¹Omorogieva, O.M,² Nwokoloh N.J, & ³Imasuen, O.I ^{1&3}Department of Geology, Faculty of Physical Sciences University of Benin, P.M.B 1154 Benin City, Nigeria ²Delta State Ministry of Water Resources, Awin Road, Asaba, Delta State **Emai**l: omorogieva@physci.uniben.edu

ABSTRACT

There is thus the need to assess the quality of groundwater sources because water quality assessments form an important aspect of environmental studies. This study is aimed at understanding the aquifer geometry and assessing the quality of groundwater of two boreholes 4.2 km apart at Okabere on $6^{\circ}1.6'23.6''N$ and 5°30'38.6"E and Evbuabogun on 6°1.6'23.6"N and 5°30'38.9"E in Recent to Miocene Benin Formation (FM) Benin City, South-South Nigeria. Water and soil samples from the borehole were collected and analysed for physico-chemical parameters, grain size and heavy minerals analysis using standard laboratory method while heavy metals were determined with Atomic Absorption Spectrometer (AAS) unican series model 969 with air acetylene flame. The results obtained revealed that PO_{4}^{3} , K^+ , Cr^{+6} , Ni^+ , Pb^{+2} , Fe^{+2} , were above the maximum threshold value permissible for drinking water proposed by WHO. The aquifer are shallow ranging with depths 54.90m and 45.76m respectively, grain size analysis revealed that the aquifer geometry were semi confined to unconfined and mainly of fine to coarse sand grains with intercalation of clay/shale. Heavy mineral analysis shows a preponderance of zircon, rutile, staurolite, gamet, tourmaline and kyanite suggesting that the sediments were from basement complex source. The foregoing revealed that the aquifer is vyInerable to contamination, the authors' advocates for routine treatment of sych water before consumption while remediation measure is advice.

Keywords: Assessment, WHO, groundwater quality, boreholes and heavy minerals

INTRODUCTION

In Benin City as of today, groundwater has become the major source of drinking water because the government is unable to meet the ever increasing water demand. The quality of these groundwater sources are affected by the characteristics of the media (geology) through

which it percolates and the anthropogenic activities going on in the areas thus, the heavy metals discharged by industries, traffic, municipal wastes, hazardous waste sites, automobile workshops as well as from fertilizers for agricultural purposes and accidental oil spillages from tankers can result in a steady rise in contamination of groundwater (Vodela *et al.*, 1997; Igwilo *et al.*, 2006; Adeyemi *et al.*, 2007; Imasuen and Omorogieva, 2013a).

The study area is characterize with heavy rainfall and moderate temperature. The expansion of Benin metropolisin recent times is currently attracting land speculators against the backdrop of distance from the city centre; consequently, the communities have been merging and have form parts of Benin City. The communities are mainly residential quarters with pockets of cottage industries coupled with agricultural activities (Omorogieva, 2016). The communities are accessed through Upper Sokponba and Sapele roads as well as Benin City bypass (Fig. 1). World Health Organization (WHO) and United Nations Children Education Fund (UNICEF) emphasized that having access to clean water under the programme of Water Sanitation and Health (WASH) particularly children and those living in the rural communities and suburbs is a priority.

Therefore, the assumptions that groundwater is clean and drilling should be done blindly are an act of ignorance and the consequences far outweigh the benefits (Imasuen *et al*, 2016). Since the stratigraphy of a terrain plays an important role in groundwater contamination especially when the aquifer geometry is unconfined, it becomes imperative to understand the lithology of an area and how it interplay with groundwater resources (Onyeobi and Akujieze, 2014; Akpoborie, 2000; Imasuen *et al*, 2016). If an aquifer is unconfined and shallow, there is a high possibility of vulnerability to contaminants of different source and kind, especially when they are close to area of high population density with high anthropogenic activities (Isikhuemen and Omorogieva, 2015 and 2015a). This study is aimed at assessing the aquifer geometry of the study locations as well as to determine the water quality in comparison with WHO standard. The study has contributes to groundwater modeling and environmental indices in the area, facilitates policy maker with respect to environmental management plans and groundwater protection and management.



