## ENVIRONMENTAL HYDROGEOCHEMISTRY OF THE BENIN FORMATION OF THE PORT HARCOURT, ABA AND OWERRI AXIS IN THE NIGER DELTA, NIGERIA

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Ph.D/SSSE/2008/249

### **DEPARTMENT OF GEOLOGY**

## SCHOOL OF NATURAL AND APPLIED SCIENCES

### FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA

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# THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGERIA, IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY (Ph.D) IN GEOLOGY

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#### ABSTRACT

Soil and water pollution are major environmental problems facing many coastal regions of the world due to high population, urbanization and industrialization. The Environmental Hydrogeochemistry of the Benin Formation of the Port Harcourt, Aba and Owerri axis in the Niger Delta, Nigeria was investigated in this study. The study area lies between latitudes 4°40<sup>I</sup>N to 5°40<sup>I</sup>N and longitudes 6°50<sup>I</sup>E to 7°50<sup>I</sup>E covering parts of Port Harcourt. Aba and Owerri a total area of about 12,056 km<sup>2</sup>. Hydrogeological investigations show that the aquifers in the area are largely unconfined sands with intercalations of gravels, clay and shale. Results of geoelectric sections, boreholes logs and sieve analysis confirm the dominance of sandy horizons in the area. Pumping test results show that the transmissivity ranged between 152.0 m<sup>2</sup>/day and 2835.0 m<sup>2</sup>/day with an average value of 1026.0 m<sup>2</sup>/day while the specific capacity varied between 828.0m<sup>3</sup>/day and 15314.0 m<sup>3</sup>/day with a mean value of 6258.0 m<sup>3</sup>/day. Well discharge ranged between 1624.0 m<sup>3</sup>/day and 7216.0 m<sup>3</sup>/day with an average value of 3218.0  $m^3/day$  while hydraulic conductivity varied between 3.2 m/day and 478.4 m/d with a mean value of 98.6 m/day. These findings indicate that the aquifer in the area is porous, permeable and prolific in groundwater. The observed wide ranges and high standard deviations and mean in the geochemical data are evidence that there are substantial differences in the quality/composition of the groundwater within the study area. The plot of the major cations and anions on Piper, Durov, and Scholler diagrams indicated six hydrochemical facies in the area: Na-Cl, Ca-Mg-HCO<sub>3</sub>, Mg-Ca-SO<sub>4</sub>, Ca-Mg-Cl, Na-Fe-Cl and Na-Fe-Cl-NO<sub>3</sub>. Heavy metal enrichment index revealed 12 elements in the decreasing order of: Fe > Ni > Cu > Zn > Mn > Cd > V > Co > Pb > Cr > As > Hg. The study identified salt intrusion, high iron content, acid-rain, hydrocarbon pollution, use of agrochemicals, industrial effluents and poor sanitation as contributors to the soil and water deterioration in the area. Saltwater/freshwater interface occurs between 5 m and 185 m while iron-rich water is found between 20 m and 175 m. The first two factors are natural phenomenon due to the proximity of the aquifer to the Ocean and probably insitu weathering and mobility of marcasite, a sulphite mineral contained in the rock. The occurrences of the marcasite are localized at depths between 150m and 180m. The last four factors are results of various anthropogenic activities domiciled in the area. DRASTICA model, a modification of DRASTIC model was developed and used in the construction of aquifer vulnerability map of the area. Modern sanitary landfill that ensures adequate protection for the soil and groundwater was designed and recommended to replace the existing open-dumpsites. Owing to the monumental and devastating effects of hydrocarbon pollution in the area, the need to eradicate gas flaring and minimize oil spills in the area was advocated. Bioremediation and phytoremediation techniques were recommended to be applied in the clean-up of soils and water contaminated with hydrocarbon in the area. The efficiency of multivariate statistical techniques in evaluating hydrogeochemical data have been demonstrated in this study.

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#### **CHAPTER ONE**

#### **INTRODUCTION**

### **1.1 Background**

1.0

Land and water are precious natural resources on which rely the sustainability of agriculture, industrialization and the civilization of mankind. Unfortunately, they have been subjected to severe exploitation and contamination due to anthropogenic activities resulting from industrial effluent, solid waste landfills, gas flaring, oil spillage and petroleum refining leading to the release of heavy metals into the environment (Bellos and Swaidis, 2005; Ahmad, Islam, Rahman, Haque and Islam, 2010). The areas around Port-Harcourt, Aba and owerri are coastal areas which have been experiencing high urbanization and industrialization as a result of exploration and exploitation of the petroleum resources of the areas. It is necessary to undertake a comprehensive study of the hydro-facies of the groundwater system of the region, to be able to assess the aquifer characteristics and consequently suggest remediation methods and processes. Industrialization and urbanization of the area necessitated the choice of the study area, considering the impact which various anthropogenic activities may have on the groundwater system of the area. The aquifer system in the area is largely unconfined, highly porous and permeable and the tendency of contaminants infiltrating into the shallow water table is quite obvious. This study has provided the means of identifying and characterizing the contaminants. This research has provided hydrogeologically based aquifer vulnerability map of the area, which is vital in aquifer security, utilization and management.

The increase in groundwater demand for various human activities has placed great importance on water science and management practice world-wide (Nouri, Mahvi, Babaei and Ahmadpour, 2006). Each source of contaminant has its own damaging effects to plants, animals and ultimately to human health, but those that add heavy metals to soils and waters are of serious concern due to their persistence in the environment and carcinogenicity to human beings. Unlike the organic pollutants which are biodegradable (Ammann, Michalke, and Schramel, 2002; Adams, Guzman-Osorio and Zavala, 2008) heavy metal ions are not biodegradable (Bird, Brewer, Macklin, Balteanu, Driga, Serban and Zaharia, 2003; Lee, Li, Zhang, Li, Ding and Wang, 2007), thus making them a source of great concern. Through food chain, the heavy metals bioaccumulate in living organism and reach levels that cause toxicological effects (Kraft, Tumpling and Zachman, 2006; Aktar, Paramasivam, Ganguly, Purkait and Sengupta, 2010). Human health, agricultural development and the ecosystem are all at risk unless soil and water systems are effectively managed (Akoto, Bruce and Darko, 2008). Close relationship exists between groundwater quality and land use as various land use activities can result in groundwater contamination.

Eastern Niger Delta is the operational base of major oil producing and servicing companies in Nigeria. Petroleum exploration and exploitation have triggered adverse environmental impacts in the Delta area of Nigeria through incessant environmental, socio-economic and physical disasters that have accumulated over the years due to limited scrutiny and lack of assessment (Achi, 2003; Caerio, Costa, Ramos, Fernandes, Silveira, Coimbra, Painho, 2005). In Nigeria, immense tracts of mangrove forests have been destroyed as a result of petroleum exploitation in the mangroves and these have not only caused degradation to the environment and destroyed the traditional livelihood of the region but have caused environmental pollution that has affected weather conditions, soil fertility, groundwater, surface water, aquatic and wildlife (Olujimi, 2010). If this trend is allowed to continue unabated, it is most likely that the food web complexes in this wetland might be at a higher risk of induced heavy metal contamination. This unhealthy situation continues to attract the interest of environmental observers and calls for evaluation of the impact of exploration and exploitation activities in the coastal areas of Nigeria and these were part of what this research intended to address.

To meet the ever-increasing water demand in the region, groundwater is being extensively used to suppliment the surface water thereby subjecting it to over-exploitation for domestic, agricultural, urban and industrial uses which results in the deterioration of groundwater in coastal areas (Macklin, Brewer, Balteanu, Coulthard, Driga, Howard and Zaharia, 2003). Increasing urbanization is taking place along the coastlines of the Niger Delta and causing increased use of groundwater and it has a large impact on the quality and quantity of groundwater system in the area. The quality of groundwater is measured in terms of its physical, chemical and biological parameters (Sargaonkar and Deshpande, 2003). In many countries around the world, including Nigeria, groundwater supplies may have become contaminated through various human activities, which have impact on the health and economic status of the people. The discharge of untreated waste water, soakaway, pitlatrine as well as agricultural water runoff from farms can all lead to the deterioration and contamination of groundwater in coastal aquifers via infiltration through the overlying formation (Abdel-Satar, 2001; Adams *et al.*, 2008).

The deterioration of water quality in the coastal region due to saltwater pollution of the freshwater aquifers of Eastern Niger Delta, Nigeria has become a major concern to stakeholders in the water sector (Oteri, 2013). Saltwater pollution is the movement of saline water into freshwater aquifers, which leads to contamination of groundwater sources which

in turn leads to waterborne diseases such as typhoid fever, dysentry, cholera, meningitis and diarrhea. Seawater intrusion is a natural process due to the hydraulic connection between groundwater and seawater. Saltwater is denser with low hydraulic head than freshwater because of its higher mineral content and has the capacity to migrate inland below the freshwater (Nwankwoala, 2011; Oteri and Atolagbe, 2003). Human activities such as pumping of groundwater from coastal freshwater wells, construction of canals and drainage networks provide conduits for saltwater to be carried inland (Oteri, 2013). Studies have shown that many of the coastal aquifers in the world already experience salt water intrusion caused by both natural and anthropogenic processes (Kar, Sur, Mandal, Saha and Kole, 2008; Venugopal, Giridharan and Jayaprakasa, 2009). Oteri, (2003) and Nwankwoala, (2011) revealed that boreholes are abandoned along the Nigerian coastlines as a result of saltwater intrusion. Some of the identified causes include indistriminate drilling of boreholes and uncontrolled abstraction of groundwater. It is therefore necessary to understand the pattern of movement and interaction between the fresh water and the salt water as well as the conditions that can influence these processes. Considering the water resources in areas bordering the ocean such as in Nigeria, the Benin Formation is a major source of groundwater (Karbassi, Nouri and Ayaz, 2007; Vinodhini and Narayanan, 2008). The aquifer constitutes a hydrological unit formed by the alluvial and shallow features as they are spread along the fluvial valley of the basin.

The shallow depth and high permeability of the coastal plain-sand aquifer of Niger Delta has made the groundwater system highly vulnerable to contamination (Amadi and Olasehinde, 2009). According to Amadi, (2007), the Benin Formation of Niger Delta is characterized by shallow water table, high porosity and hydraulic conductivity. The strategic position of the Niger Delta in the socio-economic activities of Nigeria makes it imperative to have a good knowledge of the groundwater quality status in the area.

With the discovery of oil in Nigeria, more than fifty years ago, there has been no concerted and effective effort on the part of the government, let alone the oil operators, to evaluate and control environmental and health problems associated with the industry while the host communities are on the receiving end. Niger Delta is an oil-rich region with high amount of gas reserves. It covers about 20,000 km<sup>2</sup> within wetlands of 70,000 km<sup>2</sup> formed primarily by sediment deposition (Akpokodje, 2001). It is home to over 20 million people and 40 different ethnic groups. This floodplain makes up 7.5% of Nigeria's total land mass (Nwankwoala, 2005). It is the largest wetland and maintains the third-largest drainage basin in Africa (Adelana, Olasehinde and Vrbka, 2000; Adegoke, 2002). The region sustains a wide variety of crops, economic trees and a variety of fresh water fish than any ecosystem in West Africa. But this region, if care is not taken can lose most of its natural endowments due to uncontrolled gas flaring, oil spillage and poor sanitary situation in the area (Teme, 2002; World Bank, 2004). The Niger Delta is among the world's largest petroleum provinces and its importance lies on its hydrocarbon resources. It has been rated as the sixth largest oil producer and twelfth giant hydrocarbon province (Adegoke, 2002). The oil sector provides 20% of Nigerian's GDP and 95% of foreign exchange earnings as well as 75% of budgetary revenues (World Bank, 2004).

The practice of gas flaring and incidence of oil spillage are as old as oil production in Nigeria. In Europe 99% of associated gas (AG) is used or re-injected into the ground but in Nigeria, over 75% of gas production is flared, out of which 95% is associated gas (World Bank, 2004). Statistically, about 2.5 billion standard cubic feet (scf) of gas is flared in

Nigeria in a day. This is equal to about 25% of the UK's daily gas consumption and about 40% of Africa's daily gas consumption and this amounts to an annual loss of \$2.5billion to the Nigerian economy apart from the associated health and environmental hazards. According to the World Bank (2004), more gas is flared in Nigeria than anywhere in the world and flaring in the country has contributed more greenhouse gases to the earth's atmosphere than all the other sources in Sub-Saharan Africa combined.

From available literature (Odero, Semu and Kamau ,2000; Ngah, 2002; Njenga, 2004; Ofoma and Ngah, 2006; Adekunle, Adetunji, Gbadebo, and Banjoko, 2007; Nwankwoala and Udom, 2008), some of the chemicals released in a flare include benzene, toluene, xylene, naphthalene, styrene, hydrogen sulphide, carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen dioxide, methane, ethane ethylene and acetylene. Most of these chemicals that are released are carcinogenous and have the potentials to cause other health hazards to humans after prolonged exposure while the gaseous components combine with water molecules in the atmosphere to produce acid-rain.

### **1.2 Statement of the Problem**

The impact of hydrocarbon pollution in terms of gas flaring and oil spillage on the environment and health of host communities in Niger Delta, Nigeria is of great concern. The upsurge in human activities due to the presence of oil companies in the area and the propensity of contaminant infiltrating through the porous and permeable formation into the shallow groundwater table has necessitated the study, which is intended to provide useful information on the degree of aquifer contamination resulting from anthropogenic activities in the area. This is important because the physical, chemical and bacteriological characteristics of groundwater determine its application, management and remediation processes. In view of the economic activities domiciled in the region, it becomes imperative to undertake a comprehensive study of the effects of human activities on the aquifer/groundwater quality in the area.

#### 1.3 Aim and Objectives of the Research

The study seeks to provide baseline information on the hydrofacies of the aquifer system as well as the suitability of the groundwater in the area for domestic purposes.

The specific objectives of this study include:

(i) To carryout geophysical investigation on selected locations in the area in order to obtain lithostratigraphic information on the subsurface geology.

(ii) To determine the hydraulic properties of the aquifer through pumping test and lithological logging of drilled boreholes.

(iii) To carryout laboratory analyses of groundwater, soil, surface water and rainwater samples from the area in order to determine their quality status.

