SEASONAL VARIATIONS OF HEAVY METALS IN GROUNDWATER OF WARRI AND ENVIRONS, SOUTHWESTERN NIGERIA

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Abstract

The concentrations of a suite of heavy metal in the groundwater of Warri and environs were determined using Atomic Absorption Spectrophotometer in order to assess its suitability for drinking. Forty groundwater samples were randomly collected in both rainy and dry seasons. The results showed that the mean concentrations of heavy metals (mg/kg) obtained in all the groundwater samples during the rainy season were in the order: As (0.0034) <Ni (0.0035) <Cd (0.0038) <Pb (0.0047) <Cu (0.0054) <Cr (0.0056) <Fe (0.0101) <Zn (0.0116). The mean heavy metal concentrations reported for the dry season were in the order: Cr (0.0056) <As (0.0084) <Cd (0.0115) <Ni (0.0126) <Cu (0.0162) <Fe (0.0195) <Pb (0.0200) <Zn (0.0240). The result showed that the mean concentrations of heavy metals determined during the dry season were slightly higher than those obtained during the rainy season. The result shows that the mean concentrations of Pb, Cd, and Cr in some groundwater samples were above the permissible limit of international standards for drinking water. Pearson's correlation of heavy metals in the groundwater samples showed no significant correlation was observed among all the metals in groundwater in the dry season, whereas that of the rainy season showed strong relationships among metals suggesting a similar distribution pattern and a combination of natural and anthropogenic sources.

Keywords: Heavy metals, seasonal variation, groundwater, aquifer.

Introduction

Monitoring the concentration of heavy metals in groundwater is crucial for public health, and essential for sustainable environmental management (Kot *et al.,* 2000). The groundwater of Warri and environs is an important resource because it is the chief source of drinking water for a large percentage of the increasing populace in the study area that does not have access to potable water supply. The reliance on groundwater for potable water supply is a result of the inability of government authorities to supply potable water due to lack of maintenance of existing facilities. This has made the exploitation of groundwater to become a common practice as many residential and commercial premises use untreated water from hand-dug wells and boreholes for industrial, domestic and agricultural purposes. Considering the proximity of the water table to the ground surface (varying from 0 to 4 meters) and the depth of some hand-dug wells (approximately 3 to 15 meters), the quality of groundwater for drinking in the study area is of concern considering its vulnerability to contamination by heavy metals.

Groundwater naturally contains different concentrations of heavy metal, and this is dependent on the mineralogical composition of the host aquifer system. However, unregulated human activities, industrial activities, urbanization, and increased population have caused a significantly increase in the concentration of heavy metals in the environment, when compared to those resulting from natural processes (Dasaram *et al.,* 2010). The occurrence of heavy metals in high concentration makes groundwater unsafe for drinking, domestic, industrial, and agricultural purposes (Bhaskar *et al.,* 2010). Some heavy metals, such as copper and zinc, are essential for human existence, but turn out to be toxic when their concentrations increase or, while others such as arsenic, lead, and cadmium, are non-essential to organisms even at low concentrations they exhibit toxic properties and can pollute groundwater, soil and plant resources through bioaccumulation (Jakimska *et al*., 2011; Mason, 1991). The toxic effects of heavy metals result from the inability of the body to metabolize them, hence they begin to accumulate in soft tissues of the body causing various diseases (Sonayei *et al*., 2009).

Warri and environs have experienced rapid urbanization and development since the 19th century and this has therefore led to increased industrialization, increase in the use of agrochemicals, general environmental degradation and consequently the accumulation of heavy metals in the environment. Heavy metal pollution in the Niger Delta Basin has been linked to different onshore and offshore operations in the petrochemical industry and their related activities. These activities which may contaminate groundwater resources include blow out during drilling operations, leakage of wellhead, pipelines and underground storage tanks, overflow at gathering stations, improper disposal of petroleum wastes and other industrial activities. The elevated level of heavy metals in soils, stream sediments and water resources of the Niger Delta Basin as a result of improper release of wastewater from refinery process have been examined by Spiff & Horsfall, (2004); Braide *et al.,* (2004; Ikomi & Emuh (2000).

