

Geoenvironmental Assessment of Metallic Concentration in Soils and Groundwater of Effurun and Environs, Delta State

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ABSTRACT

The study on the assessment of heavy metal contamination in soil due to leachate migration and groundwater study contamination study been carried out. The results of the analysis of heavy metal contamination study indicate that Lead, Cadmium, Calcium, Copper and Manganese have a serious impact, thus deteriorating and polluting the soil quality and microorganisms in the area.

The pollution levels of these heavy metals vary significantly with the type of solid waste that predominates in the study locations within the dumpsite. These innumerable problems call for stringent adherence to the recommended management strategies. It also serves as a clarion call for the prompt implementation of policy on waste management as established by this study. This calls for urgent, imperative and well-articulated recommended strategies which will not only stem the problem in the study area but constitute a policy implementation material for solid waste management techniques.

For the groundwater contamination study, the study reveals that the groundwater in the study area is mostly acidic with high chloride concentrations Contamination by anthropogenic sources is mainly from septic tanks and probably improper sewage disposal. Ammonium having a mean value of 3.6751mg/L, which is a very huge magnitude above the EU DWD standard of 0.5mg/L or less, suggests that the samples from the study area is heavily contaminated by anthropogenic activities (human waste is the most probable source). Cadmium having an average value of 0.0056, which is above the EU DWD recommended level of 0.005mg/L, may indicate

the presence of cadmium as an impurity in the zinc of galvanized pipes, or pipes or fittings soldered using cadmium-containing solders and associated types. Also, in areas where the soil has been acidified due to acid rain or other means, high concentrations of cadmium have been observed

INTRODUCTION

In many metropolitan cities, open, uncontrolled and poorly managed dumping is commonly practiced, giving rise to serious environmental degradation. More than 90% of municipal solid waste in cities and towns are directly disposed-off on land in an unsatisfactory manner and often pose a threat to ground water quality and has resulted in many incidents of ground water contamination in Udu Local Government Area, Delta state. Nearly all human activities generate waste, and the way in which this is handled, stored, collected and disposed of, can pose risks to the environment and to public health (Zhu et al., 2008).

Due to migration of leachate, soils have been contaminated with heavy metals such as lead, copper, zinc, iron, manganese, chromium, and cadmium and these heavy metals in solid wastes lead to serious problems because they cannot be biodegraded (Hong et al. 2002). The major sources of heavy metals in landfills are the co-disposed industrial wastes, incinerator ashes, mine wastes and household hazardous substances such as batteries, paints, dyes, inks, etc. (Erses and Onay 2003). Soil contamination by heavy metals from waste disposal sites is a serious problem in industrial and urban areas (Mandal and Seng-upta 2006). Soils are regarded as the ultimate sink for heavy metals discharged into the environment, as many heavy metals are bound to soils (Obiajunwa et al. 2002). Furthermore, when screening for pollutants in soil and leachate at contaminated sites, the results are often required directly, since classification of the soil is needed before determination of remediation techniques (Banar et al. 2007). Hence, this study has been carried out to assess the soil contamination around the local dump area where the municipal solid wastes have been disposed for so many years.

Groundwater is also commonly understood to mean water occupying all the voids within a geologic stratum. It is not usually static but flows through the rock. The ease with which water

can flow through a rock mass depends on a combination of the size of the pores and the degree to which they are inter-connected described groundwater as the main source of potable water supply for domestic, industrial and agricultural uses in the southern part of Nigeria, especially the Niger Delta, due to long retention time and natural filtration capacity of aquifers. Generally, the quality of drinking water is determined based on the appearance, taste, color and odor of the water but all these do not really tell if the water should be free from hazardous compounds as the Geology of an area, its rock types, their weathered products, precipitation from rainfall, urban storm-water runoff and human activities in an environment contributes immensely to the chemistry of subsurface and surface water. Also, the quality of water is a measure of the suitability of the water for a designated use such as; drinking, agriculture, Recreation, laundry and industrial usage based on selected physical, chemical and biological characteristics These substances occur naturally in geological structures or sometimes caused by mining, industrial and agricultural activities. These chemical can badly affect human health when they are consumed in large amount. There are two main sources of water supply that are available to man, surface water that includes: rivers, lakes, stream, drainage areas which funnels water toward the holding reservoirs and subsurface or ground water which includes wells, springs and horizontal galleries

(II) AIM AND OBJECTIVES

The aim of this work is to determine and analyze the extent of heavy metal contamination in the soil due to leachate migration from the open dumping sites and their spatial relationships within the study area using statist methods and also to determine and analyse the concentrations of the chemical constituents of groundwater and their spatial relationships within the study area using statistical methods.

Location and Accessibility

The study area are of two locations: for the study of heavy minerals concentration of the dump sites, the location (Udu) lies between latitude $05^{\circ}54'00''\text{N}$ and $05^{\circ}24'00''\text{N}$, and longitude $005^{\circ}42'00''\text{E}$ and $005^{\circ}54'00''\text{E}$ and covers a distance of 1130.61km^2 . The study area is located

in the western part of the Niger Delta, and includes the area that covers the metropolitan city of Udu in Udu Local Government Area. The area, located some 40km away from the Atlantic Ocean, has a population of over 100,000 people.



Figure 1: Map o Niger Delta showing first location (Udu L.G.A) of study area

The second location for the study of groundwater study; The 1130.61km² study area lies between latitude 5°54'00"N and 5°24'00"N, and longitude 5°42'00"E and 5°54'00"E. The

study area is located in the western part of the Niger Delta, and includes the area that covers the metropolitan city of Warri and Effurun in Warri South and Uvwie Local Government Area respectively, and Sapele Local Government Area. The area, located some 40km away from the Atlantic Ocean, has a population of over 300,000 people (Olobaniyi and Owoyemi, 2006).

