 3.30 ± 0.87 mg/kg in December to 9.34 ± 0.53 mg/kg in November. These values were above the less than 1.0 mg/kg background value in unpolluted soils (Pais and Jones, 1997) or 0.11 mg/kg recorded by GESAMP (1982) for unpolluted sediments. Thus, there is a strong suggestion of anthropogenic inputs from such agricultural practices as the application of fertilizers. The rainy season mean level of 3.39 ± 1.34 mg/kg was significantly lower (at 0.05 levels of significance) than the mean level of 5.54 ± 2.55 mg/kg in the dry season. Cadmium is a biotoxic heavy metal regarded as an important environmental pollutant in an agricultural environment (Onweremadu and Duruigbo, 2007) because of the potential adverse effects it poses to soil, food quality and human health invariably.

Table 3: Rainy season level of heavy metals in the river sediment

Month	***Concentration of heavy metals (mg/kg)**										
	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
May 2004	11.22	5.13	6.26	45.13	14.39	36.51	14.22	5.44	24.30	11.57	17.45
	± 0.08	± 0.86	± 0.83	± 2.24	± 2.60	± 4.27	± 1.57	± 1.86	± 5.23	± 1.06	± 1.28
June 2004	11.83	3.74	7.60	38.60	17.96	36.12	15.63	3.59	31.98	10.57	14.72
	± 0.62	± 0.22	± 1.14	± 2.94	± 1.57	± 1.44	± 2.58	± 0.57	± 2.04	± 1.43	± 3.82
July 2004	14.53	1.95	7.67	45.88	15.81	37.20	14.74	3.55	24.89	12.54	13.70
	±1.93	± 0.58	± 1.04	±1.07	± 1.20	± 1.87	± 3.07	± 1.96	± 3.88	± 2.07	± 0.81
August 2004	11.94	2.73	8.16	43.34	15.89	37.79	12.83	2.42	30.69	8.33	12.64
	± 0.27	± 0.48	± 0.56	± 5.65	± 2.01	± 2.93	± 0.25	± 0.77	± 6.49	± 0.87	± 1.00
Range	11.22- 14.53	1.95 - 5.13	6.26 - 8.16	38.60- 45.88	14.39- 17.96	36.12- 37.79	12.83- 15.63	2.42- 5.44	24.30- 31.98	8.33- 12.54	12.64- 17.45
Seasonal mean	**12.38**	**3.39**	**7.42**	**43.24**	**16.02**	**36.90**	**14.36**	**3.75**	**27.96**	**10.75**	**14.63**
± s.d.	**±1.59**	**±1.34**	**±1.08**	**±6.15**	**±2.11**	**±2.52**	**±2.12**	**±1.67**	**±5.37**	**±2.04**	**±2.60**

Values = mean of triplicate determinations ± s.d.

Table 4: Dry season level of heavy metals in the river sediment

Month	***Concentration of heavy metals (mg/kg)**										
	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
	15.79	9.34	8.45	49.26	17.38	44.87	15.97	4.47	39.84	9.87 ±	14.86
Nov 2004	± 0.38	± 0.53	± 0.82	± 4.37	± 0.52	± 2.58	± 1.82	± 0.74	± 7.73	0.90	± 3.74
Dec 2004	70.60	3.30	12.20	33.17 ±	15.81	40.19	26.25	5.13	44.23	11.48	21.94
	± 3.35	± 0.87	± 1.97	1.72	± 2.09	± 1.00	± 4.28	± 1.21	± 1.69	± 0.98	± 0.98
Jan 2005	71.45	3.81	8.28	32.95	21.81	45.93	30.57	4.40	32.86	10.42	24.56
	± 4.11	± 0.57	± 1.36	± 2.92	± 1.82	± 5.58	± 1.16	± 0.88	± 4.04	± 0.92	± 3.26
Feb 2005	63.58	5.70	8.24	26.59 ±	22.87	46.58	24.30	4.22	42.98	10.83	23.22
	± 5.58	± 0.78	± 0.52	4.59	± 3.76	± 4.87	± 0.30	± 1.42	± 1.67	± 1.57	± 0.97
Range	15.79- 71.45	3.30- 9.34	8.24- 12.20	26.59- 49.26	15.81- 22.87	40.19- 46.58	15.97- 30.57	4.22- 5.13	32.86- 44.23	9.87- 11.48	14.86- 24.56
Seasonal mean	**55.35**	**5.54**	**9.29**	**35.49**	**19.47**	**44.39**	**24.27**	**4.56**	**39.97**	**10.65**	**21.14**
± s.d.	**± 4.29**	**±2.55**	**±2.07**	**±1.31**	**±3.68**	**±4.27**	**±5.91**	**±1.21**	**±7.50**	**±1.14**	**±4.49**

* Values = mean of triplicate determinations ± s.d.