There is, therefore, the need for continuous research to evaluate the concentration of heavy metals in groundwater in view of the health and environmental problems associated with pollution resulting from them. The present work will investigate the seasonal variation in the concentration of some heavy metals in groundwater resources of Warri and environs as this will aid in the initial assessment of their suitability for drinking.

Study Area Description

The area under study is Warri and its environs in Delta State, Niger Delta Basin of Southwestern Nigeria (Figure.1). It is located within latitudes 5.29°N and 5.34°N and longitudes 5.41°E and 5.49°E. The study area is a well-known centre of commercial activities in southern Nigeria, as one of the three refineries in Nigeria and many other oil and gas companies are located in the study area. The climate of Warri and Environs are mainly tropical with an alternating wet and dry season. The dry season occurs annually from November to March, while the rainy season usually occurs from April to October. However, during the dry season, it rains occasionally, also a brief period without rainfall occurs during the wet season in August known as August break. Mean annual temperatures range from about 22^0C to 34^0C, while mean annual rainfall is between 1,501 mm and 2000 mm; mean evapotranspiration is 1117 mm (Akpoborie, 2011), with high humidity (Olobaniyi *et al*., 2007).

The geology of an area may be a source of contamination and a pathway along which contaminants in the area can migrate or a receptor can be affected by the contaminants (Nathanial & Bardos, 2004). Also, the geology of an area can influence whether a contaminant is likely to remain close to the source or migrate. It is important that the area under study be understood geologically, as it bears relevance to the contamination potential of the area, and will in turn help in the geo-environmental risk assessment. The Nigerian Geological Survey map indicates that the studied area is underlain by three major sub-surface lithostratigraphic units which are; Benin Formation, Agbada Formation, and Akata Formation, which are overlain by superficial deposits of alluvium of a Quaternary to Recent age known as the Sombreiro-Warri Deltaic Plain sands. The Quaternary to Recent Sombreiro-Warri Deltaic Plain sands consists of sandy silt, brownish lateritic soils (clayey/silt sand) and fine medium/coarse grained unconsolidated sands. The Benin formation is the major aquifer in the studied area, with appreciable groundwater storage and recharge of over 6.63 x 10^8m^3 per annum (Oteze, 1981). Boreholes and hand-dug wells tapping into the aquifer are the chief source of public water supply in Warri and Environs. These activities greatly increase the vulnerability of the aquifer to contamination by heavy metals and other toxic pollutants. The major water-bearing unit in the Benin Formation is found in aquifers which consist of thick gravel and sand.

Materials and Methods

A total of 40 groundwater samples were randomly collected from boreholes and hand-dug wells at different locations within the study area, during the rainy and dry season from December 2017 to July 2018. Borehole water samples were collected after the borehole was pumped for 5 minutes. From each sampling station, samples were collected in well labeled 2.5 litres polythene bottles which had earlier been washed with hydrochloric acid and then rinsed severally with distilled water. Upon sampling, the polythene sampling containers were rinsed thrice with water from the exact sampling point, and were carefully corked immediately after sampling. The samples were stored at less than 4°C in an ice packed cooler in order to prevent significant change in chemical composition, chemical absorption and ion interference prior to laboratory analysis (Galarpe &Parilla, 2014), and later sent to the laboratory for analysis of heavy metal using Atomic Absorption Spectrophotometer (AAS).

Wet Oxidation Method was used to extract the heavy metals from the groundwater samples through digestion. 50 ml of each well mixed water sample was measured into a 150 ml beaker. Then 5 ml of concentrated HNO_3 was added. The solution was evaporated until it was almost dry on a hot plate and left to cool. Another 5 ml of concentrated HNO_3 was added to the beaker, and covered immediately with a watch glass. The heating continued with the addition of HNO_3 as necessary until light coloured residue which indicated that digestion was completed was obtained. About 1 to 2 ml of concentrated HNO_3 was added to the residue and washed with distilled water. This was filtered into a 100 ml flask to remove silicate and other insoluble materials. Distilled water was added to the flask, and thereafter stored in 125 ml polypropylene bottle for Atomic Absorption Spectrophotometer (AAS) analyses, which was used to detect various heavy metals in the samples, with the use of different heavy metals cathode lamps. During the analysis and sample preparation, adequate measures were taken to prevent samples contamination and instrumental errors.