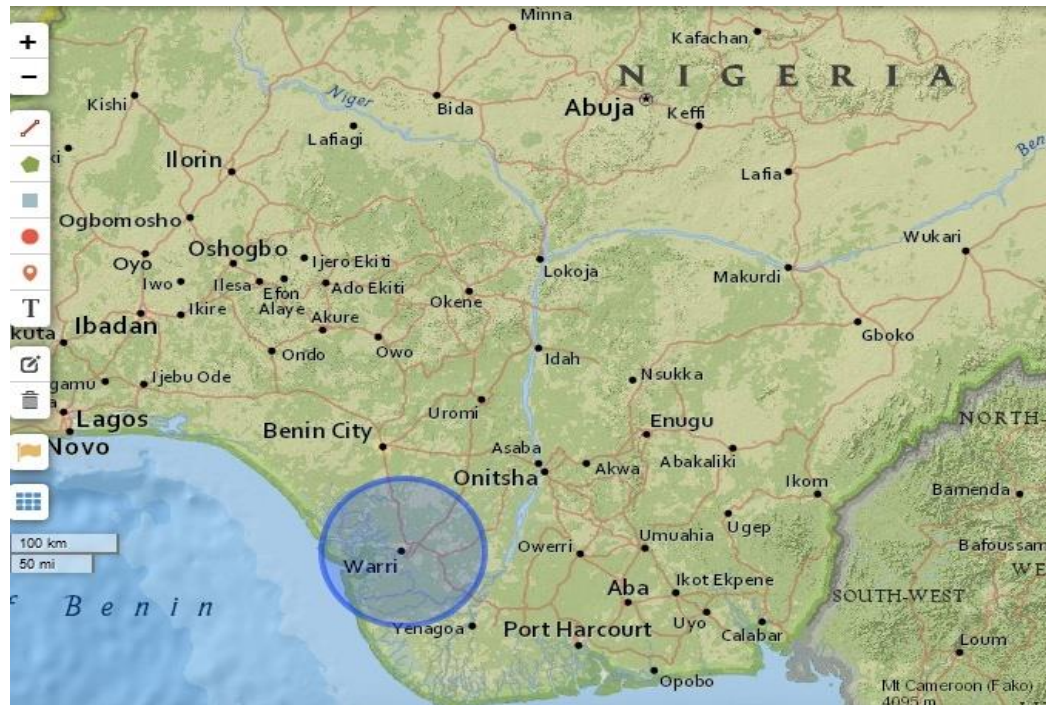


Figure. 2: Map of Nigeria indicating the second location of study area (Warri)

Topography and Drainage

The study area is a plain with rivers and swamps within relatively short distances. The topography of the area is flat to gently undulating with slopes of about 0-4° and occupies a low-lying plain consisting mainly of recent unconsolidated sediments of Quaternary age. These sediments are partly of marine and partly of fluvial origin. Land elevation is generally under 30 meters above mean sea level. There is a marked absence of imposing hills that rise above the general land surface. The area is traversed by numerous flat-floored rivers that drain into the Atlantic Ocean. The two important rivers are the Ethiope and Warri. These rivers are prone to

flooding, especially during the wet season, mainly because of the heavy rainfall, high ground water table and the flat-floored valleys.

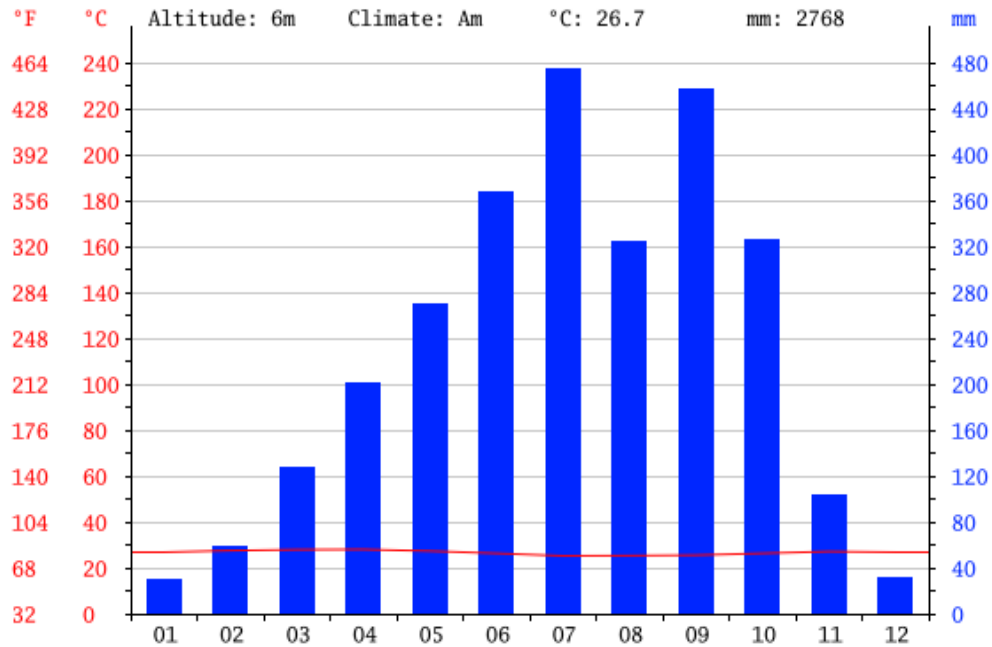


Figure.3. Histogram showing monthly distribution of yearly rainfall in Warri.

(III) MATERIALS AND METHOD

(A) HEAVY METAL STUDY

Sampling

The soil samples were collected randomly from open dumpsites within Udu Local Government Area. The GPS was used to take readings of the locations, their coordinates and elevation above sea level. The samples were then taken to the laboratory for analysis within retention time.

Leachate sampling and analysis

The leachate corresponds to rainwater that has percolated through waste, interacting with bacteriological activity and especially organic substances. Its composition is a function of the

nature and the age of the landfill, the type of wastes, the method of burying, the geological nature of the site and the climate (Amina et al. 2004). To study the physicochemical composition of leachate, the leachate samples were collected from actual leachate streams in the solid waste dumping site using 5 L polypropylene carboys that were rinsed out thrice prior to sample collection using distilled water and transported to the laboratory, stored at 4⁰C and analyzed within 2 days. A total of 10 (ten) leachate samples were collected for monitoring purpose. The physicochemical parameters such as pH, total hardness, and total dissolved solids, major cation such as iron and major anion such as Cl⁻ were determined. All the analyses in this study were repeated two or three times until concomitant values were obtained, and all the tests were carried out according to the standard methods (APHA 1998).

Sample preparation

For heavy metal contaminant evaluation such as Cd, Cu, Mn, and Pb on solid waste and soil, the collected 10 number of solid waste samples and 10 number of soil samples were air dried, then grinded, screened through a <2.360-mm sieve and subjected to acid digestion. Acid digests of solid waste and soil samples were prepared as per the procedure postulated by (NEPM1999). For the determination of total metal content, boiling aqua regia (3:1 hydrochloric/nitric acid) was used to extract the metals from the samples. The strong and concentrated acid mixture is capable of extracting inorganic metals. One gram of MSW fine fraction/soil was mixed with 18 ml of concentrated HCl and 6 ml of concentrated HNO₃ and moistened with a little deionized water. The mixture was gently boiled in a hot plate until about 5–10 ml of extract remains in the flask and allowed to cool for about 15 min. Then, 18 ml of concentrated HCl and 6 ml of concentrated HNO₃ were added and boiling was repeated till about 5-10 ml of extract remains in the flask. After cooling, the extract was filtered through Whatman No. 42 filter paper and was made up to 50 ml with distilled water. The heavy metal concentration present in the solid waste and soil samples were calculated using the following relation.

$$M = \frac{(C - B) 50}{W}$$

Where,

Where,

M = concentration of metal in the solid waste/soil, air dried basis (mg/kg),

C = concentration of metal in the digest (mg/l),

B = concentration of metal in the blank (mg/l),

W = weight of air dried solid waste and soil sample digested (g).

To analyze the heavy metal concentration in leachate, the collected 10 (ten) leachate samples from the dumping area were filtered and preserved for soluble heavy metal analysis with a drop of concentrated nitric acid. The heavy metal analysis such as Cd, Cu, Ca, Mn and Pb were determined for the preserved leachate samples.

Laboratory Analysis

The analytical methods used in the determination of the heavy metals are in accordance with the American Standard for Testing Materials (ASTM D 3867) (1969) and American Public Health Association (APHA) (1989) Standard procedures. Analyses were carried out as soon as the soil samples arrived at the laboratory.

