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THE STUDY OF POSSIBLE CHEMICAL COMPONENT OF WATER IN DUMPSITE VICINITY CONSIDERING A ZONE IN SOUTH EASTERN NIGERIA

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ABSTRACT

This study investigates the leachate contamination and assess the pollution risk associated with the Nekede dumpsite located in Owerri southeastern Nigerian. This dumpsite poses significant environmental threats particularly on ground water and soil contamination due to unregulated solid waste disposal and subsequent leachate generation. A total of eight borehole water samples were collected within the months of December, January and February to represents dry season and the months of may, June and July to represent rainy season. Six ground water samples within the vicinity of the dumpsite and two control far away from the vicinity and one leachate sample during rainy season was collected too . The soil samples were collected 100m away from each other and at a depth of three different depths (surface, 15cm and 30cm) on the dumpsite using a Dutch soil auger. The soil samples were collected from seven different location points within the dumpsite with two points serving as controls. The water and soil samples were analyzed for physicochemical properties, pollution indices, Hydro-geochemical fancies of groundwater irrigation quality, contamination level of water and soils using pollution risks models(contamination factor, pollution load index, geo-accumulation index, enrichments factor etc) health risk assessment and descriptive statistical analysis were all carried out .The soils were observed to have a PH value of averaging 5.1to 8.3 indicating slightly acidic to moderately alkaline while the groundwater were observed to have a mean PH of 4.61 and 4.49 for both dry and rainy seasons respectively indicating acidic water which fall outside the WHO sanitation standard range of 6.5-8.5 along with the Nigerian standard. The nitrate concentration (12.47mg/l) for rainy season which exceeds WHO threshold of 10mg/l this creating danger for infants while for dry seasons it has a mean value of 6.99m/l which is within the WHO specified limit of 10mg/l .The measured values of conductivity and TDS of both dry and rainy season, fall under the WHO set limits of 2500u/cm and 1000mg/l thus indicating moderate ionic contamination. The soil quality index (SQI)and water quality index (WQI)were calculated to be 531.003 and 54.31respectively and thin indication severe levels of contamination. Hence indicates all the water samples were unsuitable for mostly drinking but can be used for irrigation and industrial purposes and the need for proper treatment is required before drinking. The soil geo-accumulation index reveals that the study area is moderately to extremely contaminated with level of contaminants in this order Cu> Zn>Ni>Pb>Fe>Cr>Mn. The polluting load index of soil (PLI) suggested that the entire area is highly polluted according to PLI result which totaled 11.98 similarly the pollution load index (PLI) of ground water both for dry and rainy season suggested that the ground water is highly polluted according to PLI results which totaled 2.26 and 3.61 for dry and rainy season respectively.The Contamination factor (CF) of the collected soil samples reveals that the entire area has high concentration of Co, Fe, Cu, Ni and Si suggesting possible anthropogenic source The contamination factor of both dry season shows that Nl,K,Ca,Pb,Mn and Cr have low contamination values of <1while for rainy season K, Ca ,Ni ,and Cr have low contamination factors.In the Health risk analysis in both the rainy and dry season, the result revealed that the dermal H values for both adult and children were all greater than one (<1).the estimated weekly intake show high health risks to children ,the risks of developing cancer increase when people are exposed to hexavalent chromium as measured in Cr .EWI 0.0286 adult and 0.0437 child per week, the same is applicable to rainy season with Cr EWI 0.0218 adult and 0.0326 child . For the geochemical composition of the water(water type), Ca-Mg-Cl and Ca-So4- are the dominant water type. Descriptive statistical technique including the mean,standard deviations, variance, Pearson correlation, ANOVA, Hierarchical cluster analysis, Dendogram, Heatmaps, Barchats, principal component analysis were all employed in this study to establish a quantitative mathematical relationship between the variables.

KEYWORDS: Polluting Load Index, Water quality Index, Physico-Chemical, Leachate Contamination.

INTRODUCTION

Environmental pollution is one of the major challenges facing humanity in the 21st century. Industrialization, urbanization and developmental projects are the major cause of environmental pollution which is associated to anthropogenic activities have increased with the last century globally (Qiu, 2010; Izah et al., 2018;). Dumpsite is a widespread land meant or designed for deposition of waste and unwanted materials from household, institutions, industries or the environment and is generally open or covered with soil layer with or without liner at the bottom. Dump/landfill is a major source of contamination of groundwater (Wilfred et al.2022). Open dumpsite is common in developing countries (Mentore Vaccari et al. 2018). Open dumping system of waste disposal is the most common method of waste disposal in Nigeria.

Management of solid waste and disposal sites is a serious ecological concern all over the world (Vincent et al. 2012, Francis et al.2021), due to the tendency of such dumpsites to contaminate ground and surface water sources (Ejiogu et al. 2017). Lack of proper waste management and disposal system is an unavoidable problem in most developing countries like Nigeria due to the increasing population, rapid urbanization, industrialization, and lax environmental laws (Okere et al. 2018). The waste management practices within the study area are simply based on the collection and dumping out of the city boundaries in open excavated waste dumps (Arukwe et al.2012, Francis et al 2021). the waste dumpsites, in addition to being a major breeding grounds for micro-organisms and other disease vectors like rats which put the health of the inhabitants at risk , it also causes air pollution which results from offensive odour and uncontrolled burning of these wastes, which may jeopardize human health and deteriorate the air quality of the area (Enyoh et al., 2019; Ibe et al. 2016; Ibe et al. 2020a, ,BV.). According to (maiti, S. K. *et al* 2016), contamination of ground water and surface water in low-income countries with organic, inorganic and microbial pollutants due to contamination from leachate is a common and significant problem. Water is extensively wasted and polluted by both natural and anthropogenic activities. The enormous economic and industrial growth are often accompanied by urbanization and population growth. As a consequence, the quantity of municipal solid waste (MSW) produced in the last few decades has increased significantly throughout the world (somani *et al*;2019, Hamza *et al*;2022), despite the development of waste management practices including incineration, compositing and recycling (Aziz *et al*; 2021, Baghanam *et all* , 2020 facili *et al* 2022), The disposal of waste in land fills is still one of the widely used methods for municipal solid waste management (chidichimo *et al*; 2020, kapelewska *et al; 2019*, Hamza *et al*; 2022.

As a result, mitigation of negative environmental impacts of landfilling has become one of the most challenging issues of the world (Akoto *et al*, 2021)Water is a fundamental requirement for all living bodies, it plays a vital role for industrial operation. In near future, the availability of drinking water will be a challenge in all over the world. (H.M.A Ashar et all, 2015). Water pollution refers to the presence of a harmful and objectionable material in water, even at low concentration, which makes it unfit for drinking. Water contamination weakens or destroys natural ecosystem that support human health, food production and bio-diversity. Our water supply is more important than anything else when it comes to our natural resources. Contaminants are protected from a variety of sources. Leachate is one of the most prevalent types of liquid that can contaminate our drinking water and soil. Once contaminated, groundwater may forever remain polluted or contaminated without remedy or treatment. Diseases may spring up through water pollution, especially groundwater contamination, and rapidly spread beyond human expectation because of its flow pathway mechanism (Afolayan et al., 2012).

