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Source Apportionment of Heavy Metals in Utility Water Sources

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ABSTRACT

Heavy metals cause cancer and non-cancer health effects in humans when consumed via drinking water. Therefore, the importance of assessing the levels and sources of heavy metals in utility water sources, with a view to proffering mitigation measures, cannot be overemphasized as not all toxic metals can be removed by conventional water treatment processes. A total of 40 composite water samples were randomly collected from utility dams and their feeding rivers from January, 2010 to December, 2011. The concentrations of metals were determined by atomic absorption spectrometry and were found to vary with season. The concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (mg L^{-1}) in the water sources ranged from 0.02 to 0.49, 0.01 to 0.17, 0.03 to 0.38, 0.09 to 0.48, 0.17 to 3.25, 0.05 to 0.34, 0.02 to 0.33, 0.13 to 0.61 and 0.09 to 1.07, respectively, in the dry season, and from 0.08 to 0.68, 0.02 to 0.58, 0.13 to 0.87, 0.02 to 0.69, 0.28 to 5.62, 0.31 to 1.28, 0.09 to 1.08, 0.23 to 1.98 and 0.26 to 1.59, respectively, in the wet season, indicating that the concentrations of Cd, Cr, Fe, Ni, and Pb exceed regulatory limits in both seasons. Furthermore, the result of principal component analysis on absolute principal component scores (PCA/APCS) used to apportion sources to the metals in the dams and rivers revealed two major anthropogenic sources accounting for over 90% of the metals. Source 1 represents anthropogenic release from small-scale entrepreneurial enterprises, such as automobile-mechanic, panel beaters, vehicle sprayers and battery recharger workshops generating and spilling wastes such as lubricating oil, grease, petrol, diesel, battery electrolytes, contributing 96.2, 99.2, 95.9, 100, 99.4, 99.9, 100 and 95.2%, of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively, while source 2 represents the release from agricultural activities, such as from fertilizers and fungicides and contributes 63.2, 100 and 51.6% of Cd, Co and Cr, respectively.

Keywords: dams, human health risks, municipal supplies, rivers, treatment process

INTRODUCTION

The Ibadan metropolis is supplied with treated water by the Asejire and Eleyele water treatment utilities. These water utilities sustain many households (ADB 2009) and factories within the metropolis. The utilities get raw water from their dams, which are continuously furnished with water from the Osun/Iwo and Ona/Apete rivers respectively. Field survey revealed anthropogenic activities that may introduce heavy metals into these water sources. Also, several studies conducted in the metropolis reported high levels of inorganic contaminants in different environmental media (Adebisi *et al*. 2007; Adekunle *et al*. 2007; Ipinmoroti *et al*. 2007; Ajayi *et al*. 2008; Dawodu and Ipeaiyeda 2008; Ipeaiyeda and Onianwa 2009; Adebisi and Fayemiwo 2010; Ogedengbe and Akinbile 2010; Alao *et al*. 2010; Olusegun 2010; Pepple and Nweinewi 2011; Adelekan and Alawole 2011).

Heavy metals are known to cause cancer and non-cancer systemic health effects in humans when consumed (USEPA 2010). For instance, high rates of breast cancer amongst Nigerian females have been attributed to Cd and Pb poisoning, via intake of contaminated water (Alatise and Schrauzer 2010). Also, over 300 children under the ages of 5 years in two gold mining villages in the Northern Nigeria were reported to have died of Pb poisoning from exposure to contaminated water and soils (Punch Newspaper 2010). Therefore, the objectives of this study, is to assess the levels of toxic metals in water sources used by municipal water treatment utilities supplying water to the Ibadan metropolis, and also apportion sources to the metals. The findings from this study are expected to serve as a springboard for source water protection and improvement of the quality of municipal water supplies.

MATERIALS AND METHODS

Site description and sampling

The study site is the Ibadan metropolis, in Oyo State, South-Western Nigeria. The description of the metropolis is available elsewhere (Ajayi *et al*. 2008; Ogedengbe and Akinbile 2010).