Fig. 1: Location map of the study communities

Geology of the Study Locations

The area understudy falls within the Benin Formation (Short and Stauble, 1967) which is the youngest and topmost unit of the tertiary Niger Delta (Fig. 2).



Fig. 2: Schematic structural cross section of Niger Delta (After Short and Stauble, 1967)

It consists of over 90% sandstone usually coarse grained, granular, poorly sorted, sub angular to well-rounded with major shale intercalations; they bear lignite streak and wood fragment. The formation is thicker in the central onshore part of the delta where it reaches about 2,100metres (Avborbo, 1978; Imasuen et al., 2016; Omorogieva, 2016). It contains very little hydrocarbon accumulation. The colour is generally white to yellowish brown. In the subsurface it is of Oligocene in age in the north becoming progressively younger southwards, in general it ranges from Miocene to Recent. The Niger delta province is a sedimentary basin highly constructive with a characteristic elongated shape; the sediments that accumulate at the mouth usually formed the deltaic deposits. The Niger Delta is bounded on the west by the Okitipupa uplift which separates it from the Benin Basin. Its eastern limit is the Cameroon volcanic line. To the north it passes into a series of much older Cretaceous tectonic elements while it is open ended to the south. The cycle started from the Eocene to Recent and marked the continuous growth of the main Niger Delta. Deposition of sediments into the Niger Delta is linked with late Eocene to the present phase which is largely regressive delta sequence. Sedimentation of the Niger Delta Basin (NDB) has been controlled by the interplay between rates of sediment supply and subsidence (Evamy *et al,*1978)

MATERIALS AND METHODS

The study sites (Evbuabogun and Okabere) are suburb in Ikpoba-Okha Local Government Area of Edo state, Nigeria (Fig. 1). Evbuabogun is accessed through Sapele road by Nigeria National Petroleum Corporation (NNPC) filling station and on coordinates N 06° 1.6' 23.6" and E 005° 39'38.9" and an elevation of 76meters above sea level (ASL) while Okabere is on the coordinates N 06° 1.6'23.6" and E 005° 39' 38.6" with elevation of 85meters above sea level (ASL) and can be accessed through Upper Sakponba road by Oka market junction Benin City (Fig.1). The materials used include water and soil samples obtained from the study site.

Sample Collection and Data Acquisition

Two boreholes4.2km apart at a depth of 54.90m and 45.76m deep respectively were manually drilled by the application of rotary method at Okabere and Evbuabogun.Soil samples were taken at 4.58m intervals for grain size and heavy mineral analysis in order to determine the aquifer geometry. The samples collected were placed in a labelled polythene bag and transported to laboratory for appropriate analysis. Water samples were collected from these borehole in order to determine its quality by analysing for its physical and chemical properties.

Laboratory Analysis

SOIL (Sieve Analysis)

Sieve analysis was carried out on twenty two soil samples obtained from well log in order to determine the particle size distribution and individual grains. The samples were first air dried and 50g of soil sample was weighed and sieve analysis was carried out on each of the twenty two (22) samples with a set of mechanical shaker.50g of each sample was poured into a set of sieves arranged in descending order to mesh diameter from top to bottom and a receiving pan at the base. The topmost sieve was covered and the set of sieve mounted on an automatic electric sieve-shaker for about five (5) minutes, at the end of each sieving, samples retained on each sieve or screen was carefully

removed and weighed. Weights of each retained fraction was recorded against each sieve and later converted to percentage weight and the cumulative weight percent

HEAVY MINERAL

Soil samples collected from the boreholes were subjected to heavy mineral analysis. The apparatus used for the heavy mineral separation include; fume cupboard, separating funnel, filtering funnel with filter paper, a retort stand, flat bottom flask, Canada balsam, a hot plate, slides and hand gloves.

