

TRACE METAL LEVELS OF DRINKING WATER SOURCES IN PARTS OF OSUN STATE, NIGERIA

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Abstract

This study was carried out to investigate the portability of drinking water sources available to people in parts of Osun State, Nigeria, especially with respect to trace metal levels. The trace metal contents were determined over a period of six months covering both the rainy and dry seasons. Tap, well, stream and borehole water from five towns (Osogbo, Iwo, Ejigbo, Ile-Ife and Ilesha) in Osun State were analysed using Atomic Absorption Spectrophotometer. The concentrations of the metals analyzed range ($\mu\text{g/mL}$) as follows: Fe (0.18-0.30), Mn (0.33-0.37), Zn (0.11-0.14), Cu (0.05-1.0), Pb (0.01-0.03), Hg (Nd-0.03), As (Nd-0.03), Cd (Nd-0.04), Cr (0.02-0.05), and Ni (0.02-0.05) while the mean levels ($\mu\text{g/mL}$) were of the order: Hg (0.01) < Pb (0.02) = As (0.02) = Cd (0.02) < Ni (0.03) < Cr (0.04) < Cu (0.08) < Zn (0.13) < Fe (0.25) < Mn (0.36). The results indicated a significant correlation in the metal contents of the water samples from the various locations as well as the various water sources. The trace metals contents (Fe, Mn, Zn, Cu, Cr and Ni) were below or equal to the limits set by WHO for drinking and domestic water while the toxic metals (Pb, Hg, As and Cd), recorded values higher than the safe limits set by WHO hence, the water sources are capable of constituting serious health hazards.

Key Words: Trace Metals, Water, Borehole, Well, Stream, Tap, Toxicity

Introduction

Water has maintained a status of being one of the most essential commodities on earth owing to its indispensable roles for agricultural and household use; industrial, tourism and cultural purposes; and as a medium for numerous biochemical and physiochemical reactions (Oyekunle *et al.*, 2012).

According to WHO (2004), as of 2002, 1.1 billion people, representing 17% of the global population, were without safe drinking water and forecast has shown that more than

47% of the global population will face severe water hardship by 2030 (Robert, 2008).

Nigeria is endowed with about 267 billion cubic metres of surface water and about 52 billion cubic metres of ground water annually (Ince *et al.*, 2010). Generally, the quality of ground water in Nigeria is better than that of surface water in terms of health criteria, but much of the ground water is corrosive, and some have iron, nitrate or fluoride concentration above WHO guideline values (Ince *et al.*, 2010). In spite of the generous endowment of surface and groundwater, which are capable of meeting

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demands, the average national water supply coverage was only about 57% (about 60% for urban areas, 50% for semi-urban areas and 55% for rural areas) (Ince *et al.*, 2010). Two of the major problems that are contended with in Nigeria are the insufficient quantity (source and amount) and poor quality of water (Adeniyi, 2004) and these are problems experienced in most cities and nations in the developing nations not to mention their rural settings (Oluyemi *et al.*, 2010).

The poor state of the water and sanitation in Nigeria is reflected in the high infant mortality and morbidity rates for the country (Ince *et al.*, 2010) which are mainly caused by malaria, diarrhoea and acute respiratory infections, all of which are related to unclean and inadequate sanitation. Together with typhoid, these diseases account for more than 70% of all child mortality and morbidity in Nigeria (Ince *et al.*, 2010). In 1997, the World Health organization (WHO) reported that 40% of deaths in developing nations occur due to infections from water related diseases. Desirable quality of drinking water must be ensured in terms of levels of chemical and biological contaminants such as trace heavy metals, pH, organic matters and pathogens (WHO, 2011).

Elevation in the trace metal contents of an aquatic system may arise from daily human activities, various degrees of geochemical reactions occurring in the sub-surface of the earth, runoff addition, aerial deposition and percolation-related phenomena (Ibe and Duruik, 2005). Among the possible contaminants of water, heavy metals have attracted an unprecedented attention owing to their high toxicities even at low concentrations.

The major sources of water in major towns and cities of Osun state Nigeria is ground water (borehole and well), and sometimes streams and rivers especially during the dry season. These water sources are the alternatives to the inconsistent flow of pipe borne water, which would have been the more reliable source of safe water for the growing population (Oluyemi *et al.*, 2010).