A total of 40 composite water samples were collected from the utility water sources viz. Asejire dam (ADW), Eleyele dam (EDW), Iwo (Osun) river (IRW) and Apete (Ona) river (ARW), from January 2010 to December 2011. The sampling method is consistent with that described by Riccardi *et al*. (2008).

Preservation of samples

Nitric acid was added to the water samples to a pH < 2, in order to fix the metals in the water (Adewuyi *et al*. 2011). Samples were preserved in an ice chest before transporting to the laboratory for analysis.

Chemicals and reagents

Analytical grade reagents were used. Nitric acid (HNO_3) and the metal standards solutions were purchased from Sigma-Aldrich, Fluka, Switzerland, while the deionized water was purchased from the International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria.

Heavy metals: digestion method

Nitric acid digestion of water samples was done following standard procedures (Adewuyi *et al*. 2011; Etchie *et al*. 2012a). To ensure the removal of organic impurities from the samples and thus prevent interference in analysis, the samples were digested with concentrated nitric acid. 5 ml of the concentrated nitric acid

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was added to 5 ml of the water samples and the mixture evaporated on a hot plate to a final volume of about 3 ml. Another 5 ml of concentrated HNO_3 was added to the mixture and refluxed for 30 min, after which the mixture was heated on hot plate while the concentrated HNO_3 was added until the mixture was light colored. The resulting sample was filtered and the filtrate made up to 25 ml with deionized water before analysis.

Heavy metals analysis

The digests were analyzed for trace metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) using AAnalyst 200 and Buck Scientific 210VGP.s Flame Atomic Absorption Spectrophotometers. The instruments' setting and operational conditions were done in accordance with the manufacturers' specifications.

Quality assurance and quality control

Two replicates of the homogenized filtered water samples were subjected to recovery studies by spiking samples with metals standards of about the same concentrations with the analytes of interest. The spiked samples were then digested and analyzed. The metals' recoveries ranged from 76 to 91%. Also, each digestion and analysis procedure was done in triplicates in order to ensure precision of results. A blank was run for each digestion procedure to correct the measurements and to check all reagents and procedure for interferences and cross contamination (Etchie *et al.* 2012a).

Source apportionment

Principal component analysis on absolute principal component scores (PCA/APCS) was used to apportion sources to the metals. To apply the PCA, a spearman's correlation matrix was first prepared using all 9 selected trace metals; Cd, Co, Cr, Cu, Fe, Mn Ni, Pb and Zn. SPSS 17.0 was used to extract the components using ones as prior communality estimates and this was followed by a varimax (orthogonal) rotation. Components which displayed eigenvalues greater than 1 and factor loading of 0.5 or greater (Ravindra *et al.* 2008) were retained. The contribution of the different sources identified by the PCA after varimax rotation was then determined by performing multiple linear regression on the absolute principal component (scaled) scores.

RESULTS AND DISCUSSION

The results of analysis of water samples collected from the utility water sources in dry and wet seasons is presented in **Table 1**, while **Table 2** has the correlation matrix of metals in both seasons. **Table 3** shows the components' loadings above 0.5 and their percentage contribution.

From the result (**Table 1**), it could be seen that the levels of Cd, Cr, Fe, Ni and Pb in the utility dams (ADW and EDW) and the feeding rivers (IRW and ARW) exceed regulatory limits in all seasons, whereas Co and Mn levels only exceed regulatory limits in wet season. In spite of this, Cu and Zn levels in the water sources are within safe limits in all seasons. Though heavy metals are present in unpolluted rivers and dams, the concentrations are usually below regulatory limits. However, anthropogenic release can result in high concentrations of metals relative to normal background levels (Adelekan and Abegunde 2011). Also, high levels of toxic metals like Cd^{2+}, Cr^{6+} and Pb^{2+} in raw waters may be very difficult to remove by conventional water treatment process. Consequently, the metals remain in treated waters and exert toxic effects on exposed population, especially the children (Zeng *et al.* 2009).