The experiment was set up in a fume cupboard and bromoform was poured directly into a separating funnel arranged with a collecting flask and a filter paper fixed on a funnel and placed beneath the separating funnel. A weight of 5g of each sample was measured from the twenty two samples of each depth intervals of the borehole log. The mixture was stirred with a stirring rod until the heavy fractions are no longer observed to sink to the bottom of the flask. The mixture is allowed to settle, after complete settlement the stopper is then opened gently to allow the accumulated heavy mineral flow out and collected on top of the filter paper in the filtering funnel while bromoform drains into the flat bottom flask under the filtering funnel and the tap is closed, once complete separation of heavy mineral is ensured. The heavy minerals collected in the filter paper is drained and weighed in the chemical balance, and the result recorded. The heavy mineral is mounted on a glass slide using Canada balsam under controlled heat and allowed to cool. The glass slide is subjected to petrographic examination in order to determine the heavy mineral present.

WATER

The water sample collected during test pumping was analysed for its physical and heavy metals. In this study, the procedures proposed by America Public Health Association (APHA, 1985) and Allen *et al*, (1974) were adopted with slight modification. Heavy metals were

determined with Atomic Absorption Spectrometer (AAS) unicam series model 969 with air acetylene after digesting with $HNO_{3'}$ $HCLO_{3}$ and HCI at ratio 3:1:2. Temperature, Electrical Conductivity (EC) and pH were measured in situ with appropriate instrument. TDS were determined using gravimetric method in which case the sample was vigorously shaken and a measured volume was transferred into 100ml graduated cylinder by means of a funnel. The sample was filtered through a glass fibre filter and vacuum applied for 3 minutes to ensure that water was removed as much as possible. The sample was washed with deionised water and suction continued for at least three (3) minutes. The total filtrate was transferred to a weighted evaporating dish and evaporated to dryness on a water bath. The evaporated sample was dried for at least one (1) hour at 1800°C.

The dried sample was cooled in desiccators and weighed. Drying and weighing process was repeated until a constant weight was obtained. Total Alkalinity, TH and Cl⁻ concentrations were determined using titrimetric methods. Alkality was determined by titration of 50ml water sample with 0.1M hydrochloric acid to pH 4.5 using methyl orange as indicator while TH was analysed by titration of 50ml water sample with standard EDTA at pH10 using Erichrome black T as indicator. The Cl⁻ content was determine by argentometric method. The sample was titrated with standard silver nitrate using potassium chromate indicator.

RESULTS AND DISCUSSION

The results obtained from the sieve analysis was used to determine the grain sizes and the aquifer geometry of the study areas. Figure 2 represents the two boreholes and their lithologic description.



Fig. 3: A cross section of the borehole logs and their correlation (lmasuen *et al.*, 2016)

The boreholes were overlain with lateritic overburden of about 9.15m at both communities. At 18.30m deep in Evbuabogun, fine sands with intercalation of clay were encountered whereas at the same depth in Okabere, clay/shale with intercalation of fine sands materials were observed (Fig. 2). At Evbuabogun, the fine sands with intercalation of clay/shale were underlain with fine sands at a depth of 22.88m. The fine sands were underlain with dry coarse sands with intercalation of clay/shale at a depth of 27.45m. The coarse dry sands was underlain with fine sands from a depth of 27.76m to 41.18m; coarse wets sands which is the aquifer bearing unit was observed from the depth of 41.48m and continues down hole. On the other hand, at a depth of 32.33m to about 36.6 clay materials were observed to have cap fine sands and very fine sands with thicknesses of 4.58m each and 9.15m at a depth of 36.91m to 41.18m and 41.48m to 45.75m respectively. From the sieve analysis and litho log obtained from the boreholes, it

was observed that aquifer geometry at Okabere is semi confined to confined while that of Evbuabogun was unconfined (Fig. 2). Heavy mineral result revealed the presence of assessory minerals such as zircon, rutile, staurolite, gamet, tourmaline and kyanite, which indicate that the parent rock is basement complex origin.