This study therefore aims at investigating the portability of drinking water sources available to the people in various parts of Osun State, Nigeria, with respect to trace metal levels with the view to constantly monitor the river and ground water quality in the state so as to record any alteration in the quality, which may lead to outbreak of health disorder or serious health effect.

Materials and Methods

Study area

Drinking water samples were collected from four different sources (borehole, tap, well and stream) in five different locations in Osun State. Samples were collected from the State capital (Osogbo, 7° 46' N 4° 33' E) and from two towns each from two of the three senatorial districts of Osun State – Osun West (Iwo, 7° 38' N 4° 11' E and Ejigbo, 7° 54' N 4° 19' E) and Osun Central (Ile-Ife, 7° 27' N, 4° 34' E and Ilesa, 7° 36' N 4° 34' E). Samples were collected from these locations taking into consideration the population density and human activities in each particular area. Table 1 shows the senatorial district distribution of the four sources of water sampled for the trace metal analysis. The sampled water was from a mix of government and private properties. All of the sampled water was the main source of drinking water for the local population.

Table 1: Senatorial district spread and the types of water sampled for trace metal analysis

Senatorial District	Boreholes	Stream	Tap	Well	Total sample per area
Osun West	2	2	2	2	8
Osun Central	2	2	2	2	8
State Capital	1	1	1	1	4
Total	5	5	5	5	20

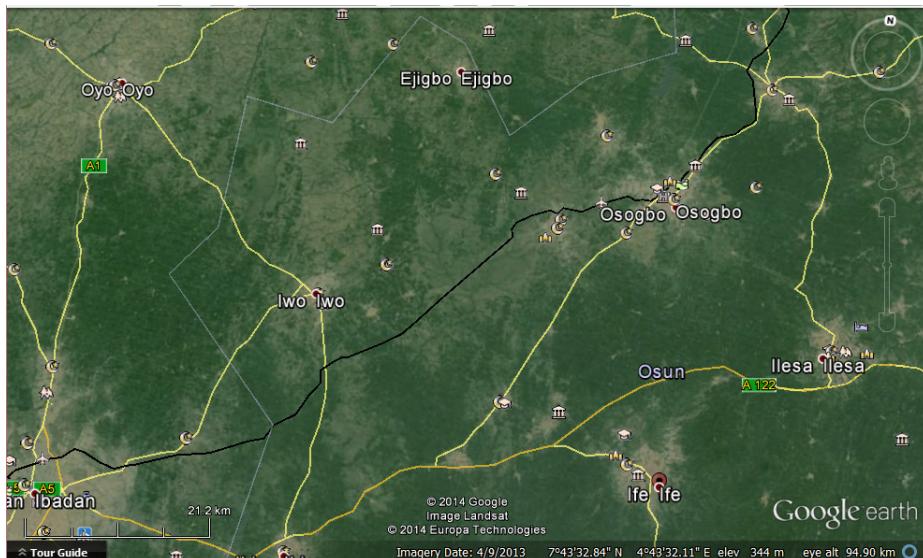


Figure 1: Map of Sampling Locations

The sampling was carried out over a period of six months, spanning the dry and wet seasons of 2009 and 2010. Samples were collected in November and December 2009 and January 2010, representing the dry season; and April, June and July 2010, representing the wet season.

Sample Collection

Samples for water quality studies were collected in 2 L plastic bottles that had been previously soaked in 10 % nitric acid for 48 hrs, and rinsed with distilled water. The container was rinsed three times on site with the sample water before collecting the water sample for water quality analysis. All samples were filtered with cellulose acetate filters and stored immediately in a cooler, in order to ensure that the physical properties of the water samples were maintained, and transported to the laboratory where they were stored in the refrigerator prior analysis.

Sample Digestion for Total Metal Determination

A 50 mL aliquot of water sample was transferred into Teflon beaker and 5 mL of concentrated HNO_3 was added. This was followed by gentle boiling on a thermostated hot plate in a fume cupboard for about 45 min. The digested samples were

quantitatively transferred into a 25 mL volumetric flask and diluted to volume with double distilled water. From this, an aliquot was taken for AAS analysis.