Unlike most metals, Cd can be taken up by several plants such as wheat, maize, rice, spinach or tobacco (Udousoro *et al*., 2010). It can also be taken up easily by aquatic animals. Human uptake of cadmium takes place mainly through food although an exposure to significantly higher Cd levels can also occur when people smoke. Foodstuffs obtained from soils heavily polluted with Cd greatly increase its concentration in human bodies. It should therefore be stressed that in a place like Oke-Osun farm settlement where upland farming system is practiced round the year and the main drainage is Ajawere River, some caution must be exercised with respect to direct consumption of products or untreated water from the river environment to avoid Cd poison.

The monthly mean concentration of Co for the two seasons ranging from 6.26 ± 0.83 mg/kg in May to 12.20 ± 1.97 mg/kg in December showed a good agreement with the usual back ground levels of 10.0 mg/kg in unpolluted soils (Pais and Jones, 1997). Although these values were higher than the 0.102 mg/kg obtained by Awofolu *et al*. (2005) for Tyume River sediment, it can still be concluded that the river sediments in this study had not suffered serious anthropogenic input of Co. The seasonal mean values indicated a higher Co level (9.29 ± 2.07 mg/kg) for dry season than the 7.42 ± 1.08 mg/kg recorded for rainy season.

On a monthly basis, the lowest level of Cr, 26.59 ± 4.59 mg/kg, was recorded in February during the dry season while the highest level, 49.26 ± 4.37 mg/kg, was recorded in November also during the dry season. These values were generally lower than the less than 100 mg/kg level in an unpolluted soil (Pais and Jones, 1997), but significantly higher than the 20.3 mg/kg value obtained by Binning and Baird (2001) for Swartkops estuary sediments. The higher rainy season mean value of 43.24 ± 6.15 mg/kg relative to the lower dry season mean value of 35.49 ± 1.31 mg/kg observed could be attributed to leaching effects through surface runoff that probably mobilized Cr containing materials into the river sediments during the rainy season period.

For Cu, the monthly mean level ranged from 14.39 ± 2.60 mg/kg in May (rainy season) to 22.87 ± 3.76 mg/kg in February (dry season). These values were higher than the 4.7 mg/kg obtained for sediments from River Wiwi in Ghana (Biney and Beeko, 1991) or 5.1 - 21.9 mg/kg obtained in the sediments from Trinidad and Venezuela (Rojas de Astudillo *et al.*, 2005), but lower than 85.6 mg/kg recorded for River Nile Estuary in Egypt (Saad and Fahmy, 1985). The anthropogenic input could not be said to be very serious considering the fact that the background Cu concentration range in an unpolluted soil is 5-30 mg/kg (Pais and Jones, 1997) while the value in an unpolluted sediment is 33 mg/kg (GESAMP, 1982). There was no significantly difference (at $p \leq 0.05$) between dry season average concentration of Cu, 19.47 ± 3.68 mg/kg, and that of the rainy season average of 16.02 ± 2.11 mg/kg. The implication of this is that the levels of Cu in the sediments were more attributable to lithogenic effects rather than anthropogenic factors. However, future slow build up of Cu in the sediments and along the food chains in the consumers of products from this aquatic environment cannot be ignored.

The monthly mean levels of Fe in the river sediments ranged from 36.12 ± 1.44 mg/kg in June to 46.58 ± 4.87 mg/kg in February while the rainy season mean value was 36.90 ± 2.52 mg/kg and the dry season mean value was 44.39 ± 4.27 mg/kg. These values were higher than 0.46 mg/kg and 20.7 mg/kg of Fe levels in sediments obtained respectively by Saad and Fahmy (1985) and Kakulu and Osibanjo (1988) for River Nile Estuary, Egypt and Niger Delta, Nigeria respectively. The values were, however, comparable to the value (41.0 mg/kg) in unpolluted sediments (GESAMP, 1982).

Monthly mean values of Mn ranged from 12.83 ± 0.25 mg/kg in August to 30.57 ± 1.16 mg/kg in January while the mean level for rainy season was 14.36 ± 2.12 mg/kg and for dry season, the mean level was 24.27 ± 5.911 mg/kg. The values were generally higher than 0.256 - 0.389 mg/kg levels recorded for Mn in coal and sediments from River Ekulu in Enugu (Adaikpoh, 2005) but lower than the usual background levels (200 - 3000 mg/kg) in unpolluted soils and those reported elsewhere in which the Mn level for Swartkops estuary sediment was measured to be 114.9 mg/kg (Binning and Baird, 2001). Again, the sources of Mn in the sediment in this study might likely be more of geochemical than anthropogenic. In certain quantities, Mn is an essential metal in both plants and animals. The deficiency and accumulation of large concentrations of manganese can have repercussions on the central nervous system of humans (Crossgrove and Yokel, 2004), and hence, its environmental monitoring is as important as those of the other metals.