The collected soil were placed on clean plastic sheet, oven dried for three hours and then sieved through a 0.2 mm mesh size to remove stones, plant roots in order to have uniform soil particle size. Following a method developed by Berghof Microwave Digestion Application (2011), a soil sample of 500 mg were transferred to digestion vessels with 7.5 ml of HCl and 2.5 ml of concentrated HNO₃(3:1 HCl : HNO₃). The vessels were carefully shaken and placed in a fume hood for about 20 min for pre-digestion and to avoid foaming before they were placed on the turntable of the microwave system. Then the pre-digested samples in the digestion vessels were closed and heated on microwave oven following the optimized procedure shown in the Table below. The total concentrations of Ca, Pb, Mn, Cu and Cd in filtrates were then determined using a Flame Atomic Absorption Spectrometer using air acetylene flame.

Table 3.3: Working condition for Varian 220 Atomic Absorption Spectrometer for Heavy Metals

Heavy metal	Wavelength	Slit width (nm)	Lampcurrent (nm)	Fuel	Support	Flame Stoichiometry
Calcium	375.2	0.5	5.0	Acetylene	Air	Oxidizing
Cadmium	228.8	0.5	4.0	Acetylene	Air	Oxidizing
Copper	324.7	0.5	4.0	Acetylene	Nitrous oxide	Reducing

(B) GROUND WATER STUDY

Sampling

For ground water study; ten samples were collected randomly from in warri axis, the study area. Sampling was carried out by collecting water samples in 1litre opaque plastic cans from the boreholes (Cased or uncased), hand dug wells and streams. The pH and electrical conductivity of the water sample was taken in-situ using the pH meter and electrical conductivity meter. The GPS took readings of the locations' coordinates and elevation above sea level. The samples were then taken to the laboratory for analysis within retention time.

pH

The samples collected were measured for pH value in the field, using a pH meter (Model Ecosense). Each sample was placed in a beaker, the electrode end of the meter was then rinse with distilled water followed by the sample and inserted into the sample in the beaker. The

READ button on the pH meter was pressed and the pH value at a stable pH reading was recorded.

Conductivity

The water samples were measured for electrical conductivity (EC) using an Electrical Conductivity Meter (datalogger). The EC meter electrode was rinsed with distilled water and the sample, the sample was poured into a beaker, and the electrode end of the meter was inserted in the sample. The READ button on the meter was pressed and the EC value was read and recorded at stable meter reading.

Field measurements:

The following data were obtained in various locations using the aforementioned methods and instruments in the field.

Borehole=BH, Hand dug well=HDW, Stream=STRM, Effurun R.A=EFF R.A, Niger cat, NGCT, Ogunu=OGN, Refinery road=REF.RD

Table 1: GPS Coordinates and elevation data

S/N	Locations	Longitude	Latitude	Elevation	Time
1	EFF R.A BH	054 ⁷ '2''	05°34'31''	15	11:40am
2	EFFR.AHDW	05°47'11''	05°34'43''	16	12:10pm

3	NIGCT BH	05°44'30''	05°34'39''	20	12:30pm
4	NIGCT HDW	05°44'30''	05°34'32''	23	12:50pm
5	OGN BH1	05°42'28''	05°31'58''	12	01:15pm
6	OGN HDW	05°42'46''	05°31'59''	14	01:30pm
7	OGN BH2	05°42'36''	05°31'52''	12	01:45pm
8	OGN STRM	05°42'43''	05°31'48''	13	02:00pm
9	REF RD.BH	05°46'50''	05°34'10''	20	02:15pm
10	REFRD.HDW	05°46'52''	05°34'28''	20	02:45pm

Table 2 : Analysis Result

S/N	Locations	Temperature (°C)	pH	TDS (ppm)	EC (g/mol)
1	EFF R.A BH	27	4.33	19	44
2	EFFR.AHDW	26.7	4.37	50	104
3	NIGCT BH	26	4.96	15	29

4	NIGCT HDW	26	5.11	236	481
5	OGN BH1	27.5	4.95	164	337
6	OGN HDW	26	5.01	300	598
7	OGN BH2	28	5.13	168	348
8	OGN STRM	28	5.09	288	576
9	REF RD. BH	26	5.37	519	261
10	REF.RDHDW	27	5.59	14	33

Laboratory Analysis

The analytical methods used in the determination of the water chemistry are in accordance with the American Standard for Testing Materials (ASTM D 3867) (1969) and American Public Health Association (APHA) (1989) Standard procedures. Analyses were carried out as soon as the water samples arrived at the laboratory, since it is usually not advisable to delay in order to accurately determine the water chemistry.

Chloride ion

The salinity and chloride in water was determined in accordance with the American petroleum Institute (API-RP 45). 100ml of sample was measured and put in a 250ml conical flask. A 1ml of K_2CrO_4 was added and titrated with 0.014N $AgNO_3$. The end point for was marked by a colour change from yellow to reddish brown. The formula for chloride calculation is:

$$\text{mg/L (Cl}^{-}\text{)} = \frac{35.5 \times C_b \times V_b}{\text{ml of sample}} \times \frac{1000}{1}$$

Where:

C_b = Concentration of AgNO_3 (Normality)

V_b = Volume of AgNO_3 (Consumed)

Nitrate / Nitrite ion

Nitrate in water was determined in accordance with the American Society for Testing and Materials (ASTM D 3867). A number of reaction tubes in a wire rack containing 10ml of sample were set up, with blank and standard solution prepared from sodium nitrate, spacing them so that empty space surrounds each tube. The rack was set in a cool water bath, 2ml NaCl solution prepared from (300g of NaCl crystals in distilled water) was added to the sample, standard and blank solution. The set up was mixed thoroughly by swirling and then 10ml H_2SO_4 prepared from (500ml of conc. H_2SO_4 to 125ml distilled water) to each of the solution. The setups was again swirl and mixed thoroughly and allow to cool. The rack of tube were replaced to mix thoroughly and placed in a well stirred boiling water bath, that maintain a temperature of not less than 95°C and left there for 20minute. The samples were then removed and immersed in a cool water bath. When thermal equilibrium was attained, the tubes were removed and dried with tissue paper. The standard and sample against the reagent blank at 410nm in the spectrometer was read.

Heavy metals and cations

Water samples were collected using acid-leached polythene bottles. The samples were preserved with concentrated HNO₃ and refrigerated to 4.0° pending analysis. Some water parameter like PH, electrical conductivity, total dissolved solids was performed immediately before preservation. For assessment of contamination, the method of Arnold (6) was used in which heavy metals extracted by molar nitric acid is assumed to represent the amount that has been acquired through contamination, in this method, 5ml concentration HNO₃ was added to 100ml of well-mixed water sample in 125ml conical flask, the solution was evaporated to about 20ml on hot plate. Another 5ml concentration HNO₃ was added and the mixture heated until digestion was completed. Additional 10ml concentration HNO₃ was added and the content filtered and made up to 100ml with distilled water. Cations and heavy metals were determined in water samples and blanks with a computerized Varian 220 Flame Absorption Spectrophotometer. The instrument working conditions and parameters for the determination of each metals were shown below.