### **1.4 Justification of the Research**

The need to identify, evaluate and categorize the hydrofacies in Eastern Niger Delta is long overdue. For more than 50 years now, petroleum prospection, exploration, exploitation and refining as well as other industrial and agricultural activities have been going on in the area and the impact of these human activities on the environment in general and groundwater in particular has not been determined and this is what this study intended to achieve. No study has provided a platform to evaluate the impact, the various human activities might have on the groundwater system as well as design a pollution control and protection measures that

will prevent pollutant coming in contact with groundwater system. The present study is targeted at addressing these deficiencies.

### **1.5 Study Area Description**

The study area lies within the eastern Niger Delta region of Nigeria between latitude 4°40<sup>I</sup>N and 5°40<sup>I</sup>N and longitude 6°50<sup>I</sup>E and 7°50<sup>I</sup>E (Figure 1.1). It covers parts of Port-Harcourt, Aba and Owerri and a total area of approximately 12,056 km<sup>2</sup>. The area is low lying with a good road network system and is drained by Imo, Aba, Kwa-Ibo and Bonny Rivers and their tributaries. The topography is under the influence of tides which results in flooding especially during the rainy season (Nwankwoaloa and Mmom, 2007). The prevalent climatic condition in the area comprises of the rainy (March to October) and dry (November to February) seasons characterized by high temperatures, low pressure and high relative humidity throughout the year. A short spell of dry season referred to as the 'August break' is often felt in August and is caused by the deflection of the moisture-laden current. Due to vagaries of weather, the 'August break' sometimes occurs in July or September.



Figure 1.1: Map of Niger Delta, Nigeria (Modified from Weber and Daukoru, 1976)

### **1.5.1 Physiography**

The area is characterized by a fairly flat topography underlain by the Benin Formation and slopes towards three major rivers (Imo, Aba, Kwa-Ibo and Bonny). It has a gentle elevation that ranges from 40m – 84m above sea level, and the landform is related to the geology of the region. Several gulley erosion sites exist in the area which can be attributed to the friable nature of the coastal plain sand dominant in the area. The slope ranges from 0 to 3% and is generally towards the rivers from north to south. The area is drained mainly by the four perennial rivers and their tributaries and flows north-south joining the Atlantic Ocean (Figure 1.2). There are swampy grounds close to the river channels due to the flat topography.



Figure 1.2: Drainage map of Niger Delta, Nigeria (After Ibe, Sowa and Osondu 1992)

### **1.5.2 Climate and Vegetation**

The climate of the region is humid and characterized by two seasons; the dry season (November to March) and a rainy season (April to October) although on the average no month of the year is entirely devoid of rainfall. Analysis of the rainfall data of the area shows that the mean monthly rainfall figure of about 172.34 mm with a maximum of about 353.33 mm recorded in September and a minimum of 5.62 mm in December (Etu-Efeotor and Akpokodje, 1990). A high percentage of this rain falls between the months of April and October. The average rainfall is about 2217.29 mm/year, but it averaged 2613.9 mm in 1999 being the maximum to have been recorded over the ten years period (Table 1.1). The mean minimum temperature and mean maximum temperature are 21.3°C and 30.0°C respectively. The dry season temperature could be as low as 17°C, and as high as 34.4°C. On the average the maximum temperature is recorded in November and December and the minimum temperature is recorded in January and February (Tables 1.2 and 1.3). The mean annual evaporation loss is estimated for the area as 969.5mm with the highest monthly evaporation loss of 113.8mm during the dry season and about 89.6mm in the rainy season. The area has an average monthly relative humidity that ranged between 50% and 93% over 24 hours during the day (Edet, 1993; Etu-Efeotor and Odigi, 1983) and between 66.5% and 86.0% (Federal Ministry of Water Resources, Port-Harcourt, 2010; Table 1.4). The average monthly relative humidity by Federal Ministry of Water Resources, Port-Harcourt was adopted in the study because it is recent and from a Federal Government Ministry.

Tropical vegetation is found along streams/river channels and often covers uncultivated farm lands. Due to intense cultivation, grasses are taking over the original tropical forest characteristic of the area. Rodents and reptiles inhabit the grassy areas. There is abundant sunshine all the year round. The temperature is highest in December and lowest in February due to the harmattan. The dry season in the area is from November to March and is characterized by dry, cold and windy weather, with little or no rainfall. This period in the region is referred to as harmattan and is usually accompanied with dust. Palm trees are very abundant in the area, which is favoured by the abundant rainfall and high temperature. Raffia palms are also grown in the area. Other crops are bananas, plantain, maize, cassava, yams and cocoyams including various vegetables. Hydro-meteorological data of the area from 1998 to 2007 was obtained from the Federal Ministry of Water Resources, Port-Harcourt (FMWR, 2010) and are summarized in Tables 1.1 to 1.4.

Year/	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Month										
Jan.	9.07	35.20	0.00	0.00	0.00	15.02	99.01	0.00	0.00	26.00
Feb.	49.04	62.05	20.05	100.00	98.23	2.23	0.08	0.00	15.00	13.02
March	103.18	101.31	72.34	146.05	69.21	98.23	73.67	111.02	185.17	143.07
April	97.02	54.18	106.04	125.29	18.33	122.05	63.79	105.68	133.16	102.06
May	177.41	463.21	131.07	207.37	274.49	174.04	113.51	226.05	351.57	149.44
June	347.63	220.38	275.69	205.49	484.53	256.98	230.64	212.58	321.00	319.21
July	407.98	554.84	218.28	165.46	172.32	296.77	474.01	371.77	285.31	290.02
Aug.	118.33	226.30	260.65	341.75	423.54	386.78	204.81	433.74	211.23	339.87
Sept	444.54	559.85	518.64	513.10	344.53	283.68	355.76	188.33	276.03	448.86
Oct.	131.99	226.30	101.26	74.49	325.05	317.92	293.09	457.66	105.14	211.03
Nov.	70.14	110.34	106.10	47.01	99.25	91.32	153.31	64.33	80.24	124.12
Dec.	0.00	0.00	12.07	5.01	5.01	0.00	0.00	12.02	22.04	0.00
Mean	163.03	217.83	151.86	160.92	192.87	170.42	171.81	181.93	165.49	180.56
Total	1956.3	2613.9	1822.2	1931.0	2314.4	2045.0	2061.6	2183.1	1985.8	2166.7

 Table 1.1: Summary of monthly rainfall in Eastern Niger Delta from 1998 to 2007

(Source: Federal Ministry of Water Resources, Port-Harcourt, 2010)

Year/Month	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
January	18.0	19.0	22.0	17.0	25.0	22.0	22.0	22.0	22.0	19.0
February	22.0	22.0	22.0	22.0	22.0	22.0	21.0	23.0	22.0	21.0
March	22.0	23.0	24.0	21.0	22.0	20.0	22.0	23.0	21.0	21.0
April	21.0	22.0	25.0	22.0	22.0	21.0	21.0	22.0	17.0	21.0
May	22.0	23.0	23.0	21.0	21.0	19.0	19.0	21.0	21.0	22.0
June	21.0	23.0	22.0	22.0	22.0	19.0	19.0	21.0	20.0	21.0
July	18.0	21.0	19.0	21.0	21.0	18.0	21.0	23.0	22.0	22.0
August	24.0	21.0	23.0	22.0	19.0	21.0	23.0	20.0	21.0	18.0
September	24.0	19.0	23.0	23.0	18.0	22.0	22.0	19.0	22.0	20.0
October	21.0	22.0	22.0	24.0	20.0	22.0	22.0	19.0	22.0	21.0
November	21.0	24.0	21.0	24.0	21.0	21.0	23.0	18.0	21.0	22.0
December	18.0	25.0	19.0	23.0	19.0	20.0	22.0	19.0	22.0	22.0
Mean	21.0	22.0	22.1	21.8	21.0	20.6	21.4	20.8	21.1	20.8
Total	273.0	286.0	287.1	283.8	273.0	267.6	278.4	270.8	274.1	270.8

 Table 1.2: Monthly minimum temperature (°C) in Eastern Niger Delta from 1998 to 2007

(Source: Federal Ministry of Water Resources, Port-Harcourt, 2010)

1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
34.3	32.0	23.2	23.2	29.0	30.0	28.5	29.6	27.6	28.4
26.5	32.2	26.0	26.2	28.3	30.2	25.5	30.5	29.5	30.2
30.2	31.0	26.2	34.0	29.2	34.0	28.5	32.0	28.6	30.4
32.1	31.0	28.3	31.0	30.3	31.6	29.4	29.7	28.8	29.3
28.2	30.0	29.4	32.0	29.2	27.6	30.5	25.6	28.4	30.0
30.0	27.0	30.2	30.0	28.3	26.5	29.0	28.4	30.2	32.4
34.4	28.0	27.0	29.1	30.0	24.2	28.2	26.2	28.4	29.7
28.0	29.2	30.0	29.3	28.3	26.0	30.5	27.0	29.3	31.2
29.2	32.2	31.0	30.2	30.2	31.3	26.0	27.0	30.3	33.3
32.3	26.4	32.2	31.3	34.0	30.4	29.2	26.0	33.2	32.,4
32.4	31.0	32.0	33.2	34.0	28.5	28.0	28.4	34.2	34.3
32.0	33.3	34.3	35.0	34.4	31.8	30.6	30.5	35.3	34.7
30.8	30.3	29.2	31.2	30.4	29.3	28.7	28.4	30.3	31.4
	199834.326.530.232.128.230.034.428.029.232.332.432.030.8	1998199934.332.026.532.230.231.032.131.028.230.030.027.034.428.028.029.229.232.232.326.432.431.032.033.330.830.3	19981999200034.332.023.226.532.226.030.231.026.232.131.028.328.230.029.430.027.030.234.428.027.028.029.230.029.232.231.032.326.432.232.431.032.032.033.334.330.830.329.2	199819992000200134.332.023.223.226.532.226.026.230.231.026.234.032.131.028.331.028.230.029.432.030.027.030.230.034.428.027.029.128.029.230.029.329.232.231.030.232.326.432.231.332.431.032.033.230.830.329.231.2	1998199920002001200234.332.023.223.229.026.532.226.026.228.330.231.026.234.029.232.131.028.331.030.328.230.029.432.029.230.027.030.230.028.334.428.027.029.130.028.029.230.029.328.329.232.231.030.230.232.326.432.231.334.032.431.032.033.234.430.830.329.231.230.4	19981999200020012002200334.332.023.223.229.030.026.532.226.026.228.330.230.231.026.234.029.234.032.131.028.331.030.331.628.230.029.432.029.227.630.027.030.230.028.326.534.428.027.029.130.024.228.029.231.030.230.231.332.326.432.231.334.030.432.431.032.033.234.028.532.033.334.335.034.431.830.830.329.231.230.429.3	199819992000200120022003200434.332.023.223.229.030.028.526.532.226.026.228.330.225.530.231.026.234.029.234.028.532.131.028.331.030.331.629.428.230.029.432.029.227.630.530.027.030.230.028.326.529.034.428.027.029.130.024.228.228.029.230.029.328.326.030.529.232.231.030.230.231.326.034.428.027.029.130.024.228.228.029.231.030.230.231.326.032.326.432.231.334.030.429.232.431.032.033.234.028.528.032.033.334.335.034.431.830.630.830.329.231.230.429.328.7	1998199920002001200220032004200534.332.023.223.229.030.028.529.626.532.226.026.228.330.225.530.530.231.026.234.029.234.028.532.032.131.028.331.030.331.629.429.728.230.029.432.029.227.630.525.630.027.030.230.028.326.529.028.434.428.027.029.130.024.228.226.228.029.230.029.328.326.030.527.029.232.231.030.230.024.228.226.228.029.231.030.230.231.326.027.029.232.231.030.230.231.326.027.029.326.432.231.334.030.429.226.032.431.032.033.234.028.528.028.432.033.334.335.034.431.830.630.530.830.329.231.230.429.328.728.4	19981999200020012002200320042005200634.332.023.223.229.030.028.529.627.626.532.226.026.228.330.225.530.529.530.231.026.234.029.234.028.532.028.632.131.028.331.030.331.629.429.728.828.230.029.432.029.227.630.525.628.430.027.030.230.028.326.529.028.430.234.428.027.029.130.024.228.226.228.430.027.030.229.328.326.030.527.029.334.428.027.029.130.024.228.226.228.428.029.231.030.230.231.326.030.527.029.334.428.027.029.328.326.030.527.029.329.232.231.030.230.231.326.030.527.030.332.326.432.231.334.030.429.226.033.232.431.032.033.234.028.528.028.434.232.033.334.335.034.431.830.630.535.3<

Table 1.3: Monthly maximum temperature (°C) in Eastern Niger Delta from 1998 to 2007

(Source: Federal Ministry of Water Resources, Port-Harcourt, 2010)
Year/Month	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
January	80.5	77.0	80.5	80.5	79.0	84.5	78.0	77.0	81.0	78.5
February	80.5	78.5	79.0	trace	78.5	85.5	75.5	75.5	77.0	82.5
March	80.0	79.5	79.0	80.0	81.5	66.5	83.0	80.5	73.0	74.5
April	81.0	80.5	72.0	76.5	79.5	84.5	80.5	83.0	75.5	82.0
May	81.0	81.5	81.5	73.5	81.0	81.0	79.5	78.5	76.0	81.5
June	84.0	83.5	78.0	83.5	79.0	82.5	78.5	82.5	79.0	82.0
July	84.5	80.5	82.5	84.5	81.5	85.0	88.0	80.5	82.0	82.5
August	83.0	82.5	86.0	83.0	80.5	80.0	81.0	84.0	82.0	86.5
September	82.0	80.5	80.5	85.0	81.0	80.0	81.0	83.5	83.0	85.0
October	79.5	80.0	79.0	81.0	84.5	81.0	83.5	83.0	84.0	83.0
November	81.0	78.0	78.5	80.5	82.5	80.5	78.0	85.5	83.0	78.5
December	82.0	77.5	79.0	81.5	86.5	81.5	82.0	82.5	84.0	82.5
Mean	81.9	80.0	80.0	80.7	81.3	81.0	80.7	81.3	80.0	81.6

 Table 1.4: Monthly relative humidity in Eastern Niger Delta from 1998 to 2007

(Source: Federal Ministry of Water Resources, Port-Harcourt, 2010)

### **1.6 Scope of Present Work**

The study involved deskwork during which preliminary assessment of feasibility of the research project and evaluation of existing data on the hydrogeology of the study area were compiled. This was followed by fieldwork which involved collection of data for geological, hydro-geophysical and hydrochemical evaluations. The detail activities of the field study involve:

i) Geological and hydrogeological mapping of the study area in order to have direct and detailed information on the aquifer system in the area. This involved rock unit mapping and logging of exposures, borehole drilling and pumping test.

ii) Geophysical surveys using Vertical Electrical Resistivity Sounding (VES) were conducted in order to delineate the subsurface geo-electrical variations/sections, depth to the aquifer and pollution (plume) mapping. The underlying factors in the choice of survey points in the study area are:

- Spatial distribution
- Proximity to major waste dumpsite/gas flaring station/flow station and
- The observed groundwater flow direction.

iii) Borehole well inventory data such as well depth, depth to water table, well location coordinates and elevations.

