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Hydrochemical Characteristics And Heavy Metal Concentrations In Groundwater Around Active Solid Wastes Dumpsites In Rumueme And Elijiji Communities In Rivers State, Nigeria

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Abstract
Levels of Physicochemical and Heavy Metal properties of groundwater and soil samples in parts of Obio/Akpor LGA, Rivers State, were assessed in this study. Heavy Metals were determined using Atomic Absorption Spectrophotometer, The results for groundwater showed maximum mean levels of Lead (0.209±0.281 mg/L), Chromium (1.904±1.542 mg/L) and Nickel (0.185±0.119 mg/L).. Chromium and Lead levels were above standard limits (0.05 mg/L and 0.02 mg/L respectively) in most stations. Plot of the Piper diagram revealed that the groundwater had sodium bicarbonate, sodium chloride and mixed water types across the sample stations, while the Durov diagram suggested that ion dissolution and mixing/uncommon dissolution processes governed the groundwater types. The study recommends that regular monitoring of activities around dump sites should be done routinely and strict environmental laws governing waste disposal be enacted and enforced.

Keywords: *Hydrochemical Characteristics, Groundwater, Heavy Metals, Solid Wastes, Dumpsites. Rivers State*

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I. Introduction

The impact of poor waste management on human health and well-being cannot be overemphasized. Individuals living adjacent to dumpsites are at high risk due to the potential of waste to pollute drinking water, food, vegetation, land and air (Njoroge, 2007). Waste comes from various sources: domestic residences, offices, institutions, commercial buildings, restaurants, agriculture, construction, and hospitals. The majority of the wastes generated from these sources ends up in dumpsites. Across many cities in Nigeria, collected wastes are usually burnt outdoors and ashes are poorly disposed of on-site. This act destroys the organic components and causes the oxidation of metals. The ashes left behind are enriched with metal, which results in pollution of the soil and drinking water quality surrounding this environment (Adeyi and Majolagbe, 2014; Henry, *et al.,* 2017; Temilola *et al.,* 2014).

Water is the most abundant environmental resource on earth but its accessibility is based on quality and quantity, as well as space and time. It may be available in various forms and quantity but its use for various purposes is the subject of quality. About 70% of the human body and about 60-70% of plant cells is made up of water (Smith and Edger, 2006). It is one of the demands of human settlement, existence and activities on the earth. Its quantity is fixed but dynamic in formation and storage. Of all the environmental concerns that developing countries face, the lack of adequate, good quality water remains the most serious (Markandya, 2004). Once contaminated, groundwater may forever remain polluted without remedy or treatment. Water is one of the determinants of human earth system. Diseases mayspring up through water pollution, especially groundwater contamination, and rapidly spread beyond human expectation because of its flow mechanism (Afolayan *et al.,* 2012). One of the major factors that make the earth habitable for humans is the presence of water. Forming the major component of plant and animal cells, it is the basis of life and therefore the development of water resources is an important component in the integrated development of any area.

Active waste dumpsites have effect on the soil and groundwater quality in Nigeria, because it is generally faced with rapid deterioration of environmental conditions due to the conventional system of collection and dumping of solid wastes. Therefore, waste management has become a major concern in cities. Little efforts have been made in order to improve the waste collection and disposal facilities. The present study therefore was conducted to assess the significant impact of dumpsites in the two selected areas in Rivers state, Nigeria (Nsirim

Road and Elejiji Dumpsites) on soil and groundwater quality since the areas are residential and an emerging commercial area.

Hydrochemical evaluation of groundwater system is usually based on availability of a large amount of information concerning groundwater chemistry. The quality of groundwater is as important as its quantity owing to the suitability of water for various purposes. Groundwater chemistry, in turn, depends on a number of factors such as general geology, degree of chemical weathering of various rock types, quality of recharge water and inputs from sources other than rock interaction. Such factors and their interaction result in a complex water quality (Aghazadeh & Mogaddam, 2010). Groundwater quality is determined by natural and anthropogenic factors. Factors affecting groundwater are nature of bedrock geology, depth from surface soil, vegetation, climatic variation, permeability of sediments, and topography, while anthropogenic are nature of human activities, urbanization, industrialization and waste management disposal, amongst others.