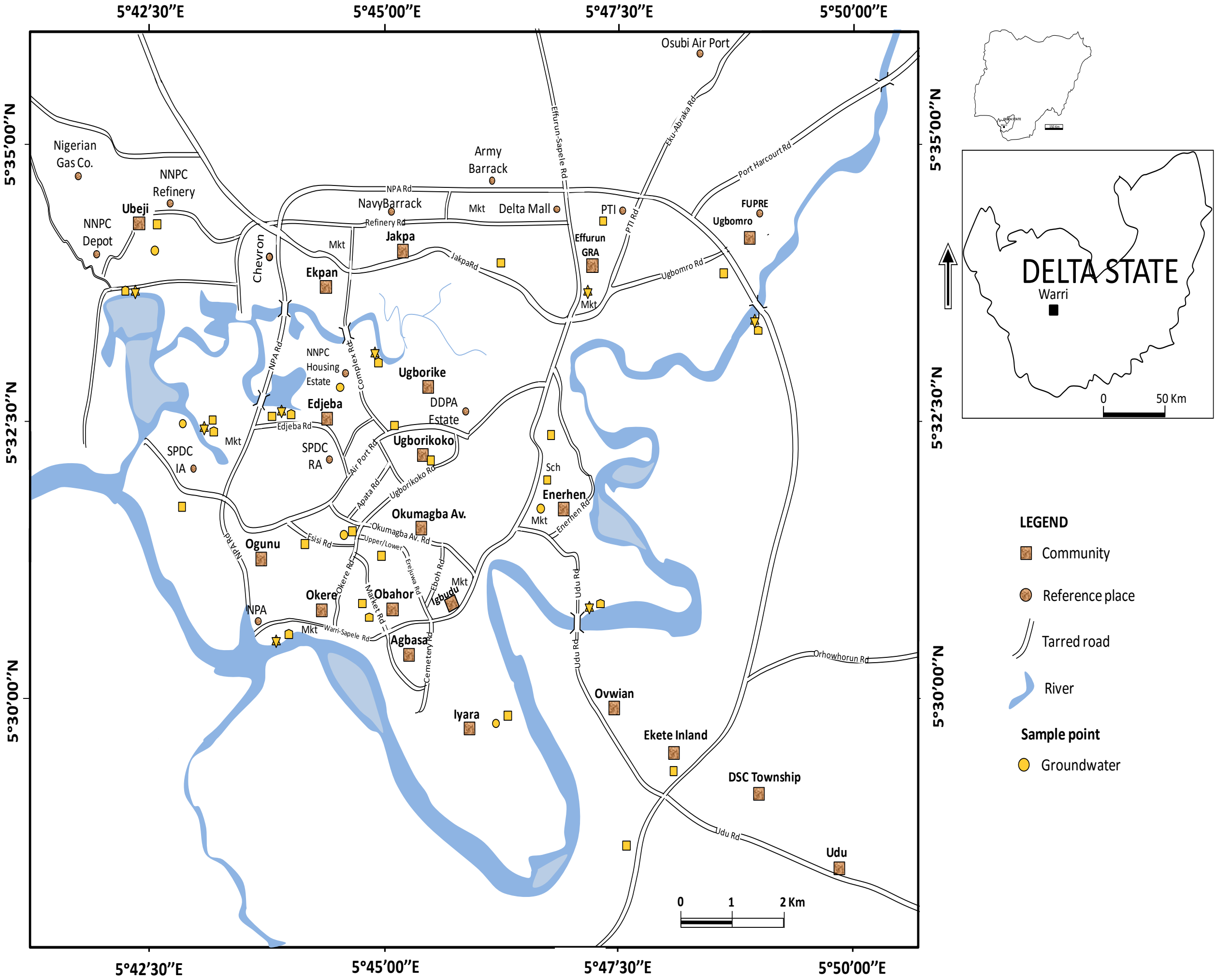

Figure 1: Map of the study area showing the groundwater sampling points.