The results obtained for cation in both boreholes are represented in the Figure 3a-d. The result shows that potassium (K⁺) ion result of 11 mg/L obtained in Okabare was above 10 mg/L upper limit set by World Health Organization (WHO, 2009) for drinking water. The major source of potassium in groundwater is attributed to the dissolution of silicate mineral which constitute over 90% of the earth materials make up in the study aquifer (Imasuen *et al.*, 2016). Other cations that were measured in this study include Na⁺ 10.5 mg/L Okabere and 9.5 mg/L Evbuabogun, Mg^{2+} 3 mg/L Okabere and 3.2mg/L Evbuabogun, Ca^{2+1} mg/L Okabere and Evbuabogun 1.5 mg/L respectively compare to WHO upper limit of 20 mg/L, 50 mg/L and 75 mg/L respectively (Fig.3a-d). Figure (e) show the distribution of the cations.



Fig. 3a-d: Results of cations obtained from both boreholes with WHO standards

Chlorde (Cl⁻), sulphate (SO_4^{2-}) , nitrate (NO_3^{-}) and phosphate (PO_4^{3-}) were some of the anions measured in Okabere and Evbuabogun borehole respectively. The values obtained in each borehole is represented in Figure 4a-d with Cl⁻having (39 mg/L and 43 mg/L), $SO_4^{2-}(8 \text{ mg/L} \text{ and } 8.8 \text{ mg/L})$, $NO_3^{-}(5.5 \text{ mg/L} \text{ and } 6 \text{ mg/L})$ and PO_4^{3-} (4.0 mg/L and 4.2 mg/L) respectively. The Figure clearly shows that values obtained in the Evbuabogun boreholes were relatively higher than those obtained from Okabere. This could be explained by the nature of earth materials and aquifer geometry (unconfined aquifer with high percentage of coarse sand).

The value obtained were however below World Health Organization (WHO) specification except phosphate (PO₄³⁻) which is higher than the threshold value specified by WHO and Nigeria Drinking Water Standard (NDWS). Phosphorus is the major source of phosphate ion in groundwater aside animal waste, plants and erosion of substances containing dissolve phosphorus, and it is highly reactive (Joseph and Henry, 2012). Soil have the capacity to store phosphorus , and once the capacity of soil to absorb phosphorus is exceeded, the excess will dissolve and move more freely with water either directly to stream or percolate to an aquifer. There is a growing awareness that long term over application of manure and chemical fertilizer also contributes to phosphorus movement into the groundwater resources. Figure 4e, represents the distribution of the anions in the study area.





CARD International Journal of Environmental Studies and Safety Research (IJESSR) Volume 1, Number 2, September 2016



Figure 5a-g: Results of metals obtained at both boreholes with WHO standards.

Eight metals were assessed in this study (Fe, Zn, Mn, Cu, Ni, V, Cr and Pb) of which Ni,Cr and Pb have a significant health impact. The values obtained in this study for Zn and Cu were below the specification of WHO and Nigeria Drinking Water Standard (NDWS) Figure 5d and 5b respectively. However, the values obtained for Fe, Mn, Ni, Cr and Pb were above the tolerable limit for drinking water purpose. Most worrisome is the level of hexavalent chromium (Cr⁶⁺), lead (Pb²⁺) and Nickel (Ni⁺) which is present above the specified WHO/NDWS limits for drinking water. Lead, Chromium and Nickel have been reported to have course health challenges which if not properly manage result in death (NRC, 1999; Omorogieva *et al.*, 2003). Figure six (6) show the trend inmetals distribution in groundwater at Okabere and Evbuabogun respectively.



Fig. 6: trend in metals distribution in groundwater at Okabere and Evbuabogun

Factors responsible for the high concentration of metals and high level of contamination in the groundwater system include the high anthropogenic activities like automobile workshop, runoff of water containing dissolve substances, long term application of fertilizer by local famers, septic tanks and the geology of the terrain combined with the aquifer geometry. The mechanism of mobility is influence by the high level of rainfall and the nature of soil which is mainly dominated with over 90% of sand and about 10% of clayinteraction at some depths. Pearson correlation represented in simple chat (Fig. 7) shows a strong relationship between the contaminants measured indicating anthropogenic influence.