(iv) Collection of soil, surface water, groundwater and rainwater samples for chemical and microbial analyses. This stage also included in-situ measurement of physical parameters,

such as pH, electrical conductivity (EC), total dissolved solids (TDS), and temperature of the sampled geomaterials using standard techniques.

However, due to the constraint regarding generation of all the relevant data needed for complete evaluation in this type of study, secondary data were sourced from reliable government agencies, oil companies, chemical industries, hospitals, borehole drilling and water engineering outfits to complement the field data collected. These data were all subjected to careful and objective analyses, followed by data processing and evaluation using manual, iterative, statistical, and analytical techniques; and the use of specialized computer software suitable for the various analyses.

Hydrofacies determinations are useful for evaluating flow patterns, origins and chemical histories of groundwater masses. They describe bodies of groundwater in an aquifer that differ in their physical, chemical and bacteriological composition. The facies are a function of the lithology, prevailing climatic condition, topography, residence time, solution kinetics, flow pattern of the aquifer and anthropogenic interference (Raghunath, Murthy and Raghavan, 2002; Abdullah, Musta, Aris and Annamala, 2004; Lambarkis, Antonakos and Panagopoulos, 2004). Hydrochemical facies can be classified on the basis of the dominant ions in the facies by means of Piper, Durov, Stiff and Schoeller diagrams. These methods combine chemically similar elements together and large data are usually cumbersome to handle. Their demerits were overcome in this study by the application of principal component analysis (PCA), factor analysis (FA), water quality index (WQI) and a newly evolved DRASTICA model. These geostatistical techniques allow for elemental analysis and interpretation of multiple mixing trends thereby providing greater precision in identifying groundwater hydrofacies and interpreting their sources and this is part of what

make this research unique. The study has helped to ascertain the level of aquifer/groundwater pollution in the area and to suggest ways to efficiently utilize and manage groundwater resources while providing the stakeholders with useful information on the aquifer/groundwater vulnerability of the area.

#### **CHAPTER TWO**

## 2.0 LITERATURE REVIEW

## 2.1 Regional Geology

The term Benin formation was first coined in 1907 and the formation outcrops in the Port-Harcourt, Aba and Owerri axix of the Niger Delta province (Figure 2.1). The formation consists predominantly of very thick coastal sands, sandstones, and clay and sandy-clay occurring in lenses (Reyment, 1965). The work of Reyment (1965) shows that the Benin Formation is not associated with lignite seams, while lignite was recognized in the Ogwashi-Asaba Formation. But according to Whiteman, 1982, both disseminated and bedded lignites occur within the Benin Formation. Generally, the Benin Formation can be recognized due to its high sand proportion (70-100%) with a few minor shale intercalations and the absence of brackish water and marine fauna. Till date, very little oil has been found and the formation is mainly water bearing (Whiteman, 1982).

In the eastern part of Niger Delta, the Afam Clay member (Figure 2.2) of the Benin Formation separates the formation into three aquifer systems; confined, semi-confined and unconfined (Uma and Egboka, 1987; Figure 2.2). The sediments of the Benin Formation have variable thickness as you transverses from one location to another. Nwankwor (1995) gave an average thickness of the Benin Formation as 800m. Basic hydraulic parameters such as transmissivity, storativity and hydraulic conductivity are vital tools used to characterize an aquifer (Amadi and Amadi, 1990).

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Figure 2.1: Geological map of Niger Delta, Nigeria (Modified from Weber and Daukoru, 1976)



Figure 2.2: Stratigraphic column of the lithofacies units in Niger Delta, Nigeria (After Doust and Omotsola, 1990)

The bottom of the upper water table aquifer unit is at a depth of about 100m. The middle semi-confined aquifer has an average thickness of 80m while the lower confined aquifer has an estimated thickness of over 600m (Uma and Egboka, 1987). Aquifer parameters indicate high storage and transmissive properties. Well yield in the area ranges from 15.06 l/s to 89.32 l/s (Amadi, 2007) and 14.25 l/s to 95.78 l/s (Amadi and Olasehinde, 2008).

Nwankwor, (1995) used the coefficient of uniformity obtained from grain size distribution curve to estimate porosity and compressibility value in the area, from which storativity was calculated. The disadvantage of the technique was that it was developed on the basis of mere approximation (relating size-sorting to porosity and compressibility of aquifer matrix). Uma and Egboka (1987) highlighted the influence of geologic and hydrological cycles that exacerbate the incidence of pollution from both point and distributed sources. They identified lack of scientific information, on which appropriate groundwater protection measures could be developed as the major constraint to water management in developing countries. Bacteriological quality and faecal contamination of groundwater appears to pose serious problem in the area due to the shallowness of the water table (Ezeigbo, 1989). This scenario is indicative of the potential ease of pollution of the surface water is poor, mainly due to contamination from widespread anthropogenic activities and industrial effluent (Ibe *et al.*, 1992).

Olobaniyi and Owoyemi, (2006) applied factor analysis in the characterization of the chemical facies of groundwater in the deltaic plain-sand aquifers of Warri, western Niger Delta, Nigeria. They identified three factors as the possible sources of contaminant in the deltaic plainsand aquifers of Warri, Western Niger Delta. According to Etu-Efeotor (1981),

two hydrogeochemical regimes exist in the area: the inland and the coastal as well as high iron content in the groundwater. Etu-Efeotor and Odigi (1983), observed that the groundwater problems in the area includes salinity and bacteriological contamination. Amadi and Amadi, (1990) outlined factors controlling saline water migration in coastal aquifers of southern Nigeria and observed that the chemistry of the natural water in Port-Harcourt and Degema areas changes with season. Etu-Efeotor and Akpokodje, (1990) identified one major and two sub-aquifer horizon within the geological and geomorphological units of the Niger Delta. Oteri, (1990) delineated the extent of seawater intrusion in the coastal beach ridge of the Forcados, Niger Delta using geoelectric survey data.

The study area falls within the Niger Delta Basin (Short and Stauble, 1967). The basin is an extensive continental margin basin situated in the Gulf of Guinea built out into the Central South Atlantic Ocean at the mouths of the Niger-Benue and Cross River systems during the Eocene (Hosper, 1971). The basin lies between latitudes 4<sup>0</sup>N and 7<sup>0</sup>N and longitudes 5<sup>0</sup>E and 8<sup>0</sup>E (Figure 2.1). It is an arcuate delta that is wave dominated and tidally influenced sand bodies whose thickness may be influenced by growth faulting (Avbovbo and Ayoola, 1981). The basin is separated from Dahomey Basin by the Okitipupa High in the West and bounded by the Cameroon Volcanics in the east. The northern margin formed the following cretaceous structures: the Anambra Basin, Abakaliki Uplift, Afikpo Syncline and the Calabar Flank (Ofoma and Ngah, 2006). The sedimentary fill of the basin was controlled by three major tectonic phases and epirogenic movements which resulted in major transgressive and regressive phases (Etu-Efeotor and Akpokodje, 1990). As a result of tectonic events, the axis of the main basin has been displaced, giving rise to three

successive basins: The Abakaliki-Benue Trough, the Anambra Basin and the Niger Delta Basin (Nwankwor, 1995).

The first phase (Albian to Lower Satonian) was characterized by movement along major NE-SW trending faults in the formation of the Rift-like Abakaliki-Benue Trough. The second phase (upper Santon'11ian to Lower Campanian) was characterized by compressional movements along the established NE-SW trend and resulted in the folding and uplifting of the Abakaliki-Benue folded belt (Onyeagocha, 1980). Contemporaneously with the Abakaliki uplift, the Anambra platform subsided and the axis was displaced to a position southwest of the Benue Fold Belt and northwest of the Abakaliki uplift. The third phase occurred towards the end of the Eocene (Lower Eocene-Recent).

Large area in the eastern part of the basin down-dip of the Abakaliki plunge and the Calabar flank show repeated period of erosion/non-deposition during the Middle-Upper Eocene, whereas a large deltaic complex was deposited in the down-dip Anambra Basin (Weber and Dankoru, 1976). The geomorphic zones recognized in the basin according to Nwankwoala (2005) are: Flood plains; Mangrove swamps; beach ridges barriers; delta front platform and pro delta slope. Apart from petroleum, the Niger Delta is very unique geologically among the deltas of the world as it typifies the most classic delta in geologic literature (Weber, 1971; Onyeagocha, 1980). The Niger Delta is a prograding depositional complex within the Cenozoic Formation of Southern Nigeria (Hosper, 1971, Okosun and Liebau, 1999).

The formation of the Niger Delta has been related to the separation of African and South American plates and the consequent opening of the South Atlantic Ocean (Weber and

Dankoru, 1976). It has been proposed that a triple junction developed at the position of what is now the outer Niger Delta (Etu-Efeotor, 1981). The failed arm of the triple junction is the Anambra-Benue rift valley within which oceanic crust did not develop (Weber and Dankoru, 1976). The African and South American continents drew apart along the ridgetransform system of the Gulf of Guinea and South Atlantic arms of the junction (Evamy, Haremboure and Karmerling, 1978). The rivers flowing along the Benue-Anambra failed arm disgorged into a regional downwrap of the oceanic crust in the area of the triple junction (Short and Stauble, 1967). The tertiary Niger Delta is one of the major regressive deltaic sequences in the world. The delta is over 12 km thick and occupies an area of 75,000 km<sup>2</sup> in the Gulf of Guinea (Ejedawe, 1981). Development of the Proto-Niger Delta began with the formation of the Benue-Abakaliki trough in the early Cretaceous as a failed arm of a rift triple junction associated with the south Atlantic during the separation of South America and Africa (Burke, Dessavuragie and Whiteman, 1971). From the Aptian to the Santonian, 6000 m of sediment was deposited in the Benue-Abakaliki trough. During the Santonian tectonism, the Benue- Abakaliki trough was folded and uplifted to form the Abakaliki high, whereas to the west, the adjacent Anambra platform subsided to form the Anambra basin. The Anambra and Afikpo basins were the site of deltaic sedimentation through the Paleocene (Bustin, 1988). Uplift of the Benin and Calabar flanks during the Paleocene – early Eocene initiated a major regressive phase represented by the Eocene to Holocene Niger Delta (Weber and Daukoru, 1976).

The general morphology of the Niger Delta is that of a wave and tide dominated delta, though more wave dominated. At present, it appears to be constructive in the center and destructive in the flanks. The sediments in the Niger Delta are mostly sandy as a result of the fact that nearly all the environments in the sub-aerial part are of upper coastal or delta plain origin. The sediment source area in the shield consists mainly of crystalline rocks of the Guinea highlands basement complex together with the cretaceous and tertiary sediments derived from the Cameroun volcanic zone. The quality and abundance of reservoir throughout the tertiary sequence of the delta indicates that there has always been a major sand contribution from the shield area. Long-shore currents carry sediments discharged at the apex of the delta both northwest and eastward along the coast to form sand beaches, beach ridges and offshore bars. The marginal portions of the delta are relatively starved of sand and in some places, suffer encroachment from the sea.

The present morphology of the Niger Delta is highly influenced by the regular strong southwestern prevailing wind and the regular pattern of long-shore current described above. This is because the Niger Delta faces a high energy dynamic environment of the Atlantic Ocean. The strength of these current diverts the sediments brought into the sea by the rivers, distributing them along the coast and preventing the formation of a bird-foot-type delta. This gives the delta its present arcuate marginal shape (Figure 2.1). The progressive out-building of the Niger delta resulted in a progressive outward shift of the coastline. The shoreline progressively migrated during deltaic progradation. This was greatly accelerated in Miocene-Pliocene times with attendant increase in growth faulting and large-scale diapiric movement of the Akata shale. This involved deep mass movement of the undercompacted and over-pressured shale towards the continental slope. Deltaic growth declined in the late Pliocene - Pleistocene during a major drop in sea level, with sediment by passing into deep sea fans. A late Pleistocene transgression flooded the Plio-Pleistocene offlap upper and lower deltaic plains, and as sea-level stabilized, a new regressive offlap sequence

developed. The shoreline was about 16 km seaward of the present shoreline in the late Miocene and about 40 km seaward by the Pleistocene.

The oldest formations (Paleocene-Eocene) in the Niger delta form an arcuate exposure belt along the delta frame. These are the Paleocene Imo Shale (fossiliferous blue-grey shales with thin sandstones, marls and limestones, and locally thick near shore sandstones); The Eocene Ameki Formation (fossiliferous calcareous clays, coastal sandstones); the late Eocene-Early Oligocene lignitic clays and sandstones of the Ogwashi-Asaba Formation and the Miocene Recent Benin Formation (coastal plain sands). These formations are highly diachronous and expanded into the subsurface where they have been assigned different formation names: The Akata, Agbada and Benin Formations are interfingering facies equivalents representing pro-delta, delta-front and delta-top environment respectively (Peters, 1991). Unconformities, large clay fills of ancient submarine canyons and deep-sea fans occur in the eastern and western delta. These were formed mainly during early Oligocene and Tertiary lowstands of sea-level (Burke, 1972; Adeniran, 1997; Okosun and Liebau, 1999).

## 2.2 Geology of the Eastern Niger Delta

The study area (Port-Harcourt, Aba, Owerri and environs) is underlain by Pliocene-Pleistocene Benin Formation (Figure 2.3) belonging to the Benin Formation. The type locality of the formation is in Port-Harcourt, Aba and Owerri where the formation overlies the older Ogwashi-Asaba Formation (Ezeigbo and Aneke, 1993).