Water is the most important resource of the whole country, and of the entire society, since no life is possible to exist without water. Water forms the major component of plant and animal cells; it is the basis of life. Acording to the Standard for drinking water and Nigerian Standard of Drinking Water Quality (NSDWQ, 2007), in the planning and operation of the systems, water allocation priorities should be broadly as follows: drinking, bathing, irrigation, hydropower system (dams, electricity generating plants etc.), ecology, agro-industries and non-agricultural industries, navigation and other uses. The major sources of water are surface water (oceans, rivers, streams, seas and brooks), groundwater, snow and ice, lakes etc.

Contamination of water bodies has increasingly become an issue of serious environmental concern. Availability of clean drinking water is a basic right for all people. Unfortunately, many of the boreholes offer water which is either unsafe for human consumption or rather has such unaesthetic quality that no one will want to use. Groundwater is particularly important as it accounts for about 88% safe drinking water, both in the rural and urban areas, where population is widely dispersed; and infrastructure needed for treatment and transportation of surface water does not exist (Cunningham’s et al, 2005). It has become an important water resource due to increasing trend of pollution on surface water and this problem is more acute in an area or areas which are densely populated and inadequately supplied with potable drinking water. The availability of groundwater is neither unlimited nor is it protected from deterioration. Man, through a variety of activities like indiscriminate dumping of refuse, and modern technologies, is dramatically changing the characteristics of groundwater system. Ground water pollution could be avoided when borehole wells are located far from any source of potential pollution. Good well design is also important in the prevention of underground water pollution. As rain drops and infiltrates into the soil, harmful substances from dumpsites, landfills find their way into boreholes, hence polluting the water body and making it unfit for domestic and other purposes.

A plume of contamination occurs whenever a reasonable permeable material exists below the soil strata. Organic contaminants called leachate drains into groundwater where there is no base lining and carries along with-it anions of iron and manganese which contaminates borehole water easily.

PROBLEM STATEMENT

Most Nigeria cities such as Nekede in Imo state have experience high rates of urbanization and industrialization with associated waste disposal problems. Associated with this urbanization and industrial growth is the influx of people from other locations due to the polytechnic being sited there. It is known that increases in population such as this are also associated with attendant increases in volume of wastes generated. This therefore has created a huge waste burden on the city, as various waste categories, ranging from domestic, through commercial to industrial are deposited at various locations of the town (Akanwa, 2014, Emeribeole, 2017). Normally, waste disposal impacts on water quality and supply dynamics. In Nekede, the practice of uncontrolled waste disposal system can render the soil, groundwater and surface water unsafe for human, agricultural and recreational use (Lazarus O. Ikwa et al 2017). Poor management of solid waste materials has resulted to a lot of disastrous effects such as aesthetics, environmental hazards and pollution. The Nekede dumpsite developed as a result of community effort (possibly due to ignorance) to stop the fast-growing gully which claimed unavailable lands and threatened residential building. Dumping of refuse at the site has continued for over 30 years at a distance of less than 20m from residential buildings. In the words of (kurakalva R.M et al (2016). Areas near dumpsites are most likely to experience subsurface water contamination as a result of leachate emanating from pollution sources. considering the effect of a contaminated commercial water source on the populace and possible outbreak of diseases and epidemic within the catchment including its short- and long-term implication. It becomes expedient for an in-depth understanding of the risk posed by the population, its modeling and assessment.

OBJECTIVES OF STUDY

The aim of the project is to

1. To analyze water from bore holes near the dumpsite.
2. To study the possible impact of leachate percolation on groundwater and soil quality.
3. Determination of heavy metal concentration in soils around the dumpsite. Their geo accumulation index, enrichment factor, degree of contamination etc. will show their distribution pattern in the soils.

SIGNIFICANCE OF THE STUDY

The significance of the study lies in the fact that inhabitants of the study area lack access to The pipe borne water supply and depend solely on groundwater sources for their domestic uses; hence the need to regularly analyze these sources. The report of this study would be a useful tool for creating awareness amongst the residents, planers and decision makers for future water supply scheme in the area.

METHODS

Groundwater Analysis

For groundwater samples, some of the physicochemical parameters thatwere determined in the field during sampling. They were measured using water- analyzer kit. These parameters are Temperature, pH, Dissolved Oxygen (DO), Electrical Conductivity (EC) and Total Dissolved Oxygen (TDS). The temperature and dissolved oxygen was measured using temperature/DO probe meter (Model JPB 607A). The electrical conductivity and total dissolve solids (TDS) were determined using a portable digital EC/TDS meter. Others were analyzed in the laboratory. They include Total Solid (TS), Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), PO_4^{-3} , SO_4^{-2} , NH_3, HCO_3^- , NO_3, K, Na, Ca, Mg etc. The concentrations of Cd, Pb, Cr, Ni, Zn, Fe, Mn, Ag, As, Hg, Cu, CN and Al were also determined with atomic absorption spectrophotometer (AAS), FS 240 Varian Atomic absorption spectrophotometer. The concentrations of these metals were quantified using calibration curves made in the same acid medium as the standard solution of the metals (Ibe, *et al*., 2018).

Hydro-Geochemical Facies of Ground waterin the StudyArea

Graphical techniques have been devised to facilitate the classification of water into similar homogeneous groups with each representing hydro geochemical facies as shown below. In this study the Piper, Durov, Stiff and Schoeller plots wereused to sort the water chemistry into groups to understand the geochemical evolution of water and to identify the chemical relationships between samples. Thesoftwareused fortheaboveplotsisRock ware Aq.QAversion1.5.0 (2015). Hydro-geochemical studies are tools used to identify those processes that are responsible for groundwater chemistry and pollution. Often, samples with similar chemical characteristics will have similar hydrologic histories, recharge area, infiltration pathway and flow paths in terms of climate, mineralogy and residence time.

Piper Diagram

A Piper diagram is a graphic procedure proposed by Arthur M. Piper in 1944 for presenting water chemistry data to help in understanding the sources of the dissolved constituent salts in water. This procedure is based on the premise that cations and anions in water are in such amounts to assure the electroneutrality of the dissolved salts, in other words the algebraic sum of the electric charges of cations and anions is zero. The Piper trilinear diagram is a graphical representation of the chemistry of a water sample or samples.