The results also show that the metals levels in wet season are higher than in dry season. This is contrary to the observations of Batayneh (2010) and Etchie *et al.* (2012a). However, considering that in wet season, heavy rainfall may cause erosion and flooding, and trace metals from polluted soils and dump sites can be washed or leached into water bodies, thus increasing metals' levels in wet season than in dry. Furthermore, the reduction of metals in the dams, relative to the levels in the rivers, could be attributed to absorption by trees planted in the dams. According to ADB (2009), the tree planting is a strategy for reducing metals' load in the dams.

In addition, water treatment utilities in Nigeria generally increase their water supplies in wet season, so as to prevent flooding due to high water levels in dams. Also, since wet season in Nigeria is about 8 months, and dry season is about 4 months, there is a higher risk of exposure in wet season than in dry season. Similar studies (Adewuyi *et al.* 2012; Etchie *et al.* 2012b) conducted in the metropolis, to ascertain the levels and risks of heavy metals in the municipal water supplies of these water utilities reported high levels of Cd, Co, Cr^{6+} Mn and Pb in their treated waters, exceeding regulatory limits for drinking water. Consequently, the health risk assessment results revealed high cancer and non-cancer systemic chronic health risks to the consumers especially their children. Apart from the direct health effects exerted by Cd, Cr^{6+} and Pb on the human system (USEPA 2010), they also interact *in vivo* with selenium (Se), a nutritionally essential trace element whose anti-carcinogenic properties have been demonstrated in numerous animal tumor model systems. The interactions are part of natural metal detoxification processes, but result in the metabolic inactivation of Se and at sufficiently high expo-

Table 1 Levels of heavy metals (mg L^{-1}) (represented in range/mean) in the utilities' water sources.

Metals	Dry season				Wet season				MCLs (mg L^{-1})		
	ADW	EDW	IRW	ARW	ADW	EDW	IRW	ARW	NIS	US EPA	WHO
Cd	0.07 – 0.13 0.12	0.20 – 0.40 0.31	0.02 – 0.28 0.19	0.02 – 0.49 0.26	0.16 – 0.28 0.20	0.19 – 0.41 0.37	0.08 – 0.32 0.24	0.10 – 0.68 0.43	0.003	0.005	0.003
Co	0.04 – 0.10 0.06	0.01 – 0.07 0.03	0.03 – 0.12 0.09	0.01 – 0.17 0.05	0.15 – 0.29 0.20	0.06 – 0.22 0.18	0.07 – 0.58 0.37	0.02 – 0.39 0.24	NM	0.1	NM
Cr	0.14 – 0.25 0.20	0.16 – 0.29 0.21	0.03 – 0.32 0.18	0.09 – 0.38 0.29	0.26 – 0.47 0.32	0.28 – 0.51 0.39	0.15 – 0.63 0.41	0.13 – 0.87 0.59	0.05	0.1	0.05
Cu	0.09 – 0.16 0.11	0.12 – 0.25 0.15	0.09 – 0.28 0.17	0.15 – 0.48 0.29	0.18 – 0.36 0.25	0.15 – 0.41 0.34	0.22 – 0.54 0.33	0.02 – 0.69 0.42	1	1.3	2
Fe	0.36 – 0.68 0.47	0.52 – 0.90 0.58	0.17 – 3.25 1.09	0.33 – 3.05 1.81	0.48 – 1.80 0.89	0.96 – 2.96 1.34	0.39 – 3.54 2.23	0.28 – 5.62 3.21	0.3	0.3	NGL
Mn	0.09 – 0.22 0.14	0.10 – 0.22 0.16	0.05 – 0.34 0.23	0.05 – 0.34 0.21	0.39 – 0.72 0.45	0.31 – 0.91 0.52	0.42 – 1.09 0.66	0.55 – 1.28 0.87	0.2	0.3	0.4
Ni	0.07 – 0.17 0.11	0.08 – 0.21 0.13	0.02 – 0.33 0.15	0.04 – 0.29 0.17	0.16 – 0.38 0.21	0.18 – 0.39 0.25	0.09 – 0.78 0.36	0.10 – 1.08 0.46	0.02	0.1	0.07
Pb	0.16 – 0.25 0.18	0.18 – 0.36 0.21	0.13 – 0.45 0.24	0.25 – 0.61 0.32	0.48 – 0.72 0.55	0.34 – 1.02 0.62	0.23 – 0.97 0.62	0.29 – 1.98 0.74	0.01	0.015	0.01
Zn	0.20 – 0.37 0.24	0.22 – 0.45 0.34	0.09 – 0.59 0.39	0.23 – 1.07 0.66	0.33 – 0.69 0.46	0.32 – 0.53 0.44	0.29 – 1.18 0.64	0.26 – 1.59 0.81	3	5	NGL