(III) RESULTS FOR DUMPSTES HEAVY METAL CONCENTERATION STUDY

Table 2 : AAS analysis result for heavy metals in soil samples

SAMPLE	Cd (mg/l)	Cu (mg/l)	Pb (mg/l)	Ca (mg/l)	Mn (mg/l)
SS – I	0.10	0.30	0.20	3.24	0.6
SS – II	0.10	0.50	0.40	13.26	0.20
SS – III	0.10	0.70	1.40	15.10	0.12
SS – IV	0.10	0.60	1.40	14.96	0.16
SS – V	0.00	0.30	1.00	3.00	0.10

SS – VI	0.00	0.30	1.00	3.74	0.30
SS – VII	0.10	1.10	1.40	4.52	0.40
SS – VIII	0.10	1.80	4.80	6.67	0.30
SS – IX	0.10	0.70	0.50	7.40	0.18
SS – X	0.10	0.80	1.60	5.46	0.20

Table 3 : Physiochemical characteristics of leachate

SAMPLE	pH	EC (μ mho/cm)	TDS (mg/l)	Chlorides (mg/l)	Iron (mg/l)	Total hardness as CaCO ₃ (mg/l)	Total alkalinity as CaCO ₃ (mg/l)
LS – I	7.49	31,940	22,000	1999	1.28	7900	5000
LS – II	7.5	44,300	34,900	6498	2.40	8500	11000
LS – III	8.27	33,150	27,500	5997	2.41	7000	9500
LS – IV	7.5	35,380	29,500	5995	1.28	8500	10000
LS – V	8.17	26,710	21,000	388.5	2.29	4700	7000
LS – VI	7.50	39540	29,450	5956	2.26	8000	8500
LS – VII	6.50	22,850	15,460	1993	5.28	4900	6800
LS – VIII	6.89	20,100	14,360	1994	5.01	4300	7000
LS – IX	7.10	21,000	16,000	1982	7.59	3900	6700
LS – X	6.5	20,222	14,000	2995	1.27	5000	6500

Leachate characteristics

Table 3 shows the wide variation in the concentration of leachate parameters within the dumping sites which is mainly due to the nature of solid waste dumped in that particular location. It can be observed that the leachate sample possesses very high concentration of chemical parameters except pH. The pH values ranges from 6.50 – 8.27, this may be attributed to the decrease in the concentration of free volatile acids due to anaerobic decomposition, as fatty acids can be partially ionized and contribute to higher pH values. Alkaline pH is normally encountered at landfills, 10 years after disposal (El-Fadel et al. 2002). Since the pH of every sample was observed below 8.3, the alkalinity of each sample might have been due to bicarbonate; a large amount of mineral species are also expected to exist in the leachate as the bicarbonate form (Seo et al.2007).

The relatively high value of electrical conductivity indicates the presence of dissolved inorganic materials in the samples. The concentration of TDS also fluctuates widely from 14,000 to 34,900 mg/l. The determined chloride concentration varies between 388.5 and 6,498 mg/l. Chloride is a non-degradable conservative parameter and the change in its concentration is commonly used to assess the variation of leachate dilution (Bilgili et al. 2007). The results with relatively high pH, alkalinity, and chloride concentration in all the leachate samples analyzed confirm the methanogenic condition of the dumpsite. The Fe concentration in the leachate sample indicates that Fe and steel scrap are also being dumped in the landfill.

Table 4: Physiochemical characteristics of soil

SAMPLE	pH	EC	Chlorides (mg/kg)	Iron (mg/kg)	Total alkalinity (mg/kg)	Total hardness (mg/kg)
SS – I	7.64	627	797	715.86	1200	1000
SS – II	8.01	255	1999	793.50	1600	2100
SS – III	7.99	320	1998	927.55	900	1500
SS – IV	7.55	124.8	2998	793.73	600	2100

SS – V	7.56	114.8	399	573.42	1200	3200
SS – VI	7.55	134.3	599	708.55	800	2400
SS – VII	7.80	326	499	837.59	900	2200
SS – VIII	7.66	281	699	617.28	1000	2300
SS – IX	7.71	266	5978	771.65	700	2900
SS – X	7.31	290	4998	801.7	3000	9000

Characteristics of soil

The collected soil samples from the dump sites were analyzed for index properties and for various physicochemical parameters as reported in Tables 3 and 4, respectively. From Table 3, it was observed that the organic content of the soil ranges from 1.70 to 4.32 %. The maximum organic content was observed in SS – VIII (soil sample 8). The moisture content of the soil samples ranged from 0.65 to 4.00 %. The results indicated that the moisture content was high in the top layer (1 m from the ground level) in all the locations. The specific gravity of soil ranges from 2.12 to 2.25. From the physicochemical characteristics of the soil sample, it was observed that the pH value of the soil sample was alkaline in nature with the range from 7.31 to 8.01. The electrical conductivity of the soil sample ranges from 114.8 to 627 μ mho/cm. The range of parameters such as chlorides, total alkalinity and total hardness varies in the ranges of 399 – 5978, 600–3,000, and 1,000–9,000 mg/kg, respectively. The presence of high value of pH, alkalinity, chloride and iron concentration in the soil samples (SS – IX and SS – X: nine and ten) nearby dumping site suggested that the soil samples were contaminated by leachate migration from open dumping site.

Heavy metal assessment

Table 5: Concentration of heavy metal for the collected leachate sample

SAMPLE	Cu	Cd	Mn	Pb
LS - I	1.4190	0.1131	0.0555	5.1221
LS - II	0.0151	0.3331	1.0551	0.7551
LS - III	0.7521	0.1621	0.6553	0.7654
LS - IV	1.9172	0.3410	0.1605	1.7011
LS - V	1.1549	0.6124	0.5534	2.8221
LS - VI	2.6776	0.7512	1.0582	3.5013
LS - VII	1.5419	1.0370	1.6872	3.1285
LS - VIII	0.5461	0.0040	1.6962	0.0311
LS - IX	0.3445	0.0010	1.4689	3.2200
LS - X	1.4555	0.7662	1.0445	3.3333