Groundwater is the main sources of water supply for many countries. In many urban Africa, groundwater is a primary source for domestic use (Altchenko *et al.,* 2011, Lapworth *et al.,* 2017). According to Siebert et al. (2010), groundwater also accounts for 43% of the global irrigation water use and is more suitable for irrigation purpose compared to surface water. However, degradation of water quality is one of the problems of the 21st century (Oki and Akana, 2016). Globally, anthropogenic activities such as urbanization, industrial development and agricultural intensification are degrading groundwater quality (Li, 2016, Li *et al.,* 2017, Foster *et al.,* 2002, Nair *et al.,* 2015).

Groundwater is a major source of water for drinking and industrial use in Ethiopia. In Main Ethiopian rift, groundwater is highly used for drinking water supply (Reimann *et al.,* 2003). Many studies (Gizaw, 1996, Gizaw, 2002, Ayenew, 2005, Ayenew, 2008, Kebede *et al.*, 2008, Rango *et al.*, 2010, Furi *et al.*, 2011, Demlie and Wohnlich, 2006, Demlie *et al.*, 2007a, Demlie *et al.*, 2007b, Demlie *et al.*, 2008, Yitbarek *et al.*, 2012, UNDP, 1973, Chernet, 1982, Wood and Talling, 1988, Halcrow., 1989, Kebede et al., 2005) reported on the hydrochemistry of the Ethiopian rift. The hydrochemistry of the highlands and the rift valley aquifers is different. High F^- concentrations in rift valley groundwater were reported by many researchers (Ayenew, 2005, Rango *et al.*, 2010, Reimann *et al*., 2003, Furi *et al.,* 2011) and it is main geogenic problem of drinking water supply. Volcanic aquifers composed of mica; pyroxene and amphiboles are sources of fluoride in the ground water of study area (Furi *et al*., 2011). In addition, anthropogenic activities such urban sewages, industrial and agricultural expansion are deteriorating surface and groundwater quality in Main Ethiopian Rift particularly in Modjo River basin. Domestic and industrial wastes are polluting Modjo River (Amanial, 2015). As a result, groundwater abstraction wells located along and close to Modjo River are highly polluted (Berehanu, 2007). Despite the fact that groundwater resources are serving the survival of millions of people in Main Ethiopia rift, there was no water quality monitoring system, no aquifer and well head protection zones for groundwater quality protection. In study area, Modjo River basin, producing a spatial variation map of major cations and anions is essential for proper development of new groundwater schemes and management of groundwater resources. Thus, the objectives of the study are to evaluate groundwater suitability for drinking purpose and irrigation purpose. Spatial variation map of major cations and anions in groundwater of Modjo river basin were produced using IDW interpolation in GIS.

Waste disposal has assumed a frightening dimension with its attendant effects on the environment, health and wellbeing of people hence, approaching it holistically is a non-negotiable alternative for a healthy and sustainable living (Ahmad et al., 2013). Population growth and economic development lead to enormous amounts of solid waste generation by the dwellers of the urban areas (Verge and Rowe, 2013). Furthermore, waste is usually generated from human settlements, small industries and commercial activities (Singh et al., 2011). Soil contamination through waste discharges, particularly hazardous wastes, is a worldwide phenomenon and carries different metals which are then transferred to plants by different ways (Akinbile and Yusoff, 2012).

Many studies show evidence of seriousness of hazards caused by open waste dumping ultimately affecting the plant life on the planet leading towards an irreversible erosion trend unless the present land use pattern is checked (Phil-Eze, 2010). Solid waste pollutants serve as an external force affecting the physicochemical characteristics of soil ultimately contributing towards the poor production of vegetation (Christensen et al., 2014).

The contamination of soil by heavy metal can cause adverse effects on human health, animals and soil productivity (Smith *et al.,* 1996) and depending on the tendency of the contaminants, they end up either in water held in the soil or leached to the underground water. Contaminants like Cd, Cu, Ni, Pb and Zn can alter the soil chemistry and have an impact on the organisms and plants depending on the soil for nutrition (Voutsa *et al.,* 1996).