Quantification Process

Trace metal concentrations in the drinking water samples were determined using a Buck Model 205 Flame Atomic Absorption Spectrophotometer from East Norwalk, United States of America.

Recovery Analysis

This was conducted to assess the error levels arising from contamination and adsorption losses in the speciation procedure and also to ascertain the precision of the analytical procedures used in this study. A 25 mL water sample was put into a Teflon beaker and was spiked with 25 mL of 50 $\mu\text{g}/\text{mL}$ of the metals and digested as earlier described. The digested spiked sample was made up to the mark in a 25 mL volumetric flask with doubly distilled water. Also, 25 mL each of 50 $\mu\text{g}/\text{mL}$ of the standard heavy metal solution mixture was taken for analysis. The levels of these metals in the two samples were determined using the AAS. The percentage recovery (% R) for each metal was calculated using the relationship:

$$\% R = \frac{A - B}{C} \times 100$$

where A = concentration of a metal in the spiked sample; B = concentration of a metal in the unspiked sample; and C = the amount of metal (ppm) used for spiking.

Statistical Analysis of Data

The mean and standard deviation for the metals from three replicate measurements, as well as the correlation matrix were determined using statistical package for social sciences (SPSS) software. Coefficient of variation was adopted to evaluate the intra- and inter-state temporal variability of the metals.

Table 2: Value of recovery analysis and calibration curve

	Fe	Mn	Zn	Cu	Pb	Hg	As	Cd	Cr	Ni
r ²	0.9961	0.9898	0.9896	0.9794	0.9585	0.9856	0.9987	0.9975	0.9892	0.9973
%	87.50±	89.73±	98.38±	96.23±	86.99±	84.72±	92.88±	92.99±	89.15±	93.20±
R	6.60	6.31	6.97	3.06	3.53	4.02	3.54	4.55	3.97	3.91

* Value = mean of triplicate analysis ± s.d.

The mean total trace metal levels ($\mu\text{g/mL}$) for the water samples are presented in Table 3. The total metal concentrations were of the order: Iwo (0.76) < Ile-Ife (0.83) < Ejigbo (0.89) < Osogbo (1.14) < Ilesa (1.23). The high metal load observed at Ilesa could be as a result of anthropogenic and industrial input, in addition to geochemical composition of the underlying rocks of the area, which might possibly contain some of the metals assessed (Aiuppa *et al.*, 2003).

The six months mean metal content for all the four sources of water ($\mu\text{g/mL}$) was of the order: Hg (0.01) < Pb (0.02) = As (0.02) = Cd (0.02) < Ni (0.03) < Cr (0.04) < Cu (0.08) < Zn (0.13) < Fe (0.25) < Mn (0.36). The concentrations of these trace metals were below the WHO recommended limits for drinking water with exception of Pb, Hg, As and Cd that were slightly above the recommended limit for drinking water by WHO (2011).

Results and Discussion

The result of the recovery analysis of metal analysed for water samples drawn from all the five locations are presented in Table 2 below. Under the experimental conditions used, the standard calibration curves obtained showed high linearity level with r^2 values between 0.9585 for Pb and 0.9973 for Ni. Recoveries of trace metals in water ranged from $84.72 \pm 4.02\%$ for Hg to $98.38 \pm 6.97\%$ for Zn. These values are adjudged acceptable, and hence, the results obtained are reliable.

Table 4 represents the mean of the concentrations of metals in different water samples. The concentrations of the metals ($\mu\text{g/mL}$) range as follows: Fe (0.18-0.30), Mn (0.33-0.37), Zn (0.11-0.14), Cu (0.05-1.0), Pb (0.01-0.03), Hg (Nd-0.03), As (Nd-0.03), Cd (Nd-0.04), Cr (0.02-0.05), and Ni (0.02-0.05).

Concentration of Fe in all the water sources was generally below the WHO maximum permissible limit except stream water which was exactly equal to the recommended limit. The high concentration of the element in the stream might be due to direct release of domestic waste from anthropogenic activities and vehicular exhaust.