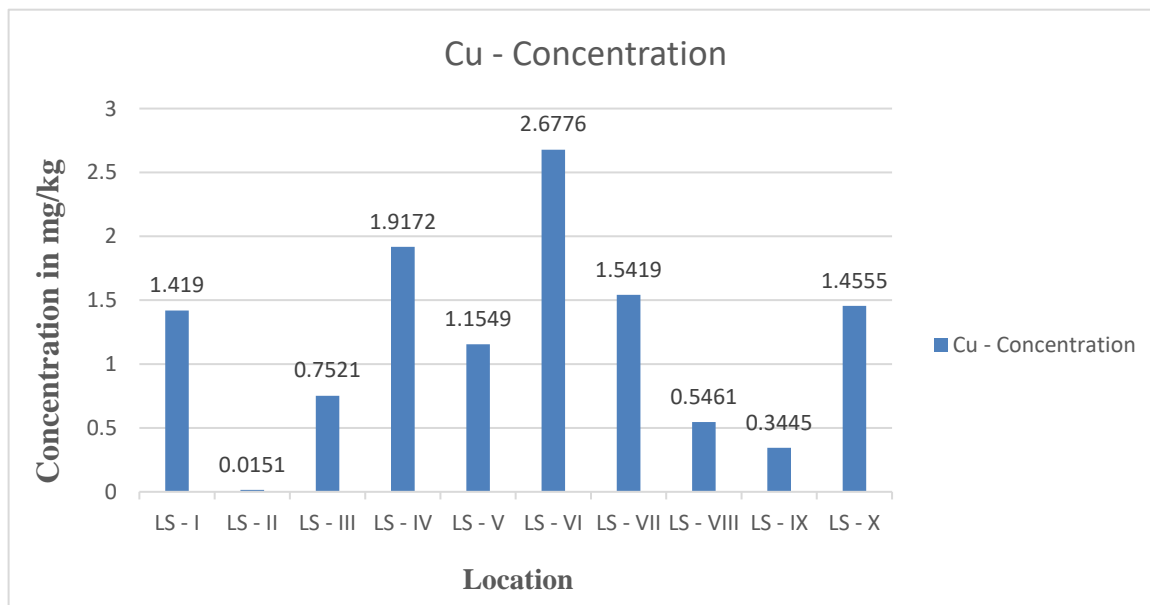


Figure 4: Histogram showing variation of copper concentration in the leachate samples

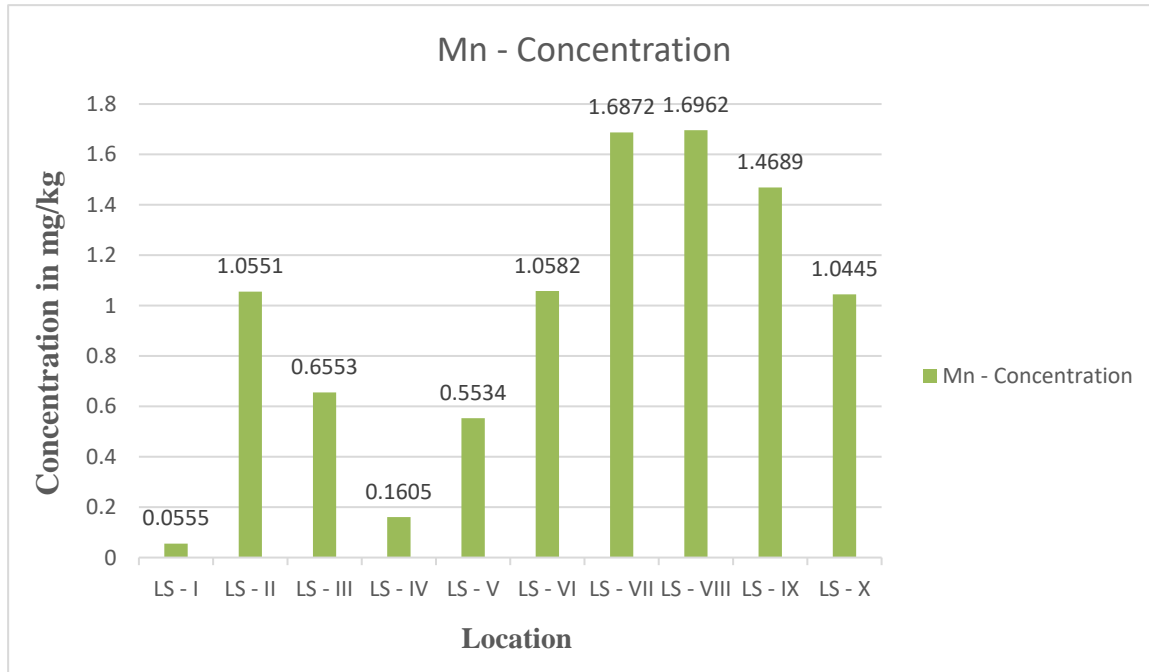


Figure 5: Histogram showing variation of copper concentration in the leachate samples

Leachate

Heavy metals are typically released by acidic pH. Usually these heavy metals are found at moderate concentration levels in municipal landfill leachates (Jensen et al. 1999). From Table 5, it can be observed that Cu, Cd, Mn and Pb concentration values are in the ranges 0.0151–2.6776, 0.0010–0.7662, 0.0555–1.6962, and 0.0311–5.1221 mg/l, respectively, for the collected leachate samples. The high level of Pb (5.1221 mg/l) in the leachate samples indicates the disposal of Pb batteries, chemicals for photograph processing, Pb-based paints and pipes at the landfill site (Moturi et al. 2004; Mor et al. 2005). Based on the average concentration, the heavy metal concentration in the collected leachate sample was found in the following order: Pb>Mn>>Cu>Cd.

Table 6: Concentration of heavy metals for the collected soil samples

SAMPLE	Cu	Cd	Mn	Pb
SS – I	72.52	35.63	148.70	40.09
SS – II	30.21	39.11	144.11	111.40
SS – III	39.10	9.59	137.45	153.34
SS – IV	28.77	5.14	116.48	203.22
SS – V	4.59	10.01	130.51	201.20
SS – VI	39.27	17.12	161.11	69.23
SS – VII	28.88	20.47	40.07	70.11
SS – VIII	5.73	29.41	52.51	73.27
SS – IX	30.30	38.72	141.40	120.60
SS – X	27.90	34.13	115.33	168.18

Soil

Contamination of heavy metals in the environment is of major concern because of their toxicity and threat to human life and the environment (Purves 1985). Many investigators have conducted researches on heavy metal contamination in soils resulting from various anthropogenic sources such as industrial and municipal wastes (Haines and Pocock 1980; Parry et al. 1981; Culbard et al. 1983; Gibson and Farmer 1983; Olajire and Ayodele 1998). In this study, the concentrations of heavy metal present in the collected soil sample were reported in Table 6. Cu was observed and it is well known that copper is a rather immobile element in soils, and the greatest amounts of adsorbed copper have always been found for Fe and Mn oxides (Kabata-Pendias and Pendias 2000). The concentration of Cd in the collected soil sample was observed to be very less, because the concentration of Cd in the solid waste and leachate was found to be very meager. The manganese concentrations were totally observed for all the 10 samples with the ranges

between 40.07 and 161.11 mg/kg. Lead has highly chalcophilic properties. Thus, its primary form in its natural state is galena (PbS), and the natural lead content of soil is inherited from parent rocks (Kabata-Pendias and Pendias 2000; Son and Jung 2011). From Table 6, the concentration of lead was observed in the ranges from 40.09 to 203.22 mg/kg. The distribution of metal among specific forms varies widely based on the metal's chemical properties and soil characteristics (Soon and Bates 1981; Olajire and Ayodele1998). Based on the average concentration, the heavy metal concentration in the collected soil sample was found in the following order: Mn >Pb>Cu>Cd.