The cations and anions are shown by separate ternary plots. The apexes of the cation plot are calcium, magnesium and sodium plus potassium cations. The apexes of the anion plot are sulfate, chloride and carbonate plus hydrogen carbonate anions. The two ternary plots are then projected onto a diamond. The diamond is a matrix transformation of a graph of the anions (sulfate + chloride/ total anions) and cations (sodium + potassium/total cations). The Piper diagram is suitable for comparing the ionic composition of a set of water samples but does not lend itself to spatial comparisons. The Piper diagram can be used to determine water type, hydro-chemical facies and ion exchange (Hounslow 1996; Freeze and Cherry 1979). The diamond part of piper diagram may characterize waters of different types.

Durov Diagram

Durov plots as proposed by Durov (1948) as an alternative to piper diagram to remove some its short comings. In the diagrams, the major ions are plotted as percentage milli equivalents per litre(meg/L) in two base triangles. The total cations (Na^+,K^+, Ca^{2+},Mg^{2+}) are plotted in the right triangle while the total anions (Cl^-, $HC03^-$, $SO4^{2-}$) are plotted in thelefttriangleand theyaresetequalto 100 percent.Eachpointinthetwobasediagramsis projected into square combined field of (Na^+ + K^+ and $HCO3^-$) of the main field which lies perpendicular to the third axis in each triangle. Durov diagram shows clustering of water quality data point to indicate samples that have similar compositions as well as displaying some possible geochemical process that could affect the water genesis.

Schoeller Diagram

Schoellerdiagramsaresemi-logarithmicdiagramusedtoshowtherelativeconcentrationsof anions and cations expressed in milli equivalent per liter. It allows the major ions of many samples to be representedonasinglegraphthroughwhichsampleswithsimilarpatternscan be easily distinguished in the ratios of anions and cations. These patterns maybe used to differentiate common or disparate source areas of water drawn from multiple wells.

Stiff Diagram

Was first developed by Stiff (1951). He suggested a pattern diagram where four parallel horizontal axes extend on either side of one vertical axis. Concentrations (meq/L) of the majorcations (Na^+, K^+, Ca^{2+}, Mg^{2+}) areplotted on each horizontal lineon the left side ofthe vertical zero axis while the concentration (meq/L) of the major anions (HCO^{3-} , Cl^-, $SO4^{2-}$,$NO3^-$+$PO4^{2-}$)ontheright.Stiffdiagramsareusedinmakingvisualcomparismbetweenwater from different sources because waters of similar qualities have a distinctive shape. With the diagram changes in the ionic composition of water body over time and space can also be determined.

Analysis of Impact of groundwater quality on Agricultural Activities

Several ratios are determined from the geochemical data which help to show the impact of groundwater quality of agricultural production. They are presented below:

Sodium Adsorption Ratio (SAR)

For a groundwater to be used for irrigation purposes its suitability in relation to its mineral constitution and its effects on both soil and plant is ascertained. SAR is highly recommended in determining the suitability of groundwater for irrigation purposes because of its direct relationship to Na^+, adsorption by soil (Nazzal, *et al* 2014). Na^+reacts with soil to reduce its permeability through ion exchangethat leads to alkalinesoil that will result in stunted growth in plants. The sodium hazard classes include low S1(SAR <10) this is permissible for all types, medium S2(SAR 10-18) good for coarse textured soils and high, S3(SAR 18-26); and veryhigh,S4(SAR>26).SARforcategoryS3andS4mayhaveharmfuleffectonmosttypes of soils (Ejiogu et al, 2017). The SAR was calculated after Richards (1954) as follows:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \qquad (3)$$

All parameters are in meq/L

Sodium Percentage

Calculating Na % for irrigation water is important. Na % is an expression that is used to determine the Na content in irrigation water.High content of sodium in water relative to Calcium + Magnesiumingroundwatercandamagethesoil. Highsodiumcontent leadsto the dissolution of soil organic matter as well as dispersion of clay. This results in poor soil structure by reducing permeability causing water to move very slowly into and through the soil. TheNa%wascalculatedafter Wilcox (1955) as shown in equation 4:

$$Na\% = \frac{Na^{+}+K^{+}}{Na^{+}+K^{+}+Ca^{+}+Mg^{+}} x\ 100 \qquad (4)$$

All parameters are in meq/L. There are five classes of Na% and they are<20is anexcellentwater,20 – 40isgood,40– 60 permissible,60 – 80 doubtful and > 80 unsuitable.

Magnesium Adsorption Ratio(MAR).

Magnesium is an important element in determining the quality of irrigation water. Naturally, Ca^{2+}andMg^{2+}maintainastateofequilibriuminwater but behave differently in soil. Highly saline water deteriorates soil structure which leads to high concentration of Mg^{2+} in soil because of exchangeable Na^{+} in irrigated soil. This adversely reduces crop yield. The groundwater samples can be classified as suitable (MAR < 50) and unsuitable (MAR > 50) for irrigation. The MAR was calculated after Raghunath(1987) as follows:

$$MAR = \frac{Mg}{Ca+Mg} \qquad (5)$$

All parameters are in meq/L.

Kelly'sRatio

Thisratioisusedtosortouttheproblemofsodiuminwaterforirrigationbyevaluatingthe level of sodium measured against calcium and magnesium. TheKRwas calculated after Kelly *etal*., (1940)as follows:

$$KR = \frac{Na^{+}}{Ca^{2+}+Mg^{2+}} \qquad (6)$$

All parameters are in meq/L.A Kelley’s ratio of more than one indicates an excess level of sodium in waters. Hence, waters with a Kelley’s ratio less than one are suitable for irrigation, while those with a ratio more than one are unsuitable.

Residual Sodium Carbonate

When water contains carbonate and bicarbonate more than allowable limits over thealkaline earth mainly Calcium and Magnesium, it affects agriculture unfavorably. Water having high concentration of bicarbonate, allows calcium and magnesium to precipitate as bicarbonates. This deterioratessoil structuremaking themovement ofair within thesoil to be restricted (Gorthi and Mohan, 2015). In order to qualify this, an experimental parameter termed residual sodium carbonate can be calculated using the formula below.

$$RSC = [HCO_3^- - CO_3^-] - [Ca^{2+} + Mg^{2+}] \qquad (7)$$

All parameters are in meq/L. Water having less than 1.25 or equal to 1.25 meq/L of RSC is safe water for irrigation purpose, water having 1.26 – 2.5 meq/L values of RSC are doubtful whereas water having more than 2.5 meq/L of RSC is not suitable for irrigation purpose.

Assessment of the Contamination Level of Water and soils using pollution risks models Pollution Assessment models of Water resources.

The presented study evaluated the pollution and risk inherent in the consumption of groundwater in the study area because of the impact of solid waste dumpsite and exploitation activities. Pollution assessment is the process of evaluating the impact and characteristics of various compounds, ranging from excess nutrients to toxic substances, on the environment. The present study is therefore aimed at the application of risk and pollution models to evaluate the quality of groundwater samples within the study area. The study also determined the concentration of metallic pollutants in the soil. This was done to reveal the identity, intensity, percentage, and concentration of the metallic contaminants. Finally, the groundwater samples from the area were analyzed for the presence of the recognized metallic pollutants in the soil samples.