Results and Discussion

The descriptive statistics of the concentrations of heavy metals in surface water and groundwater are presented in Table 1. The concentration of lead in groundwater in the rainy season ranged from 0.015 to 0.012 mg/l with a mean value of 0.0047 mg/l. Groundwater concentration of lead in the dry season ranged from 0.015 to 0.027 mg/l, with a mean value of 0.02 mg/l. The concentration of lead in some locations was, however above the maximum allowed limits of WHO (20017) of 0.01 mg/l in some groundwater samples collected in the dry season. The sources of Pb in water resources include; dumpsites soak away pits, Pb based paints, old automobiles and fertilizers. Also water pipelines which are made of Pb may still be used in archaic houses, and this could be a source of Pb contaminated water. During rainy seasons the surface runoffs from the above mentioned source may transport heavy metals to both surface and groundwater via infiltration, hence the elevated heavy metal levels. According to Mebrahtu & Zerabruk (2011), Pb is considered very important heavy metals because it is toxic, very common and hazardous even in low concentration. There are several ways through which led could go into the human body; these include ingestion of lead contaminated food, especially fishes, and intake of lead contaminated water. Although Pb could be removed from humans via urine, however increased exposure to Pb over a long period may result to excessive accumulation, especially in children. High concentration of Pb in the body can cause various symptoms related to the nervous system, concentration and behavioural disturbances in children, death, brain damage and kidney failure (Mebrahtu & Zerabruk, 2011).

The concentration of cadmium in groundwater in the rainy season ranged from 0.001 to 0.009 mg/l with a mean value of 0.0038 mg/l. Groundwater concentration of cadmium in the dry season ranged from 0.007 to 0.017 mg/l, with a mean value of 0.0115 mg/l. The results for Cd concentration in surface water and groundwater resources of the studied area during dry and wet season was above the World Health Organization (WHO, 2017), European Union and Standard Organization of Nigeria (SON, 2007) of 0.03mg/l, 0.005 mg/l and 0.003 mg/l respectively, indicating that the levels of Cd in some locations of the studied area was not within the safe level and has been influenced by human activities. The principal source of Cd into the atmosphere is through combustion processes, mainly in the form of oxides (Wieczorek et al., 2004), once released, it is known to have elevated mobility in biological and environmental systems. Chronic exposures to cadmium can cause renal dysfunction, calcium metabolism disorders, high blood pressure, destruction of red blood cells and cancer (Selinus & Alloway, 2005; Taha, 2004). Anthrpogenic sources of Cd in the environment include; combustion of fossil fuel, phosphate fertilizers, sewage sludge, mining and refining of metal ores, (Challa & kumar, 2009). Cd is also used in the production of Nickel-Cadmium batteries which when improperly disposed, contributes significantly to the concentration of cadmium in the environment (Challa & kumar, 2009). Most of these uses of cadmium increase its availability and transport to the environment which eventually comes in contact with groundwater resources.

The concentration of chromium in groundwater in the rainy season ranged from 0.001 to 0.015 mg/l with a mean value of 0.0056 mg/l. Groundwater concentration of chromium in the dry season ranged from 0.001 mg/l to 0.037 mg/l, with a mean value of 0.0056 mg/l. Raji *et al.* (2010) recorded values in drinking water ranging from 0.510-0.800 mg/l. The results obtained for chromium in the present study were above the WHO (2007) acceptable limit. The increasing concentration of chromium in the aquatic environment has been linked to several industrial activities such as petroleum refining, metal refining, electroplating factories, car and textile manufacturing, leather tanneries, detergents, wood preservation, chromium plating, leather tanning, amongst others (Adeleken & Abegunde, 2011; Hilgenkamp, 2006; Huang *et al*., 2004; Panov *et al*., 2003). Chromium can also leach from contaminated soils into the groundwater system. Because chromium can accumulate on various parts of humans such as on the skin, lungs, liver, hair, nails and placenta (Adeleken & Abegunde, 2011), several human health effects have been attributed to short and long term ingestion and contact with chromium contaminated water. These health effects include cancer, irritation of the eye and lungs, dermatitis and skin and nasal ulcers, vertigo, convulsion, liver and kidney failure (Sarkar, 2005).