Temilola ***et al.,*** (2014), studied a comparative assessment of the impact of a functional and an abandoned waste dump site on the quality of neighbouring groundwater was carried out at in Lagos Nigeria. The levels of some physico-chemical, microbial and heavy metals of two soil samples obtained from the dumpsites and nine hand-dug wells at different proximities to the dumpsites were accessed. pH, Conductivity, Total solids, Total dissolved solids, Dissolved oxygen, Biochemical oxygen demand, Chloride, Acidity, Alkalinity, Hardness, Phosphate, Nitrate, Sulphate, copper, cadmium, chromium, iron, lead and zinc, Total heterotrophic bacteria, Total heterotrophic fungi and Total coliform, were determined in the water samples while pH, Total organic carbon and some potentially toxic metals were determined in the soil samples. Mean concentration of the physico-chemical parameters except sulphate and phosphate were found to be greater at wells near the functional dumpsite at Olusosun. However, all the parameters determined were within World Health Organization (WHO) and Nigerian Standard for Drinking Water Quality (NSDWQ) permissible limits. Metals in the water sample were within WHO and NSDWQ permissible limit except for Lead in both dumpsites with mean concentration of 0.069 ± 0.075mg/l for wells near Oke-Afa dumpsite and 0.17 ± 0.086mg/l for wells near Olusosun dumpsite. The soil samples in both dumpsites show a considerable level of pollution as all the metal determined exceeded the specified WHO limit. The comparative analysis of the abandoned dumpsite with the active dumpsite reveals no significant difference in the concentration of soil and water parameters measured. However, this study is similar to Temilola *et al.,* (2014) and Henry, *et al.,* (2017), but defer in terms of number of parameters of solid heavy metals and groundwater reactive parameters measured and also the locations/positions of heavy metals of soil/groundwater samples.

II. Materials And Methods

The Study Area

Obio/Akpor Local Government Area of Rivers State is located between latitudes 4˚45′ N and 4˚60′ N and longitudes 6˚50′ E and 8˚00′ E (Fig. 1). Rivers state is found in the coastal plain of the Eastern Niger Delta (UNEP, 2011). Temperature ranges from 21.2 ˚C to 33.4 ˚C. Annual rainfall is 4,700 mm/year (UNEP, 2011). Major economic activities of environmental significance in the study area include primary, secondary and tertiary institutions, hotels, hospitals, mechanic workshops, petrol stations and small-scale industries. The communities in the study area are densely populated, thus, large quantities of domestic and household wastes are generated and most of the time, dumped indiscriminately at several dumpsites at various locations within the communities.

Sample Collection

Water samples were collected in polyethylene bottles of one to two litre capacities. Prior to the collection of samples, the bottles were washed thoroughly and rinsed with water, dilute HNO_3, distilled water and a small quality of the water to be sampled. All collected samples were properly and carefully labelled instantly according to the name of the place or location. Water samples collected were transported to the laboratory and then filtered using the Whatman filter paper, then acidified using concentrated HNO_3 to maintain the pH at 2, and then kept in a dark room. Field measurements of pH, specific conductivity, water level, turbidity and temperature were performed using multimeter.

