

## Original Research Article

## Metals contamination of Aquifer in Warri and Port- Harcourt (Niger – Delta Region)

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### Abstract

Heavy metal concentrations of hand-dug wells from twelve (12) locations within Warri and Port Harcourt metropolis of (Niger - Delta region) were studied. Twenty – four (24) hand-dug well water samples were analysed. The physicochemical parameters of the water samples were analyzed using Standard methods within 24 hours. The metal cations were also determined using Atomic Absorption Spectrophotometer (AAS) method, hardness, chloride and bicarbonate concentrations were determined using titrimetric method, sulphate was determined by spectrophotometer method. Most physicochemical parameters were found to be within the WHO acceptable limits for drinking water in all sample locations. Rumagbo and Udu has the highest (108.5 and 288.55 mg/L) while Elewere and Enware lowest (36.08 and 36.05 mg/L) concentrations of bicarbonate ( $\text{HCO}_3^-$ ) respectively, the highest concentration of sulphate ( $\text{SO}_4^{2-}$ ) was recorded in Waterline and Efurun (72.00 and 82.75 mg/L). chloride ( $\text{Cl}^-$ ) (96.75 and 107.25 mg/L) for Mgbuoba and NPA meanwhile nitrate ( $\text{NO}_3^-$ ) (0.05 and 0.06 mg/L) have their highest concentrations observed at Eligbolo and NPA respectively. Eligbolo, and Udu have the highest concentration of manganese (Mn). Meanwhile arsenic (As) concentration was found to be highest in Rumuola and Udu (0.75 and 0.77mg/L) with the lowest concentration found in Elewere and Enware (0.38 and 0.46mg/L) respectively. In all, the concentrations of metals from the water samples observed were above the WHO limits of heavy water concentrations in drinking water. The results from this study show that there is high level of contamination of the aquifer (groundwater) in the studied areas. The long-term effect of continuous consumption of this groundwater can be of pose a threat to the health of the people.

### Environmental Science.

**Keywords:** *Heavy metals, toxicity, hand dug well*

### Introduction

Earth is known as the blue planet or the water planet because of the reality that most of its surface is covered by water, and it is the only planet in the solar system that has this huge quantity of water (Balasubramanian, 2017 and Ryecroft *et.al.*, 2019)

Groundwater is the main potable water supply used in many nations; also provides water for agriculture and industry (Hassan *et al.*, 2021 and Abdulhadi *et al.*, 2019) According to Megdal ,2018 and Omran *et al.*, 2019, in their work stated that the excessive use of freshwater in agriculture and industrial activities with regards to population growth have all led to increasing reliance on groundwater which is as a result effect of global warming, climate change, . Groundwater is the sole source of drinking water to about 2.5 billion people around the world (Grönwall and Danert 2020)

Approximately one-third of the global population depends on groundwater for drinking water (International Association of Hydrogeologists 2020). Contamination of water sources can arise from leaching of rocks, industrial and agrochemical discharges that are washed into them (Lawal and Lohdip, 2011), especially during the rainy season (Obaroh *et al.*, 2015). Contaminants, such as toxic metals, hydrocarbons, trace organic contaminants, pesticides, nanoparticles, microplastics, and other emerging contaminants, are a threat to human health, ecological services, and sustainable socioeconomic development (Li 2020; Li and Wu 2019). Freshwater aquifers are one of the most important sections of the Critical Zone (CZ), which extends from the top of the vegetation canopy down to the bottom of the aquifer (Lin 2010). As part of the global effort to understand the functions, structures, and processes within the CZ, a range of investigations have been performed that contribute to our knowledge of the circulation and evolution of groundwater (Sawyer *et al.* 2016; Goldhaber *et al.* 2014). A recent survey found that an estimated 65 million Nigerians had no access to safe water (Majuru *et al.* 2011). The provision of clean, reliable and portable water in rural areas and urban slums remains a huge task for governments throughout the world especially that a larger fraction of the population lives in the urban areas (Ahaneku and Adeoye 2014).