Figure 2.3: Geological Map of Eastern Niger Delta, Nigeria (Amadi and Olasehinde, 2008)

The formation outcrops sometimes in both surface (outcrop) and subsurface in mode of occurrence. Reyment (1965) described the formation as extensive reddish earth made up of loose, poorly sorted sands underlying recent Quaternary sedimentary deposits of southern Nigeria. It consists mainly of sands, sandstone and gravel with clays occurring in lenses (Onyeagocha, 1980). The sands and sandstones are fine to coarse grained, partly unconsolidated with varying thickness (Avbovbo, 1978). The formation is recognized in burrowed pits, river channels, and boreholes in the area. The upper horizon contains reddish-brown clayey sand covered by brownish humic soil. The formation has a thick sequence of sediments about 2100 m thick deposited in the continental phase of the Niger Delta (Short and Stauble, 1967; Weber and Daukoru, 1976). Within the study area the thickness of the formation is probably 900m and its maximum thickness near the sea is about 1,820 m. The Benin Formation is composed mostly of high resistant fresh water bearing continental sand and gravel with clay and shale intercalations (Ofoegbu, 1998). The sediments represent upper deltaic plain deposits (Peters, 1991).

However, the formation lacks faunal content and this makes it difficult to date although an Oligocene–recent age is generally accepted (Avbovbo, 1978). The environment of deposition is partly lagoonal and fluvio–lacustrine/deltaic (Rayment, 1965). The formation comes in contact with the Ogwahi–Asaba Formation in the northern part and with Alluvium in the southern part and thickens southwards into the Atlantic Ocean (Figure 2.3). The sandy unit which constitutes about 95% of the rock in the area is composed of over 96% guartz (Onyeagocha, 1980).

### 2.3 Stratigraphy of Tertiary Niger Delta

The first information on the subsurface distribution of stratigraphic units in the basin was given by Short and Stauble (1967) while previous works on the surface outcrops was given by Reyment (1965). The outcropping units are present in the northern parts of the delta and continue in the subsurface equivalents, only getting younger basinward. The chronostratigraphic units of the Niger delta after Short and Stauble, (1967) and Etu-Efeotor (1981) are contained in Tables 2.1 and 2.2 respectively. Both recognized three lithostratigraphic units in ascending order: the Akata, Agbada and Benin Formations. The stratigraphic succession is an overall coarsening-upward sequence more than 12 km thick (Bustin, 1988). The Niger delta lithostratigraphic units are strongly diachronous. The age of the Akata Formation ranges from Paleocene in the proximal parts of the delta to Recent in the distal offshore; the oldest deposits of the Agbada Formation are of Eocene age in the north and are presently being deposited in the nearshore shelf domain, while the Benin Formation first occurs in Oligocene times in the northern delta sector (Reijers, Petters and Nwajide, 1996). Along the northern perimeter of the Niger Delta, where the proximal parts of these lithostratigraphic units are exposed and partly grade into the lithofacies of the Anambra basin, the same formations have been termed Imo Shale (Akata), Ameki (Agbada) and Ogwashi-Asaba (upper Agbada facies).

Ancient and persistent submarine canyons are common in the eastern (Afam channel) and western (Opuama channel) parts of the Niger delta succession. They are locally incised more than 1,000 m deep and contains a polyphased fill of deep marine clays, lowstand fans and shallow estuarine clastics which correspond to various successions of lowstand (deep

marine deposits) to transgressive (wave and tide-dominated deposits) systems tracts formed during Oligocene to Pliocene time.

Subsurface			S		
	Benin				
Recent	Formation	Oligocene	Pleistocene	Benin Formation Ogwashi-Asaba	Miocene
	Agbada		Miocene	Formation	Oligocene
Recent	Formation	Eocene	Eocene	Ameki Formation	Eocene
	Akata		Late Eocene	Imo Shale	Paleocene
Recent	Formation	Eocene	Paleocene	Nsukka Formation	Maastrichian
			Maastrichian	Ajali Formation	Maastrichian
			Campanian	Mamo Formation	Campanian
No sub-surface equivalent			Campanian	Nkporo Shale	Santonian
			Coniacian	Agwu Shale	Turonian
			Turonian	Eze-Aku Shale	Turonian
			Albian	Asu River Group	Albian

Table 2.1: Correlation of Subsurface and Surface Formations of Niger Delta Basin

(After Short & Stauble, 1967)

#### Table 2.2: Stratigraphic Units of the Niger Delta Basin

Outcropping Unit	Subsurface Unit	Present-day Equivalent
Benin Formation	Benin Formation	Continental (fluviatile) deposits mainly sandstones
Ogwashi –Asaba Formation	Agbada Formation	Mixed continental brackish water and marine deposits, sandstones and clays
Ameki Formation Imo Shales	Akata Formation	Marine deposits, mainly clays

(After Etu-Efeotor, 1981)

## 2.3.1 The Akata Formation

It is predominantly of marine sedimentary sequence laid down in front of advancing delta. It is characterized by uniform medium dark gray marine shale with lenses of siltstones and sandstones. The shales become darker towards the base and richer in fossil remains. The upper part contains some plant remains and mica. It is the lateral equivalent of the outcropping/surface Imo Formation. The thickness is over 1300m (Avbovbo, 1978) and the age ranges from Paleocene in the proximal parts of the delta to recent in the distal offshore. The Akata Formation is generally an open marine and pro-delta dark grey shale with lenses of siltstone and sandstone (Figure 2.4). The Akata Formation is under-compacted/overpressured in much of the delta and has not been drilled except in the delta margins (Bustin, 1988). Some sand beds considered to be of continental slope channel fill and turbidite are present (Weber and Daukoru, 1976). Thin sandstone lenses occur near the top particularly near the contact with the overlying Agbada Formation (Table 2.1). An estimated maximum thickness of the Akata Formation is possible only in the northern part of the delta where the formation has been drilled through into the Cretaceous (Avbovbo, 1978).

Weber and Daukoru (1976) proposed a greater depth (600m) for Akata Formation hydrocarbon source and migration routes that include growth faults. Evamy *et al.*, (1978) suggest that based on maturation studies that Akata Formation is the main source rock in the eastern part of the delta. In the western part, where the Akata Formation is more deeply buried, the Agbada provided a significant source. Akata Formation is known to be very rich in microfauna (Adeniran, 1997; Okosun and Liebau, 1999). Planktic formation may account for over 50% of the rich microfauna and the benthic assemblage indicates shallow marine shelf depositional environment (Weber and Daukoru, 1976).

### 2.3.2 The Agbada Formation

The Agbada Formation consists of cyclic coarsening-upward regressive sequences resulting from distributaries migration and abandonment (Figure 2.4). Short and Stauble, (1967) attributed the cyclicity of the sequences to differential subsidence, variation in sediment supply and shifts of the depositional axes of the delta resulting in local transgressions and regressions. The coarsening upward sequences are composed of shales, siltstones, and sandstones which include delta front and lower delta plain deposits (Weber, 1971). In other words Agbada Formation is a paralitic sequence consisting of inter-bedded sands and shales. The thickness of the Agbada sequences is highly variable (from 300 m up to about 4500 m). Transgressive deposits, although locally present, are thin and not every where distinguishable. Avbovbo (1978) said that the Agbada Formation ranges in age from Eocene to Holocene and is up to 4,000 m thick in the central part of the delta, thinning seaward and toward the delta margins (northern and northeastern flanks). Surface outcrops of equivalent strata along the delta margin are assigned to the Ogwashi-Asaba and Ameki Formations (Short and Stauble, 1967). Most exploration wells in the Niger Delta penetrated the bottom of this lithofacies (Awosika, 2006). The sandstones are medium to fine-grained and are fairly clean. Accessory glauconite and shell materials are found embedded within the sandstone and they contain kaolinite and small amounts of mixed layers of illite and smectite (Avbovbo, 1978).

Generally, the upper part of the formation has higher sandstones percentage than the lower part. This is as a result of irregular seaward advance of the basin through geologic time despite the occurrence of regional transgressive sequences (Achi, 2003). The formation is rich in microfauna at the base decreasing upward and thus indicating an increasing rate of deposition in the delta front (Peters, 1991). A fluviatile origin is indicated by the coarseness of the grains and the poor sorting (Avbovbo, 1978). Agbada Formation (Table 2.1) forms the hydrocarbon prospective sequence in the Niger Delta with sands as reservoirs and the shales contributing as source rocks and seals (Short and Stauble, 1967). Weber (1971) supported the idea that Agbada Formation is the main hydrocarbon source rock, he stated that the high wax content of the oil reflects terrestrial organic sources and thus an Agbada source. Isotopic studies by Uma (1993) further confirmed a terrestrial organic source rock of Niger delta oils. The sands range from 75% in the upper parts to 50% in the lower parts and thickness of the formation is 300m (Adeniran, 1997).

## 2.3.3 The Benin Formation

The Benin Formation is the uppermost unit in Niger Delta (Figure 2.4). The Benin Formation comprises a succession of Eocene to Holocene massive poorly indurated sandstones, thin shales, coals, and gravels of continental to upper delta plain origin (Table

2.1). Other accessory minerals include yellowish brown limonite coatings and lignite. The sands and sandstones which are dominantly of quartz and potassium feldspars are coarsegrained, angular to sub-angular and poorly sorted (Onyeagocha, 1980). The sands and sandstones are thought to represent point-bar deposits, channel fills or natural levees where as the shale may be back-swamps deposits and ox-bow fills (Weber and Daukoru, 1976).

The Benin Formation is up to 2,000 m thick in the central onshore part of the delta and thins towards the delta margins (Bustin, 1988; Ozumba and Amajor, 1999) and occurs across the whole Niger Delta from Benin to Onitsha area in the north to beyond the present coastline. Short and Stauble (1967) defined the contact between the Agbada and Benin Formations as the highest shale bearing a marine fauna (foraminifera) in the Agbada Formation. However, the contact is more practically defined at the base of the massive sandstones typical of the Benin Formation and generally corresponds to the base of freshwater-bearing strata (Bustin, 1988). Benin Formation lacks marine or brackish water microfauna (Short and Stauble, 1967, Ozumba, 1995).



Figure 2.4: Stratigraphic and structural cross-section of the Niger Delta, Nigeria (Source: Bustin, 1988)

## 2.4 Subsurface Structures

Sedimentary structures occur in the upper and lower surfaces of beds as well as within beds and develop through physical, chemical and biogenic processes before, during and after deposition. They aid in depicting the process and condition of deposition of sediments and paleocurrent direction (Offodile, 2002). Growth faults, rollover anticlines and mud diapirism are among the commonest subsurface structures in the Niger Delta (Figure 2.5). Progradation of the delta has been accompanied and helped by formation of growth faults, associated rollover anticlines and mud diapirism (Ejedawe, 1981).

Growth faults are synsedimentary gravitational faults generated by rapid sedimentation load and the gravitational instability of the Agbada sediment pile accumulating on the mobile, under-compacted Akata shales. Merki (1972) defined growth faults as faults that offset an active surface of deposition. Growth faults (Figure 2.6) are said to be triggered by the movements of deep seated, over-pressured ductile marine Akata shale due to gravitational slumping aided by slope instability (Weber, 1971; Weber and Daukoru, 1976). Greater amounts of sediments accumulate close to the fault in the down thrown block compared with the upthrown block (Merki, 1972).

Merki (1972) established that the growth index varies between the minimum value of 1 and a maximum of 2.5. Niger Delta growth faults are frequently crescent-shaped with the concave side facing the downthrown block (Weber, 1971; Merki, 1972). They are also found to be steeply dipping about  $60^{\circ}$  at the surface but flattened out with depth.



Figure 2.5: Structural and Stratigraphic formations in Niger Delta, Nigeria (Source: Merki, 1972)



Figure 2.6: Growth fault in Niger Delta, Nigeria (Source: Hospers, 1971)

The Akata and Agbada facies are mostly affected by the fault while they die out upward either in or below the base of the Benin sand facies which implies that there is little or no growth faulting extending into the Benin Formation. Growth faults comprise antithetic faults and the major structure building faults (some of which bound the depobelts), steep parallel crestal faults which cut the rollover structures. Associated with the structure building faults are the rollover anticlinal structures.

The rollover anticlines result from the rotation of the downthrown block about an axis roughly paralleling the growth fault. When the block is sufficiently rotated, an elongated anticline rollover structure develops in front of the curved plane (Weber, 1971; Merki, 1972). The rotation of the downthrown layer is caused by the downward movement along the concave fault plane coupled with sedimentation. Evamy *et al.*, (1978) described the formation, distribution and importance of growth faulting on delta development. The growth faults are (Figure 2.5) of great importance as the act as migratory paths for the hydrocarbon generated in the Akata shales into the upper Agbada reservoirs sands. The rollover anticlines on the other hand form where hydrocarbon accumulated in the Agbada reservoir sands (Figure 2.6). Growth fault related rollover structures are the dominant hydrocarbon traps in the Niger delta (Reijers, Petters and Nwajide, 1996).

Toe thrusting at the delta front lateral flow and extrusion of the Akata pro-delta shales during growth faulting (Figure 2.7) and related extension also account for the diapiric structures on the continental slope of the Niger delta in front of the progading depocentre with paralic sediments (Reijers *et al.*, 1996). The diapiric structures are shale bulges found in the offshores on the continental slopes.



Figure 2.7: Roll-over anticline in the Niger Delta, Nigeria (Source: Reijers *et al.*, 1996)

They resulted from the differential loading of deltaic sediments (sand and silt) over the ductile shale of Akata Formation. In response to this loading, the highly watered, undercompacted mobile clays of the Akata Formation then bulges out forming diapirs and domelike structures, Merki (1970) and Hospers (1971). This is followed by the warping, thinning and wedging out of the overlying paralic sequence.

The complexity of these structures is dependent on the overall sediment burden in the initial phase of growth faulting, displacement only occurs along the major bounding faults. With increased overburden and increased horizontal displacement, accommodation becomes more complex and finally occurs along numerous small faults which form the typical collapsed crest structures. Series of fault blocks can be grouped to define macrostructure. Macrostructures can be grouped into sets to form mega-structures. The mega-structures are defined by major rollovers or counter regional faults. Along the axis of the delta, the mega-structures are 30-60km wide and well defined whereas along the margins they narrow and coalesce (Evamy *et al.*, 1978).