Notes: ADW: Asejire's dam water; EDW: Eleyele's dam water; IRW: Iwo (Osun) river water; ARW: Apete (Ona) river water; MCL: maximum contaminants level; NGL: no guideline limit; NM: not mentioned. Reference: NIS, Nigerian Industrial Standard (2007); Gebrekidan and Samuel (2011); Etchie *et al.* (2012a, 2012b)

Table 2 Correlation matrix of metals.

	Metals	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Dry season										
Correlation	Cd	1.000	-0.644	0.425	0.467	0.295	0.182	0.467	0.434	0.477
	Co	-0.644	1.000	-0.442	-0.086	0.154	0.587	0.155	0.017	-0.076
	Cr	0.425	-0.442	1.000	0.873	0.767	0.181	0.641	0.814	0.861
	Cu	0.467	-0.086	0.873	1.000	0.971	0.635	0.933	0.993	1.000
	Fe	0.295	0.154	0.767	0.971	1.000	0.761	0.957	0.988	0.972
	Mn	0.182	0.587	0.181	0.635	0.761	1.000	0.860	0.718	0.652
	Ni	0.467	0.155	0.641	0.933	0.957	0.860	1.000	0.965	0.942
	Pb	0.434	0.017	0.814	0.993	0.988	0.718	0.965	1.000	0.995
	Zn	0.477	-0.076	0.861	1.000	0.972	0.652	0.942	0.995	1.000
Wet season										
Correlation	Cd	1.000	-0.300	0.813	0.897	0.637	0.665	0.599	0.864	0.502
	Co	-0.300	1.000	0.145	0.138	0.443	0.376	0.477	0.120	0.468
	Cr	0.813	0.145	1.000	0.953	0.951	0.970	0.938	0.993	0.910
	Cu	0.897	0.138	0.953	1.000	0.901	0.906	0.880	0.981	0.795
	Fe	0.637	0.443	0.951	0.901	1.000	0.997	0.999	0.935	0.974
	Mn	0.665	0.376	0.970	0.906	0.997	1.000	0.994	0.950	0.977
	Ni	0.599	0.477	0.938	0.880	0.999	0.994	1.000	0.917	0.981
	Pb	0.864	0.120	0.993	0.981	0.935	0.950	0.917	1.000	0.868
	Zn	0.502	0.468	0.910	0.795	0.974	0.977	0.981	0.868	1.000

Table 3 Components' loading above 0.5 and % contribution (R^2).

Metals	Dry season		R^2 (%)	Wet season		R^2 (%)
	Component 1	Component 2		Component 1	Component 2	
Cd		0.711	63.2	0.870		96.2
Co		-0.983	100		0.962	93.5
Cr	0.702	0.588	*51.6	0.993		99.2
Cu	0.957		98.9	0.979		95.9
Fe	0.991		98.3	0.929		100
Mn	0.827		88.5	0.946		99.4
Ni	0.986		97.4	0.911		99.9
Pb	0.984		99.6	1.000		100
Zn	0.962		99.3	0.863		95.2

*Adjusted R^2

sure levels may over time produce a state akin to Se deficiency. Mn also occurs in manganese superoxide dismutase (MnSOD), which exists in several genotypes of which some are believed to cause oxidative damage to DNA and increase breast cancer risk (Alatise and Schrauzer 2010). In addition, Cr, which is absorbed in its hexavalent state, is converted to the trivalent form in cells and forms tightly bound adducts with DNA and proteins, thus initiating the formation of cancer (Williams *et al*. 2000).