Nickel had monthly mean ranged values of 2.42 ± 0.76 mg/kg in August and 5.44 ± 1.86 mg/kg in May with rainy season mean level of 3.75 ± 1.67 mg/kg and dry season mean value of 4.56 ± 1.21 mg/kg. The values fell below the normal background range of 30 - 40 mg/kg in unpolluted soils (Pais and Jones, 1997). They were however, higher than the 0.401mg/kg obtained by Awofolu *et a*l. (2005) for River Tyume, or the 0.064 - 0.067 mg/kg Ni levels measured in coal and sediments from River Ekulu in Enugu, Nigeria (Adaikpoh *et al.*, 2005) but comparable to the 4.7 - 24.1 mg/kg Ni obtained for sediments from Trinidad and Venezuela (Rojas de Astudillo *et al.*, 2005). Agricultural fertilizers, especially phosphates, have been identified as a significant source of nickel in soil (McGrath, 1995) in addition to weathering of the parent rocks rich in Ni. Thus, the Ni levels in the sediments could be attributed to agricultural runoff from the adjacent farm lands, on one hand, and to lithogenic inputs, on the other hand. Above certain threshold levels, Ni can cause allergic skin reactions in sensitized individuals following either dermal or oral exposure (Environment Agency, 2009).

In this study, the monthly mean levels of Pb varied from 24.30 ± 5.23 mg/kg in May to 44.23 ± 1.69 mg/kg in December and the its seasonal mean level of 27.96 ± 5.37 mg/kg in rainy season was significantly lower (at $p \leq 0.05$) than its 39.97 ± 7.50 mg/kg mean level in dry season. This could be because of fewer fluxes of lead-bearing suspended particles which had settled as part of the sediments during the dry season. The Pb levels were similar to the 32.9 mg/kg value of Binning and Baird (2001), but significantly higher (at $p \leq 0.05$) than the 0.042 mg/kg value of Awofolu *et al*. (2005) or the 19 mg/kg Pb level for unpolluted sediments (GESAMP, 1982). Obviously, the Pb levels could be ascribed more to anthropogenic effects than to lithogenic factors. While soil affected or ammended by this sediment may not be harmful for planting crops such as pepper and tomatoes which are known to bioconcentrate Pb to a less extent, broad-leaf vegetables and root crops should be propagated on this soil with caution as they easily bioconcentrate Pb substantially. Pb is a highly toxic naturally occurring metal and too much of it in the human body can cause damage to the brain, kidneys, nervous system and red blood cells.

The geochemical background values of V in average shale and unpolluted soils were given as 20 mg/kg and 100-1000 mg/kg respectively (Turekian and Wadepohl, 1961; Pais and Jones, 1997). The values in this study, ranging from 8.33 ± 0.87 mg/kg in August to 12.54 ± 2.07mg/kg in July, were quite lower than the background values earlier reported. Thus, it could be presumed that the source of V in the sediment was majorly geochemical especially that the seasonal levels of 10.75 ± 2.04 mg/kg (rainy season) and 10.65 ± 1.14 mg/kg (dry season) showed no significant difference (at $p \leq 0.05$) from one another. Anthropogenic sources as secondary sources could not be ruled out altogether since there had been no earlier reports to indicate previous levels of V, vis-à-vis other metals in the sediment. Vanadium occurs naturally in fuel oils and coal and is found in many petroleum products. As a result, increases in anthropogenic vanadium emissions due to the combustion of fossil fuels, now equal natural emissions from continental dust, marine aerosols, and volcanic activity [Irwin *et al.,* 1997]. It is also a by-product of petroleum refining. Vanadium and its compounds are toxic; its toxicity depends on the valence and it increases with increasing valence, with pentavalent vanadium being most toxic [van Zinderen Bakker and Jaworski, 1980]. It has been reported that higher plants do not bioaccumulate V to any significant degree [Welch and Cary, 1975; Cary *et al*., 1983] and that on the average, plants in general have a soil bioconcentration factor (BCF) of 0.1 for vanadium [van Zinderen Bakker and Jaworski, 1980; WHO, 1988]. Hence, from the point of view of V levels in the sediments of the study area, the aquatic environment of the farmland appeared to be safe for food crop propagation.

For Zn, the monthly mean levels in the river sediment ranged from 12.64 ± 1.00 mg/kg in August to 24.56 ± 3.26 mg/kg in January. The rainy season mean level was 14.63 ± 2.60 mg/kg while the dry season mean level was 21.14 ± 4.49 mg/kg. Although these values were closely comparable with the 20 mg/kg level of Zn in average shale (Turekian and Wadepohl, 1961), they were quite lower than the 70 mg/kg reported for unpolluted sediments (GESAMP, 1982) or the 62 mg/kg value obtained for the sediments from Niger Delta, Nigeria (Kakulu and Osibanjo, 1988). The values were also lower than the 35.9 mg/kg recorded by Binning and Baird (2001) for Swartkops estuary. Despite these observations, it still could be inferred that both geochemical and anthropological factors would have contributed to Zn levels in the river sediment considering the fact that Zn level in unpolluted soils is normally between 10 mg/kg and 300 mg/kg; the values obtained being above the lower limit.