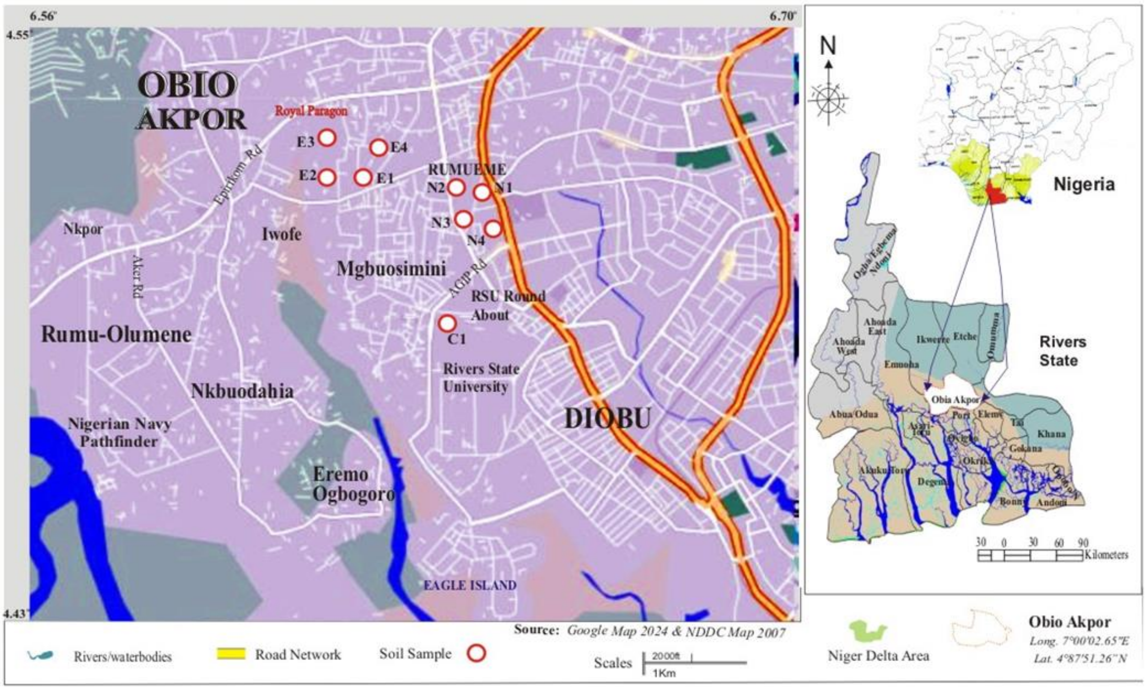

Figure 1: Map showing Sampling Locations for Groundwater Samples [N= Nsirim; E = Elejiji; C = Control]

Analytical Methods

The research adopted method proposed by American Public Health Association (APHA, 1995). All groundwater sample containers were checked and confirmed for proper type, adequate volume, integrity, temperature, preservation and holding time.

Heavy Metals; Samples collected from the study area were analysed for heavy metals using GBC XplorAA atomic absorption spectrophotometer instrument as stated in the Operational Manual (GBC 2016). To determine the concentrations of heavy metals, the sample was aspirated into a flame where it became atomized. A beam of light was directed through the flame into a monochromator and later into a detector that measured the intensity of the light energy absorbed. The intensity of light produced by a specific lamp, absorbed in the flame is directly proportional to the concentration of the element in the sample.

Hydrogeochemical Analysis; The quality of groundwater depends on the nature of bedrock, topography, geology, soils, atmospheric precipitation and anthropogenic pollution sources that result from agricultural and industrial activities; thus, having an understanding of the main factors governing groundwater chemistry is important for managing groundwater resources. The hydrogeochemical analysis of the groundwater samples was done using plots of the Piper, Durov and Gibbs diagrams.

III. Results

Heavy Metals

The heavy metal properties of the groundwater samples are shown it Table 3

Mean chromium levels fell between 0.545±0.766 - 1.904±1.542 mg/L and 0.001±0.000 mg/L at the control station; Mean nickel levels fell between 0.001±0.000 - 0.185±0.119 mg/L and 0.006±0.004 mg/L at the control station; Mean iron levels fell between 0.043±0.053 - 0.318±0.169 mg/L and 0.001±0.000 mg/L at the control station; Mean lead levels fell between 0.010±0.000 - 0.209±0.281 mg/L and 0.001±0.000 mg/L at the control station; while Mean manganese levels fell between 0.068±0.047 - 0.245±0.102 mg/L and 0.133±0.004 mg/L at the control station.