Fig. 7: correlation matrix of contaminants measured at P < 0.05

Geochemistry of Lead and Chromium in Water

The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. The primary source of leadin the study area include lead battery from automobile workshop, condemn engine oil, vehicular emission and lead contaminated wastes (Imasuen and Omorogieva, 2013a). Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead-metal oxyanion complexes (Smith *et al.*, 1995). Lead exhibit oxidation state of o or +2; however Pb²⁺ is the more common and reactive form of lead and forms mononuclear and polynuclear oxides are the most stable forms of lead (Smith *et al.*, 1995). At low solubility,inorganic(Cl⁻, CO₃²⁻, SO₄²⁻,

 $PO_{4^{3^{-}}}$ and organic ligands (humic and fulvic acids, EDTA, amino acids)compounds are formed (Bodek *et al.*, 1988). Lead released to the environment is retained in the soil and are eventually washed down. Factors such as adsorption, ion exchange, precipitation, and complexation with sorbed organic matter are responsible for the mobility of lead in soil. These processes limit the amount of lead that can be transported into the surface water or groundwater (Smith *et al.*, 1995).

Like other metals, chromium (Cr) does not occur naturally in elemental form, but only in compounds. The major source of chromium in groundwater is the weathering of $FeCr_2O_4$ the major ore of chromium and chromium containing wastes which infiltrates into aquifer especially when they are shallow and unconfined. The availability of Cr^{+6} and Cr^{+3} is the function of pH and redox conditions; at low pH, Cr^{+3} is dominant and at high pH, Cr^{+6} is dominant these influence the mobility and availability of the species in water system. Chromium $six(Cr^{+6})$ is dominant in shallow aquifers where aerobic conditions exist but can be reduced to Cr^{+3} by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions in deeper aquifer whereas Cr_{3}^{+} forms solution complexes with NH3, OH⁻, Cl⁻, F⁻, CN⁻, $SO_{4^2}^{-}$, and soluble organic ligands/Smith *et al.*, 1995). Chromiumsix (Cr^{+6}) is the more toxic and is also more mobile. Chromium (III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3(s)$, Chrotowski *et al.*, [1991].

CONCLUSION

Chemical and physical properties of the contaminated matrix influence the mobility of metals in soils and ground water. The study revealed that metals elevation in the boreholes were influenced by anthropogenic actives couple with the geology and soil type. The unconfined shallow aquifer at Evbuabogun were observed to have higher values of the contaminants measured compare to Okabere borehole which was relatively deeper and semi confined. Water treatment plant is advocated

CARD International Journal of Environmental Studies and Safety Research (IJESSR) Volume 1, Number 2, September 2016

in these study communities in order to forestall the implication of consuming water laden with such deleterious metals. Metals such hexavalent chromium, lead and nickel undergo bioaccumulation and result in toxic effects on humans that are victims, therefore all hands must be on deck to ensure availability of potable drinking water and to protect the available water resources for sustainable development of which the government has a role to play. The study show that shallow unconfined aquifer are vulnerable to contamination; study such as this is of paramount important in environmental planning and decision making process for sustainable development.

Authors Contributions: OOM designed the research and write the manuscript for publication while NNJ did the analysis and OOM interpreted the results. OOM and NNJ went to field for investigation and samples collection as well as proof reading the manuscript for publication.

Acknowledgements: The author appreciates the head of department and technical staffs of geology and chemistry as well as splendid research laboratory manager for their effort and contributions towards the success of material analysis.

Funding: The research was self-funded.

Conflicts of interest: None declared

Ethical Approval: All field investigation, samples analysis and experiment were carried out in line with current and best practice in the field of Geosciences.