Currently, Nigeria has no established sediment quality guidelines. As a result, the US National Oceanic and Atmospheric Administration (NOAA) Effect Range-Low (ERL) and Canadian Sediment Quality (CSQ) Threshold Effects Level (TEL) guidelines stated by Rojas de Astudillo *et al*. (2005) were used as interim measures to assess whether the concentrations of heavy metals in sediments could have adverse biological impacts. The ERL and TEL for a given sediment parameter are the concentrations above which adverse biological effects are expected to occur (Long *et al*., 1995). Results of heavy metal concentrations showed that Cd at all sites sampled for both seasons occurred at concentration levels greater than the 1.2 mg/kg ERL or 0.7 mg/kg

TEL levels indicating that the existing concentrations of Cd in all the sites were sufficiently high to cause adverse biological effects to the aquatic biota. Similarly, Pb concentrations were only greater than the 30.2 mg/kg TEL value in June during the rainy season, but greater than the TEL value throughout the dry season. The existing concentrations of Pb were, however, less than the 46.7 mg/kg ERL value during both seasons.

The pollution status of the sediments was assessed using the geoaccumulation index (I-geo). The I-geo was originally used by Muller (1969) to assess the pollution status of the Rhine River sediments. It was computed from the relationship:

$$\textbf{I-geo} = \log_2 [C_n/1.5B_n],$$

where Cn is the measured total metal concentration in soil; B_n is the background value;
and 1.5 is the background matrix correction factor due to lithogenic effects.

During the two seasons, the calculated I-geo values presented in Table 5 indicated that the river sediment was practically unpolluted with respect to CO, Fe, Mn, Ni, V and Zn; moderately polluted with respect to Cr, Cu and Pb; and heavily polluted/very heavily polluted with respect to As and Cd. Undoubtedly, the river sediment had experienced elevated heavy metals anthropogenic inputs in addition to lithogenic inputs when metals like Cr, Cu, Pb, As and Cd are considered.

In Table 6, the correlation coefficients of the metals within the river sediment are presented. Significant positive correlations existed for As and Co, As and Cu, As and Fe, As and Mn, As and Pb, As and Zn, Cd and Pb, Co and Pb, Cu and Fe, Cu and Mn, Cu and Zn, Fe and Mn, Fe and Zn, Mn and Pb, Mn and Zn, and Ni and V. The positive correlation therefore suggests common sources for these metals. It also implies that metals that are positively correlated might displace each other in their ecological functions within the environment where they existed. Also, significant negative correlations existed for As and Cr, Cr and Mn, Cr and Pb, and Cr and Zn. The negative correlations showed that there is antagonism in the association of these metals, hence the correlation in the opposite directions.

Levels of Heavy Metals in River Water

Rainy and dry seasons' levels of heavy metals in the river water are presented in Tables 7 and 8 respectively. On a monthly basis, the mean levels (µg/L) of As ranged from 2.69 ± 0.56 in July to 3.54 ± 0.38 in February. The rainy season mean was 3.02 ± 0.72µg/L while the dry season mean was 3.12 ± 0.64µg/L. These values were quite lower than the concentration levels of As with a range of between 0.70 and 5.5 mg/L in the water of a contaminated lake (Wegman and Greve, 1980). The values of As obtained in this study were below the maximum contaminant levels of As in fresh water (EEC, 1980; USEPA, 2005; SON, 2007). The future possible bioaccumulation of As in the tissues of those who use the river water for long-term domestic purposes, may however, be of concern because of bio-magnification.

Table 5: The Geo-accumulation Index (*I-geo*) Values in River Sediments

Element	**C_n**		**B_n**	**I-geo**		**Class**		**Pollution Intensity (PI)**	
	Rainy season	**Dry season**		**Rainy season**	**Dry season**	**Rainy season**	**Dry season**	**Rainy season**	**Dry season**
As	12.38	55.35	1.0	3.04	5.21	3	6	MP-HP	VHP
Cd	3.39	5.54	0.035	6.01	6.72	6	6	VHP	VHP
Co	7.42	9.27	10.0	-1.03	-6.90	0	0	PU	PU
Cr	43.24	35.49	11	1.39	1.10	2	2	MP	MP
Cu	16.01	19.47	4	1.42	1.70	2	2	MP	MP
Fe	36.91	44.39	3800	-7.27	-6.97	0	0	PU	PU
Mn	14.36	24.27	200	-4.38	-3.63	0	0	PU	PU
Ni	3.75	4.56	20	-3.00	-2.71	0	0	PU	PU
Pb	27.97	39.98	9	1.05	1.57	2	2	MP	MP
V	10.75	10.65	20	-1.47	-1.47	0	0	PU	PU
Zn	14.63	21.15	20	-1.03	-4.94	0	0	PU	PU