The concentration of arsenic in groundwater in the rainy season ranged from 0.001 to 0.008 mg/l with a mean value of 0.0034 mg/l. Groundwater concentration of arsenic in the dry season ranged from 0.0013 to 0.017 mg/l, with a mean value of 0.0084 mg/l. Arsenic is a widely distributed heavy metal, occurring in rock, soil, water and air. High concentrations of inorganic arsenic in water resources are acutely toxic and may cause gastrointestinal disorders, cardiovascular and central nervous systems disorders, and eventually death.

The concentration of nickel in groundwater in the rainy season ranged from 0.001 to 0.008 mg/l with a mean value of 0.0035 mg/l. Groundwater concentration of nickel in the dry season ranged from 0.007 to 0.018 mg/l, with a mean value of 0.0126 mg/l. The concentration of copper in groundwater in the rainy season ranged from 0.001 to 0.015 mg/l with a mean value of 0.0054 mg/l. Groundwater concentration of copper in the dry season ranged from 0.008 to 0.031 mg/l, with a mean value of 0.0162 mg/l. Copper is an essential component of several enzymes. It is essential for the utilization of iron (Curtis *et al*., 1996). High concentrations of copper in drinking water may cause chronic anaemia, make the water bitter and could intensify the corrosion of galvanized iron and steel fittings (Chukwu *et al*., 2008).

The concentration of iron in groundwater in the rainy season ranged from 0.001 to 0.029 mg/l with a mean value of 0.01 mg/l. Groundwater concentration of iron in the dry season ranged from 0.0012 to 0.043 mg/l, with a mean value of 0.0195 mg/l. Iron is an essential element which is abundant on the Earth's surface. Iron generally occurs in groundwater in the form of ferric hydroxide, in concentrations less than 500 µg/L (Oyeku & Eludoyin, 2010). Although, iron is an essential dietary requirement in humans, however when its concentrations in the human body becomes excessively high, it is stored in body organs such as the heart, liver, pancreas, and spleen, where it may cause diseases and ultimately organ failure (Rajappa *et al*., 2010; Bhaskar *et al*., 2010; Chukwu et al., 2008). It is also known that deficiency of iron in humans causes anaemia. In addition, the presence of high concentrations of iron in drinking water gives a bitter taste, and may also promote the growth of iron bacteria, which expedites the rusting of water storage tanks and pipes, made of iron (Chukwu et al., 2008).

The concentration of zinc in groundwater during the rainy season ranged from 0.001 to 0.039 mg/l with a mean value of 0.0116 mg/l. Groundwater concentration of cadmium in the dry season ranged from 0.01 to 0.067 mg/l, with a mean value of 0.024 mg/l. All obtained results for zinc are below the guideline value of 3 mg/l suggested by WHO for zinc content in drinking water. Zinc is an essential trace element for humans, plants, and animals, and is important in the synthesis of proteins. Zinc usually occurs at low concentration in surface water because of its limited mobility after weathering. Zinc toxicity is uncommon but at concentrations of up to 40 mg/l, toxic effects such as irritation, pain and muscle stiffness may occur (Al-Weher, 2008). Some of the anthropogenic sources of zinc in groundwater resources include the use of fertilizers, paints, wood preservation and indiscriminate disposal of smelter slag and waste containing high concentrations of zinc (Lew, 2008).

Table 1: Summary statistics of heavy metals in groundwater during the rainy and dry seasons.

Parameter (mg/l)	Rainy Season (n=20)		Dry Season (n=20)		WHO (mg/l)	EU (mg/l)	NIS (mg/l)
	Range	Mean	Range	Mean			
Pb	0.015 – 0.012	0.0047	0.015 – 0.027	0.0200	0.01	0.01	0.01
Cd	0.001 – 0.009	0.0038	0.007- 0.017	0.0115	0.003	0.005	0.003
Cr	0.001- 0.015	0.0056	0.001 – 0.037	0.0056	0.05	0.05	0.05
As	0.001 – 0.008	0.0034	0.0013 – 0.017	0.0084	0.01	0.01	0.01
Ni	0.001 – 0.008	0.0035	0.007 – 0.018	0.0126	0.02	0.02	0.02
Cu	0.001 – 0.015	0.0054	0.008 – 0.031	0.0162	2.0	2.0	1.0
Fe	0.001 – 0.029	0.0101	0.0012 – 0.043	0.0195	No guideline	0.2	0.3
Zn	0.001 – 0.039	0.0116	0.01 – 0.067	0.0240	3.0	N/A	3