As a result of this gross absence of potable water, most people depend on groundwater for consumption, domestic, agricultural and industrial uses globally (Hvitved-Jacobson and Yousef, 1991; Ebong and Etuk, 2017) this can be observed in Nigeria with the Niger-Delta region as a case study. It was reported that only 58% of Nigerians living in the urban and semi-urban areas and 39% of the rural dwellers have access to potable water supply; others largely rely on ground and surface water for their domestic water supply (FGN, 2012). It was also reported by Adeyemi *et al.*, 2007, that the quality of groundwater sources is affected by the features of the media through which the water passes on its way to the groundwater zone of saturation. The heavy metals discharged by industries, traffic, municipal wastes, hazardous waste sites as well as fertilizers for agricultural purposes and accidental oil spillages from tankers can result in a steady rise in pollution of groundwater (Igwilu *et al.*, 2006: Momodu and Anyakora, 2010).

According to Basu *et al.*, 2014; Pandey *et al.*, 2016; Subba Rao *et al.*, 2020; He *et al.*, 2020a, many of the contaminants in groundwater are of geogenic origin as a result of dissolution of the natural mineral deposits within the Earth's crust. Contaminants can come from natural and anthropogenic sources (Elumalai *et al.*, 2020). These natural sources may become serious sources of contamination if human activities upset the natural environmental balance, such as depletion of aquifers leading to saltwater intrusion, acid mine drainage as a result of exploitation of mineral resources and leaching of hazardous chemicals as a result of excessive irrigation (Su *et al.*, 2020; Wu *et al.* 2015; Li *et al.*, 2016, 2018).

Groundwater quality differs from place to place, and this may therefore affect its suitability for consumption (Taiwo, *et al.*, 2015). Water dissolves more substances than any other solvent; thus,

a lot of toxic substances which can cause malfunctioning of the human body and chronic ailments are present in it (Nkem, *et al*, 2002; Adeyeye, 2000). Among the chemicals dissolved in groundwater are heavy metals such as arsenic lead etc. Drinking groundwater and surface water contaminated by heavy metal ions can be detrimental to health (Ohwohere 2012), especially at concentrations above a certain minimum. Groundwater contamination is defined as the addition of undesirable substances to groundwater caused by human activities (Government of Canada 2017).

Heavy metals are elements having atomic weights between 63.546 and 200.590 and a specific gravity greater than 4.0 i.e. at least 5 times that of water. They exist in water either as colloid, particle or dissolved form with their existence in water bodies being either of natural origin (Adepoju-Bello *et al.*, 2009) (e.g. eroded minerals within sediments, ore deposits leachate and products of volcanic eruption) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic effluents, harbour channel dredging) (Marcovecchio *et al.*, 2007).

Some of the metals like calcium, magnesium, potassium and sodium are essential for sustaining life and must be present for normal body functions. Also, cobalt, copper, iron, manganese, molybdenum and zinc are needed at low levels as catalyst for enzymatic reactions (Adepoju-Bello *et al.*, 2009), however, exposure to these metals at high levels can result in toxicity. Heavy metals can cause serious health problems with symptoms depending on the nature and quantity of the metal ingested (Adepoju-Bello and Alabi, 2005).

The Niger – Delta region of Nigeria is richly blessed with abundant deposits of natural resources including gas and oil. The groundwater in this delta is made up of a large multilayered aquifer that supplies millions of people that live within the region (Abam and Nwankwoala 2020). According to Clement (2013), an estimated population of 70% surrounding the delta depends on the natural environment for their livelihood. The Niger – Delta region of Nigeria is blessed with abundant resources, but as a result of the heavy mining and refining activities that are associated with crude oil exploration in the region, the groundwater in the region is not fit for consumption due to contamination. The level of contamination of groundwater in this region is on a continuous basis. Contaminated groundwater can lead to soil contamination and degradation of land quality. For example, in many agricultural areas in arid regions, high groundwater salinity is one of the major factors influencing soil salinization (Wu et al. 2014).