The Fe levels in this study were lower than the $31.78 \pm 0.80 \mu\text{g/mL}$ (river) levels reported by Oluyemi *et al.* (2010) for the Ife North Local Government area of Osun State. The highest level of Mn ($0.40 \mu\text{g/mL}$) was recorded in the stream. This value was

equivalent to the maximum recommended level by WHO (2011) while all others sources were lower than this limit. The result obtained in this study was lower than the value ($11.32 \mu\text{g/mL}$) reported for stream water by Oluyemi *et al.* (2010) or $76.79 \pm 12.89 \mu\text{g/mL}$ reported by Oyekunle *et al.* (2012) for the groundwater of Ile-Ife. On the other hand, Nsi and Ogori (2005) reported $0.005\text{--}0.0055 \text{ mg/L}$ levels for well water and 0.15 mg/L for borehole waters of Markurdi, which are lower than what is being reported in this study. Mn toxicity constitutes a serious health hazard, resulting in severe pathological disorder of the central nervous system (Keen & Ziderberg-Cherr, 1996). The toxicity can be manifested by a permanent crippling neurological disorder of the extra pyramidal system similar to Parkinson's diseases. In its milder form, the toxicity is expressed by aggressiveness, hallucinations, disturbances of libido and improper coordination (Oyekunle *et al.*, 2012).

The Zn concentration ranges from $0.11(\text{well})$ to $0.14 \mu\text{g/mL}$ (stream). These values were lower than the $147.3 \pm 30.4 \mu\text{g/mL}$ (hand dug well) and $6.19 \pm 0.24 \mu\text{g/mL}$ (stream) levels reported by Oluyemi *et al.*, (2010) and $31.86 \pm 3.64 \mu\text{g/mL}$ reported for groundwater by Oyekunle *et al.* (2012) for Ife North LGA and Ife Township respectively. However, the values were much higher than the $0.04 \pm 0.06 \mu\text{g/mL}$ reported for Ojota area in Lagos (Oyeku and Eludoyin, 2010). These variations may have resulted from the geological differences of the areas (Oyekunle *et al.*, 2012). Zn is an essential element required for life processes of various enzymes (Wordstron, 1982). It also interferes at different levels in the endocrine system and lipid and carbohydrate metabolism. Acrodermatitis enteropathica is a disease characterised by low serum zinc and at elevated levels, Zn may be carcinogenic (Schwartz, 1975). Zn deficiency symptoms include nausea, dizziness, gastric ulcers,

lethargy, muscle pain, impairment of immune function, headaches, vomiting, dehydration, stomach aches, poor muscle coordination, fatigue, fever, depression, malaise, cough, possible renal failure and increased blood level of insulin-like growth factor and testosterone, both of which are related to prostate cancer (Michael and Stanford, 2003; Bacha *et al.*, 2010). Histopathology signs of Zn poisoning, including fibrosis and vacuolization were associated with elevated pancreatic Zn concentration (Van der Merwe *et al.*, 2011).

Cu is an essential trace metal to human life at moderate levels, functioning as part of several enzymes such as tyrosine, cytochrome oxidase, super oxide dismutase, amine oxidases and uricase (Oyekunle *et al.*, 2012). The mean concentrations of Cu in this study range from 0.11 (stream) to $1.00 \mu\text{g/mL}$ (borehole). The values of Cu in all water sources analysed were lower than the permissible limit set by WHO (2011). Oyekunle *et al.* (2012) reported a higher Cu content ($8.28 \pm 0.91 \mu\text{g/mL}$) in the underground water of Ile-Ife. The value of Cu obtained for borehole in this study was similar to the value of $1.16 \pm 0.05 \text{ mg/L}$ obtained for borehole in Ife North LGA of Osun State but the hand dug well recorded values lower than the $46.35 \pm 0.07 \text{ mg/L}$ reported for hand dug well by Oluyemi *et al.*, (2010). The level in underground water (borehole and well) reported in this study was higher compared to stream and tap water. Geochemical environment might have been responsible for the levels of Cu detected in the water samples while anthropogenic inputs could not have seriously impacted the underground waters of the studied areas (Oyekunle *et al.*, 2012).