Contamination Factor (CF) and Pollution Load Index

This is the ratio of the individual he avy metalstoits back ground values. It was calculated using Equation 8:

$$Cf = {}^{C_{metal}}\!/_{C_{background}} \qquad (8)$$

Where, C metal and C background represent the concentration of heavy metal and background value of the metal respectively. Background values were obtained from the Nigerian standard for drinking water quality (NSDWQ 2007). The values areCd-0.003,Pb – 0.01, Cu – 1, Ni – 0.02, As – 0.01, Fe – 0.3, Zn – 3, Cr – 0.05, Hg – 0.001, Al – 0.2, Mn – 0.2, CN – 0.01 mg/lrespectively. Theindividual PLIby Tomlinsonetal.(1980) was used tocalculate the groundwater pollution load using the equation below:

$$PLI = \sqrt[n]{CF1\ xCF2xCF3x \ldots CFx} \qquad (9)$$

Where, Cf1, Cf2, Cf3,Cfn are the individual contamination factors and n is the number of heavy metals under investigation. The value of PLI was divided into four groups i.e.,<1 –no pollution, 1.0 < 2—moderate pollution, 2.0 < 3—heavy pollution, and ≥ 3.0—extreme pollution.

3.7.1.2 Potential Ecological Risk Factor (Er)

Theecologicalriskfactorwasusedtoascertaintheextentofheavymetalpollutionofthe groundwater in the study area using the equations below:

$$E_r = T_r x P_I \qquad (10)$$

$$P_I = {}^{C_x}\!/_{C_n} \qquad (11)$$

$$RI = \sum_{i=1}^{n} E_r \qquad (12)$$

Pi is the pollution index for a single metal, Cx is the concentration of metals in the sample, and Cn is the metal reference value. RI is the potential ecological risk. The reference valuesof metals were taken from the NSDWQ (2007). The toxic response factors (Tr) for Pb, Cd, Cr, Cu, Zn, Ni, and Mn are 30, 2, 5, 1, 5, and 1 respectively (Hakanson, 1980). In this study, the $E^i_r$and RI of Cd, Pb, Cu, Ni, As, Fe, Zn, Cr, Hg, Al, Mn, CN were calculated for each pollutant. There are four categories of RI and five categories of Er as shown below.

Table 3: Potential Ecological Risk Categoriesbasedon E^i_r and*RI*values(Hakanson., 1980).

E^i_rValue	**Single-potentialecologicalrisk (E^i_r)**	**RIvalue**	**Comprehensive-potential ecological risk**
$E^i_r<40$	Lowrisk	RI<150	Lowrisk
$40\leq E^i_r<80$	Moderaterisk	150≤ RI<300	Moderaterisk
$80\leq E^i_r<160$	Considerablerisk	300≤RI< 600	Considerablerisk
$160\leq E^i_r<320$	High risk	600≤RI	Veryhighrisk
$320\leq E^i_r$	Veryhighrisk		

Transfer Factor

Thetransferfactorwasusedtoinvestigatethetransferofheavymetalsfromsoiltothe ground water using Eq.21(Lato et al. 2012, Ibe et al. 2017):

$$TF = \frac{M_w}{M_s} \qquad (13)$$

Where

TF=Transfer Factor

MW = concentration of metals in Water,

MS = concentration of metals in soil samples.

However, a higher transfer factor means a higher risk of metal exposure.

Water Quality Index

Sixteen physiochemical parameters of the groundwater were used to evaluate the water quality index according to Equations 23 to 25 (Ibe, *et al.*, 2019). First, each of the 16 parameters was assigned a weight (wi) according to its relative importance in the overall quality of water for drinking purposes. The maximum weight 5 was assigned to that major importance in water quality assessment; minimum weight 1 was assigned tothe least significant role. Second,the relative weight(Wi) of the chemical parameter was computed using the following equation:

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad (14)$$

Where Wi is the relative weight, wi is the weight of each parameter, and n is the number of parameters. In the third step, a quality rating scale (qi) for each parameter is assigned by dividing its concentration in each water sample by its respective standard according to guidelines (BIS, 1991), and the result is multiplied by 100:

$$q_i = \left(\frac{C_i}{S_i}\right) x\ 100 \qquad (15)$$

Where, qi is the quality rating, Ci is the concentration of each chemical parameter in each water sample in mg/L, and Si is the water standard for each chemical parameter in mg/L. For computing WQI, the sub index (SI) is first determined for each chemical parameter, as given below:

$$SI_i = W_i x q_i \qquad (16)$$

$$WQI = \sqrt{SI_{i-n}} \qquad (17)$$

Where,SI$i$is the sub index of ith parameter; Wi is relative weight ofith parameter;
Qi is the rating based on concentration ofith parameter,and n is the number of chemical parameters. Note: The computed WQI values are classified into five categories: Excellent water(WQ<I50);good water (WQI=50–100);poor water(WQI=100–200);very poor water (WQI=200–300); and water unsuitable for drinking (WQI >300).

Health risk Assessment

The health risk considers the impact of anthropogenic activities like oil exploration on groundwater sample measurements. This is to assess the activities in the area that are of a risk of likely contaminating groundwater in the area. The individual's daily human exposure risk pathways to harmful substance could be through inhalation via nose or mouth, direct ingestion (Exping) and adsorption (Expderm) through the skin exposure. Since groundwater is the main source of domestic use for inhabitants in the study area, human exposure risks through intake and adsorption through skin were calculated separately for adult and children because water exposure differs among different age groups or brackets. Equations used to calculate EXPingand EXPderm was adapted from the US EPA risk assessment Guidance for superfund (RAGS) methodology (USEPA1989).

$$EXP_{ing} = \frac{C_{water} x\ IRxEFxED}{BW\ xAT} \qquad (18)$$

Where Exping = exposure ose through ingestion of water (mg/kg/day); C water = averageconcentrationoftheestimatedmetalsinwater(mg/L);IR=ingestionrateinthisstudy(2.2L/dayforadults;1.8L/day for children). EF = is exposure frequency (365 days/year); ED= exposureduration (70yearsforadults;6yearsforchildren);BW:averagebodyweight (70 kg for adults; 15 kg for children);AT=averagingtime(365days/year x70yearsforan adult;365 days/yearx 6years for child).

Where,

$$EXP_{derm} = \frac{C_{water} x\ DPCxSAxEFx\ ETxEDxCf}{BW\ xAT} \qquad (19)$$

EXP derm=dermal absorption exposure dose (mg/kg/day),

Cwater=estimated average metal concentration in water (µg/L)

EF=exposure frequency (365 days/year),ED is the duration of exposure (6 years was taken for children, while for adults, 70 years was chosen), BW is average body weight (70kg for adults and15kg for children);SA is the skin area that is exposed (adult=19,400cm2 andchildren=16,200 cm2), Dpc= coefficient of dermal permeability in water (cm/h), which is given as 0.0006 for Zn, while its value for Cd, Fe, Cu, CN, Hg, Al, As and Mn is 0.001, 0.002 for Cr, 0.001 for Pb, 0.0002 for Ni and 0.0006 for Ag (Ibe *et al*., 2018; EPA, 2011).ET=time of exposure(adult=0.58h/day and children=1h/day), CF= conversion factor taken as 0.001 L/cm3),AT=averagingtime (365days/year×70yearsforadultsand 365days/year×6yearsfor children).