## **Materials and Method**

Twenty- Four (24) water samples were collected from hand – dug wells from 4 different locations in Warri and 8 locations in Port Harcourt metropolis (Niger - delta region), on two (2) different occasions. The project area was divided into quadrants so that water collected was from each of the quadrants to represent the areas that fall within each section of the quadrant. After this has been done, the sampling location was studied before the commencement of the work.

Samples were collected in a 1.5 L. polyethylene bottles after rinsing them with the water being sampled and were properly sealed. The moment the water sample was collected at the various point of sampling; it was wrapped with foil paper and then labeled accordingly with the name of the location where the sample was collected.

The information that was collected from the point of sampling, are the sampling environment and activities that take place in the area.

### Physicochemical parameters analysis

The samples collected were analyzed for the following physicochemical parameters such as Temperature, pH value, total dissolved solid and conductivity within 24 hours of sampling using Standard methods.

The samples were taken to the laboratory in Institute of Agricultural Research and Training (I. A. R & T) in Ibadan, Oyo State for analyses

### Chemical parameters analysis

The Samples were analyzed quantitatively for metal ions, hardness, Chloride, Sulphate, Bicarbonate and Nitrate.

The metal cations were determined using the Atomic Absorption Spectrophotometer (AAS) method as described in APHA 3111B and ASTM D3651. The method involve digestion of samples by measuring of 100ml of the water sample into different conical flask and 5ml of concentrated HCL and HNO<sub>3</sub> was measured into different conical flask and was heated for 15 minutes. Thereafter, 100ml of the digested sample was standardized with 100ml of distilled water, this sample was then analysed by AAS using their (each metal) respective lamp and wavelength. Also, hardness, chloride and bicarbonate concentrations were determined using titrimetric method, sulphate was determined by using spectrophotometric method while nitrate was determined as nitrogen content using the Kjeldhal method.

### Statistical analysis

Data obtained were analysed using descriptive statistics for the mean and standard deviation, one-way ANOVA was used to test the significant differences in the concentrations of the metals in wells.

### Result and Discussion

The result of Physicochemical and heavy metals analysis of Twelve (12) locations shows that the temperature of the water ranged from 30 to 31.5°C (Table 1 and 2) which fall within the recommended standard of 30 – 32 °C according to world health organisation that must be for good drinking water quality by WHO (2011).

**Table 1: Result of physicochemical parameters for Port-Harcourt**

Parameters	pH	EC (µS/cm)	TDS (mg/L)	T (°C)
Rumukoro	4.20	182.50	77.50	30.75
Elewere	4.20	150.00	85.00	31.03
Rumuigbo	4.74	242.50	96.75	31.20
Lagos street	3.94	232.50	432.00	31.50
Water line	4.03	247.50	450.00	30.65
Mgbuoba	4.26	227.50	297.00	31.28
Rumuola	3.97	175.00	468.75	31.05
Eligbolo	4.64	207.00	342.50	31.35
WHO (2011)	6.5 – 8.5	150.75	1000	30 – 32
Average	4.25	208.69	281.19	31.10

Source: Ossai *et al.*, (2021)

**Table 2: Result of physicochemical parameters for Warri**

Parameters	P <sup>H</sup>	Ec (µS/cm)	TD (mg/L)	T (°C)
Efurun	5.60	435.00	332.50	31.05
Enware	5.74	372.50	242.50	31.00
Udu	4.53	225.00	287.50	31.50
NPA	5.97	427.50	255.00	30.75
WHO (2011)	6.50	150.75	100.00	30 - 32

**Table 3: Result of the mean concentrations of anions present in the samples from 8 locations in Port-Harcourt**

Location	HCO <sub>3</sub> <sup>-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	Cl <sup>-</sup> mg/L	NO <sub>3</sub> <sup>-</sup> mg/L	F <sup>-</sup> mg/L
Rumukoro	72.23	47.50	38.00	0.01	1.75
Elewere	36.08	67.25	26.75	0.03	2.40
Rumuigbo	108.50	47.75	69.00	0.01	1.80
Lagos str	36.25	70.75	90.00	0.02	1.78
Water line	36.18	72.00	35.00	0.03	3.05
Mgbuoba	38.18	48.00	30.00	0.03	4.70
Rumuola	72.18	57.00	40.50	0.03	6.85
Eligbolo	108.20	60.25	91.5	0.05	6.85
WHO (2011)		200.00	250.00	45.00	

