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Seasonal Variations of Heavy Metals in Water Samples from Selected Hand-Dug Wells Close to Petrol Stations in Ile-Oluji, Ondo State, Nigeria

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ABSTRACT

Availability of drinking water is a great challenge to many communities in Nigeria. Hence, majority of rural area dwellers depend on groundwater for drinking and other purposes. This study was conducted to evaluate the effects of anthropogenic activities from petrol stations on the quality of groundwater in selected locations at Ile-Oluji, Nigeria. The samples were analysed for seven heavy metals using Atomic Absorption Spectroscopy (AAS). The statistical analysis of variance (using Tukey test) revealed no significant difference at $p<0.05$. The percent coefficients of variation for all the heavy metals analysed varied widely, except for Cd. From the foregoing results, it is evident that the groundwater located near petrol stations is unsuitable for drinking and other domestic applications. Thus, there is need for government to take urgent measures to enact and enforce appropriate legislation to regulate the locations of wells for groundwater especially in areas that are prone to anthropogenic activities.

Keywords: *Concentration, heavy metals, Ile-Oluji, petrol stations, pollution, hand-dug wells,*

INTRODUCTION

Water is requisite and crucial to life, the existence of life in this sphere originated in water; no other substances serve the society more other than water for the well-being individuals [1, 2]. Drinking water is not a delicacy but one of the most indispensable desires of life itself [3]. Water is also described as thirst-free resources that pre-determine life existence; therefore, water is an elixir of life [4]. Water does not only fulfil the basic means of life but also functions in transportation, recreation, power generation, manufacturing industries, cooling, irrigation, food production and processing to mention a few [5, 6]. Water quality has no fixed definition, but a term that is most frequently used to reflect the source and the activities of man, including the use and management measures for sustainable development [7]. More than 1.5 billion people worldwide estimated depend on groundwater [8]. Due to incapacity of governments to convene the ever-increasing water demand abate in the country, people in rural areas resort to groundwater. Thus, humans can obtain groundwater through boreholes or hand-dug wells, which are drilled or bored into the aquifer for domestic and industrial use. Sometimes water which is on the top of the impervious layers may only be reached by digging deep down the water table. Such openings are known as wells [9]. However, groundwater resources are commonly vulnerable to pollution that could affect their quality especially in the area where petrol filling stations are commonly located. Discharge of toxic chemicals and materials, over pumping of aquifer and contamination of water bodies with substances that promote algae growth are some major cause for water quality degradation nowadays [10]. The non-availability of good water is responsible for major health concerns in our environment today. Ile-Oluji is a town with a population of above 170,000 as at 2006 national census, accessibility to tap water has long ago been put on hold till date because of poor infrastructures, and as a result, the only source of drinking water is groundwater. In most cities, towns and villages, valuable man-hours are spent on seeking and fetching water, often of doubtful quality, from distant sources. The concentrations of some physicochemical properties in some studies conducted have been characterized for some small and medium size cities in the country namely: Iwo [11], Port Harcourt [12], Akure [13, 14], and Imo river basin [15]. There is a need to extend studies to areas that are close to petrol stations in the country so as to ascertain the quality of groundwater in those areas. Recently our findings on physicochemical and microbiological assessments of water from hand-dug wells sited close to petrol filling stations in Ile-Oluji, Nigeria were reported [16]. Adebawore et al. (2016) [17] also evaluated the polycyclic aromatic hydrocarbons in water samples from the hand-dug wells. The water quality assessment of the *Elemi River* water sample in Ado-Ekiti, Ekiti State, Nigeria was also reported [18].This paper examines the influence of petrol stations on the levels of heavy metals in groundwater from Ile-Oluji, Nigeria with a view to determining the suitability of these groundwater sources for domestic applications.

MATERIALS AND METHOD

Sampling location

Ile-Oluji is the headquarters of Ile-Oluji/Okeigbo Local Government, Ondo State, Nigeria. It lies between longitudes 6° 40' N and 7° 14' N, and latitudes 4° 38' E and 4° 53' E. It has an area of 698 km² and a population of 172,870 as at the 2006 census. It is bounded in the south by Otasun Hills, Okurughu and Awo rivers, south west by Okeigbo; North East by Oni rivers and Ikeji Hills in the East, partly by river Owena and partly by Ondo town; and in the West by the tributary of the Oni River. Her immediate neighbours are Ondo, Okeigbo, Idanre (Ondo State) and Ipetu-Ijesha (Osun State) as shown in Figure 1.