#### 2.5 Hydrogeology

### 2.5.1 Surface Water Hydrology

The study area has wide flood plains which incise and run straight on their course and form major tributaries to the Aba, Imo, kwa-Ibo and Bonny Rivers (Figure 1.2). The rivers flow is in the northwest-southeast direction (Uma, 1993). They have large area of recharge by the abundant rainfall in the region, a large percentage of the area being open grasslands. These Rivers are prone to pollutions along their course due to anthropogenic activities and so the inhabitants do not rely on them for potable water supply. The continuous rural-urban

drift of people to Port-Harcourt, Aba and Owerri is further aggravating the pollution of these Rivers as they form the effluent discharge point for untreated industrial waste as majority of them are sited along the banks of these rivers. Also Port-Harcourt, Aba and Owerri and its environs have no functional municipal water supply and so the populace depends on private boreholes for their domestic water supply.

### 2.5.2 Groundwater Hydrology

The study area is marked by flat terrain, and the land structure is related to the rock type underlying it. It is underlain by the Tertiary Benin Formation which is loose, coarse grained, friable, poorly sorted with sub-angular to well rounded sediments. It is over 90% sandstone with minor clay and shale intercalations (Uma, 1984). The Benin Formation extends across the whole of Eastern Niger Delta including Port-Harcourt, Aba and Owerri (Figure 2.8). The thickness is variable but it generally exceeds 1800m (Aseez, 1976). Offodile, (2002) reports gravelly beds up to 10m thick in the Aba and Owerri portion of the Benin Formation.

The formation is permeable and so allows infiltration of rain water. The Benin Formation is the water-bearing aquifer, and it is unconfined. The clayey portions of the formation are discontinuous and so are not enough to make it a confined aquifer. The Benin Formation is overlain by iron-stained laterite, often reddish in colour. The Benin Formation aquifer is prolific and contains abundant water with no confining uppermost layer, hence the aquifer in the study area is phreatic.



Figure 2.8: Hydrogeological Map of Niger Delta, Nigeria

(Modified from Ibe et al., 1992)

The soil which includes weathered sediments has a significant impact on the amount of recharge that infiltrates to the aquifer. The presence of fine textured materials such as silts and clays decrease relative soil permeability and hence the amount of recharge to the aquifer. The sediments of the Benin Formation are more permeable than those of the deltaic areas (Offodile, 2002). Due to high rainfall, run-off is also high as the underlying formations are saturated and in most cases it results to erosion and flooding. This explains the dominance of gully erosion sites in most part of the study area. The Benin formation in the area is prolific in groundwater. Though Port-Harcourt, Aba and Owerri are significantly built up areas, there are still so much open spaces all over the area allowing unhindered infiltration of rain water into the aquifer. Also the neighbourhoods have wide expanse of farmlands through which rain water readily infiltrates to the water table. The abundant rains in the area ensure that much water is always recharged in the aquifer.

#### 2.5.3 Water Supply in parts of Eastern Niger delta

These urban areas in Port-Harcourt, Aba and Owerri get their daily water supply mainly from groundwater sources due to the inadequate supply from public pipe borne water. Many industries like oil servicing companies in Port-Harcourt; manufacturing, breweries and pharmaceutical industries in Aba and agro-allied industries in Owerri source their water supplies from private boreholes. The groundwater is contained in the Benin Formation which geologically underlies these areas. Rain-water harvesting complements the groundwater supply during the rainy season. Problems associated with unsupervised and unregulated siting of boreholes as well as uncontrolled abstraction (pumping) of boreholes by private and corporate entities is common in the area (Nwigwe, 1998).

#### **CHAPTER THREE**

# 3.0 MATERIALS AND METHODS

## **3.1 Geological Mapping of the Area**

The field work commenced in February, 2009 to July, 2009 with geological mapping on a scale of 1:50km covering an area of about 12,056 km<sup>2</sup>, aimed at providing knowledge of the geology of rock units underlying the study area and updating of the already existing geological map. The mapping involved rock unit description as observed on exposures along road cuts, burrowed pits, gully erosion sites, river terraces and borehole cuttings. Traverses were made and exposed soil profiles in burrow pits and gully erosion sites were studied to ascertain the nature of the subsurface geology and stratification. The mapping exercise revealed that the Benin Formation which outcropped in the study area is faintly cross-bedded, poorly sorted, friable, sub-angular to rounded in nature.

## **3.2 Pre-drilling Geophysical Survey**

The purpose of electrical surveys was to determine the subsurface resistivity distribution by making measurements on the ground surface. The ground resistivity was related to various geological parameters such as salt/fresh water interface, plume migration, porosity and degree of fluid saturation in the rock (Olasehinde, 1999). Electrical resistivity survey has been used for many decades in hydrogeological, geotechnical and environmental investigations (Nwankwo and Etche, 1990). The survey provided information about the nature of the sub-surface geology in terms of lateral and vertical variation as well as the possible extent of leachate migration. A synergy between the geoelectric section and the borehole logs enabled the delineation of saltwater/freshwater interface and the iron-rich zone. The geophysical survey was also aimed at acquiring information on the hydrogeology

in order to predict the thickness of the aquifer and pollution plume if any around selected flow stations, crude oil pipelines, gas-flaring stations and dumpsites (Appendix A). A total of 18 Vertical Electrical Sounding (VES) (Figure 3.1) was carried out and it coincides with the 18 drilled boreholes. An *ABEM SAS 1000 Terrameter* was used for the electrical resistivity survey. Recommendations were based on careful study and interpretation of the field data using *Resist and IpI2win Computer softwares* as well as curve matching method of interpretation of the apparent resistivity values.

### **3.2.1 Vertical Electrical Sounding (VES)**

Schlumberger electrode configuration (Figure 3.1) was used, a total spread of 165 m was covered with maximum current electrode separation (AB/2) of 82.5 m. The instrument, in this array measures vertical changes in ground resistivity with depth. After field corrections, the actual depth of penetration was 115.5 m. The array consists of 2 current and 2 potential electrodes.  $C_1$  and  $C_2$  are the current electrodes and  $P_1$  and  $P_2$  are the potential electrodes. The spacing (MN) between the potential electrodes is much smaller than the spacing (2L) between the current electrodes. It works under the principles of the wider the current electrodes, the deeper the current penetration (Olasehinde and Taiwo, 2000).



Figure 3.1: Schlumberger Array

### **3.3 Borehole Logging and Pumping Test**

The Niger Delta Development Commission (NDDC) awarded contract to Dammes Associates LTD for the drilling of 6 boreholes in each of the 6-oil producing states tagged: Micro-Project Programme (MPP-6). The states include; Abia, Rivers, Imo, Akwa-Ibom, Cross-River and Edo. The drilling of the boreholes was supervised by the researcher, who was the Consultant Hydrogeologist for the project. Borehole litho-sample cuttings were collected at the sedimentation pit, and washed thoroughly with clean water and air-dried before transferring it into the sample box. The sampling was done at 3m penetration intervals, except where there is a sudden change in lithology. Sampled formations were useful in establishing the lithological successions transversed in a given site. These are important tools used to assess the hydrological properties of an aquifer. A detailed and sequential description of samples contained in the sample box gives rise to the strata-log. It is used for the design of the borehole screening to enhance productivity. Sampling was meticulously carried out for each of the 18 drilled boreholes that falls within the study area and the strata-log for each of the locations was prepared.

Seven hours constant rate pumping and recovery tests were carried out on the selected boreholes. Prior to the pumping test, the initial static water level (SWL) was measured using an electric dipper at each location at the commencement of the pumping. Subsequent drawdown of water level were measured at interval of 1 minute and later increased to 2 and 5 minutes respectively until the dynamic water level (DWL) of the borehole has been attained. At this point in the pumping test procedure, increment of the measuring time by 30 minutes or 1 hour interval does not affect the (DWL) and at this point, the pumping was stopped. As soon as pumping is terminated, recording of water level recovery started. The

interval of measurements for recovery was similar to that of constant rate test. A period was reached when the residual drawdown is very negligible and at this juncture, equilibrium was reached which implied that the borehole has fully recovered. The data obtained were recalculated and values were used to plot the drawdown/recovery graph.

#### 3.4 Sieve Analysis of Soil and Borehole Samples

In order to determine the textural characteristics of the uppermost layer of the underlying lithology, which invariably influences infiltration rate of rain water and contaminants into the groundwater table, borehole cuttings and soil samples were collected and analyzed. The collected soil samples were subjected to both sieve analysis and falling head permeameter test. About 500g of each of the soil samples between 2 and 3 m depth of each location was weighed on a balanced and poured into an aluminium bowl. It was washed with distilled water to remove cementing materials. After washing, the sample was transferred into an oven and oven dried under temperature range of  $105 - 110^{\circ}$ C for about 24 hours. It was thereafter removed from the oven and allowed to cool for about 30 minutes, and then poured in the upper test sieve, which was then shaked for a minimum of 20 minutes. Finally, each sieve in which soil was retained was weighed and recorded (Plate I).



Plate I: Sieve Analysis of Soil and Borehole samples in the laboratory (Amadi, 2010)

# 3.5 Soil and Water Sampling

Community leaders and inhabitants of host communities where flow stations are domiciled were interviewed and vital information on the impact of oil and gas activities on their health, aquatic and terrestrial environment were obtained based on prepared questionaires. The result was complemented with reconnassance survey, leading to selection of specific pollution zones (flow stations, gas flaring points and dumpsites). Extensive fieldwork was embarked upon in order to generate data for the determination of hydrofacies of the coastal plain-sand aquifer of the area. The fieldwork comprises of geological, hydrogeological and geophysical as well as sampling of geomaterials (soil, groundwater, surface water and rainwater). The co-ordinates (longitude, latitude and elevation) of each sampling point and the static water level of each drilled borehole were taken with the aid of Global Positioning
System (GPS) and the data was used to construct the contour map and the groundwater flow direction of the area. The groundwater flow direction obtained coincides with the regional groundwater flow direction (NE-SW) for entire Niger Delta region, though slight local variation exist (Uma, 1984).

Boreholes drilled at the selected points where geophysical survey was carried out were sampled and logged. A total of 40 groundwater samples, 26 surface water samples, 22 rainwater samples (comprising of 12 direct rainwater and 10 roof-top collected rainwater) and 20 soil samples (Figures 3.2) were collected seasonally (twice per year) from the vicinity of the flow stations, gas flaring point, industries and dumpsites (Figure 3.3) and monitored for a period of four years, from March, 2008 to April, 2012. Control samples were collected far away from the flow stations, gas flaring point and dumpsites and also sent to the laboratory for relevant analyses.

Physical parameters such as pH, temperature, conductivity and turbidity of the sampled geomaterials were determined insitu in the field using standard pH meter, thermometer, conductivity meter and turbidiometer respectively. Their determination followed standard sampling procedures prescribed by American Public Health Association (APHA, 1995); Nigerian Standard for Drinking Water Quality (NSDWQ, 2007); United States Environmental Protection Agency (USEPA, 1998) and Federal Environmental Protection Agency (FEPA, 1999). The laboratory analyses include sieve analysis of soil samples, chemical and bacteriological analyses of soil and water samples.



Figure 3.2: Sampled locations in Eastern Niger Delta, Nigeria (Amadi, 2010)



Figure 3.3: Locations of sampled flow stations, industries, dumpsites and gas flare stations in Eastern Niger Delta, Nigeria (Amadi, 2010)

## 3.6 Laboratory Studies

For temporal monitoring of the physico-chemical and bacteriological characteristics of the soil and water samples collected, sampling was conducted in the months of February and September, which correspond to the peaks of dry and rainy seasons respectively, for a period of four consecutive years (2008-2012). After each sampling, the samples were transported to the respective laboratories in Port-Harcourt for relevant analysis. Sample preparation and preservation followed American Public Health Association (APHA, 1992) guidelines, which included cooling the samples to 4°C and in some cases preservation with acid. All the physico-chemical and microbial analyses were carried out according to the procedures outlined by Analysis of the Association of Analytical Chemist (AOAC, 1990).

## **3.6.1 Preparation of Soil Samples**

The soil samples were air-dried under shade and ground to pass through a 0.5 mm sieve for metal determinations and analyzed using the "total digestion" method. 0.5 g soil was weighed into a 100 cm<sup>3</sup> beaker. 5 cm<sup>3</sup> of concentrated HNO<sub>3</sub> was added and this was boiled gently for 30 min on a hot plate. The beaker was cooled and 2 cm<sup>3</sup> HClO<sub>4</sub> and 5 cm<sup>3</sup> concentrated HNO<sub>3</sub> were added. The mixture was heated to near dryness. The corners and walls of the beakers were washed with distilled water, and the solution was again heated until dense white fumes developed. The beaker was cooled and 10 cm<sup>3</sup> HNO<sub>3</sub> was added to dissolve the salts. The solution was transferred into a 50 cm<sup>3</sup> standard flask and then diluted with distilled water. The solution was analyzed by means of Atomic Absorption Spectrophotometer (AAS). Triplicate samples were extracted and analyzed with the Spectrophotometer.

## **3.6.2 Analytical Procedures**

# 3.6.2.1 pH

## A. Principles

pH, which is an accepted measure of acidity or alkalinity is determined by change in potential of glass – saturated calomel electrodes, as measured by the apparatus standardized against standard buffer solutions whose pH values are assigned by National Institute of Standard and Technology (NIST).

# **B.** Apparatus and Reagent

- i. pH meter
- ii. Standard buffer solutions

# C. Determination

Thoroughly wet electrodes and prepared in accordance with manufacturer's instructions was standardized with standard buffer solution whose pH value is near that of sample and then with 2 others to check linearity of electrode response. The samples were analyzed as soon as possible (within few hours) after collection. The sample bottles were not open before analysis. The immersed electrodes were washed 6 - 8 times with portions of sample, particularly when unbuffered solution follows buffered solution. Equilibrium as shown by absence of drift was established before readings were accepted (APHA, 1995).

## 3.6.2.2 Temperature

The temperature was always determined at the source of the sample-using thermometer in <sup>0</sup>C after having taken the sample into the sampling bottles.

# **3.6.2.3** Total Dissolved Solids

# A. Principles

A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 108 <sup>o</sup>C. The increase in dish weight represents the total dissolved solids.