Source: Ossai *et al.*, (2021)**Table 4: Result of the mean concentrations of anions present in the samples from 4 locations in Warri**

Location	HCO <sub>3</sub> <sup>-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	Cl <sup>-</sup> mg/L	NO <sub>3</sub> <sup>-</sup> mg/L	F <sup>-</sup> mg/L
Efurun	72.30	82.75	38.50	0.03	5.08
Enware	36.05	80.50	93.50	0.04	3.75
Udu	288.55	69.25	52.00	0.04	5.70
NPA	108.33	75.00	107.25	0.06	3.18
WHO (2011)		200.00	250.00	45.00	

**Table 5: Result of the mean concentrations of cations present in the samples from 8 location Port-Harcourt**

Location	Na mg/L	K mg/L	Ca mg/L
Rumukoro	113.4	137.25	92
Elewere	125.25	166	47.88
Rumuigbo	113.45	137.75	195.25
Lagos str	124.15	146.25	543.25
Water line	126	168	575.75
Mgbuoba	122.4	180.5	354.5
Rumuola	158.35	174	674.5
Eligbolo	135	157.75	304.25
WHO (2011)	200		75

Source: Ossai *et al.*, (2021)

**Table 6: Result of the mean concentrations of cations present in the samples from 4 locations in Warri**

Location	Na mg/L	K mg/L	Ca mg/L
Efurun	104.10	120.00	773.75
Enware	114.02	179.00	340.75
Udu	134.75	157.76	449.10
NPA	162.23	176.25	352.50
WHO (2011)	200		75

**Table 7: Result of the mean concentration of heavy metals presents in the samples from 8 locations in Port-Harcourt**

Location	Mn mg/L	Cd mg/L	Pb mg/L	Fe mg/L	As mg/L
Rumukoro	0.81	7.3	7.08	1	0.61
Elewere	0.75	6.85	6.03	1.2	0.38
Rumuigbo	0.8	7.3	7.08	1	0.6
Lagos str	0.72	7.4	7.13	1	0.58
Water line	0.7	6.33	6.2	1.73	0.51
Mgbuoba	0.84	7.73	7.53	1.18	0.7
Rumuola	0.84	8.3	7.8	1	0.75
Eligbolo	0.88	8.1	7.78	1.2	0.62
WHO (2011)	0.1	0.003	0.01	0.3	0.01

Source: Ossai *et al.*, (2021)

**Table 8: Result of the mean concentration of heavy metals presents in the samples from 4 locations in Warri**

Location	Mn mg/L	Cd mg/L	Pb mg/L	Fe mg/L	As mg/L
Efurun	0.76	7.08	6.80	1.18	0.67
Enware	0.89	7.73	7.33	1.15	0.46
Udu	0.94	9.73	9.16	1.21	0.77
NPA	0.68	6.78	6.33	1.00	0.57

The results obtained (Tables 1 and 2) shows that groundwater pH from all the sites were generally less than 6.0 indicating slight acidic conditions The pH value of the water ranged from 3.94 to 5.97, which fall below the standard requirement limits (6.5-8.5) recommended by W.H.O (2011) and NIS (2007). The pH values (Table 1 and 2) showed that the lowest value of 3.94 was recorded in Lagos Street Port-Harcourt, this may be as a result of the discharge of acidic materials into the groundwater through industrial and domestic activities, while Rumuigbo and NPA have the highest pH value of 4.74 and 5.97 respectively as can be seen too from the above Tables 1 and 2 This may pose a risk for human consumption due to metal toxicity. Under a high acidic (low pH) condition, metals become more water soluble, thereby making it readily available for exposure.