Table 6: Matrix of Correlation Coefficient of Metals in the River Sediments

	As	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
As	1.00										
Cd	- 0.06	1.00									
Co	**0.54***	- 0.05	1.00								
Cr	**-0.69***	0.14	- 0.39	1.00							
Cu	**0.53***	0.11	- 0.06	- 0.40	1.00						
Fe	**0.53***	0.36	0.19	- 0.31	**0.62***	1.00					
Mn	**0.93***	- 0.02	**0.40***	**-0.53***	**0.59***	**0.51***	1.00				
Ni	0.24	0.23	0.09	0.16	0.10	0.20	0.34	1.00			
Pb	**0.54***	**0.40***	**0.54***	**-0.43***	0.22	0.35	**0.42***	0.16	1.00		
V	0.10	- 0.14	0.02	0.12	0.02	- 0.19	0.18	**0.48***	0.02	1.00	
Zn	**0.85***	0.03	0.33	**-0.59***	**0.46***	**0.62***	**0.82***	0.37	0.38	0.20	1.00

*** Correlation is significant at 0.05 level (n=24)**

Mean Cd levels (µg/L) on monthly basis ranged from 6.35 ± 2.06 in May to 23.91 ± 6.01 in February. The seasonal means were 8.08 ± 2.66µg/L for rainy season and 15.19 ± 8.73µg/L for dry season. The values far exceeded the recommended 2.0 µg/L acute contaminant level or 0.25 µg/L chronic contaminant level (USEPA, 2005) and 5 µg/L maximum contaminant level (EEC, 1980; WHO, 1993) or 3µg/L level of SON (2007). It goes without saying that the levels of Cd in the river water poses serious health problems for both the aquatic ecosystem and the humans who use the water from time to time for both domestic and agricultural purposes. For Co, the monthly mean concentration ranged from 1.30 ± 0.13 µg/L in May to 5.18 ± 1.93 µg/L in August while the rainy season mean level was 3.07 ± 1.95 µg/L and dry season mean level was 3.09 ± 1.65 µg/L. Obviously, there was no significant difference between the rainy season and dry season levels of Co in the river water indicating little or no short-term anthropogenic input. Compared with the 0.1-15.7 µg/L levels of Co obtained by FOREGS- Euro Geo Surveys for stream water (GESAMP, 1982), it can be concluded that the stream water was not so heavily

Table 7: Rainy Season Mean Levels of Heavy Metals in River Water

Month	**Concentration of Elements (mg/L)**										
	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
May 2004	2.98 ±0.43	6.35 ±0. 06	1.30 ± 0.13	36.68 ± 8.02	4.07 ± 1.50	164.00 ±27.18	83.14 ±16.68	3.74 ± 0.56	35.82 ±14.88	20.28 ±5.09	70.22 ± 1.62
June 2004	3.05 ± 0.52	7.87 ±0.81	4.09 ± 1.25	12.62 ± 2.83	4.24 ± 0.84	196.08 ± 4.34	92.02 ± 0.97	3.64 ± 0.99	16.72 ±1.46	17.28 ± 5.97	87.89 ± 14.86
July 2004	2.69 ± 0.56	8.15 ±4.41	1.72 ± 0.10	14.31 ± 4.01	12.86 ± 1.80	164.75 ±19.72	86.23 ±10.75	4.01 ± 1.37	14.24 ± 0.67	17.08 ± 3.28	108.34 ± 25.49
August 2004	3.39 ± 1.30	9.96 ± 2.18	5.18 ± 1.93	16.86 ± 3.10	14.39 ± 3.25	193.13 +2.55	96.74 ± 5.77	6.45 ± 1.00	23.43 ± 9.98	16.51 ± 3.72	93.19 ± 26.01
Range	2.69- 3.39	6.35- 9.96	1.30- 5.18	12.62- 36.68	4.07- 14.39	164.00- 196.08	83.14- 96.74	3.64- 6.45	14.24- 35.82	16.51- 20.28	70.22- 108.34
Seasonal mean ± s.d.	**3.02 ±0.72**	**8.08 ±2.66**	**3.07 ±1.95**	**20. 12 ±19.26**	**8.89 ±5.28**	**179.49 ±21.45**	**89. 53 ±13. 70**	**4.46 ±1.49**	**22. 55 ±11. 73**	**17.79 ±4.24**	**89.91 ±22. 01**

* Values = mean of triplicate determinations **±** s.d.