Lead is a highly toxic naturally occurring metal that have been present in soils, surface waters and groundwater (Olutona *et al.*, 2012). The levels of Pb range from 0.01 (tap water) to 0.03 (borehole and stream). These

findings were low compared to 0.18 ± 0.04 $\mu\text{g/mL}$ obtained in underground water of Ile-Ife by Oyekunle *et al.* (2012); 4.01 ± 3.82 $\mu\text{g/mL}$, 4.9 ± 0.18 $\mu\text{g/mL}$, and 2.4 ± 3.3 $\mu\text{g/mL}$ Pb levels respectively reported for the underground water resources from Ife North Local Government area, Ibadan and Lagos by Oluyemi *et al.* (2010) and Oyeku and Eludoyin (2010). The values of Pb in different water sources obtained in this study was higher than WHO (2011) recommended limit except tap water that has equivalent amount to the recommended limit of 0.01 mg/L. Elevated Pb levels of groundwater may be an indication of surface pollution resulting from the several years of automobile combustion of petrol containing organolead additives in the past, unguarded disposal of used lead-acid batteries, alloys, soldering metal and uninformed open air incineration of waste material at dump sites (Oyekunle *et al.*, 2012). All these anthropogenic activities have tendency to increase the metal contents of underground water resources via percolation related phenomena if the Pb or its related compounds become soluble at lower pH levels (Oyekunle *et al.*, 2012). Pb can cause serious health problems, especially for infants, children and pregnant women (Oyekunle *et al.*, 2012). Acute and chronic effects of Pb poisoning include psychosis (Okunola *et al.*, 2011). Pb poisoning also have ill-defined symptoms such as nausea, vomiting, abdominal pains, anorexia, constipation, insomnia, anaemia, irritability, mood disturbance and coordination loss (Grandjean and Nielson, 1979). In blood, Pb concentrations of less than 10 $\mu\text{g/dL}$ in children and adolescents can cause cognitive defects (Wu *et al.*, 2003). Pb effects especially on the foetus and children may include behavioural changes and impaired performance in IQ tests (Fatoki *et al.*, 2003).

Elemental mercury is basically released from industrial, agricultural, household,

commercial and medicinal products containing mercury, sewage discharge and soil. Inorganic mercury is found in batteries used in cars, mechanical and chemical industries. Inorganic mercury is the most common form that is present in drinking water but is not considered to be very harmful to human health, in terms of the levels found in drinking water. Inorganic mercury compounds are rapidly accumulated in the kidney; about 7-8% of ingested mercury in food is absorbed (WHO, 2005a). Absorption from water may be 15% or less depending on the compound (IPCS, 1990). In this study, the levels of Hg ranged from 0.00 in tap water to $0.03\mu\text{g/mL}$ in stream water. The levels of Hg obtained from borehole, stream and well water sources were higher than the $0.006\ \mu\text{g/mL}$ recommended for drinking water by WHO (2011).

Arsenic (As) can be found in traces in nature. Elevated levels can be found naturally in groundwater which may be as a result of contamination caused by hazardous waste or industries that make use of As. Elevated levels of arsenic in drinking water may cause thickening and discolouration of skin, nausea, vomiting, diarrhoea, numbness in the hand and feet (Farrell-Poe, 2010). In this study, arsenic was not detected in tap water but levels of arsenic in all other sources of water were higher than the recommended WHO limit of $0.01\ \mu\text{g/mL}$. Concentration of arsenic is generally higher in groundwater than surface water which may be as a result of the dissolution of naturally occurring As-containing minerals.

Cadmium is a modern toxic metallic environmental pollutant. With exception of tap water where Cd was not detected, all other sources of water had values higher than the recommended level of $0.003\ \text{mg/L}$ by WHO (2011). By comparison, the values of Cd in various water sources in this study were lower than the values $0.08\text{-}0.11\ \mu\text{g/mL}$ and $0.98\pm0.67\ \mu\text{g/mL}$ reported (Oyekunle *et*

al., 2012; Oluyemi *et al.*, 2010) for Ife North Local Government area and Ife township. The high level of Cd in the various water samples, with exception of tap water, could be as a result of its long anthropogenic inputs which leached into the stream and the underground waters from contaminated sites. Cd has mutagenic, carcinogenic and teratogenic effects (Goyer and Clarkson, 2001) and is toxic to humans at extremely low levels (Okunola *et al.*, 2011). Prolonged exposure to the metal may result in mental dysfunction, characterised by tubular proteinuria. Exposure to high concentration of Cd leads to obstructive lung disease and Cd pneumonitis, which is characterized by chest pain, cough with foamy and bloody sputum, and death of the lung tissues lining because of excessive accumulation of water fluids (Okunola *et al.*, 2011).