The risk inherent in exposure to contaminants like heavy metals and Cyanide due to the useofthegroundwater werecalculated as the hazard quotient(HQ) according to the equation 20-23 below:

$$HQ_{ing} = \frac{EXP_{ing}}{RFD_{ing}} \qquad (20)$$

$$HQ_{derm} = \frac{EXP_{derm}}{RFD_{derm}} \qquad (21)$$

$$HI = \sum_{i=1}^{n} HQ_{ing} = \sum HQ_{Cd} + HQ_{Pb} + HQ_{Cu} + HQ_{Ni} + HQ_{Fe} + HQ_{Zn} + HQ_{Ag} + HQ_{Cr} + HQ_{Hg} + HQ_{Al+M_n+C_n} \qquad (22)$$

$$HI = \sum_{i=1}^{n} HQ_{derm} = \sum HQ_{Cd} + HQ_{Pb} + HQ_{Cu} + HQ_{Ni} + HQ_{Fe} + HQ_{Zn} + HQ_{Ag} + HQ_{Cr} + HQ_{Hg} + HQ_{Al+M_n+C_n} \qquad (23)$$

Where RFDing and RFD derm are the reference dose value for oral toxicity and dermal toxicity inmg/kg/day(USEPA,1989),HI=HazardIndexfororaldoseanddermaldose.HQ<1is an indication that it poses no health effect, while HQ > 1 may pose a potential health effect on human exposure (Ibe, *et al*., 2018; USEPA,1989).

Table 4a. RFDoral Values used for calculation Hazard Index across the study area.

	Metals	**RFDoral**	**Sources**
1	Cd	0.0005	OnyeleandAnyanwu,2018.USEPAIRIS2011
2	Pb	0.0035	OnyeleandAnyanwu,2018.USEPAIRIS2011
3	Cu	0.04	Patrick-IwuanyanwuandNwokeji, 2018.
4	Ni	0.02	Patrick-IwuanyanwuandNwokeji, 2018.
5	As	0.0003	Patrick-IwuanyanwuandNwokeji, 2018.
6	Fe	0.007	OnyeleandAnyanwu,2018.USEPAIRIS2011
7	Zn	0.03	Patrick-IwuanyanwuandNwokeji, 2018.
8	Ag	0.005	Vetrimuruetal2016
9	Cr	0.0003	OnyeleandAnyanwu,2018.USEPAIRIS2011
0	Hg	0.0001	USEPAIRIS,2011
11	Al	1	Johannetal
12	Mn	0.014	Patrick-IwuanyanwuandNwokeji, 2018.
13	CN	0.00063	USEPAIRIS,2011

Table 4b.RFDoral Values used for calculation Hazard Index across the study area.

		RFDdermusingGI fraction.
1	Cd	1.3E-05
2	Pb	0.00175
3	Cu	0.0228
4	Ni	0.0008
5	As	0.00019
6	Fe	0.014
7	Zn	0.15
8	Ag	0.0002
9	Cr	7.5E-05
10	Hg	4.5E-05
11	Al	0.0022
12	Mn	0.00084
13	CN	0.2209

Pollution Assessment of Soil Contamination Level

Heavy metals at high concentrations in the soil cause metabolic activities in plants to be retarded or inhibited and thereby resulting in the decrease of the sensory quality and disorder of metabolic processes in plants (Luning, 2018). Pollution occasioned by heavy metals occur majorly in smelting, electroplating, chemical and mining industries. The level and types of heavy metals differ from region to region (Zhe & Luyu, 2018; Lei, 2018). Certain geochemical approaches and pollution indices which are useful tools in ecological risk assessment can interpret the impact of heavy metals on soil ecology and understanding contamination possibilities of the soil, help in providing details about the pollution degree and quality of the soil. These pollution indices include, contamination factor or index (CF), pollution load index (PLI), modified contamination degree (mCD), geo-accumulation index (Igeo), potential ecological risk coefficient (Ei,) ecological risk index (RI), Nemerow integrated pollution index (NIPI) and anthropogenicity (APn%). These pollution assessment models give information on the intensity of anthropogenic input on the contamination of the soil (Mugosa et al., 2016; Nwankwoala & Ememu, 2018). The contamination of the soil by heavy metals can lead to the contamination of the ground and surface water bodies that abound in the study area.

The levels of contamination in soils around the study area were therefore quantitatively assessed using the several single element geochemical pollution indices; geo-accumulation index (Igeo), Contamination Factor (CF) and pollution Load Index, and enrichment factor (EF). These indexes are methods widely used for the assessment of the impacts of anthropogenic activities on soils, and it involves calculating the Individual element concentrations at the study area against uncontaminated background levels used to evaluate metal contamination (Kolawole *et al.*, 2018).These indexes have been extensively used in different studies (e.g., Okoro *et al*., 2020, Ichu *et al*., 2021) and are discussed in detail in the following section.

Geo-accumulation Index (Igeo)

The geo-accumulation Index (Igeo) was introduced by Muller (1971). It is to compare current concentrations of heavy metals in a system to pre-industrial concentrations. The method has been commonly used to evaluate heavy metal contamination in urban soils. Index of Geo-accumulation can be calculated using the equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right) \qquad (24)$$

Where $C_n$is the measured concentration of element in question measured at a certain site, B_n is the geochemical background value in the soil (Muller, 1979). In the present work, the global Earth's shale values (Pb =20;Mn=900;Cu =45;Cd=0.3;Ni=68;Cr=90; Zn=95;Hg=0.4;Ag=0.07;Al=80,000;Fe=47,200;mg /kgdryweight) for heavy metals as documented by Turekian & Wedepohl (1961)were used as background values for metals and was employed in calculating Igeovalues.The constant 1.5 was used in the **Igeo**equation to reduce possible effects of varying background values which may have resulted from varying soil lithology as well as accommodating anthropogenic influence influences no matter how small it may be (Ichu, *et al*., 2021). The geo-accumulation index has been subdivided into 7 pollution grades which range from practically uncontaminated, to extremely contaminated based on their values (Muller, 1969). These grades are given in Table 36.

Table 5: Classification of index of geo.

Igeoclass	**Igeovalue**	**Category**
0	<0	Practically unpolluted
1	0-1	Unpolluted to moderate polluted
2	1-2	Moderately polluted
3	2-3	Moderately to strongly polluted
4	3-4	Strongly polluted
5	4-5	Strong to very strong polluted
6	>5	Very Strongly polluted

Accumulation (Muller,1979, Vineethkumar*et al.*, 2020).