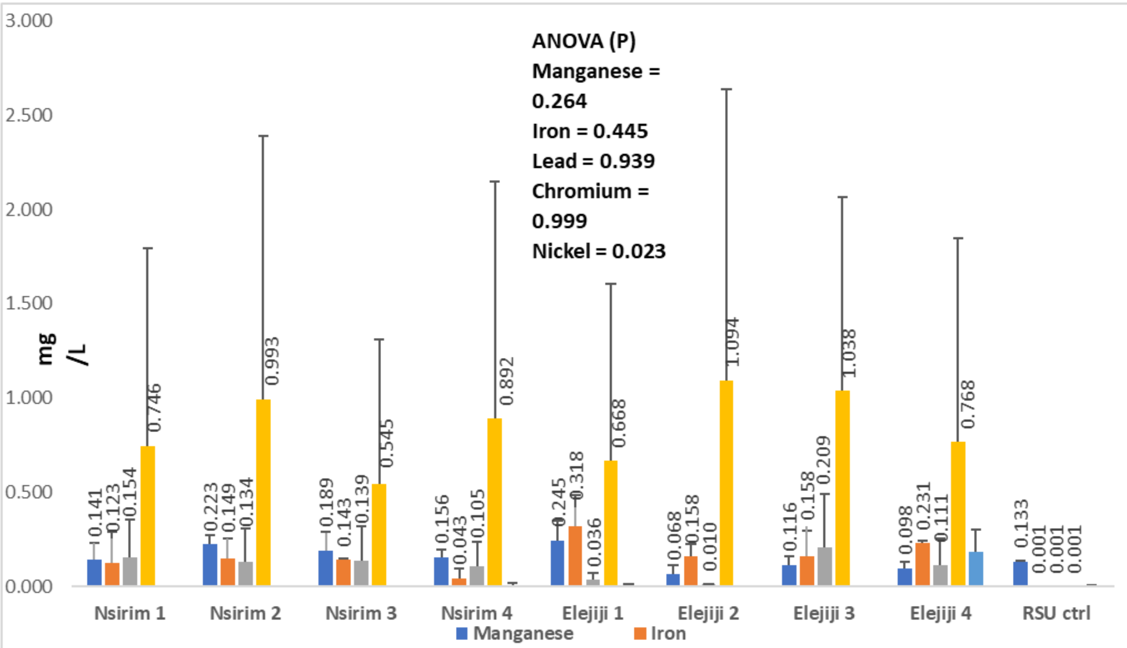

Fig. 2: Mean Levels of Heavy Metals

Piper Trilinear Diagram

Piper (1944) developed a trilinear diagram (Fig. 3) which evaluates the evolution of water and relationship between rock types and water composition. Plotting of samples on the Piper Trilinear Diagram reveals the composition of the water in the different sampling stations, indicating the water type. The milliequivalents of the various anions and cations are used and are plotted in two different triangular graphs. The points of these anions and cations on the x, y and z axes of the triangular graphs are extrapolated to determine the dominant ion types. The extrapolated points on the triangular graphs are further projected onto the diamond graph to determine the water type.

Durov diagram

The Durov diagram is a useful graphical tool that is widely used to identify the chemical relationship and evolution of groundwater samples (Chen *et al*, 2019), and helps in the interpretation of the evolutionary trends and the hydrogeochemical processes occurring in the groundwater system. Like the piper diagram, milliequivalents of cations and anions are plotted on the triangular graphs and the extrapolated points are projected onto the square plot to determine the hydrogeochemical process (Fig. 4). Water in the study areas was plotted on the Durov diagram and classified according to Lloyd and Heathcoat (1985)