Cr as a common contaminant is usually encountered in the environment in two oxidation states, Cr(III) and Cr(VI). Cr(III) is considered as an essential micro nutrient for human, plant and animal metabolism (Rafati *et al.*, 2010; Patil and Ahmad, 2011) while Cr(VI) is very soluble and hazardous to health (Rafati *et al.*, 2010). The values of Cr from different water sources in this study were lower than the recommended limit by WHO (2011) with exception of stream which was equivalent to the recommended limit (Table 4).

The primary source of nickel in drinking water is leaching from metals in contact with

drinking water, such as pipes and fittings. However, nickel may also be present in some groundwater sources as a consequence of dissolution from ore-bearing nickel (WHO, 2005b). The levels of nickel in this study range from 0.02 μ g/mL (tap) to 0.05 μ g/mL (stream). In all the water sources, the concentration of nickel was lower than the 0.07 mg/L maximum permissible level (WHO, 2011). Nickel concentrations in groundwater depend on the soil use, pH and depth of sampling (WHO, 2005b). This could be the reason why the concentration of Ni in borehole is slightly higher than well water (Table 4). High concentration of Ni in stream water could be due to the ‘stainless’ materials used in households and metal industries been eroded into the stream as a result of dumping waste.

Conclusions

Results obtained from this study revealed that the metals analysed were found mostly within the WHO limits (WHO, 2011). Few exceptions were observed in Pb, Hg, As and Cd which were found to be a little above the set standard. The users of these untreated sources of water from the study area may suffer from several heavy metal-induced toxicity symptoms. It is therefore recommended that the waters should be subjected to further treatment that will reduce drastically, the levels of the few trace metals identified that may pose serious health hazards to the society.

Table 3: Mean levels ($\mu\text{g/mL}$) of trace metals in water sources for different Cities in parts of Osun State, Nigeria

	Fe	Mn	Zn	Cu	Pb	Hg	As	Cd	Cr	Ni	Total burden	Metal	Correlation matrix
Ejigbo	0.24	0.33	0.11	0.08	0.02	0.01	0.02	0.02	0.03	0.03	0.89	1	
Ile-Ife	0.19	0.35	0.11	0.07	0.02	0.01	0.01	0.01	0.03	0.03	0.83	0.352**	
Ilesa	0.32	0.39	0.14	0.13	0.03	0.02	0.04	0.04	0.06	0.06	1.23	0.351**	
Iwo	0.20	0.33	0.13	0.05	0.01	Nd	Nd	Nd	0.02	0.02	0.76	0.556**	
Osogbo	0.30	0.41	0.14	0.09	0.04	0.02	0.03	0.03	0.04	0.04	1.14	0.591**	
Range	0.19-0.32	0.33-41	0.11-0.14	0.05-0.13	0.01-0.04	Nd-0.02	Nd-0.04	Nd-0.03	0.02-0.06	0.02-0.06			
Mean	0.25	0.36	0.13	0.08	0.02	0.01	0.02	0.02	0.04	0.03			
WHO*	0.3	0.4	3.0	2	0.01	0.006	0.01	0.003	0.05	0.007			

** Correlation is significant at the 0.01 level (2-tailed)

Table 4: Mean levels ($\mu\text{g/mL}$) of trace metals in water sources in the areas studied

	Fe	Mn	Zn	Cu	Pb	Hg	As	Cd	Cr	Ni	Correlation matrix	
Borehole	0.27	0.37	0.13	1.0	0.03	0.01	0.02	0.02	0.04	0.04	1	
Stream	0.30	0.40	0.14	0.11	0.03	0.03	0.03	0.04	0.05	0.05	0.808**	
Tap	0.18	0.33	0.12	0.05	0.01	Nd	Nd	Nd	0.02	0.02	0.548**	
Well	0.25	0.35	0.11	0.07	0.02	0.01	0.02	0.02	0.03	0.03	0.952**	
WHO*	0.3	0.4	3.0	2.0	0.01	0.006	0.01	0.003	0.05	0.07		

** Correlation is significant at the 0.01 level (2-tailed)

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