3.7.2.2 Enrichment Factor

This is a geochemical model that is used to differentiate heavy metals originating from human activities from those of natural sources. Enrichment Factor (EF) of an element in the studied samples is based on the standardization and integration of a measured element against a reference element. A reference element is often the one characterized by low occurrence variability. Enrichment factor is determined by this by the relationship:

$$EF_s = \frac{[C_s/CFe_{soil}]}{[C_s/CFe_{(rference\ value)}]} \qquad (25)$$

where: EFS=the enrichment factor for the element S, CS= the concentration of element of interest in soil sample, CFe(soil)= the concentration of the element in the crust and CFe(ref) = the concentration of the reference element used for normalization in the crust (Taylor, 1964, Taylor & Meclenan, 1995 and Rudnick and Gao, 2003). In this study Iron (Fe) was selected as the reference element. The continental crust value of Taylor (1964) was adopted for Pb = 12.5, Zn = 70,

Cu=55, Mn, Fe = 56,300, Cr =100,

Cd=0.2,andNi=76.WhileTaylorandMeclenan,(1995)wasadoptedforAg=50Rudnick and Gao (2003) was adopted for Hg = 0.05 mg/kg.Five contamination categories are documented based on the enrichment factor by Kartal et al as shown in table below.

3.8 Multivariate Statistical Analysis

Microsoft Excel and R version 3.6.1 (2019) software were used for statistical analysis at 95% confidence limit and the graphs. The mean values of obtained for the various locations were compared with the various permissible limits of the parameters set by Standard organization ofNigeria(SON),FEPAandWHOforwatersamples.WhileNESARAwasthestandardused for soil mean values. These helped to identify areas of problems in quality of drinking water from the study area. Multivariate statistics, in terms of principal component analysis (PCA) and hierarchical component analysis (HCA), were performed using R statistical software. The PCA was used to establish the major variation and relationships among the different metals as well as cyanide. Pearson correlation was calculated for different pollutants in the water and soil samples and significant principal components (PC) were selected based on the varimax orthogonal rotation with Kaiser normalization at eigen values greater than one. The HCA was performed using Ward's method for linkages and square Euclidean distance was used to identify groups that show similar characteristics or variables. Dendrogram was used to provide a visual summary of the results based on dimensionality of the original data.

RESULT AND DISCUSSION

CROSS PLOT OF SOME PHYSICO-CHEMICAL PARAMETERS IN WATER

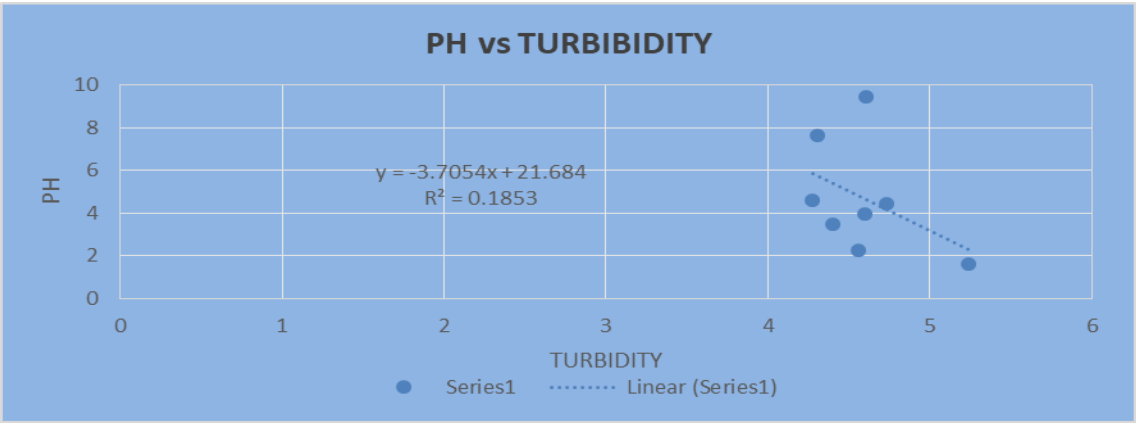

Fig. 1: PH vs Turbidity.

The cross plot between the turbidity and pH in the sampled borehole waters in the vicinity of the dumpsite revealed a weak positive correlation indicating that the relationship between the two parameters across the study area is weak. This is reflected in the coefficient of determination (R^2) evaluated from the study area which is given as (R^2=0.1853). The relationship is mathematically a power relationship.

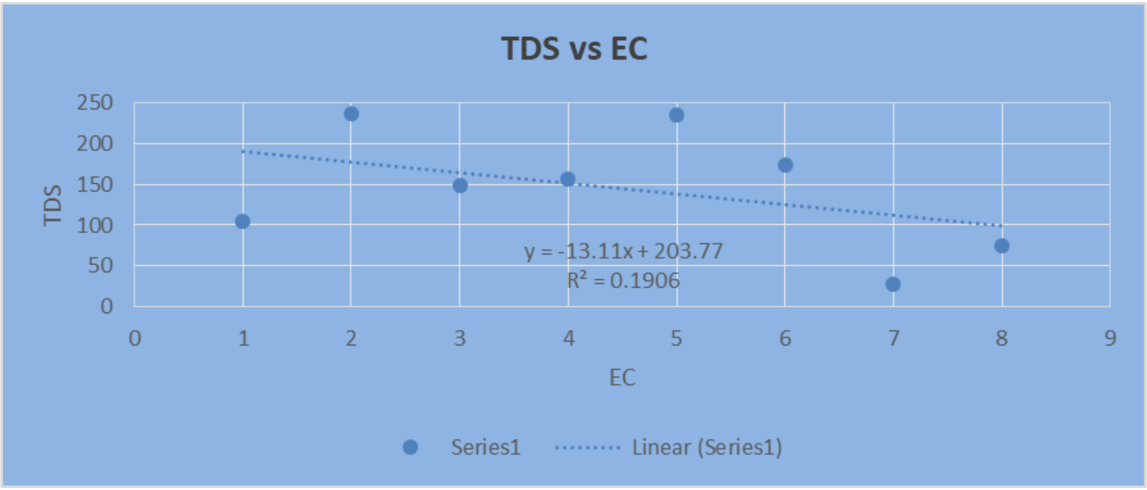

Fig. 2: TDS vs EC.

Similarly, the cross plot between the total dissolved solids (TDS) and the electrical conductivity (EC) revealed an exponential relationship. The TDS and the EC in the sampled borehole waters in the vicinity of the dumpsite also revealed a weak positive correlation indicating that the relationship between the two parameters across the study area is weak. This is reflected in the coefficient of determination (R^2) evaluated from the study area which is given as (R^2=0.1906).