The electrical conductivity of the groundwater samples from these areas (Tables 1 and 2) ranges between 150.00  $\mu$ S/cm and 435.00  $\mu$ S/cm, these are within the standard requirement limits as recommended by WHO (2011). The highest result of electrical conductivity was observed to be in samples from Waterline and Efurun area (435.00  $\mu$ S/cm and 247.50  $\mu$ S/cm respectively) while the lowest is from Elewere and Udu water samples (150.00  $\mu$ S/cm and 225.00  $\mu$ S/cm respectively). These results are higher than 12.73  $\mu$ S/cm - 32.46  $\mu$ S/cm that was reported by (Ebong and Etuk, 2017) groundwater from Itu area.

The result from table 1 and 2 above, further shows that the total dissolved solids in the water samples from all the sampling sites are well below the WHO (2011) limit for drinking water. The highest value of 468.75 was recorded in Rumuola Port-Harcourt and 332.50 in Efurun from Warri while the lowest value of 77.50 mg/L and 242.50 mg/L was observed in Rumukoro and Enware respectively.

Furthermore, the result obtained of some Anions concentrations present in the water samples collected from Port Harcourt and Warri are as shown in Table 3 & 4 above shows that Rumuigbo and Udu has the highest values of 108.50 mg/L and 288.55 mg/L respectively while the lowest concentrations of 36.08 mg/L and 72.30 mg/L of  $\text{HCO}_3^-$  were found in Elewere and Efurun respectively, more so, the highest concentration of  $\text{SO}_4^{2-}$  was recorded in Waterline and Efurun. Meanwhile,  $\text{Cl}^-$  and  $\text{NO}_3^-$  both have their highest concentrations observed at Eligbolo as (91.50 mg/L) and (0.05 mg/L) with 107.25 mg/L and 0.06 mg/L in NPA, while the highest concentration for  $\text{F}^-$  was obtained in Rumuola and Eligbolo from Port Harcourt, and Efurun in Warri. The above concentrations result for all the anions were found to be below the permissible limits set by WHO (2011). Nitrate is predominantly from anthropogenic sources, including agriculture (i.e., fertilizers, manure) and domestic wastewater (Hansen *et al.*, 2017; He and Wu 2019; He *et al.*, 2019; Karunanidhi *et al.*, 2019; Li *et al.*, 2019a; Serio *et al.*, 2018; Zhang *et al.*, 2018). High nitrate concentrations in water show presence of organic pollutants and it has been reported that women and young babies are more vulnerable to the negative effects associated with its high concentration (Ebong and Etuk, 2017).

Rumuola and NPA have 158.35 mg/L and 162.23 mg/L respectively of Highest concentration for Sodium while the lowest concentration was recorded at Rumukoro and Efurun (113.4 mg/L and 104.10 mg/L respectively) this was observed in table 5 & 6. The result shows that Sodium ions concentrations observed were found to be below the limit set by WHO (2011). The result in tables 5 & 6 further show that only Rumukoro and Elewere samples have moderate concentrations of Calcium (92 mg/L and 47.88 mg/L respectively), although Elewere site is below the limit set by WHO (2011), all samples from other sites were well above the 75 mg/L limit set by WHO. According to (Gianfredi, *et al.*, 2017), groundwater with appropriate enrichment of Ca and Mg, together with dissolved bicarbonates as a pH regulator, is protective against cardiovascular diseases (CVDs), osteoporosis, cognitive dysfunction, diabetes mellitus, acidosis, and probably cancers. With regard to the result obtained it shows that the health of an average population of the people in this region is at risk since the groundwater in the region is being polluted/ contaminated by oil spill resulting from the activities of oil exploration.

Subsequently, Potassium concentrations were found to be lowest at Rumukoro and Efurun while Enware and Mgbuoba have the highest concentrations observed from all the sampling sites

In Tables 7 & 8 as shown above, the lowest and highest concentration of Manganese metal ions obtained from the water sample twelve (12) different sampling sites in Port Harcourt and Warri, range from 0.7 mg/L and 0.68 mg/L in sample from Water line and NPA with 0.88 mg/L and 0.94 mg/L in the sample from Eligbolo and Udu respectively. The maximum permissible limit by WHO is 0.1 mg/L. It was observed that the concentrations of these metals ions in all the samples were above WHO limit for drinking water. The trace essential metals (e.g., Mn, Fe, Cu, and Zn), likewise, can be health-harmful if their concentrations are elevated above recommended daily intake (WHO, 2011). Therefore, the regular consumption of this groundwater in this region could

be of treat to the health of the populace.