RESULTS AND INTERPRETATION FOR GROUNDWATER STUDY

Table 7: Table showing the samples and their parameters

Sample	pH	TDS(mg/L)	EC(mg/L)	Ca(mg/L)	Mg(mg/L)	K(mg/L)	Na(mg/L)	
EFFRABH	4.33	194	46.59	3.18	0.014	0.096		
NIGCATBH	4.96	147	28.76	8.21	8.71	8.65		
OGNBH1	4.95	164	33.76	0.21	8.52	7.76		
OGNBH2	5.13	168	34.85	9.18	9.24	7.17		
REFRDBH	5.59	143	33.31	1.19	0.005	0.03		
EFFSPHDW	4.37	50	10.49	5.62	0.02	0.05		
NIGCATHDW	5.11	236	48.14	9.19	9.85	2.11	32.11	
OGNHWDW	5.01	300	59.87	9.23	7.27	9.31	1.13	
REFHWDW	5.37	519	26.14	9.19	9.64	1.42	27.62	
OGNSTRM	5.09	288	57.6	10.35	2.13	0.91	5.74	
MIN	4.33	142	28.73	1.11	1.19	0.005	0.03	
MEAN	4.99	177.27	281.07	6.60	4.20	4.42	2.0059	16.6356



M A X	. 5 . 5 9 5 1 9 5 9 8	10.353	. 1 8 5 . 2 1 3 2 . 1 1
S . D	. 0.370309 155.6109 211.7065 2.083719 0.472952 1.711463 13.07735		
SKEWNESS	-0.5924 0.901263 0.196603 0.355421 0.965524 0.436657 -0.23974		
U S E P A	6.5-8.5 5 0 0		2 0 0
E U D W D	6.5-9.5		2 0 0

Table 7 continued.

S a m p l e	NH4(mg/L)	NO2(mg/L)	NO3(mg/L)	Cl(mg/L)	SO4(mg/L)	HCO3(mg/L)
EFFRABH	0 . 0 0 1 0 . 0 1 0 . 1 6 4	15.021	1 . 0 8 5 0 . 0 1			
NIGCATBH	4 . 9 8 0 . 0 0 1 1 . 8 9 5	84.531	7 . 1 0 9 0 . 2 1			
OGNBH1	2 . 9 1 0 . 0 0 1 2 . 1 0 9	76.084	7 . 7 1 6 0 . 2			
OGNBH2	5 . 8 6 0 . 0 0 1 1 . 3 5 2	41.543	5 . 4 9 3 0 . 1 9			
REFRDBH	0 . 1 9 0 . 0 0 1 0 . 0 0 1	14.352	1 . 0 3 4 0 . 1			
EFFSPHDW	0 . 4 4 0 . 0 0 1 0 . 2 7 5	31.032	2 . 1 1 5 0 . 0 9			
NIGCATHDW	9 . 5 1 0 . 0 0 1 2 . 5 7 8	92.603	10 . 5 4 3 0 . 2 6			
OGNHWDW	0 . 9 5 0 . 0 0 2 4 . 2 5 4	70.584	18 . 2 3 4 0 . 3 6			
REFHWDW	0 . 5 1 0 . 0 0 1 3 . 1 4 3	62.142	11 . 0 3 2 0 . 3			
OGNSTRM	1 1 . 4 0 . 0 2 4 . 2 5 7 0 . 6	18 . 2 3 0 . 2 4				
M I N	. 0 . 0 0 1 0 . 0 0 1 0 . 0 0 1	14.352	1 . 0 3 4 0 . 0 1			
M E A N	3 . 6 7 5 1 0 . 0 0 3 9 2 . 0 0 2 1	55.8492	8 . 2 5 9 1 0 . 1 9 6			
M A X	. 1 1 . 4 0 . 0 2 4 . 2 5 4	92.603	18 . 2 3 4 0 . 3 6			
S . D	. 3.928574 0.005991 1.502293 26.95692 6.020892 0.099519					
SKEWNESS	0.966379 2.328945 0.168038 -0.42099 0.551914 -0.31581					
U S E P A		0 . 5 0 1 0 2 5 0 2 5 0				
E U D W D	0 . 5 0 . 5 0 5 0 2 5 0 2 5 0					

Of the 18 parameters analyzed, only pH, ammonium and cadmium were observed to exceed United States Environmental Protection Agency and European Union Drinking Water Directives standards (observed mean value for pH, ammonium and cadmium are 4.991, 3.6751mg/L and 0.0056; US EPA recommended pH level is between 6.5-8.5, and the EU DWD recommended level for ammonium and cadmium are 0.50mg/L and 0.005mg/L, respectively). With the exception of the aforementioned three parameters, all other parameters values observed were less than the recommended levels. With a mean value of 4.991, the pH of water samples from the Warri area is mostly acidic. Ammonium having a mean value of 3.6751mg/L, which is a very huge magnitude above the EU DWD standard of 0.5mg/L or less, suggests that the samples from the study area is heavily contaminated by anthropogenic activities (human waste is the most probable source). Cadmium having an average value of 0.0056, which is above the EU DWD recommended level of 0.005mg/L, may indicate the presence of cadmium as an impurity in the zinc of galvanized pipes, or pipes or fittings soldered using cadmium-containing solders and associated types. Also, in areas where the soil has been acidified due to acid rain or other means, high concentrations of cadmium has been observed. REFHDW (TDS=519mg/L), a sample from a hand dug well, has a TDS higher than the recommended 500mg/L; this must suggest that the shallow water table in the area is somewhat contaminated, or at least there are impurities in that sample.

From Table 6, TDS, Mg and NH₄ are the only parameters close to having a normal distribution based on their skewness, the other parameters are either positively or negatively skewed thereby justifying the normalization of the data before the application of multivariate statistics. All the parameters with mean values above the recommended values and also having a wide range of values, suggests that they may be influenced by anthropogenic activities.

Piper Diagram

A piper diagram is a graphical representation of the chemistry of a water sample or group of 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 bicarbonate anions. The two ternary plots are then projected up onto a diamond. The diamond is a matrix transformation of a graph of the anions and cations. It is used to classify water types by hydrochemical facies. The piper diagram below (6) show the samples analyzed and their corresponding cation and anion concentrations in relative proportions.