Statistical Analysis

The geochemical results were statistically analyzed using Pearson's Correlation to find out the significant relationships that exist among the analyzed heavy metals. Correlation coefficient is a statistical evaluation method generally used to determine the relationship between two variables. Correlation coefficient analysis is helpful in establishing possible associations between variables. It is a simple measure to exhibit how well one variable predicts the other. A correlation coefficient (r) of +1 indicates that two variables are perfectly related in a positive linear sense, but if r = -1, it indicates a negative linear correlation. However, if r = 0, it implies that there is no relationship between the two variables (Fashiola et al., 2013). This implies that when two metals or parameters have a positive correlation coefficient, they may have a common source, while a negative correlation coefficient signifies a different source. Correlations are considered significant when the *p*-value is less than the 0.05 level of significance.

The Pearson correlation matrix of the heavy metals in groundwater samples in the rainy season (Tables 2 and 3) showed significant correlations among the metals. This includes Lead which had a moderate negative correlation with Nickel with a value of - 0.611 and a *p*-value of 0.027. No other significant correlations were observed among the other metals. No significant correlation was observed among all the metals in groundwater in the dry season.

Table 2: Pearson correlation matrix of heavy metal concentrations of groundwater in Warri and environs during the rainy season.

	Pb	**Cd**	**Cr**	**As**	**Ni**	**Cu**	**Fe**	**Zn**
Pb	1							
Cd	-.474	1						
As	.168	.066	1					
Ni	-.396	.045	-.025	1				
Cu	-.611*	.332	.199	.471	1			
Fe	.103	.254	.104	-.227	.194	1		
Zn	-.137	.042	.478	-.038	.215	-.099	1	
Cr	-.269	.118	-.068	-.066	-.442	-.335	-.011	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Table 3: Pearson correlation matrix of heavy metal concentrations of groundwater in Warri and environs in the dry season.

	Pb	**Cd**	**Cr**	**As**	**Ni**	**Cu**	**Fe**	**Zn**
Pb	1							
Cd	-.133	1						
As	-.365	.032	1					
Ni	-.027	-.135	-.045	1				
Cu	.057	.323	.461	-.337	1			
Fe	.042	.285	.525	.247	.486	1		
Zn	-.008	-.111	.167	.539	.328	.241	1	
Cr	-.327	.332	-.264	.040	-.309	-.402	-.060	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Conclusion

This study determined the concentration of heavy metals in groundwater of Warri and environs in order to ascertain its suitability for drinking. The results showed that the mean concentrations of heavy metals (mg/kg) obtained in all the groundwater samples during the rainy season were in the order: As (0.0034) <Ni (0.0035) <Cd (0.0038) <Pb (0.0047) <Cu (0.0054) <Cr (0.0056) <Fe (0.0101) <Zn (0.0116). The mean heavy metal concentrations reported for the dry season were in the order: Cr (0.0056) <As (0.0084) <Cd (0.0115) <Ni (0.0126) <Cu (0.0162) <Fe (0.0195) <Pb (0.0200) <Zn (0.0240). The result showed that the mean concentrations of heavy metals determined during the dry season were slightly higher than those obtained during the rainy season. The mean concentration of the examined heavy metals in the groundwater of the study area, when compared against standards, showed that all the metals found in the groundwater of the area was within international standards for drinking water, apart from Pb, Cd and Cr. Pearson’s correlation of heavy metals in the groundwater samples showed no significant correlation was observed among all the metals in groundwater in the dry season, whereas that of the rainy season showed strong relationships among metals suggesting a similar distribution pattern and a combination of natural and anthropogenic sources. It was recommended that groundwater from the study area should be treated using appropriate methods prior to drinking, and the concentrations of heavy metals in the groundwater should be monitored regularly to check on their levels. More so, best practices should be employed by industries in the disposal of effluent. The populace should be informed by public health officials of the effects of heavy metals on human health and the environment at large.

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