# **B.** Apparatus

- i. Glass fiber filter disk (Whatman grade 934 AH)
- ii. Filtration apparatus
- iii. Suction Flask
- iv. Dry oven, for operation at  $108 \ ^{\circ}C$
- v. Pipettes

# C. Procedure

i. Preparation of glass-fiber filter disk

Disk with wrinkled side up was inserted into filtration apparatus. Vacuum was applied and disk was washed with three successive 20 cm<sup>3</sup> volumes of deionised water. The suction was continued to remove all traces of water. The washing was discarded.

ii. Preparation of evaporation dish

The clean dish was heated to 108 <sup>0</sup>C for 1 hour in an oven and stored in desicator until needed. It was immediately weighed before use.

## iii. Sample analysis

The sample was stirred with magnetic stirrer and a measured volume was pipeted into a glass fiber filter with applied vacuum. It was washed with three successive 10 cm<sup>3</sup> volumes of reagent grade water, allowing complete drainage between washings, and continued suction for about 3 minutes after filtration was completed. 50 cm<sup>3</sup> of the filtrate was transferred to a weighed evaporating dish and evaporated to dryness on a steam bath. It was then dried for at least 1 hour in an oven at 108 <sup>o</sup>C and cooled in a desiccator to balance temperature, and weighed. The cycle of drying, cooling, desiccating and weighing was repeated until a constant weight was obtained or until weight change was less than 4 % of previous weight. Duplicate determinations agree within 5 % of their mean.

# **D.** Calculation

mg, total dissolved solids/dm<sup>3</sup> =(A –B) x 1000/sample volume,  $cm^3$ 

Where:

A =Weight of dried residue + dish, mg and

B = Weight of dish, mg

## 3.6.2.4 Total Suspended Solid (TSS)

Total suspended solid was determined by differences of the total solids and total dissolved solids. Mathematically: TS = TDS + TSS, this implies that: TSS = TS - TDS.

## 3.6.2.5 Conductivity

The portable conductivity meter type MC. 3 EIL was used in determining the electrical conductivity. The cell was rinsed with the sample and the sample poured into the cell unit

until it was up to the top at the edge of the bore. The selector switch was set to the appropriate range X1, X10, X100 or X1000 the "ON" key depressed and the conductivity was recorded.

## 3.6.2.6 Chloride

## A. Principles

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed (AOAC, 1990).

# **B.** Apparatus

- i. Erlenmeyer flask, 250 cm<sup>3</sup>
- ii Burette, 50 cm<sup>3</sup>

# C. Reagents

- i. Potassium chromate indicator solution: 50 g of  $K_2CrO_4$  was dissolved in a little distilled water and AgNO<sub>3</sub> solution was added until a definite red precipitate was formed. It was allowed to stand for 12 hr, filtered and diluted to 1 litre with distilled water.
- ii. Standard silver nitrate titrant, 0.0141M: 2.395 g AgNO<sub>3</sub> was dissolved in distilled water and diluted to 1000 cm<sup>3</sup>. This was standardized against NaCl and stored in a brown bottle;  $1.00 \text{ cm}^3 = 500 \ \mu \text{g Cl}^-$
- iii. Standard sodium chloride, 0.0141 M: 824.0 mg NaCl (dried at 140°C) was dissolved in distilled water and diluted to 1 litre;  $1.00 \text{ cm}^3 = 500 \text{ }\mu\text{g} \text{ Cl}^-$
- iv Special Reagents for removal of interference:

- a. Aluminum hydroxide suspension: 125 g of Aluminum potassium sulphate (AlK(SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O) or aluminum ammonium sulphate (AlNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O) was dissolved in 1 litre distilled water
- b. Phenolphthalein indicator solution.
- c. Sodium hydroxide, 1M.
- d. Sulphuric acid, 1M
- e. Hydrogen peroxide, 30 %

## D. Procedure

100 cm<sup>3</sup> sample was transferred into a conical flask. If the sample was highly coloured, 3 cm<sup>3</sup> of Al(OH)<sub>3</sub> suspension was added, mixed, allowed to settle, and filtered. If sulphide, sulphite, thiosulphite were present, 1 cm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> was added and stirred for 1 minute.

The samples were directly titrated in the pH range of 7 to 10. The sample pH was adjusted to between 7 and 10 with  $H_2SO_4$  or NaOH when it was not in this range. 1 cm<sup>3</sup> of K<sub>2</sub>CrO<sub>4</sub> indicator solution was added and titrated with standard AgNO<sub>3</sub> titrant to a pinkish yellow end point. End-point recognition was consistent. AgNO<sub>3</sub> titrant was standardized and reagent blank value was established by titration method outlined above. A blank of 0.2 to 0.3 cm<sup>3</sup> was usual

# E. Calculation

mg Cl<sup>-</sup>/dm<sup>3</sup> = (A-B) x M x 35 450/ cm<sup>3</sup> sample

Where  $A = cm^3$  titration for sample.

 $B = cm^3$  titration for blank  $M = Molarity of AgNO_3$  $mg NaCl = (mg Cl^-/ dm^3) \times 1.65$ 

### 3.6.2.7 Sulphide

**A. Principle**: Sulfide is determined by absorption in iodine-potassium iodide solution and subsequent titration with sodium thiosulfate.

## **B.** Reagents

i. Hydrochloric acid, HCl, 6M: Prepared by dissolving 120.2 cm<sup>3</sup> of concentrated HCl (36% purity and specific gravity of 1.18) with distilled water and the solution was made up to 1dm<sup>3</sup> (Iodometric Method, AOAC, 1990).

ii. Standard iodine solution, 0.025 M: 25 g of KI was dissolved in a little water and 3.3 g of iodine was added. After iodine had dissolved, it was diluted to  $1000 \text{ cm}^3$  and standardized against 0.025 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, using starch solution as indicator.

iii. Standard sodium thiosulphate solution, 0.025 M: 6.205 g of

 $Na_2S_2O_3.5H_2O$  was dissolved in distilled water. 1.5 cm<sup>3</sup> of 6 M NaOH or 0.4 g solid NaOH was added and the solution diluted to 1000 cm<sup>3</sup>. The solution was standardized with biiodate solution.

iv. Starch solution: 2 g laboratory – grade soluble starch was dissolved with 0.2 g salicylic acid, as a preservative in  $100 \text{ cm}^3$  hot distilled water.

# C. Procedure

i. An amount of iodine solution estimated to be an excess over the amount of sulphide present was measured and distilled water was added to bring the volume to about 20 cm<sup>3</sup>. 2 cm<sup>3</sup> of 6 M HCl was added. 200 cm<sup>3</sup> of the sample was pipeted into flask by discharging sample under solution surface. If iodine colour disappears, more iodine was added so that colour remained. It was back titrated with  $Na_2S_2O_3$  solution adding a few drops of starch solution as end point was approached, and continued until blue colour disappeared.

ii. If sulphide was precipitated with zinc and ZnS filtered out, the filter paper was returned with precipitate to original bottle and about  $100 \text{ cm}^3$  of water added. Iodine solution and HCl were then added and titrated as in (i) above.

# **D.** Calculation

One milliliter of 0.025 M iodine solution reacts with 0.4 mg S<sup>2-</sup>:

mg  $S^{2-}/dm^{3} = (A \times B) - (C \times D) \times 16000/cm^{3}$  sample

Where:  $A = cm^3$  of iodine solution

B =Molarity of iodine solution  $C = cm^3$  of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution D = Molarity of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution

# 3.6.2.8 Nitrate

# A. Principles

Sample is digested with  $H_2SO_4$  to convert organic N to  $NH_3$ , which is distilled after alkalinization and determined by nesslerization or titrimetry.

Method is applicable to surface and saline waters as well as domestic and industrial waste. Some industrial waste containing materials such as amines, nitro compounds, hydrazones, oximes, semicarbazones, and some refractory tertiary amines may not be converted to NH<sub>3</sub> (Kjeldahl Method, AOAC, 1990).

# **B.** Apparatus

- i. Digestion apparatus
- Distillation apparatus or all-glass apparatus with 800 or 1000 cm<sup>3</sup> digestion flask and 500 cm<sup>3</sup> Erlenmeyer, marked at 350 and 500 cm<sup>3</sup>, as receivers.

- iii. Nessler tubes.
- iv. Spectrophotometer or filter photometer for use at 425 nm

# C. Reagents

- i. Distilled water- NH<sub>3</sub> free
- ii. Mercuric sulphate solution: 8 g of red HgO was dissolved in 50 cm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> (1+5) and diluted to 100 cm<sup>3</sup> with water.
- iii. Digestion solution: 267g K<sub>2</sub>SO<sub>4</sub> was dissolved in 1300 cm<sup>3</sup> H<sub>2</sub>O and 400 cm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>, and 50 cm<sup>3</sup> HgSO<sub>4</sub> solution added. Solution was then made up to 2 litres.
- iv. Sodium hydroxide-sodium thiosulphate solution: 500 g NaOH and 25 g  $Na_2S_2O_3$ 5H<sub>2</sub>O was dissolved in H<sub>2</sub>O and diluted to 1 litre.
- v. Phenolphthalein indicator solution: 5g of phenolphthalein was dissolved in 500 cm<sup>3</sup> alcohol or isopropanol and 500 cm<sup>3</sup> of  $H_2O$  was added. 0.02M NaOH was added until colour turned faint pink.
- vi. Sulphuric acid standard solution, 0.02M: 1.07 cm<sup>3</sup> of sulphuric acid was dissolved in distilled water and diluted to 1000 cm<sup>3</sup>.
- vii. Ammonia standard solution- (1) stock solution, 1.00 mg/ dm<sup>3</sup>: 3.819g of NH<sub>4</sub>Cl was dissolved in distilled water and diluted to 1 litre. (2) Working solution, 0.01 mg/ dm<sup>3</sup>: 10 cm<sup>3</sup> of stock solution was diluted to 1 litre
- viii. Boric acid indicator: 20 g of H<sub>3</sub>BO<sub>3</sub> was dissolved in distilled water and diluted to 1
  litre

- ix Mixed indicator: 2 volumes of 0.2 % alcoholic methyl red was mixed with 1 volume of 0.2 % alcoholic methylene blue prepared freshly every 30 days.
- X. Nessler reagent: 100 g HgI<sub>2</sub> and 70 g KI were dissolved in small amount of water.
  Cooled solution of 160g NaOH in 500 cm<sup>3</sup> of water was added slowly, with stirring and diluted to 1 litre. (The reagent is stable for 1 year if stored in Pyrex container out of direct sunlight). Reagent gave characteristic colour, and no precipitate with 0.04 mg NH<sub>4</sub>-N in 50 cm<sup>3</sup> of H<sub>2</sub>O within 10 min.

# D. Digestion and distillation

The sample was placed into 800 cm<sup>3</sup> Kjeldhal flask and 100 cm<sup>3</sup> digestion solution was added. It was boiled until SO<sub>3</sub> fumes were evolved and solution became colorless or pale yellow. The solution was cooled and diluted with 300 cm<sup>3</sup> with H<sub>2</sub>O. NaOH-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was added slowly down neck of tilted flask to underlay acid solution in amount sufficient to make final solution strongly alkaline as shown by phenolphthalein indicator. The flask was connected to condenser, with tip of condenser dipping into 50 cm<sup>3</sup> 2% H<sub>3</sub>BO<sub>3</sub> solution in 500 cm<sup>3</sup> Erlenmeyer. 200 cm<sup>3</sup> of the distillate (distilled NH<sub>3</sub> in boric acid) solution was used for titration.

# E. Titrimetric determination

3 drops mixed indicator was added to the distillate and titrated with  $0.02M H_2SO_4$ , matching end point against blank containing same volume of NH<sub>3</sub>-free H<sub>2</sub>O, H<sub>3</sub>BO<sub>3</sub> solution, and indicator.

Total N (mg/dm<sup>3</sup>) = (S – B) x M x 14.01 x 1000/ cm<sup>3</sup> sample digested

Where  $S = cm^3$  standard  $H_2SO_4$  for sample

 $B = cm^3$  standard  $H_2SO_4$  for blank

 $M = Molarity of standard H_2SO_4$ 

## 3.6.2.9 Biochemical Oxygen Demand

## A. Principle

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO (AOAC, 1990).

# **B.** Apparatus

- i Incubation bottles -250 or 300 cm<sup>3</sup> with glass stoppers
- ii Gallenkamp Incubator thermostatically controlled at 20 <sup>o</sup>C

# C. Reagents

i. Phosphate buffer solution -8.50 g of KH<sub>2</sub>PO<sub>4</sub>, 21.75g K<sub>2</sub>HPO<sub>4</sub> , 33.40 g Na<sub>2</sub>HPO<sub>4</sub>.7H<sub>2</sub>O and 1.70 g NH<sub>4</sub>Cl in 500 cm<sup>3</sup> H<sub>2</sub>O were mixed and diluted to 1 litre. The pH was 7.2 without further adjustment.

ii. Calcium Chloride Solution – 27. 5 g of anhydrous  $CaCl_2$  was dissolved in distilled water and diluted to 1 litre

iii. Ferric Chloride Solution -0.25 g of FeCl<sub>3</sub>.6H<sub>2</sub>O was dissolved in distilled water and diluted to 1 litre iv. Alkaline Iodide Solution -125 g of NaOH was dissolved in 125 cm<sup>3</sup> of distilled water and 37.50 g of potassium iodide was added. The solution was kept hot until the iodide dissolved. This was called solution (a)

v. Sodium azide solution: 2.5 g  $NaN_3$  was dissolved in 10 cm<sup>3</sup> distilled water. This was called solution (b)

vi. Alkaline iodide – azide solution: This was prepared by mixing solutions (a) and (b) above and making it up to  $250 \text{ cm}^3$ .

vii. Sodium thiosulphate solution-(a) 0.75 M - 46.54 g of  $Na_2S_2O_3.5H_2O$  was dissolved in 250 cm<sup>3</sup> of distilled water.-(b) 0.0375 M solution was prepared by diluting 50 cm<sup>3</sup> of solution above to 1 litre. This was standardized with potassium dichromate solution.

viii. Magnesium Sulphate Solution -22.5 g of MgSO<sub>4</sub>. 7H<sub>2</sub>O was dissolved in distilled water and diluted to 1 litre.

ix. Dilution Water:

The desired volume of water was placed in a suitable bottle and 1 cm<sup>3</sup>/litre each of phosphate buffer, MgSO<sub>4</sub>, CaCl<sub>2</sub> and FeCl<sub>3</sub> solutions were added. Before use, the bottles were placed in the incubator for 24 hours.