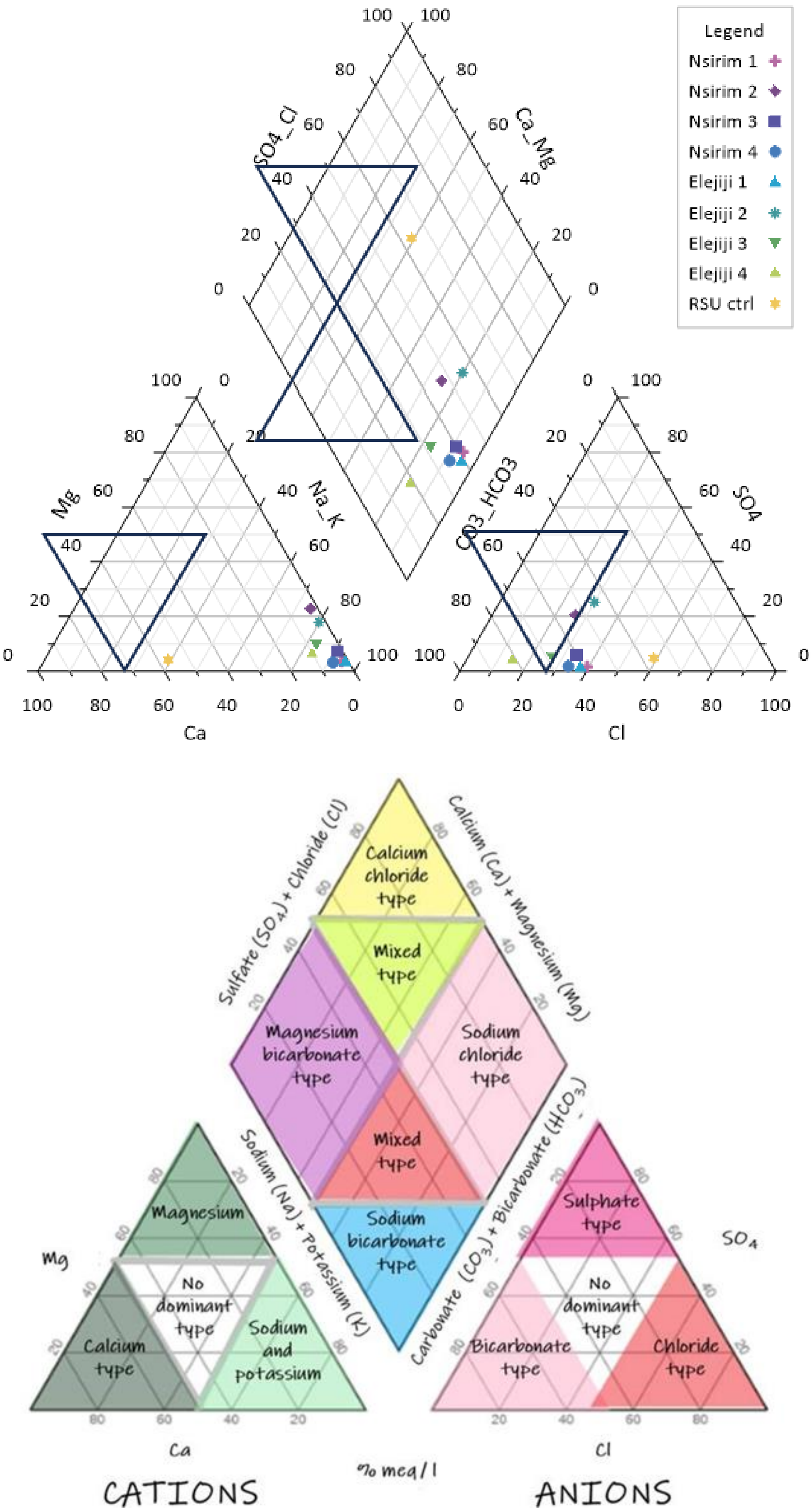

Fig. 3: Piper Trilinear Diagram

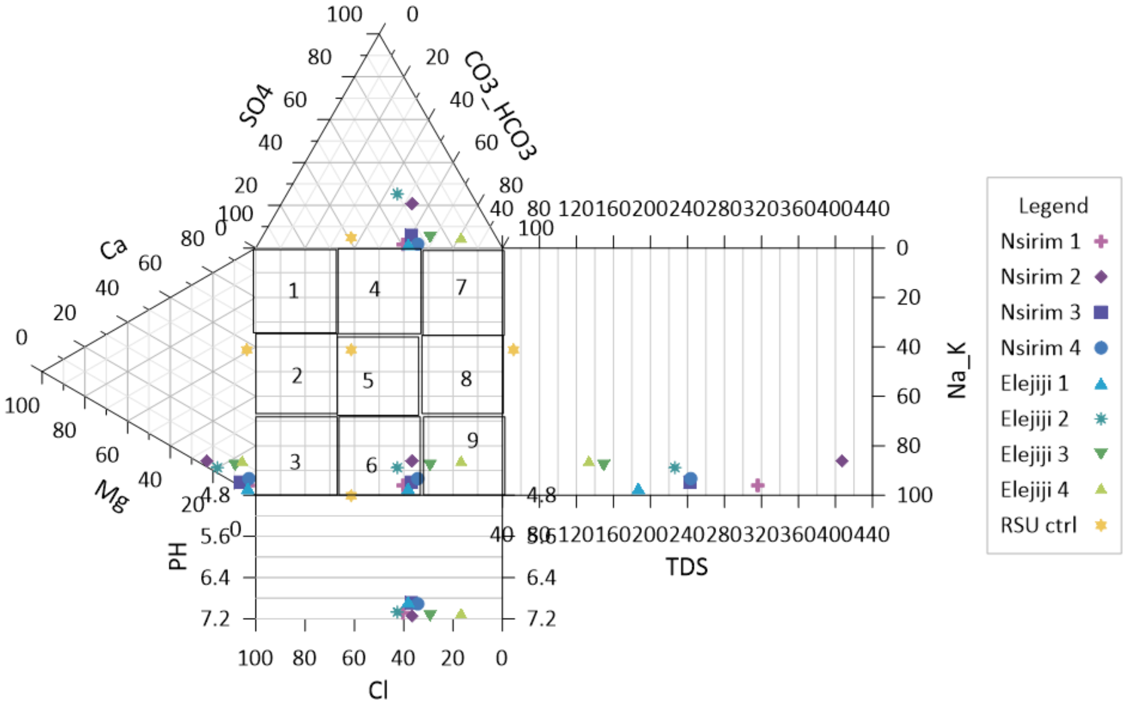

Fig. 4: Durov Diagram

IV. Discussion

Heavy Metal Properties

The permissible limit for chromium in drinking water is 0.05 mg/L as set by NSDWQ (2015) and WHO (1996). All stations had mean chromium levels above the set limit with Elejiji 2 recording the highest level of 1.094 mg/L. the control station recorded chromium level below the permissible limit. A study by Tukura *et al* (2014) recorded high Chromium concentrations in 52 borehole water sources from twelve local governments in Nasarawa State and attributed it to surface contamination originating from anthropogenic and geological sources. Excess chromium ions in water may have an erythropoietin impact, such as an expanded event of goiter among people and animals (Oyeku and Eludoyin, 2010). ANOVA results revealed there was no statistical significance between the mean chromium levels across stations the study area.

The NSDWQ (2015) set limit for nickel in drinking water is 0.02 mg/L. Only Elejiji 4 (0.185 mg/L) had mean nickel level above the acceptable limit. The control station recorded nickel level below the permissible limit. Victor and Fortune (2020) reported high nickel levels in a study carried out at Rumuola. Nickel may be present in groundwater as a consequence of dissolution from nickel ore-bearing rocks, influenced by high acidity (low pH) of the water (WHO, 2005). ANOVA results revealed there was no statistical significance between the nickel means across stations the study area.

The permissible limit for iron in drinking water is 0.30 mg/L as set by NSDWQ (2015) and USEPA (2004). Only Elejiji 1 recorded a level of 0.318 mg/L, slightly above the set limit, while other stations, including the control station, recorded mean iron levels below the permissible limit. Uzoije *et al* (2014), in a similar study at Buguma, reported higher iron levels in most of the sample areas in the range of 1.07 – 4.64 mg/L. Biologically iron is the most important nutrient for most living creatures as it is the cofactor for many vital proteins and enzymes (Jaishankar *et al*, 2014). Water containing an excessive concentration of iron has been reported to constitute a human health hazard leading to hemochromatosis, whose signs include fatigue and eventually, heart disease, liver complications, and diabetes (Nwachukwu *et al*, 2014). Children are highly susceptible to iron toxicity as they are exposed to a maximum of iron containing products (Albretsen, 2006). ANOVA results revealed there was no statistical significance between the mean iron levels across stations the study area.