More so, Rumuola (8.3 mg/L) and Udu has 9.73 mg/L which are the highest concentrations of cadmium metal ions in the sample from the result obtained with the lowest concentration observed in the sample from Waterline and NPA (6.33 mg/L & 6.78mg/L respectively). This was above the maximum level according to WHO is (0.003 mg/L) which indicates that all the samples did not agree with the maximum permissible limit for drinking water. Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems (Goyer and Clarkson 2001). When accumulated in the human body, they can damage various organs, sometimes causing them to malfunction (Wu *et al.*, 2016), long-term exposure to cadmium (Cd) may cause cancers in the prostate, lungs, and liver, as well as injuries to the pulmonary, testicular, and nervous systems (Wu *et al.*, 2016; Monika *et al.*, 2021).

Rumuola and Udu have high concentrations of 0.77 mg/L and 0.75 mg/L of Arsenic respectively, even though all other samples are more than the maximum limit 0.01 mg/L as recommended by WHO (2011) Arsenic according to US Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC), is ranked as a Group 1 human carcinogen and As<sup>3+</sup> can react with sulfhydryl (-SH) groups of proteins and enzymes to upset cellular functions and eventually cause cell death (Abbas *et al.*, 2018; Rebelo and Caldas 2016). It causes damage to blood, kidney, skin, central nervous and digestive systems (Khadse, *et al.*, 2008). Long-term exposure to As even at levels slightly above MCL is related to health problems of the skin (e.g., skin lesions, Bowen's disease), cardiovascular system (e.g., hypertension, coronary heart disease), neurological system (e.g. dysfunction of the central nervous system), genitourinary system (e.g., kidney and bladder cancers), and respiratory system (e.g., asthma, chronic cough, and bronchiectasis) (Yadav *et al.*, 2021). This means that groundwater in this region pose a risk to the people as it is the major source of water consumption for them.

The highest concentration of Lead was recorded in the sample from Rumuola and Udu (7.8 & 9.16 mg/L respectively) with the lowest concentration found in the sample from NPA and Elewere (6.33 mg/L & 6.03 mg/L). According to, Hardy *et al.*, (2008) Lead finds extensive use in storage batteries, solders, bearings, cable covers, ammunition, plumbing, pigments, caulking, sound vibration absorbers the two routes of exposure to lead are from inhalation and ingestion and the effects from both are the same. Lead metal ion concentrations in all the samples were observed to be above the maximum permissible limit set by W.H.O for drinking water. Source of lead in the water samples analysed in this study could be from runoff from indiscriminately disposed lead-acid batteries, lead-based solder; metallic alloy, lead-based paints, used oil, waste incineration, scrap and junk auto part.

Furthermore, there is always some level of Iron in most groundwater, this is due to the fact that it is common in many aquifers, and it is found in trace amounts in practically all sediments and rock formations. Tables 7 & 8 show that the samples from Waterline and Udu have the highest concentration of (1.73mg/L & 1.21mg/L accordingly) of iron from the water samples, while the minimum concentration (1.00 mg/L) was recorded in Samples from four sites (Rumukoro, Rumuigbo, Lagos Street, Rumuola and NPA). The maximum limit according to WHO is 0.3mg/L for iron. Meanwhile, all the samples were observed to be above the maximum permissible limit set by WHO for drinking water. This indicates that the local mineral deposit in the studied area may have high levels of iron.



Hashim *et al.*, (2011) in their own reported that exposures to toxic metals at high concentrations can lead to severe poisoning, although some of these elements are essential micronutrients at lower doses

### Conclusion

The result of the research work from the analysis carried out on the various water samples from Warri and Port Harcourt, in Niger – Delta region shows that there is a high level of contamination of the groundwater in the studied areas. The long-term effect of continuous consumption of this groundwater can be of pose a threat to the health of the people.

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