# **D. Procedure:**

A suitable volume of sample was diluted with dilution water and mixed well avoiding entrainment of air. The mixed solution was siphoned into two BOD bottles. One was incubated at  $20^{\circ}$ C for 5 days while dissolved oxygen in the other was determined immediately as follows:

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 $2 \text{ cm}^3 \text{ MnSO}_4$  was added followed by  $2 \text{ cm}^3$  alkaline iodide – azide solution well below the surface of the sample. It was stoppered carefully and mixed by inverting it for many times. The precipitate was allowed to settle. After carefully removing the stopper,  $2 \text{ cm}^3$  of conc. H<sub>2</sub>SO<sub>4</sub> was added by running down the neck of the bottle. It was restored and mixed by gentle inversion. The contents of the bottle was decanted into a 500 cm<sup>3</sup> conical flask and titrated with 0.0375 M sodium thiosulphate using starch as indicator.

# E. Calculation

Each cm<sup>3</sup> of 0.037 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 1 cm<sup>3</sup> DO when the entire bottle contents are titrated.

 $BOD = (DO_1 - DO_2)/P$ 

Where DO<sub>1</sub> =initial DO before incubation

 $DO_2 = DO$  after incubation

P = % dilution used

## 3.6.2.10 Chemical Oxygen Demand

# A. Principles

Organic substances are oxidized by  $K_2Cr_2O_7$  in  $H_2SO_4$  (1+1) at reflux temperature with  $Ag_2SO_4$  as catalyst and  $HgSO_4$  to remove chloride interference. Excess dichromate is titrated with  $Fe^{2+}$  using orthophenanthroline as indicator. Method is independent determination of organic matter in sample and has no definable relationship to biological oxygen demand (BOD). The method is applicable to surface and saline waters and industrial wastes (AOAC, 1990).

## **B.** Apparatus and Reagents

i. Reflux apparatus: -  $500 \text{ cm}^3$  Erlenmeyer or  $300 \text{ cm}^3$  round botton flask with T joint connected to  $30 \text{ cm} (12^0)$  Allihn condenser.

ii. Distilled water: - Ordinary distilled water was satisfactory: Deionized water was not used.

iii. Potassium dichromate standard solution – (a) 0.25M:  $12.259g K_2Cr_2O_7$  primary standard grade, previously dried for 2 hr at  $103^{0}C$  was dissolved in distilled water and diluted to 1 litre. (b) 0.025M:  $100 \text{ cm}^3$  of 0.25M was diluted to 1 litre with distilled water.

iv. Sulphuric acid reagent: -  $23.5g Ag_2SO_4$  was dissolved in 1000 cm<sup>3</sup> concentrated H<sub>2</sub>SO<sub>4</sub>. (1 to 2 days was required for dissolution).

v. Ferrous ammonium sulphate standard solution –(a) 0.25M: 98 g Fe (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>. 6H<sub>2</sub>O was dissolved in distilled water, 20 cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> was added and cooled, and diluted to 1 litre. This was standardized daily against 0.25M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. (b) 0 .025M: 100 cm<sup>3</sup> of 0.25M was diluted to 1 litre with distilled water and standardized daily against 0.025M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

vi. Phenanthroline ferrous sulphate (ferroin) indicator solution: 1.48g of 1,10 - (ortho)-phenanthroline and 0.70 g FeSO<sub>4</sub>.7H<sub>2</sub>O were dissolved in 100 cm<sup>3</sup> distilled water.

# vii. Standardization of Ferrous Solutions

a. Concentrated solution: To 25 cm<sup>3</sup> of 0.25M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> diluted to 250 cm<sup>3</sup> with distilled water was added 75 cm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> and cooled. This was titrated with 0.25M Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> using 10 drops of ferroin indicator.

Molarity =  $(\text{cm}^3 \text{ K}_2\text{Cr}_2\text{O}_7 \text{ x molarity})/\text{ cm}^3 \text{ Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ 

b. Dilute solution: -15 cm<sup>3</sup> H<sub>2</sub>O was added to 10 cm<sup>3</sup> of 0.025M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> followed by 20 cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> and the solution cooled. This was titrated with 0.025M Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> using 1 drop of ferroin indicator. The blue green to reddish brown colour change was sharp. The molarity was calculated as in (a).

# C. Procedure

Several boiling chips and 1 g of HgSO<sub>4</sub> was placed in reflux condenser. 5 cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> was added and swirled until HgSO<sub>4</sub> dissolved. This was placed in ice bath and 25 cm<sup>3</sup> 0.25M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 70 cm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> reagents were slowly added with swirling. While still in the bath, 50 cm<sup>3</sup> sample (or aliquot diluted to 50 cm<sup>3</sup>) was added. The condenser was attached and refluxed for 2 hr.

The condenser was cooled and washed down with 25 cm<sup>3</sup> distilled water. About 8 to 10 drops of ferroin indicator were added and excess  $K_2Cr_2O_7$  was titrated with 0.25M Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> to sharp, reddish end point (S cm<sup>3</sup>). Blank determination was performed with all reagents, including refluxing, on distilled water in place of sample and cm<sup>3</sup> of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> required was determined (B cm<sup>3</sup>).

 $COD (mg/dm^3) = (B-S) \times M \times 8000/V$ 

Where M = Molarity of  $Fe(NH_4)_2(SO_4)_2$  solution

V= Volume of sample used

## **3.6.2.11 Bacteriological Analysis**

Coliform organisms were enumerated using the most probable number (MPN) multiple tube fermentation technique. The most probable number method using fire test tubes in each series were inoculated with 10ml/1.0ml of water sample were used. (APHA, 1985).

## **Presumption Test**

Exactly 48.5g of Mac Conkey broth were weighed and dispended in 1 liter of de-ionized water and allow soaking for 10mins and swirled to mix. A sterile pipette was used to transfer 10ml of the Mac Conkey broth for double and samples strength into all the fermentation test tube of the sets. This was followed by transferring 10ml portion of the collected water sample was transferred into the second set of the fermentation tubes of single strength of Mac Conkey broth for higher dilution 0.1ml portion of the water was transferred into the third set of the fermentation test tubes of 10ml simple strength of Mac Conkey broth. All the inoculated test tube were incubated at 37 degree centigrade and 44 degree centigrade respectively and examined for gas production after 24 hours of incubation respectively.

### **Confirmed Test**

Exactly 34.5g of eosin methylene blue agar (EMBA) were weighed dispensed into 1 liter of de-ionized water, allowed to soak and then swirled to mix. It was sterilized by auto calving at 121 degree centigrade for 15mins. Poured into places and allowed to dry in a drier. The ability of the organism to ferment lactose was shown by the production of acid with or without gas. Acid production was shown by a change in colour of the Mac Conkey broth for purple to yellow and gas production by the collection of bubbles in the inverted Durham tubes. Confirmed test was performed by streaking the cutler of positive presumptive tubes across the surface of the eosin ethylene blue agar plates by using a sterile wire loop. The inoculated plates were incubated of 37oC for 24 hours.

### E-Coli

This test was performed by transferring a colony (which formed greenish metallic sheen) from the eosin ethylene blue agar (EMB) to nutrient agar and Mac Conkey agar. The plates were then incubated at 37 degree for 24 hours. Pure cultivar was maintained on nutrient agar slant.

## **Total Coliform**

The sets of fermentation tubes were inoculated with 10m/s 1.0m/s (APHA, 1985). The set of tubes were incubated at 44 degree for 24 + vet result after 24 hours indicates fecal contamination of samples.

### **3.6.3** Atomic Absorption Spectrometer (AAS)

The Atomic Absorption Spectrometer (AAS) is a very common technique for detecting metals and metalloids in environmental samples (Figure 3.4). It is very reliable and simple to use. The technique is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve.

### 3.6.3.1 Principle

The AAS technique requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide (Figure 3.4). The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 °C. The characteristic wavelengths are element specific and accurate to 0.01-0.1nm. To provide

element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A device such as photon-multiplier can detect the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample. Flame atomic absorption hardware is divided into six fundamental groups that have two major functions: generating atomic signals and signal processing. Signal processing is a growing additional feature to be integrated or externally fitted to the instrument. Proper nebulization is required to break up an aqueous sample into a fine mist of uniform droplet size that can be readily burned in the flame. Most instruments utilize the direct aspiration.

During aspiration, the gas flow breaks down the liquid sample into droplets, and the nebulization performance depends on the physical characteristics of the liquid. Only about 10% of the sample gets into the flame. Another option for nebulization is the use of an ultrasonic wave beam, which generates high frequency waves in the liquid sample. This causes very small liquid particles to be ejected into a gas current forming a dense fog. Different flames can be achieved using different mixtures of gases, depending on the desired temperature and burning velocity. Some elements can only be converted to atoms at high temperatures. Even at high temperatures, if excess oxygen is present, some metals form oxides that do not re-dissociate into atoms. To inhibit their formation, conditions of the flame may be modified to achieve a reducing, non-oxidizing flame.

During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths, Flame atomic absorption is very convenient and widespread, and has an acceptable level of accuracy for most analytes. However, there are other devices which allow for better sensitivity and more control over the chemical environment of the analyte. Depending on the information required, total recoverable metals, dissolved metals, suspended metals, and total metals could be obtained from a certain environmental matrix. Appropriate acid digestion is employed in these methods. Hydrochloric acid digestion is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because it can cause interferences during furnace atomization.



Figure 3.4: Atomic Absorption Spectrometer (Adapted from Otto, 1998)

Since each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used and this makes the method relatively free from spectra or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments are also equipped for operation in an emission mode.

## **B.** Apparatus

- i. Hot plate
- Conical (erlenmeyer) flasks, 125 cm<sup>3</sup>, or Griffin beakers, 150 cm<sup>3</sup>, acid washed and rinsed with water.

# C. Reagents

- i. Nitric acid, HNO<sub>3</sub>, conc. (% purity and sp. gravity 1.42)
- ii Aqueous stock (concentration) solutions.
  - a. Sodium solution, 0.04 M: This was prepared by dissolving 2.542 g NaCl (dried at 140<sup>o</sup>C) in water and made up to 1 litre.
  - b. Potassium solution, 0.03 M: Potassium solution was prepared by dissolving
    1.9068 g of KCl (dried at 110 °C) in water and diluted to 1 litre.
  - c. Calcium Solution, 0.02 M: 2.7693 g CaCl<sub>2</sub> was dissolved in water and made up to 1 litre.
  - Cadmium solution, 0.01 M: was prepared by dissolving 1.142 g CdO in 5 cm<sup>3</sup> HNO3 and diluted with water before making up to 1 litre
  - e. Copper Solution, 0.02 M: was prepared by dissolving 3.7980 g Cu(NO<sub>3</sub>)<sub>2</sub>. 3H<sub>2</sub>O in 5 cm<sup>3</sup> HNO<sub>3</sub> and made up to 1 litre with water.

- f. Iron solution, 0.02 M: was prepared by dissolving 4.840 g FeCl<sub>3</sub>. 6H<sub>2</sub>O in 5 cm<sup>3</sup> HNO<sub>3</sub> and made up to 1 litre with water.
- g. Magnesium solution, 0.02 M: was prepared by dissolving 3.9160 g
  MgCl<sub>2</sub>.6H<sub>2</sub>O in water and 10 cm<sup>3</sup> conc. HNO<sub>3</sub> and made to 1 litre.
- Linc solution, 0.02 M: was prepared by dissolving 1.2450 g ZnO in 5 cm<sup>3</sup> of water and 25 cm<sup>3</sup> of conc. HNO<sub>3</sub> and made to 1 litre.
- Manganese solution, 0.02 M: was prepared by dissolving 3.6077 g
  MnCl<sub>2</sub>.4H<sub>2</sub>O in 50 cm<sup>3</sup> Conc. HCl and made to 1 litre.
- j. Lead solution, 0.02 M: was prepared by dissolving 1.5890 g Pb(NO<sub>3</sub>)<sub>2</sub> in 5 cm<sup>3</sup> conc. HNO<sub>3</sub> and made up to 1 litre with water.
- k. Chromium solution, 0.02 M: was prepared by dissolving  $3.7350 \text{ g K}_2\text{CrO}_4$  in  $10 \text{ cm}^3 \text{ HNO}_3$  and made to 1 litre with water.
- Nickel solution, 0.02 M: was prepared by dissolving 4.9530 g Ni(NO<sub>3</sub>)<sub>2</sub>.
  6H<sub>2</sub>O in water and made to 1 litre.

# D. Procedure

# i. Preparation of Calibration

Appropriate working standards were prepared for each metal by serial dilution of stock solutions and then aspirated into the flame and their absorbance recorded. A calibration curve was prepared by plotting absorbance against concentrations for each metal. For calcium and magnesium 100 cm<sup>3</sup> of each standard was mixed with 10 cm<sup>3</sup> lanthanum solution (prepared by dissolving 3.1175 g of La(NO<sub>3</sub>)<sub>3</sub> in 200 cm<sup>3</sup> of water and diluted to a litre) before aspirating. For chromium 100 cm<sup>3</sup> standard was mixed with 1 cm<sup>3</sup> of 30 volume of H<sub>2</sub>O<sub>2</sub> before aspirating. 100 cm<sup>3</sup> standard was mixed with 25 cm<sup>3</sup> of calcium

solution prepared by dissolving 630 mg  $CaCO_3$  in 50 cm<sup>3</sup> of 1 + 5 HCl and diluting to 1 litre for iron and manganese determinations. Samples were similarly treated before aspirating.

## ii. Analysis of Samples

 $100 \text{ cm}^3$  of mixed sample was transferred into a 125 cm}^3 conical flask or beaker. 5 cm}^3 of conc. HNO<sub>3</sub> was added with few boiling chips. It was brought to a slow boiling and evaporated on a hot plate to the lowest volume possible (about 10 to 20 cm}^3) before precipitation occurred. The heating and adding of concentrated HNO<sub>3</sub> was continued as necessary until digestion was completed as shown by a light coloured, clear solution. The sample was not allowed to dry during digestion.

The flask or beaker walls were washed down with water and then filtered.