Ile-Oluji has a variety of land forms which can be classified into three broad physical units; the plains, the undulating highlands, and river valleys. The highlands however dominate the landscape. The township is surrounded by many granite rocks such as Ota-Ororo, Ota-Akoko, Ota-Didu, Ota-Upote and Iguruguru. Their major occupations are farming and trading.

Sample Collection

Water samples used for this study were collected from four hand-dug wells close to petrol stations, and a control sample away from petrol station at Ile-Oluji, Ondo State, Nigeria. Figure 2 shows the samples locations and each sampling site was identified by a hand-held Garmin-GPSMAP 76S-type global positioning system (Table 1).

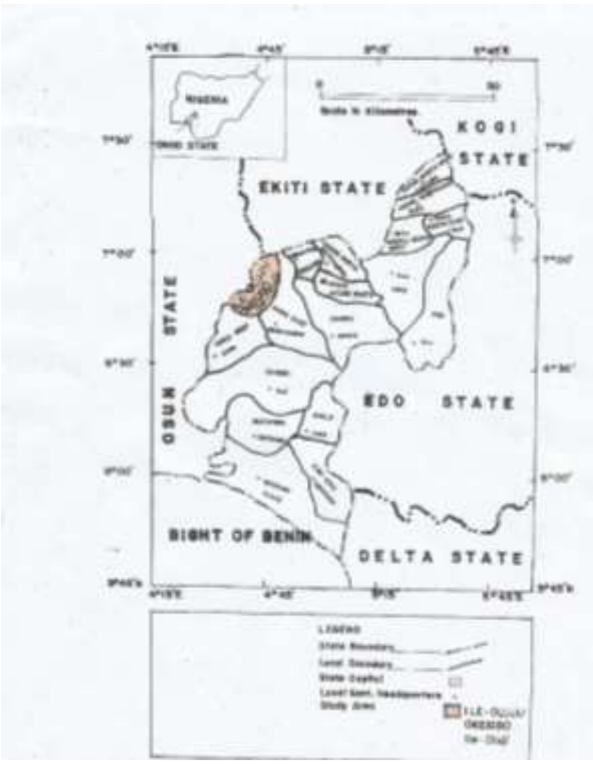

Figure 1: Map of Ondo State in Nigeria indicating Ile-Oluji/Okeigbo Local Govt. Area (Adebawore *et al.,* 2016) [16].

Figure 2: Map of Ile-Oluji showing well water sampling locations A, B, C, D and E (control) (Adebawore *et al.*, 2016) [16].

Table 1: Description of sampling locations

Sample code	Sampling location	Coordinates
A	Social petrol station	7°13'24" N and 4°52'08" E
B	Alfanpetrol station	7°13'42" N and 4°52'10" E
C	Sokapetrol station	7°10'52" N and 4°52'07" E
D	Ade Oil petrol station	7°11'06" N and 4°52'09" E
E (Control)	GRA, Temidire	7°13'24" N and 4°51'60" E

Sample Preparation and Digestion

Samples for heavy metals analysis were collected in 120 mL plastic containers which were initially washed with detergent and rinsed with distilled water. The containers were finally rinsed with 20% Nitric acid (HNO_3) before sampling. The samples were fixed by adding 1.5 mL of conc. HNO_3 to 1 L of each sample and the pH adjusted to 2.0 by the use of Hanna HI7007 pH meter. The samples were stored in a refrigerator at about 4°C, where necessary, for subsequent analysis. As samples may contain particulate or organic materials, pre-treatment in the form of digestion is required before analysis. Nitric acid digestion was employed in accordance with APHA, (1995) [19]. The digested sample was taken for Atomic Absorption Spectrophotometer (AAS) model, PG 990 for analysis.

The analytical procedure involves selection and adjustments of various units of the machine (i.e. lamp selection, wavelength selection, slit adjustment and flame adjustment for each metal). The machine was standardized by aspirating distilled water to get zero absorbance. Standard solutions of 1000mg/L for all the metals were prepared and from them working solutions (with concentrations within the range of 0-5mg/L) were prepared by serial dilution [19] for the establishment of calibration curve for each metal. After digestion, the solutions were taken for AAS analysis.

Statistical analysis

All determinations were performed in triplicate. The statistical analyses were conducted using Tukey test analysis of variance (ANOVA).