FIG. 3: Electrical conductivity versus salinity

Similarly, the cross plot between salinity) and the electrical conductivity (EC) revealed a power relationship. The salinity and the EC values in the sampled borehole waters in the vicinity of the dumpsite revealed a strong positive correlation indicating that the relationship between the two parameters across the study area is indeed strong. This is reflected in the coefficient of determination (R^2) evaluated from the study area which is given as (R^2= 0.6168).

CROSSPLOTS OF SOME CATIONS & ANIONS

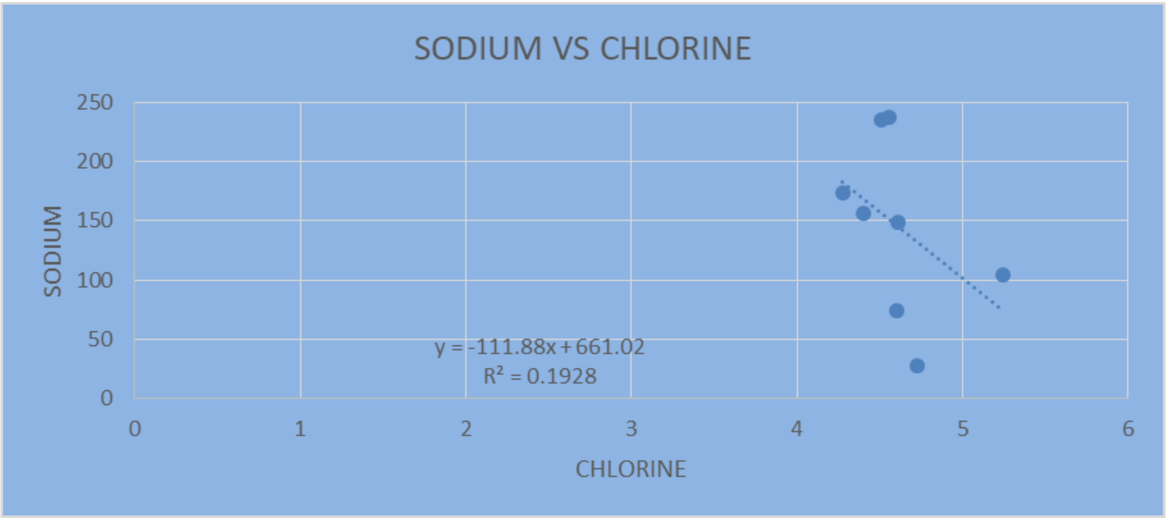

Fig. 4: Sodium versus Chlorine.

On the other hand, the cross plot between chloride concentrations versus the sodium concentrations in the sampled water revealed a power relationship. The chloride and sodium concentration values in the sampled borehole waters in the vicinity of the dumpsite revealed a weak positive correlation indicating that the relationship between the two parameters across the study area is weak. This is reflected in the coefficient of determination (R^2) evaluated from the study area which is given as (R^2= 0.1928).

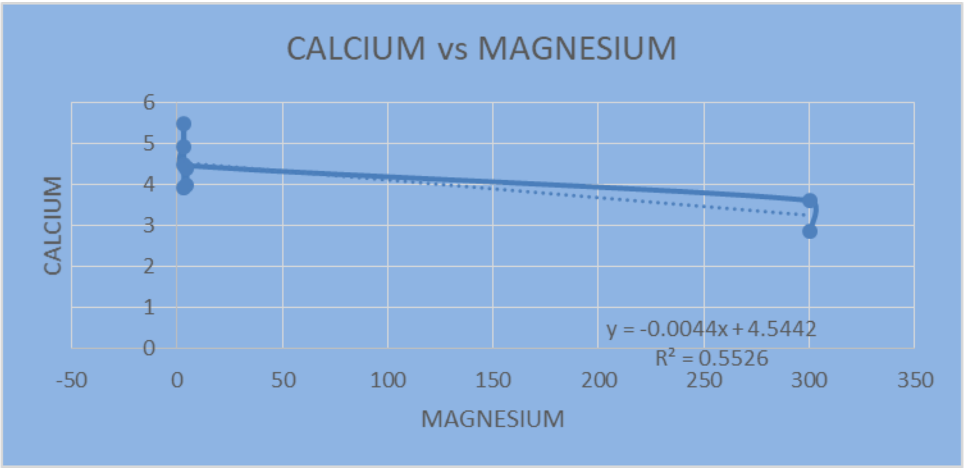

Fig. 5: Calcium versus Magnesium.

The cross plot between magnesium and calcium concentrations in the sampled water revealed a power relationship. The magnesium and calcium concentrations in the sampled borehole waters in the vicinity of the dumpsite revealed a very strong positive correlation indicating that the relationship between the two parameters across the study area is exceedingly well established. This is reflected in the coefficient of determination (R^2) evaluated from the study area which is given as (R^2= 0.5526).

The results of the physicochemical analysis of groundwater around the Nekede dumpsite are shown in Appendix A. The descriptive statistics of some of the physicochemical water are shown in table 4.1. From the table the pH values ranges from 3.983 to 4.90 with a mean value of 4.4944 in the rainy season and 4.275 to 5.242 with a mean value of 4.53125 in the dry season against the NIST and FEPA standard of 6.50 – 8.50. These average pH values show the acidic nature of the groundwater in this area throughout the sampling periods. This indicates the presence of toxic metals in the water (Akinbile and Yussof, 2011). It can also be attributed to landfill gases arising from the dumpsite as a result of the decay of organic matter from the dumpsite which has percolated through the porous subsurface to the aquifer as well as the quality of leachate from the dumpsites. This result is in agreement with the findings of Akinbile and Yussof (2011) who discovered that groundwater samples from boreholes around a landfill had an acidic pH values.

Table 1: Some Physicochemical variations in water samples for rain and dry seasons.

parameter	Min rain	Min (Dry)	Max (Rain)	Max (Dry)	Mean (Rain)	Mean (Dry)	STDEV (Rain)	STDEV (Dry)	FEPA	SON
PH	3.983	4.275	4.9	5.242	4.4944	4.53125	0.33410	0.28876	6.50-8.50	6.50-8.50
Turbidity	3.45	1.61	16.75	9.47	5.9522	4.67875	4.112261	2.646388		
EC	0.265	27.8	196.3	237	68.0406	144.95	60.42467	73.6071	1000	1000
TDS	14.02	14.02	1471	137.1	204.0033	75.865	476.78872	39.88764	500	500
Salinity	100	3.00	3555	300	628.3333	77.69625	1099.70451	137.2103		
ORP	129.6	111.5	258	165.3	163.6667	145.8625	39.18871	15.94508		
Nitrate	4.8	3.9	245	8.495	12.4662	6.992625	6.86185	1.707393	50	50
Phosphate		3.6		9.878		7.917375		2.484666		
Alkalinity		9		20		12.375		4.718883	NS	
Sulphate	1.16	4.6	57	128.234	9.7100	94.05119	17.85588	25.93744	10	
Chloride	1.29	56	13.8	102	4.4533	85.375	3.79505	16.4050	250	
TSS		0.026		0.148		0.0894		0.047161		
Bicarbonate	6.45	5.6	168	14.2	38.8811	8.475	49.30466	3.065359	NS	
Carbonate	5.72	2.5	225	8.1	78.5878	4.275	71.25256	1.92558	NS	
Sodium	1.68	1.846	126	4.394	4.4833	3.3925	3.33329	0.947635	NS	
Magnesium	3.75	1.004	20	3.272	10.5244	1.890125	5.31629	0.763146	100	20
Potasium	4.53	1.132	19	4.382	2.9756	2.405375	6.02081	1.217946	200-400	
Calcium	3.47	2.864	37	5.481	11.3156	4.2055	10.09927	0.804741	250	

Electrical Conductivity is a measure of the ability of a solution to conduct electric current.