Table 8: Dry Season Mean Levels of Heavy Metals in River Water

Month	**Concentration of Elements (mg/L)**										
	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Nov 2004	3.36 ±0.68	7.76 ±1.43	4.92 ±2.04	23.74 ±4.44	16.97 ±2.50	290.76 ±99.50	135.32 ±52.81	6.63 ±1.79	25.46 ±8.50	16.83 ±1.66	89.55 ±15.79
Dec 2004	2.83 ±0.53	7.53 ±1.27	1.83 ±0.93	27.81 ±6.43	17.11 ±2.58	275.88 ±18.71	193.20 ±5.62	5.42 ±1.02	32.49 ±15.01	12.67 ±1.78	109.00 ±6.08
Jan 2005	2.74 ±0.80	21.55 ±5.83	2.20 ±0.17	55.41 ±2.23	16.58 ±2.32	288.59 ±53.17	188.29 ±13.93	5.01 ±1.56	25.81 ±10.71	16.56 ±2.45	113.67 ±16.22
Feb 2005	3.54 ±0.38	23.91 ±6.01	3.39 ±1.08	94.61 ±3.37	16.04 ±4.49	260.41 ±24.69	164.98 ±54.44	5.92 ±2.98	31.51 ±4.62	19.40 ±1.62	124.17 ±17.45
Range	2.74- 3.54	7.53- 23.91	1.83- 4.92	23.74- 94.61	16.04- 17.11	260.41- 290.76	135.32- 193.20	5.01- 6.63	25.46- 32.49	12.67- 19.40	89.55- 124.17
Seasonal mean ± s.d.	**3.12 ±0.64**	**15.19 ±8. 73**	**3. 09 ±1.65**	**50.39 ±29.78**	**16.67 ±2.68**	**278.81 ±51. 59**	**169. 70 ±40.41**	**5.76 ±1. 84**	**29.57 ±9. 32**	**16.36 ±2. 99**	**109.10 ±18.08**

* Values = mean of triplicate determinations ± s.d.

polluted with Co. The values of Co in this study were also lower than the 0.059 mg/L (59µg/L) obtained by Awofolu *et al*. (2005) for Tyume River in South Africa.

The monthly mean levels (µg/L) of Cr ranged from 12.62 ± 2.83 in June to 94.61 ± 3.37 in February; the rainy season mean concentration was 20.12 ± 19.26µg/L while the dry season mean concentration was 50. 39 ± 29.78 µg/L. These values were higher than the 16 µg/L and 11 µg/L values stipulated by the USEPA (2005) as maximum contaminant level (MCL) for acute contaminant level (ACL) and chronic contaminant level (CCL) respectively or the SON standard level of 50 µg/L. They were also higher than the < 0.001 - 43.0 µg/L given as the range of Cr in stream water by FOREGS- Euro Geo Surveys. It is no contradictory to infer that the stream water appeared polluted with respect to Cr. Monthly variations of Cu in the river water gave a mean range of 4. 06 ± 1.50 µg/L in May to 17.11 ± 2.58µg/L in December while the seasonal variations gave a rainy season mean of 8.89 ± 5.28µg/L and a dry season mean of 16.67 ± 2.68 µg/L. These values were either comparable to or higher than the 13 µg/L or 9.0µg/L, the ACL and CCL respectively set as the MCL by USEPA (2005). The values were however, lower than 0.383 µg/L obtained for Tyume River (Awofolu *et a*l., 2005). The values were clearly lower than the MCL of 2.0µg/L in drinking water (WHO, 1993) implying that the water may be free from copper induced health problems for the humans relying on the water from this river for agricultural and domestic purposes.

The monthly mean values of Fe ranged from 164.00 ± 27.13 µg/L in May to 290.76 ± 99.50 µg//L in November. The rainy season had a mean level of 179.49 ± 21.45 µg/L of Fe while the dry season mean level was 278.81 ± 51.59 µg/L. Although these values were below the 1.0 mg/L WHO maximum permissible value of Fe for drinking water, they were higher than the 0.1mg/L WHO highest desirable level for water meant for drinking (Fatoki *et al*., 2002) but comparable with the 200 µg/L MCL in fresh water set by EEC (1980). Some levels of caution must be exercised with respect to its Fe content before the water can be considered for domestic uses. Mean values of Mn, on monthly basis, ranged from 83.14 ± 16.86 µg/L in May to 193.20 ± 5.62 µg/L in December. The seasonal mean levels were 89.53 ± 13.70 µg/L for rainy season and 169.70 ± 40.41µg/L for dry season. All the rainy season values were only slightly lower than the MCL of 100µg/L (USEPA, 1975; 1979) while all the dry season monthly values were found to be higher than the MCL. The limit of Mn in water meant for aquatic ecosystem use is 0.18mg/L (DWAF, 1996) and WHO provisional guideline value for drinking water is 0.5mg/L (WHO, 2002). These two limits were not exceeded in most cases. However, possibility of future bioaccumulation in the biota is a cause for concern as this may lead to manganese toxicity. In humans, manganese toxicity represents a serious health hazard resulting in severe pathologies of the central nervous system (CNS).