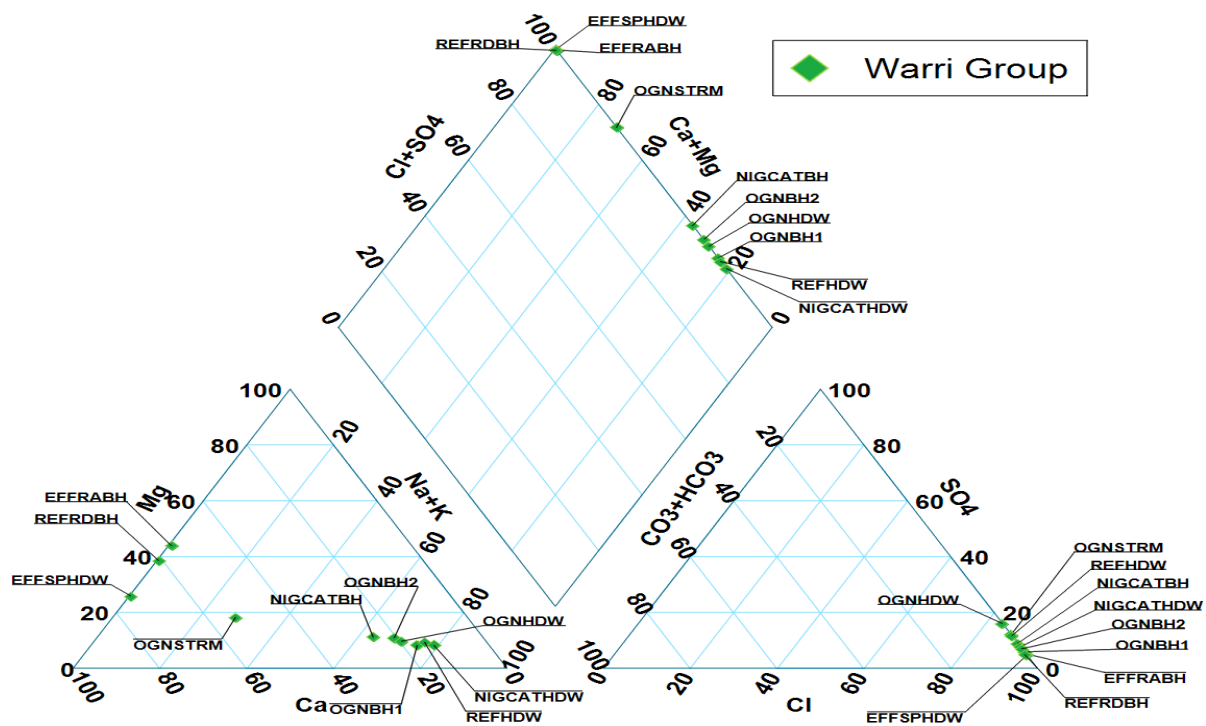


Figure 6: Piper diagram showing the samples analyzed.

The Piper diagram (Fig. 6) shows the dominant cation and anion in the water samples and also the hydrochemical facies the samples belong to. The dominant anion is chloride (Cl) as shown on the right-hand side triangle in figure 6 above, all the samples are seen aligning close to where chloride has a magnitude of 100. There are two dominant cations; the calcium (Ca) type and the sodium (Na) type or potassium (K) type as seen on the left-hand side triangle with EFFRABH, REFRDBH, EFFSPHDW, and OGNSTRM falling under the calcium type, and are therefore hard

water. The sodium type or potassium type dominate OGNBH2, NIGCATBH, REFHDW, OGNBH1, NIGCATHDW, and OGNHDW. REFRDBH, EFFSPHDW, AND EFFRABH make up the Cl-SO4-Ca-Mg groundwater group. The Cl-SO4 groundwater group includes NIGCATBH, NIGCATHDW, OGNBH1, OGNBH2, OGNHDW, and REFHDW. OGNSTRM is the only surface water sample and it stands out on the Piper diagram (Fig.6), it has a higher sulfate concentration than the Cl-SO4 group and it belongs to that group except for the fact that it is a surface water sample.

Pearson's Correlation Matrix

This type of correlation matrix is used to examine the strength and direction of the linear relationship between variables. The correlation coefficient (values) range from -1 to +1. The higher the value (closer to +1), the stronger the relationship between the variables. Also, a positive sign indicates that the variables have a positive relationship, and vice versa for a negative sign.

Cadmium is our primary concern here, and we employed a Pearson's correlation matrix to analyze the data and find if there are any meaningful relationships between cadmium and the other variables. For example, pH and hydrogen carbonate increases together. Cadmium correlates moderately with magnesium in the Pearson's correlation matrix (Table 4.2). Although it might seem that cadmium and magnesium increase and decrease together since the correlation coefficient is positive, these two elements are not known to coexisting a stable manner within a system. Magnesium has been observed to have an adverse effect on the absorption, accumulation and toxicity of cadmium.

Table 8: Pearson's correlation matrix for the parameters analyzed.

N O 3 C I S O 4 H C O 3 A I C d Z n F e C u

p	H	0.7364	0.5137	0.3442	0.0443	0.7864	0.913	0.1364	0.1287	0.7108
T	D	0.0223	0.0475	0.0053	0.0438	0.4257	0.5171	0.202	0.0716	0.6596
E	C	0.0295	0.0545	0.0076	0.0636	0.3199	0.6185	0.4116	0.1078	0.4977
C	a	0.0733	0.3683	0.2956	0.9545	0.1398	0.9351	0.1442	0.7699	0.3315
M	g	0.1243	0.864	0.7058	0.2305	0.7887	0.1045	0.4263	0.4891	0.4544
K		0.0015	0.0002	0.0004	0.0113	0.8277	0.2661	0.1702	0.0075	0.4704
N	a	0.003	0.0005	0.0007	0.0164	0.8709	0.2704	0.1961	0.0098	0.5513
N	H	0.1429	0.0064	0.0174	0.0008	0.3665	0.8922	0.4606	0.006	0.0397
N	O	0.7337	0.6599	0.8718	0.2601	0.0114	0.3648	0.0596	0.5282	0.6986
N	O	0.31	0.0018	0.0017	0.1391	0.4964	0.2087	0.6311	0.0642	0.4746
C	1	0.8511	1	0.0002	0.0056	0.5658	0.5793	0.2124	0.0003	0.0794
S	O	0.8535	0.9205	1	0.0039	0.2643	0.4715	0.2886	0.0011	0.1454
H	C	0.5022	0.7985	0.8170	1	0.6501	0.7769	0.0941	0.0003	0.052
A	1	0.2443	0.2072	0.3907	0.1643	1	0.7977	0.2065	0.4888	0.4175
C	d	0.4353	0.2001	0.2581	-0.1031	0.0933	1	0.8644	0.8811	0.3686
Z	n	-0.1738	-0.432	-0.3729	-0.5574	0.4372	-0.0622	1	0.0892	0.4878
F	e	-0.6043	-0.9035	-0.8692	-0.9058	-0.2485	0.0545	0.5644	1	0.0301
C	u	-0.2564	-0.5791	-0.4954	-0.6277	-0.2893	0.3193	0.249	0.6812	1

Principal Component Analysis (PCA)

Table 9: Principal components

Component	Variance	Difference	Proportion	Cumulative
Comp1	6.69036	3.8187	0.3717	0.3717
Comp2	2.87166	0.106816	0.1595	0.5312
Comp3	2.76485	0.422719	0.1536	0.6848
Comp4	2.34213	0.114681	0.1301	0.8149
Comp5	2.22745	.	0.1237	0.9387

The results of the PCA shows that there are five components worth retaining . These components are responsible for the hydrochemistry of the study area. The first component accounts for some 37.17% of the total variation. Component 2 is responsible for 15.95% of the variation, and component 3 has 15.36% of the variation. Components 4 and 5 holds 13.01% and 12.37% of the variation respectively. Cadmium is one of the variables that make up component 5, along with sodium and copper (Table 9).

Table 10: Principal component loadings and explained variance for the five components with Varimax normalized notation applied.