RESULTS AND DISCUSSION

The concentrations of heavy metals in the samples A to D and the control sample are given in Table 2. Table 3 shows the maximum permissible levels (MPLs) stipulated by Nigerian Industrial Standards (NIS); United States Environmental Protection Agency (USEPA) and World Health Organization (WHO).

From the results, chromium was not detectable in all the samples in both seasons. The concentration of iron, (Fe) in samples A to D ranged between 0.54 to 1.83 mg/L (DS) and 0.30 to 1.55 mg/L (RS). The levels of iron in the control sample were however much lower being 0.42 mg/L (DS) and 0.30 mg/L (RS) respectively. The concentration of iron was highest in sample B and least in D for both seasons. The results obtained for Fe in this study exceeded the limits set by USEPA/WHO [20, 21] except for sample D (RS) located at the outskirts of the town with little activities taking place; and the control sample (RS) which is not close to any filling station. Iron sinks as water percolates through soil and rock when dissolved and washed into groundwater [18, 22]. From previous report, it is generally observed that high iron concentration is mostly associated with relatively shallower wells and boreholes (<40 m deep) as concentration in relatively deeper boreholes (>40 m deep) are observed to be low [23].

The concentrations of copper (Cu) in samples A to D ranged from 0.05 – 8.52 mg/L (DS) and 0.14 – 6.47 mg/L (RS). The highest concentration of Cu was found in sample C, and the least in sample B for both seasons. The control sample had Cu concentrations of 0.22 mg/L (DS) and 0.12 mg/L (RS). The concentrations of Cu in samples A, B and D and the control sample were well within the limits set by NIS [24] except in sample C. The major factor contributing to the observed higher concentrations of Cu in all these samples from Ile-Oluji community could be due to the application of the agrochemical $CuSO_4$ on the large cocoa plantations in Ile-Oluji community which might have permeated into the ground water.

The concentration of lead (Pb) in samples A to D ranged between 0.82 to 11.2 mg/L (DS) and 0.69 to 9.60 mg/L (RS). Pb concentrations in the control sample were however much lower being 0.40 mg/L (DS) and 0.39 mg/L (RS). The concentrations of lead were found to be highest in sample B and the least in sample A for both seasons. The concentration of lead in all the samples including the control sample exceeded the MPLs set by NIS [24]; USEPA/WHO [20, 21]. The relatively high concentration of Pb in all the samples A, B,C and D could be associated to possible leakage of petrol and other petroleum products around the petrol stations, similar report was posited by Lolomari [25]. High Pb concentrations may not be unconnected to anthropogenic activities close to the well, like discharge of automotive fuel, grease and car battery water [26]. High Pb concentration in this study could be due to accumulation of automotive fuel, grease among other oils which could spill during discharge or dispense to different users.

Table 2: Concentrations (mg/L) of heavy metals in water samples from locations (A – D) at Ile-Oluji

Heavy metals	A		B		C		D	
	DS	RS	DS	RS	DS	RS	DS	RS
Cd	0.38	0.28	0.32	0.42	0.59	0.50	0.62	0.42
Cr	ND	ND	ND	ND	ND	ND	ND	ND
Cu	0.52	0.48	0.05	0.14	8.52	6.47	0.18	0.25
Fe	0.83	0.65	1.83	1.55	0.54	0.69	0.58	0.30
Ni	0.86	0.52	0.03	0.05	0.08	0.1	0.04	0.02
Pb	0.82	0.69	11.2	9.6	3.67	2.88	5.8	4.25
Zn	0.24	0.35	0.06	0.29	1.25	0.97	0.46	0.44

A, B, C and D represents sample codes (see Table 1: Description of sampling locations on page 4 for identification); DS – Dry season; RS – Rainy season; ND – Not detectable

Table 3: Concentrations (mg/L) of heavy metals in the control sample from Ile-Oluji and some MPL Standards

Heavy metals	Control		NIS	USEPA	WHO	Mean (A – D)		CV (%) (A – D)	
	DS	RS				DS	RS	DS	RS
Cd	0.22	0.14	-	0.005	0.003	0.48±0.15	0.41±0.09	31.4	22
Cr	ND	ND	0.05	0.100	0.050	ND	ND	ND	ND
Cu	0.22	0.12	1.00	1 – 3	1 – 2	2.32±4.14	1.84±3.09	179	168
Fe	0.42	0.30	0.30	0.300	0.300	0.95±0.60	0.80±0.53	63.9	66
Ni	0.02	0.12	0.02	-	0.070	0.25±0.41	0.17±0.23	161	135
Pb	0.40	0.39	0.01	0.015	0.010	5.36±4.37	4.36±3.79	81	87
Zn	0.26	0.27	3.00	5.000	3.000	0.50±0.52	0.51±0.31	104	61