The monthly mean concentration of Ni ranged from 3.64 ± 0.99 µg/L in June to 6.63 ± 1.79 µg/L in November. The rainy season mean level was 4.46 ± 1.49 µg/L while the dry season mean level was 5.76 ± 1.8 µg/L. These values were below the 50 µg/L maximum contaminant level of Ni in fresh water (EEC, 1980) and the 20 µg/L Ni level of maximum allowable concentration in drinking water (WHO, 2002). Nevertheless, because Ni can be extremely toxic to man even at low concentrations in domestic water supply when consumed (Stoepper, 1991) and cause mutagenic, carcinogenic and tetraogenic effects (Fishbein, 1987), there is the need for its near total removal in water meant for domestic purposes. The monthly mean levels of Pb in the river water ranged between 14.24 ± 3.67 µg/L in July to 35.82 ± 14.88 µg/L in May while the rainy season mean was 22.55 ± 11.73 µg/L and the dry season mean was 29.52 ± 9.32 µg/L. These values were generally above the 10 µg/L and 15µg/L being the WHO recommend maximum allowable and maximum contaminant levels respectively (WHO, 2002). It is thus imperative to have the water properly treated before being used for domestic and agricultural purposes.

Vanadium consumption has been implicated for serious health problems including nervous depression and kidney damage (Barceloux, 1999). The monthly mean levels of V in river water in this study ranged from 12.67 ± 1.78µg/L in December to 20.28 ± 5.09 µg/L in May. For rainy season, the mean level was 17.79 ± 4.25µg/L while in the dry season the mean was 16.36 ± 2.99 µg/L. Natural sources of V release to water include wet and dry deposition, soil erosion and leaching from rocks and soils. The largest amount of V release occurs naturally through water erosion of land surfaces. It has been estimated that approximately 32 300 tons of V are dissolved and transported to the oceans by water, and an additional 306 650 tons are thought to be transported in the form of particulate and suspended sediment (Van Zinderen and Jaworski, 1980).

The monthly level of Zn in the river water ranged between 70.22 ± 1.62 µg/L in May to 124.17 ± 17.45 µg/L in February while the rainy season mean concentration was 89.91 ± 22.01µg/L and dry season mean concentration was 109.10 ± 18.08 µg/L. These values fell below the 5mg/L highest desirable level of Zn in drinking water (WHO, 1984; Ogunfowokan *et a*l., 2006) but the levels far exceeded the 20 µg/L Zn level for water meant for aquatic ecosystem (Fatoki *et al*., 2002; Ogunfowokan *et a*l., 2006). Thus, while the water from the river might not pose Zn related health problems for now, the same cannot be said of aquatic biota.

The two-tailed correlation coefficients of metals in the river water, at 0.05 level of significance (for n = 24), showed significant positive correlations for Cr/Cd, Cu/Cd, Fe/Cd, Fe/Cu, Mn/Cd, Mn/Cr, Mn/Cu, Mn/Fe, Ni/Fe, Ni/Mn, Pb/Cr, Pb/Mn, Zn/Cd, Zn/Cu, Zn/Mn and significant negative correlation for V/Cu only. The metals with high positive correlations might have been contributed to the environmental matrices via similar factors.

On a general note, the dry season mean levels of the heavy metals were higher, in most cases, than the rainy season mean levels in both the sediments and water samples of the river (Tables 3, 4, 7 and 8). This could be attributed to more gentle flow of the river during the dry season coupled with conditions of low dissolved oxygen when temperatures are slightly heightened during the dry season in which case most of the metal-bearing suspended particles had settled to form part of the sediments. Likewise, water volume had reduced during the dry season making the dissolved metals to be at higher concentration levels in the liquid phase.

Coefficient of variation (CV) is a useful statistical tool that can be employed to interpret the temporal and spatial distribution and variability patterns of pollutants in an environmental matrix. The CV values of the heavy metals in the sediment samples are given in Figure 2.

Table 9: Correlation Coefficients of Heavy Metals in River Water

	As	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
As	1.00										
Cd	0.16	1.00									
Co	0.06	- 0.01	1.00								
Cr	0.06	**0.71***	-0.11	1.00							
Cu	0.11	**0.41***	0.12	0.31	1.00						
Fe	0.29	**0.48***	0.16	0.32	**0.64***	1.00					
Mn	0.13	**0.53***	-0.11	**0.48***	**0.62***	**0.80***	1.00				
Ni	0.38	0.28	0.38	0.13	0.39	**0.59***	**0.45***	1.00			
Pb	-0.12	0.06	-0.09	**0.46***	0.02	0.15	**0.40***	0.05	1.00		
V	0.22	0.15	0.09	0.02	**-0.43***	- 0.21	- 0.29	0.16	-0.04	1.00	
Zn	0.05	**0.57***	-0.11	0.39	**0.60***	0.36	**0.45***	0.11	-0.15	- 0.22	1.00