Variable	Comp 1	Comp 2	Comp 3	Comp 4	Comp 5	Unexplained
p H		-0.5952				0 . 0 2 4 4 1
T D S			0.6399			0 . 0 1 5 3 1
E C			0.6231			0 . 0 5 6 8 7
C a		0.4982				0 . 0 3 2 5 6
M g		0.4517				0 . 0 3 2 8 6
K						0 . 0 2 3 9
N a					0.3175	0 . 0 5 2 8 4
N H 4	0.3805					0 . 1 2 2 8
N O 2				0.5461		0 . 0 6 7 3 1
N O 3						0 . 0 1 6 2 2

C	l	0.3826			0 . 0 1 7 8 6
S	O	4			0 . 0 2 1 7 4
H	C	O	3	0 . 3 0 4	0 . 0 3 1 2
A	l			0.6535	0 . 0 2 2 8 1
C	d			0.6957	0 . 1 2 4 4
Z	n			0 . 4 0 3	0 . 2 0 1 2
F	e	-0.3605			0 . 0 7 5 4 8
C	u	-0.4045		0.3367	0 . 1 6 3

Proportion % 37.17 15.95 15.36 13.01 12.37

Cumulative % 37.17 53.12 68.48 81.49 93.87

The five components collectively account for 93.87% of the total variation of the hydrochemistry. This is very good, and shows that PCA was a useful tool in revealing the latent factors within the data. Component 1 holds ammonium, chloride, hydrogen bicarbonate, iron and copper as the culprits for the 37.17%, which is very high for one component. Ammonium is associated with anthropogenic pollution and its presence in component 1 indicates that this component can also be called the “anthropogenic effect” component. The relationship between ammonium, chloride, bicarbonate, iron and copper is not clear but there seems to be a false-dependence between these five variables. Chloride and bicarbonate do increase and decrease together, same for iron and copper. The five variables are contaminants and they degrade the quality of groundwater. Component 5 has the variable the variable of interest here, cadmium, and also has sodium and copper.

Component 5 accounts for only 12.37% of the variance, and has cadmium, sodium and copper as its variables. Cadmium does not correlate highly with neither sodium nor copper, although what little correlation that exists between them is positive, it is not enough to say they increase

together or that their relationship is a dependent one. This is supported by works of research on their relationship .

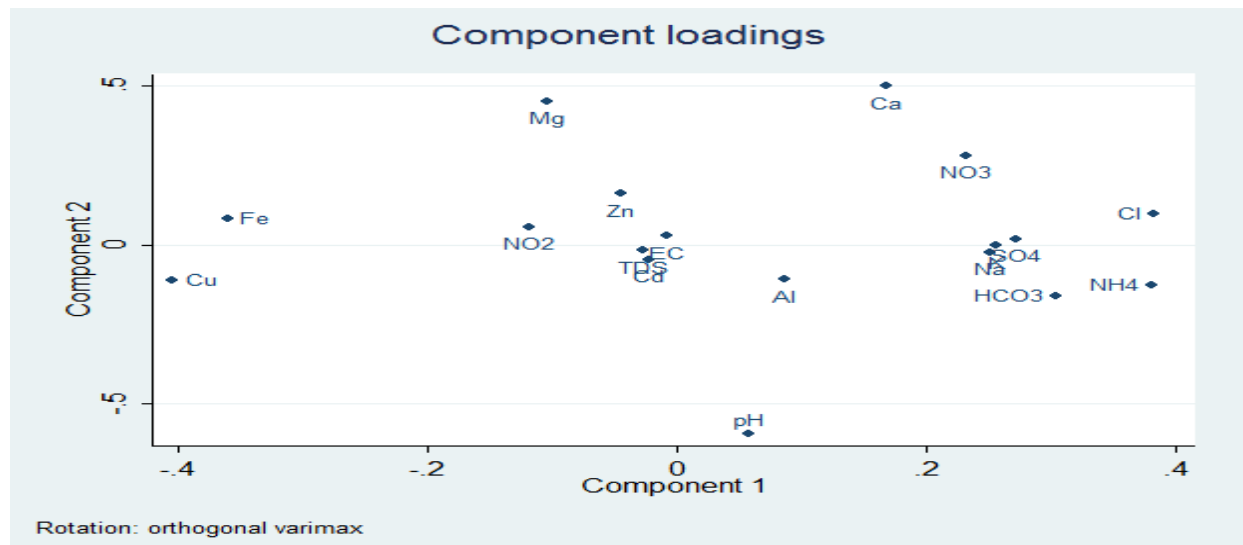


Figure 7: Components loadings for Principal Components 1 vs. 2.

DISCUSSION

Cadmium is a metal used in electroplating and as an anticorrosive on steel, in batteries, electrical components, paint pigment and nuclear reactors. Cadmium in water is highly influenced by its pH, acidic water such as that dominant in this study increases its solubility. It is present in bottom sediments and suspended particles in streams and rivers, this is evident in the values for the element in NIGCATHDW (max. value for this study 0.013mg/l, well above the EU DWD recommended standards) and OGNSTRM (0.005mg/l).

It is highly toxic, as toxic as mercury, the kidney is the most sensitive organ to cadmium, but it could also lead to tubular dysfunction in humans. Cadmium could contaminate drinking water as a result of the presence of impurities in the form of galvanized zinc pipes, cadmium-containing solders in electronics, water heaters, taps and fittings .Other sources of cadmium includes sewage

sludge (used for soil amendment), waste incineration and recycling of electronic waste, smoking cigarettes is also a source of cadmium.

Warri is a city that is notorious for having bad waste disposal policies or a lack of laws for waste disposal. Improperly disposed waste with impurities in the form of those mentioned earlier could easily dissolve in the soft and acidic water may dissolve cadmium readily within our study area leading to high concentrations of the highly toxic metal. The water table in Warri is very shallow, and contaminants can easily migrate from poorly sited landfill and waste disposal sites into the water table.

Health problems attributed to cadmium always involves kidney problems. The carcinogenic effects of cadmium in the human body are not fully understood, but it has been known to induce carcinogenesis by inhalation and parental routes of exposure in other animals. Epidemiological studies of people chronically exposed to cadmium via the diet as a result of environmental contamination have not shown an increased cancer risk, but humans exposed to cadmium by inhalation of high concentrations in the workplace revealed some evidence of an increased cancer risk but the conclusion here wasn't definite.

The silver lining here if there is any, it is that magnesium has a protective effect on cadmium in animals (humans included). Magnesium is known to protect the kidney from the accumulation and toxicity of cadmium. This is corroborated by the fact that they correlate moderately high in the Pearson's correlation matrix (0.5434mg/l) (Table 4.2). Cadmium intoxication or poisoning can therefore be treated with magnesium supplementation.

Fig. 7 shows the components loadings for components 1 through 4, with each graph showing the pairing between two of the components in each of the graphs. Cadmium loads very lowly on component 1 and component 2, close to the zero mark. It has no influence on the both of the first two components which combine for 53.12% of the total variation. This doesn't mean that the effects of cadmium is negligible but since it is a trace element, its effect usually goes unnoticed

until there is an epidemic due to its effects. Bioaccumulation could go on for a long time before it eventually reaches a level or concentration in human tissues to cause severe health problems.

The groundwater within the study area is mostly acidic with high chloride concentrations. Contamination by anthropogenic sources is mainly from septic tanks and probably improper sewage disposal. Ammonium having a mean value of 3.6751mg/L, which is a very huge magnitude above the EU DWD standard of 0.5mg/L or less, suggests that the samples from the study area is heavily contaminated by anthropogenic activities (human waste is the most probable source). Cadmium having an average value of 0.0056, which is above the EU DWD recommended level of 0.005mg/L, may indicate the presence of cadmium as an impurity in the zinc of galvanized pipes, or pipes or fittings soldered using cadmium-containing solders and associated types. Also, in areas where the soil has been acidified due to acid rain or other means, high concentrations of cadmium have been observed

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