The NSDWQ (2015) and WHO (1996) set limit for lead in drinking water is 0.02 mg/L. Only Elejiji 2 and the control station recorded mean lead level below the permissible limit. Other stations recorded higher mean lead levels, above the permissible limit, with Elejiji 3 recording the highest mean level of 0.209 mg/L. Lead causes damages to the nervous connection most especially in young children and also cause blood and brain disorder (Elinge *et al*., 2011). Lead in drinking water could have significant medical effects on renal functions (Alasia *et al*., 2009). Other symptoms of acute lead poisoning are headache, irritability, and abdominal pain (Jarup, 2003). ANOVA results revealed there was no statistical significance between the mean lead across stations the study area.

The permissible limit for manganese in drinking water is 0.2 mg/L as set by NSDWQ (2015). Nsirim 2 (0.223 mg/L) and Elejiji1 (0.245 mg/L) recorded had mean manganese levels above the set limit. The control station recorded manganese levels below the permissible limit. Uzoije *et al* (2014), in a similar study at Buguma, reported similar manganese levels in most of the sample areas in the range of 0.001 – 0.12 mg/L, with only two sample stations having high levels of 0.079 and 0.12 mg/L. ANOVA results revealed there was no statistical significance between the mean manganese levels across stations the study area.

Hydrogeochemical Analysis

Plot of the Piper diagram showed that 100 % of the groundwater samples were predominantly of the Na^+-K^+ cation type, while the control station was of the Ca^{2+} type. The groundwater samples also had 87.5 % of the samples (Nsirim 1, Nsirim 2, Nsirim 3, Nsirim 4, Elejiji 1, Elejiji 3 and Elejiji 4) was predominantly of the HCO_3^- anion type while 12.5 % (Elejiji 2) was of the no dominant anion type, while the control station was of the Cl type. The diamond section of the Piper diagram showed that 12.5 % of the groundwater samples (Elejiji 2) was classified as the Sodium Chloride type; 12.5 % (Nsirim 2) classified as the Mixed type while 75 % (Nsirim 1, Nsirim 3, Nsirim 4, Elejiji 1, Elejiji 3 and Elejiji 4) were classified as the Sodium Bicarbonate water type, while the control station was classified as the mixed type.