*Correlation is significant at 0.05 level (n=24)

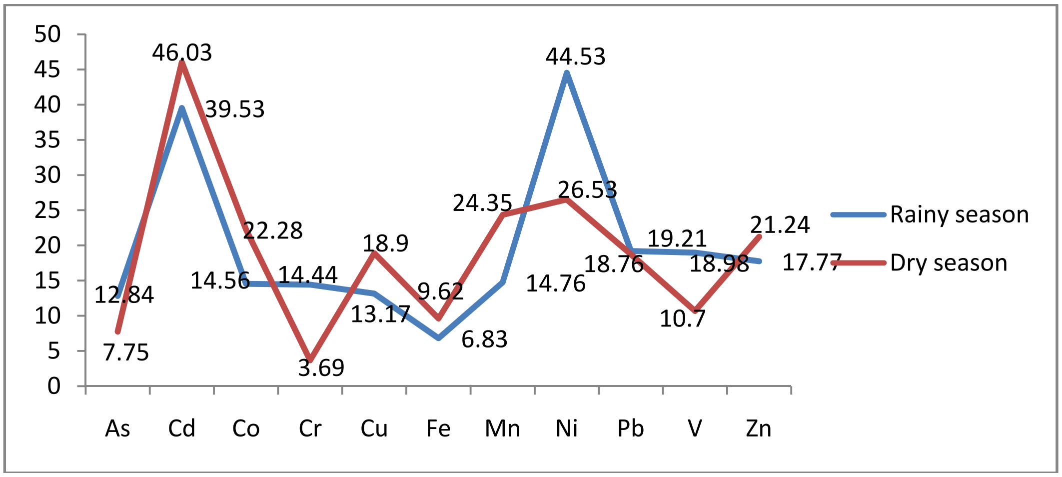

Figure 2: Coefficient of Variation of Heavy Metals in River Sediments

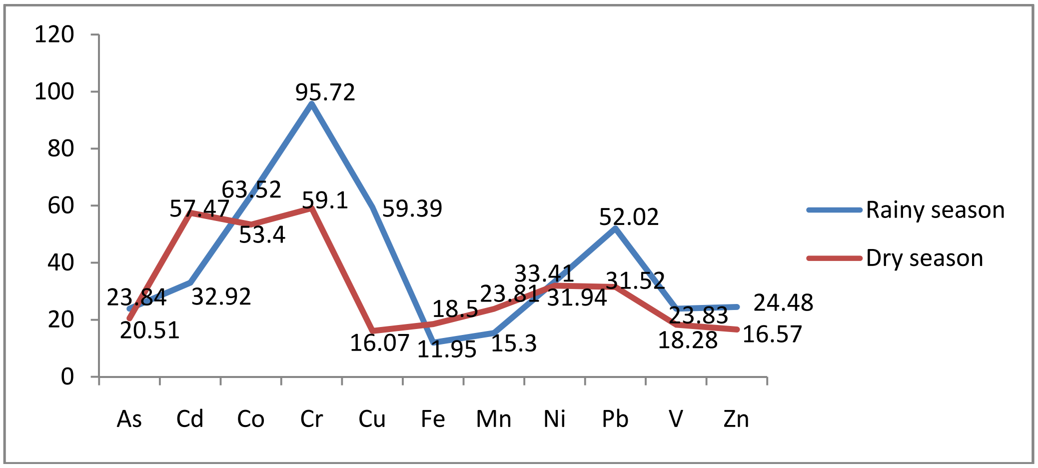

Figure 3: Coefficient of Variation of Heavy Metals in River Water

The distribution of heavy metals in the river sediment varied widely during both seasons; both the temporal and spatial distributions showed pronounced differences for Cr, Cu, Mn, Ni, V and Zn. Related trends of variability were observed for As, Cd, Co and Cr on one hand, and Fe, Mn, Ni, Pb and V on the other. The implication is that metals with related trends of variability were similarly introduced into the environmental matrix and their distributions were governed by similar factors. In the river water, the CV revealed that for both spatial and temporal distribution, only As, Ni and V had closely related patterns of distribution; the other metals were markedly differently distributed during both seasons.

Conclusion

This paper established that the river sediment was moderately polluted with respect to Cr, Cu and Pb, and was either heavily polluted or very heavily polluted with respect to As and Cd. Metal levels in the river water, in many cases, were also above the specified guideline limits for natural waters. Serious cation must therefore be exercised in using the sediments or water from this river for continuous agricultural practices as the levels of toxic heavy metals within the aquatic environment was on a high side. A follow up investigation is recommended to determine the extent to which some of the biotic species including fish and food crops from the vicinity of the study area have been affected by the status of the river.

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