REFERENCES

- Adeyemi, O. Oloyede, O.B. and Oladiji, A.T. Physicochemical and Microbial Characteristics of Leachate Contaminated Groundwater. *Asian J. Biochem. 2007Vol.2/5/pp343-348.*
- Akpoborie, I.A. Ekakite, A. O.; Adaikpoh, E.O. The Quality of Groundwater from dug wells in Parts of the Western Niger Delta. *Knowledge Review 2000 2:72-79*.
- Allen, S. E. Grinshaw, H. W. Parkinson J. A. and Quarmby, C. Chemical Methods of Analysing Ecological Materials. London, UK, Blackwell Scientific Publication 1974pp565.
- AmericaPublic Health Association. Standard Methods for the Examination of Water and Waste Water. 18th Edition, Washington D.C. 1985pp 4-17
- Avbovbor, A. A. Tertiary lithostratigraphy of Niger Delta. American Association of Petroleum Geologists Bulletin, 1978 vol. 62 pp. 295-300
- Bodek, I. Lyman, W.J. Reehl, W.F. and Rosenblatt, D.H. Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods. *Pergamon Press, Elmsford, 1988* NY
- Chrotowski, P., Durda, J.L., and Edelman, K.G. "The Use of Natural Processes for the Control of Chromium Migration. *Remediation, 1991 Vol.2, pp. 341-351*
- Evamy, B.D., Haremboure, J., Kamerling, P., Knaap, W.A., Molloy, F.A., and Rowlands, P.H. Hydrocarbon habitat of Tertiary Niger Delta: *American Association of Petroleum Geologists Bulletin, 1978 Vol. 62, pp. 277-298*.

- lgwilo, I.O., Afonne, O.J., Maduabuchi, U.J., and Orisakwe, O.E. Toxicological study of the Anam River in Otuocha, Anambra State, Nigeria. Arch. Environ. Occup. Health. 2006 Vol.61/5/ pp205-208
- Imasuen, O.I. and Omorogieva, O.M. Sources and Environmental Implication of Heavy Metal Pollution in Plants Grown Around Contaminated Site in Edo State, Nigeria. Resource Journal in Engineering and Applied Sciences, 2013a Vol.2/5/385-391 USA
- Imasuen, O.I. Omorogieva, O.M and Nwokolo, N.J (: Grain size and Heavy Mineral Analysis of two Boreholes from Recent to Miocene Aquifer in Benin Formation. Nigeria Journal of Technology 2016 (accepted for publication)
- lsikhueme, I. M. and Omorogieva, O.M. Hydrogeology and Water Quality Assessment of the Middle Aquiferous Horizon of Onitsha in Anambra Basin, Eastern Nigeria. *British Journal of Applied Science and Technology. 2015a 9 (3/ 475 - 491.*
- Joseph, L.D. and Henry, J. Phosphorus and groundwater: Establishing Links between Agricultural use and Transport Systems. *USGS* 2012 pp1-6.
- National Research Council. Arsenic in Drinking Water. National Academic Press, Washington DC.1999
- Omorogieva, O.M. Geoenvironmental Characterization of Leachate and Hydrogeochemical Properties of Ikhueniro Dumpsite and Environs in Benin City, Edo State. Unpublished Master of Philosophy thesis submitted School of Postgraduate studies, University of Benin, Benin City. 2016 pp135

- Omorogieva, O.M. Imasuen, O.I and Sanni E.B. Analysis of heavy metals Hg, As, Cd, Pb, Cr and Ni in Waste Currency Dumpsite and its Environmental and Health Implications. *Journal of Science Research 2013Vol 12 pp 87-94*
- Onyeobi, T. U S and Akujieze, C.N. Characterization of Soils and Sediment Parameters of Jisik- Izombi Upper Aquifer System for Assessment of the Potential of Groundwater Pollution. J. Appl. Sci. Environ. Manage. 2014 Vol. 18 (4/ pp 677-683
- Short, K.C. and Stauble, A. Outline of the Geology of the Niger Delta. AAPG Bulletin.1967 Vol. 51, p761-779
- Smith, L.A. Means, J.L. Chen, A., Alleman, B. Chapman, C.C. Tixier, J.S., Brauning, S.E. Gavaskar, A.R. and Royer, M.D. Remedial Options for Metals-Contaminated Sites. Lewis Publishers,1995 Boca Raton, FL
- Vodela, J.K., Renden, J.A., Lenz, S.D., Mchel Henney, W.H., and Kemppainen, B.W. Drinking water contaminants. *Poult. Sci., 1997 Vol.76 pp 1474-1492*
- WHO. Guideline Values for Chemicals that are of Health Significance in Drinking Water Quality. *World Health Organization, Geneva 2009pp41-49.*