The Durov diagram using Table 1 suggests that Ion Dissolution was the predominant process controlling groundwater type of Elejiji 3 and Elejiji 4 stations, while Mixing/Uncommon Dissolution was the predominant process controlling groundwater quality of Nsirim 1, Nsirim 3, Nsirim 4, Elejiji 1 and Elejiji 2 stations; while simple dissolution/mixing of ions was the predominant process at the control station.

V. Conclusion

The assessment of groundwater in this study showed that Chromium and lead levels were above their respective permissible limits in almost all the sample stations. The assessment of the groundwater in this study from the Piper diagram revealed that the groundwater had sodium bicarbonate, sodium chloride and mixed water types across the sample stations. The Durov diagram suggested that ion dissolution and mixing/uncommon dissolution processes governed the groundwater types.

Regular monitoring of activities around dump sites; types of wasted deposited, disposal method, volume of environmentally unfriendly materials, etc, should be done routinely and strict environmental laws governing waste disposal be enacted and enforced.

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Table 1: Levels of some Water Quality Parameters in Groundwater at the Study Areas

STATIONS	Cl^- mg/l		Ca^{2+} mg/l		Mg^{2+} mg/l		Na^+ mg/l		K^+ mg/l		HCO_3^- mg/l		CO_3^{2-} mg/l		SO_4^{2-} mg/l	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
Nsirim 1	10.60	5.90	11.39	3.08	1.58	1.64	31.52	46.82	5.58	8.76	12.00	3.00	0.28	0.19	11.00	35.20
Nsirim 2	9.90	4.90	11.70	4.62	1.35	1.51	51,61	50.57	10.68	9.65	10.00	4.00	0.22	0.35	7.60	6.40
Nsirim 3	7.00	2.90	9.23	4.62	1.28	1.62	27.32	33.34	5.97	5.96	8.00	4.00	0.14	0.13	11.20	12.90
Nsirim 4	4.90	3.00	6.77	4.93	1.28	1.58	24.49	40.64	6.15	5.86	6.00	1.00	0.11	0.04	1.00	1.00
Elejiji 1	4.90	2.10	6.46	4.93	0.79	1.09	24.54	36.76	1.47	0.97	5.00	3.00	0.07	0.12	14.50	1.00
Elejiji 2	4.90	1.10	5.85	12.31	0.23	0.25	28.89	43.92	1.13	4.71	7.00	6.00	0.10	0.54	3.10	15.70
Elejiji 3	4.00	3.50	2.77	4.62	0.16	0.47	30.27	21.74	4.20	0.10	44.00	2.00	1.23	0.14	15.90	24.50
Elejiji 4	2.10	3.60	1.85	4.79	0.95	0.55	8.85	9.32	11.91	7.54	40.00	3.00	0.99	0.55	1.00	20.20
RSU ctrl	9.90	9.90	13.99	5.81	0.62	0.25	4.43	4.41	6.82	4.76	4.00	16.00	0.25	0.23	1.00	1.20

Table 2: Levels of Heavy Metals in Groundwater at the Study Areas

STATIONS	Cr mg/l		Ni mg/l		Mn mg/l		Fe mg/l		Pb mg/l	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
Nsirim 1	1.488	0.003	0.001	0.001	0.203	0.079	0.005	0.240	0.010	0.297
Nsirim 2	1.983	0.003	0.001	0.001	0.258	0.187	0.225	0.072	0.010	0.257
Nsirim 3	1.086	0.003	0.001	0.001	0.261	0.117	0.148	0.137	0.010	0.268
Nsirim 4	1.781	0.003	0.017	0.001	0.183	0.129	0.005	0.080	0.010	0.200
Elejiji 1	1.332	0.003	0.009	0.001	0.317	0.173	0.437	0.198	0.010	0.062
Elejiji 2	2.184	0.003	0.001	0.001	0.101	0.035	0.207	0.108	0.010	0.010
Elejiji 3	1.766	0.309	0.001	0.001	0.148	0.083	0.061	0.254	0.010	0.407
Elejiji 4	1.532	0.003	0.269	0.101	0.123	0.072	0.240	0.222	0.010	0.211
	0.001	0.001	0.003	0.008	0.13	0.135	0.001	0.001	0.001	0.001