This therefore depends on the concentration of ions in water. Therefore the higher the concentration of ions, the higher the electrical conductivity while the lower the concentration, the lower the electrical conductivity implying low inorganic content. The range of the Electrical conductivity values are 0.265 – 196.3 (µS/cm) in the rainy season and 27.8 – 237 (µS/cm) in the dry season with an average of (68.0406 µS/cm) in the rainy season and 144.95 (µS/cm) in the dry season. All the samples apart from Leachate sample in the rainy season are below the permissible limit of 1000 (µS/cm). Using salinity classification by Wilcox 1955, the quality of water in the study area falls within the safe water category apart from leachate in the rainy season which falls in tolerable to some extent category as in table 4.2.

Table 2: Classification of Groundwater (after Wilcox, 1955) EC (µS/cm).

Class	Conductivity Range (Wilcox, 1955)	Quality of water
I	< 1000	Safe
II	1000 – 1500	Tolerable
III	1500 – 2000	Tolerable to some extent
IV	2000 – 2500	Intolerable
V	>2500	Health Hazard

The large variation in EC values may be attributed to the anthropogenic influences in the area. The total dissolved Solids (TDS), has a range of 14.02-1471 with an average of 204.00 in rainy season and 14.02 – 137.1 with an average of 75.865 in the dry season. Only the leachate sample is >500 the permissible limit. According to TDS classification by Freeze and Cherry in Table 4.3, the water type is fresh water type because TDS < 1000. (Freeze and Cherry 1979).

Table 3: Simple Groundwater Classification Based on Total Dissolved Solids.(Freez and Cherry, 1979).

Category	**Total dissolved solids (mg/l or g/m3**
Fresh water	0-1000
Brackish water	1000-10,000
Saline water	10,000-100,000
Brine water	More than 100,000

The high concentration of EC and TDS in the leachate and BH 20 can be attributed to the presence of inorganic components from the disposal of large quantities of industrial waste within the dumpsite. Maiti *et al*., 2016 also obtained high level concentration of EC and TDS from leachate sample.

The variations for Ca, Mg and Na are as follows 3.47-37 and 2.864-5.481, 3.75 – 20 and 1.004-3.272, 1.68 – 126 and 1.846 – 4.394 in rainy season and dry season respectively. Sulphate varied from 1.16 – 57 in rainy season to 4.6 – 128.234 in dry season. These are within the range as described by Akobundu and Nwankwoala (2013), which shows that the groundwater around the study area is free from possible sulphate toxicity which includes gastrointestinal irritation. The low level of sulphate could be as a result of Sulphate reducing bacteria (SRB) present in the water which are capable of reducing sulphates (SO4 2-) to sulphides (S-) (Oyelami *et al*, 2013, Abdurafui et al, 2011). These are represented in Appendix A. The mean values of all the physicochemical parameters were below the permissible limits in both seasons . In a similar analysis carried out by Giadom et al., 2014, in Ariaria dumpsite in Aba, similar results were also obtained

Heavy Metal Characteristics of Groundwater Samples

Table 4: The heavy metals variations in water samples for both rainy and dry season

Metals	Min (Rain)	Min (Dry)	Max (Rain)	Max (Dry)	Mean (Rain)	Mean (Dry)	STDEV (Rain)	STDEV (Dry)	FEPA	SON
Lead	0.008	0.008	0.34	0.086	0.09	0.03025	0.112	0.025297	0.05	0.01
Manganese	0	0.003	0.978	0.214	0.3499	0.126625	0.33539	0.065829	0.2	0.4
Nickel	0	0.0	0.064	0.166	0.01	0.0377	0.021	0.055067	0.02	0.007
Iron	0	0.006	2.145	0.3632	24	0.151825	0.713	0.111471	0.3	0.1
Chromium	0	0.0	0.56	0.029	0.0121	0.017875	0.01784	0.011655	0.05	0.05

Lead (Pb)

Lead is a metal that its presence in the environment can be attributed to either natural source by the dissolution of mineral in the formation or by human and industrial activities. It is a toxic chemical hazard that is wide spread in air, water, soil and food as a result all human has lead in their system (Nduka and Orisakwe, 2010). Its cumulative intake can result in poison when present in drinking water (Pazand et al, 2018). Lead intake from drinking water far exceeds its intake from air and food since there is a decline in the use of lead containing additives in fuel and food processing industries (Obasi and Akudinobi, 2020). However, even with the decrease of up to 0.66g/L of Lead in fuel, national consumption of fuel is estimated at 20 million liters per day giving rise to15,000 kg of Lead emission into the environment through combustion (Nduka and Orisakwe, 2010). Lead is very mobile in water especially at low pH. Acidic water corrodes pipes and fixtures containing Lead used in plumbing in homes releasing Lead into drinking water. Hence excessive Lead in drinking water may be from household plumbing materials (Pazand *et a.,l* 2018). From the analysis, lead values for Rain season and Dry season ranges from 0.008 to 0.34 mg/L and from 0. 008 t0 0.086 mg/L respectively. This shows 88% and 100% of samples from rain and Dry season containing lead above the WHO and SON standard of 0.01 mg/L. This indicates high pollution of lead in the groundwater around the dumpsite.

Iron (Fe)

Naturally, Fe can be mobilized in the environment through weathering of Fe and Mn rock bearing minerals. Iron may be considered as an essential human nutritional need of up to about 10 – 50 mg/L. Groundwater may contain iron (II) at concentrations up to several mg/L without the water having any discoloration or turbidity especially when pumped directly from a well. But on exposure to the atmosphere, Fe (II) oxidizes to Fe (III), this usually gives a reddish – brown colour to the water. Concentration of Fe to about 0.3 mg/l, can lead to the staining of laundry and plumbing fixtures below this level no staining is noticed. It is not considered as a health risk; therefore, no health-based guideline value is proposed for Fe (WHO, 2011). It ranged from 0.00- to 0.2145 in rain season and from 0.006 to 0.3632 in dry season (Table 4.4).

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