Also, information collected on the utility water treatment process show that the utilities use conventional water treatment process for water purification. The conventional process may involve the use of hydroxide salt to precipitate soluble metals from solution, so that the resulting insoluble hydroxide salts can then be removed by clarification process. This is not a suitable method for removing toxic metals especially Cr^{6+} Co, Mn and Pb from contaminated water. Cr^{6+} is not affected by hydroxide precipitation, while the theoretical solubilities of Co, Fe, Mn and Pb hydroxides in pure water at 25°C are 0.22, 0.89, 1.2 and 2.1 mg L^{-1}, respectively (EM 2001). Thus hydroxide precipitation of these metals may cause their levels in treated water to exceed regulatory limits for drinking purpose, so may only be suitable for wastewater treatment. Also, during water treatment process, aeration of water, and addition of Cl_2 as water disinfectant may increase the concentrations of toxic and soluble Cr^{6+} in the treated water, by oxidizing essential Cr^{3+} to the toxic Cr^{6+} in the water. These are some of the reasons that public water supplies in 42 States of the United States of America contain toxic levels of Cr^{6+}, and consequently, over 74 million Americans are chronically exposed (EWG 2011). Presently there is agitation and massive campaign for improved methods of Cr^{6+} removal, to be incorporated into water treatment process for municipal consumption. Technologies suggested to being effective in removing Cr^{6+}, and other toxic metals from waters meant for municipal consumption include: membrane filtration by nanofiltration and reverse osmosis anion exchange reduction followed by coagulation and precipitation, and adsorption (EWG 2011).

Furthermore, **Table 2** shows strong correlations among metals. This is an indication that the metals are likely to be from a common source. Also, the result of the PCA/APCS (**Table 3**) revealed two principal sources (components) accounting for about 92.1% and 97.7% of metals in dry and wet seasons respectively. Source 1 which consists of Cr, Cu, Fe, Mn, Ni, Pb and Zn, and Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in dry and wet seasons, respectively, represents anthropogenic release from automobile-mechanic workshops, panel beaters, vehicle sprayers and battery recharger workshops, and other related small scale enterprise around the rivers and dams that release waste containing heavy metals. This source releases about 51.6, 98.9, 98.3, 88.5, 97.4, 99.6 and 99.3% of Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively in dry season and 96.2, 99.2, 95.9, 100, 99.4, 99.9, 100 and 95.2%, of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively in wet season. Adelekan and Abegunde (2011) posited that there are over 50 automobile-mechanic villages in the metropolis and each of these villages contains conglomerates of workshops generating and spilling mixed wastes of lubricating oil, grease, petrol, diesels, battery electrolytes, paints and other materials containing heavy metals into bare soils and are washed into water bodies.

Source 2 contributes about 63.2, 100 and 51.6% of Cd, Co and Cr in dry season, and 93.5% of Co in wet season. This source represents anthropogenic release from agricultural activities. High levels of Cd and Co have been detected in phosphate fertilizers (WHO 2004; WHO 2006; Kumber 2011), while the use of Cr in the manufacture of fungicides has been documented (WHO 2003).

CONCLUSION

Water samples collected from utility source of raw water in Ibadan metropolis has shown high levels of Cd, Cr, Fe, Ni and Pb in all seasons, and Co and Mn in wet season, indicating contamination by heavy metals. Also, higher levels of metals were detected in wet season than in dry season, and this was attributed to inputs by surface run-offs from contaminated soils and dumpsites during heavy rainfall. PCA/APCS revealed two principal anthropogenic sources. The first source is from small scale entrepreneurial enterprises around the rivers and dams, and the second is from agricultural activities. The combined sources contribute about 92.1 and 97.7% of the total metals load in dry and wet seasons, respectively.

The bottom line is the raw water sources for water utilities in Oyo state are contaminated with heavy metals. This may reduce the quality of their treated water, which may in turn pose health threats to consumers, especially children. Therefore, there is need for source water protection. The utility should also consider shifting to other water sources, drawing less water from these contaminated sources. Furthermore, technologies which can effectively remove toxic metals like Cd^{2+}, Cr^{6+} and Pb^{2+} should be introduced, instead of the conventional water treatment process. The utilities should also monitor their treated water, to ensure compliance with regulatory standards. Cleaning up metals pollution has its costs, but ignoring it is not an option (EWG 2011).

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