DS – Dry season; RS – Rainy season; ND – Not detectable

The concentrations of cadmium (Cd) in samples A to D ranged from 0.32 – 0.62 mg/L (DS) and 0.28 – 0.50 mg/L (RS). During the (DS), sample D has the highest concentration while the lowest concentration was obtained in sample B; during the RS, sample C had the highest concentration, and sample A, the least. The control sample recorded 0.22 mg/L (DS) and 0.14 mg/L (RS) which were lower than the levels in samples A to D. The Cd levels in all the samples, including the control sample exceeded the limits set by USEPA/WHO [20, 21]. Higher levels of Cd in the samples A to D could be as a result of anthropogenic activities from automobile batteries and car paints/pigments around the petrols station through which cadmium could be released from automobile batteries or car pigments into the ground water [27].

The concentration of nickel, (Ni) ranged between 0.03 and 0.86 mg/L (DS) and 0.02 and 0.52 mg/L (RS). Ni concentrations were highest in sample A for both seasons and lowest in sample B (DS) and sample D (RS). However, the values were generally higher than the values of 0.02 mg/L (DS) and 0.12 mg/L (RS) obtained at the control site. The Ni levels in some of the samples, including the control sample (RS) exceeded the limits set by NIS [24] and

WHO [21] except for samples B, D and the control sample (DS); B and C (RS).

The concentration of zinc (Zn) in samples A to D ranged from 0.06 – 1.25 mg/L (DS) and 0.29 – 0.97 mg/L (RS). The highest concentration of Zn was obtained at site C, and the least at site B for both seasons. During the DS, the concentration of Zn in the control sample (0.26 mg/L) was higher than the concentrations in samples A and B but lower than those at sites C and D (DS). During the RS, the concentration of Zn in the control (0.27 mg/L) was higher than the concentrations in samples A, B and D except at site C. The concentration of Zn in all the samples including the control sample however fell below the MPLs set by NIS [24]; USEPA/WHO [20, 21].

The percent coefficient of variation obtained in this study (Table 3) showed a wide variation between samples (A – D) for DS and RS respectively except for Cd. A Tukey test of variance equality using the analysis of variance (ANOVA) revealed that there was no significant difference in the concentrations of heavy metals across the well samples (A – D) giving $F_{(0.696\ =\ 0.746)}$ at $P < 0.05$. However, results of heavy metals concentrations obtained during dry season (DS) were strongly correlated with that of rainy season (RS) with a correlation coefficient of (0.989) at $p < 0.01$.

CONCLUSION

This study shows that the general belief in the rural areas that groundwater is clean and potable is not absolutely true and that hand-dug water despite being underground can still be contaminated by mineral elements and other activities around the wells. It was found that changes in the seasons do have impact on the concentrations of heavy metals and the quality of drinking water. All the heavy metal concentrations investigated have higher values in (DS) more than in (RS) except Cr and Zn which were almost at par for both seasons. From the data obtained on the levels of heavy metals in all the samples during dry and wet seasons, it was observed that the concentrations of heavy metals decreased in this order Pb > Cu > Fe > Zn > Cd > Ni > Cr. The results also revealed that Cr, Cu and Zn concentrations in some samples fell within the permissible limits set by international standards. However, Cd, Fe, Ni and Pb were above, this point to the fact that users especially children are exposed to serious health risk. The relatively wide variations amongst these samples points to variability in water quality and the inherent potential dangers call for water treatment. It is recommended that wells meant for providing water for drinking and other domestic purposes should therefore not be located close to petrol filling stations. Appropriate remediation measures should be taken on the contaminated wells located near the petrol stations and urgent public awareness should be created on the danger/risk associated with the drinking of the water from these wells. Furthermore, government at federal level should enact a law prohibiting the location of hand dug wells in the vicinity of petrol stations. Lastly, efforts should be made by the Ondo State Government to resuscitate the abandoned pipe-borne water supply system in Ile-Oluji which has been non-functional for many years now.

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