The filtrate was transferred into a 100 cm<sup>3</sup> volumetric flask with two 5 cm<sup>3</sup> portions of water which was added to the volumetric flask. This was diluted to mark and mixed thoroughly. The solution was taken for required metal determinations by atomic absorption spectrophotometer.

## 3.7 Data Treatment

## **3.7.1 Descriptive Statistics**

The most often used descriptive statistics are range, minimum, Maximum, mean, variance, standard deviation, skewness and kurtosis. These statistics indicate the type of distribution being dealt with. This information is useful for making decisions on how to handle the data statistically (Kaough, 1998). For instance, highly skewed data with a large range may require using logarithms transformation of the data for the analysis. These basic statistics

were determined using the descriptive statistics tool built into the software called Statistical Package for Social Sciences (SPSS), window version 16.0 of 2010.

- The kind of distribution indicated by the data set: It is important to know to what degree the data follows a normal distribution. Most of the statistical procedures used in this analysis require the data to be normally distributed to be fully valid (Kaough, 1998).
- ii. The closeness of mean to each other: A normal distribution is indicated if the mean of the data set are nearly equal.
- iii. The bigness of the standard deviation: This value gives an indication of the spread of the data value around the mean. Coupled with the mean, the standard deviation gives a good indication of the range of values in a data set.
- iv The skewness and kurtosis values of the data set: An important aspect of the "description" of a variable is the shape of its distribution, which gives the frequency of values from different ranges of the variable. Typically, a researcher is interested in how well the distribution can be approximated by the normal distribution. Simple descriptive statistics can provide some information relevant to this issue. For example, if the skewness (which measures the deviation of the distribution from symmetry) is clearly greater then 2, then that distribution is asymmetrical, while normal distributions are perfectly symmetrical. If the kurtosis (which measures "peakedness" of the distribution) is clearly different from 0, then the distribution is either flatter or more peaked than normal;

v. The maximum/minimum falling within an expected range: This analysis cabe useful for editing bad data out of the data set. They are also useful for describing how much variability there is in the data set.

vi Degree of Freedom: Assuming the result of mean of water analysis from two locations were exactly the same, the mean difference would be zero. It would be rare to find the means from two treatments to be exactly the same. The statistical test tells us how likely it is that the obtained mean difference is due to chance variation.

We want to know if the obtained mean difference is significantly different from zero. When the variances are homogeneous the degrees of freedom value (df) is found as the sum of the degrees of freedom in each cell. The degree of freedom in a cell is given as:

n-1 and  $df = (n_1-1) + (n_2-1)$ .

When the variances are not homogeneous the formula for the degrees of freedom is more complicated. It normally results in a fractional value for degrees of freedom, as in the example above. The formula is:

$$df = \frac{\left(SD_{1}^{2}/n_{1} + SD_{2}^{2}/n_{2}\right)^{2}}{\left(SD_{1}^{2}/n_{1}\right)^{2}/(n_{1}-n) + \left(SD_{2}^{2}/n_{2}\right)^{2}/(n_{2}-1)}$$

When the variances are homogeneous, the standard error of the difference is computed by summing the standard deviations (SD) and dividing by the square root of the sum of the numbers. This is also called the standard error of the difference with pooled variance estimates.

$$SE_{diff} = \left(SD_1 + SD_2\right) / \sqrt{n_1 + n_2}$$

When the variances are not homogeneous, the standard error of the difference is found using separate variance estimates. The formula is -

$$SE_{aigr} = \sqrt{\frac{SD_1^2}{n_1} + \frac{SD_2^2}{n_2}}$$

## **3.7.2 Correlation Analysis**

Correlation analysis is a statistical technique that evaluates the relationship between two variables; i.e., how closely they match each other in terms of their individual mathematical change. The question addressed is: if one variable (X) moves or changes in a certain direction does the second variable (Y) also move or change in a similar or complementary direction?

The amount of correlation between two variables is found by comparing the sum of the products of the deviations of the two distributions; i.e,

$$\sum_{i=1}^{n} (X_i - \overline{X})(Y_i - \overline{Y})$$

with a measure that combines the sum of squared deviations of the X distribution and the Y distribution

$$\sqrt{(\sum_{i=1}^{n} (X_i - \overline{X})^2)(\sum_{i=1}^{n} (Y_i - \overline{Y})^2)}$$

The result is a ratio that is a statistical measure called the Correlation Coefficient and is (by convention) represented by the lower case letter "r":

$$r = \frac{\sum_{i=1}^{n} (X_i - \overline{X})(Y_i - \overline{Y})}{\sqrt{\sum_{i=1}^{n} (X_i - \overline{X})^2)(\sum_{i=1}^{n} (Y_i - \overline{Y})^2)}}$$

The numerical value of the correlation coefficient has two properties that make it an important tool for evaluating the relationship between two variables.

- i. The magnitude of the correlation coefficient is independent of the scales of measurement for X and Y. This means that what each of the two variables represent has no impact on the calculation of the correlation coefficient. In other words, the correlation coefficient can compare the relationship between "apples" and "oranges," or any other variables regardless of what is being represented by the variables.
- ii. The value of a correlation coefficient is limited to a range of between +1.0 and -1.0.A value of either +1.0 or -1.0 is considered to be perfect, because the movement of the two variables is in an absolute similar or complementary direction.

## **3.7.3 Principal Component Analysis**

Principal Component Analysis (PCA) is a statistical technique that calculates latent, new variables by a combination of the original variables, representing the multi-dimensional data structure in an optimal way. The direction of the first principal component PC-1, to which the studied objects are projected, is calculated in the way that the maximum variance of the studied objects is preserved. Then the second principal component PC-2, orthogonal to the PC-1 is calculated using the same principle so that it again preserves the maximum possible residual variance. Subsequent PCs are determined using the same concept. The aim of PCA is to transform the observed (usually correlated) variable to a new set of variables which are uncorrelated. The new variables are linear combinations of the original variable and are derived in decreasing order of importance such that the first principal component accounts for as much as possible of the variation in the original data. The

objectives of PCA are to identify new meaning underlying variable and to reduce the dimensionality of the problem as a prelude to further analysis. This method ensures that the first few components accounts for most of the variation in the data so that we can reduce the dimensionality of the data.

The PCA technique starts with the covariance matrix describing the dispersion of the original variables (measured parameters), and extracting the eigenvalues and eigenvectors. An eigenvector is a list of coefficients (loading or weightings) by which we multiply the original correlated variables to obtain new uncorrelated (orthorgonal) variables called principal components (PCs), which are weighted linear combination of the original variables. A principal component is the product of the original data and an eigenvector; the result of projecting the data on to a new axis is a new variable. There are as many PCs as original variables, however PC provides information on the most meaningful parameters, which describe the whole data set affording data reduction with minimal loss of information (Adams, 1998; Otto, 1998; Vega, Pardo, Barrado and Debn, 1998; Helena, Pardo, Vega, Barrado, Fernandez and Fernandez, 2000).

### **3.7.4 Factor Analysis**

In practice, Factor Analysis (FA) follows principal component analysis (PCA). The main purpose of FA is to reduce the contribution of less significant variable in order to simplify even more of the data structure coming from PCA. This last purpose can be achieved by rotating the axis defined by PCA according to well-established rules, and constructing new groups of variables, also called varifactors (VFs). It should be noted that PC is a linear combination of observable water quality variables, while a VF can include unobservable, hypothethetical, "latent" variables (Chapman, 1992; Otto, 1998; Vega et al., 1998; Helena et al., 2000). During the computation of PCA and FA in this work, a varimax rotation (raw) of the PCs coming from the original standardized variables was performed in order to reduce the contribution of variables with minor significance. Thus, we simplify the data structure. The number of PCs/VFs considered for each situatioin was mainly decided on the basis of the percentage of explained variance. The decision of when to stop extracting factors basically depends on when there is only very little "random" variability left, which means that the extraction of a new factor does not significantly improve the overall information. We only have selected factors with eigenvalues higher than 1. That is unless a factor contributes to improve the overall information at least as much as the equivalent of one original variable, we drop it. The criteria is similar to the Screen-test, which is a graphical method that plots the eigenvalues until the place where the smooth decrease of the eigenvalues appears to level off to the right of the plot (Otto, 1998).

Factor analysis focuses on data reduction, to identify a small number of factors that explain most of the variable observed in a much larger number of manifest variables. It attempts to identify new underlying variables or factors that give a better understanding of the pattern of correlation within a set of observed variables. Factor analysis is based on a proper statistical model which is more concerned with explaining the covariance structure of the variable than with explaining the variances. The purpose of factor analysis is to interpret the structure within the variance-covariance matrix of a multivariate data collection. The technique which it uses is extraction of the eigenvalues and eigenvectors from the matrix of correlation or covariance.

## **3.7.5 Water Quality Index**

Water quality index (WQI) is one of the most effective tools to communicate information on the quality of water to the concerned stakeholders and policy makers. It has becomes a useful tool for the assessment and management of water resources. Water Quality Index is a scale which helps to estimate an overall quality of water based on the values of water quality parameters. It expresses the overall water quality at a certain location and time based on several water quality parameters. The word "Water Quality" is a widely used expression, which has a broad spectrum of meaning depending upon each individual interest of water for an intended use.

The objective of WQI is to turn complex water quality data into information that is understandable and useable by the public. Over the years and even today a decision regarding "quality" of water is made using a series of judgments and can be expressed using several scores of parameters obtained from water analysis in the laboratory. In response to the need for a uniform understandable yardstick of water quality, water scientists worked out to compile all the water quality parameters into what is now known as the water quality index (WQI).

#### **3.7.5.1** Calculation of WQI

The Water Quality Index (WQI) was calculated using the Weighted Arithmetic Index method. The quality rating scale for each parameter  $q_i$  was calculated by using this expression:

$$q_i = (C_i / S_i) \times 100$$

A quality rating scale  $(q_i)$  for each parameter is assigned by dividing its concentration  $(C_i)$ in each water sample by its respective standard  $(S_i)$  and the result multiplied by 100. Relative weight  $(W_i)$  was calculated by a value inversely proportional to the recommended standard  $(S_i)$  of the corresponding parameter:

$$W_{i} = 1/S_{i}$$

The overall Water Quality Index (WQI) was calculated by aggregating the quality rating (Q<sub>i</sub>) with unit weight (W<sub>i</sub>) linearly as shown below:

i = nWQI = ( $\Sigma w_i q_i$ )

Where:

q<sub>i</sub>: the quality of the ith parameter,

w<sub>i</sub>: the unit weight of the ith parameter and

n: the number of the parameter considered.

Generally, WQI were discussed for a specific and intended use of water. In this study the WQI for drinking purposes is considered and permissible WQI for the drinking water is taken from the overall WQI given as:

Overall WQI = 
$$\frac{\sum q_i w_i}{\sum w_i}$$

Water quality and its suitability for drinking purpose can be examined by determining the water quality index.

### **3.7.6 Metal Pollution Index**

Metal Pollution index (MPI) is a method of rating that shows the composite influence of individual parameters on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance individual quality considerations. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the water (Amadi, 2011). It is also a combined physio-chemical and microbial index which makes it possible to compare the water quality of various water bodies

(Tamasi and Cini, 2004; Prasad and Kumari, 2008). It has wide application and it is used as the indicator of the quality of sea (Filatov, Pozdnyakov, Johannessen, Pettersson and Bobylev 2005) and river water (Lylko, Ambalova and Vasiljeva, 2001; Mohan, Nithila and

Reddy, 1996), as well as drinking water (Nikoladis, Mandalos and Vantarakis, 2008; Amadi, Yisa, Okoye and Okunlola, 2010). The MPI (Table 4.8) represents the sum of the ratio between the analyzed parameters and their corresponding national standard values.

$$MPI = \sum_{i=1}^{n} \left[ \frac{Ci}{(MAC)i} \right]$$

where:  $C_i$ : mean concentration

MAC: maximum allowable concentration

Metal pollution index is an effective means of communicating water quality to stakeholders in the water sector.

# **3.7.7 Contamination Factor and Geo-accumulation Index**

Contamination factor (CF) and geo-accumulation index (GeoI) are quantitative check used to describe concentration trend of metals in soils. Contamination factor (CF) is a quantifier of the degree of contamination relative to either the average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area (Tijani et al., 2004). It is expressed as:

$$CF = C_m / B_m$$

Where  $C_m$  is the mean concentration of metal m in soil and  $B_m$  is the background concentration (value) of metal m, either taken from the literature (average crustal abundance) or directly determined from a geologically similar material.

Geo-accumulation index (GeoI) as proposed by Mueller (1979) and cited by Lokeshwari and Chandrappa (2006) have been widely used to evaluate the degree of heavy metal contamination in terrestrial and aquatic environments as expressed:

GeoI = 
$$\ln [C_m / 1.5 * B_m)$$

Where  $C_m$  and  $B_m$  are as defined above, while 1.5 is a factor for possible variation in the background concentration due to lithologic differences. GeoI is classified into seven descriptive classes as follows: <0 = practically uncontaminated; 0 – 1 uncontaminated to slightly contaminated, 2 – 3 = moderately to highly contaminated, 4 – 5 = highly to very strongly contaminated, >5 = very strongly contaminated. The latter is an open-end class that is indicative of all values greater than 5, and a GeoI of 6 is said to be indicative of 100-fold enrichment of a metal with respect to the baseline value (Mueller, 1979).

## **3.7.8 Drastic Index**

DRASTIC index has been used to efficiently map aquifer vulnerability in porous and permeable aquifers like the Benin Formation in the Niger Delta. DRASTIC is one of the mapping systems which provide a systematic way for planners, administrators, and managers to address the relative vulnerability of an area's water table aquifer to contamination when making decisions that may impact the groundwater resource. DRASTIC was developed by the U.S. EPA and the National Water Well Association (Aller, Bennet, Herh, Petty and Hackett, 1987). Interest has been growing in Virginia since DRASTIC map training workshops were initiated by the Virginia (Ground Water Protection Steering Committee). The name DRASTIC is derived from the seven factors that go into the maps, these are:

"D" Depth to water

"R" Recharge

"A" Aquifer Media

"S" Soil Media

"I" Impact of Vadose Zones

"T" Topography

"C" (Hydraulic) Conductivity.

The methodology was developed around a set of basic assumptions concerning a generic contaminant. They are:

1) Material introduced at the land surface as a soluble solid or liquid travels to the aquifer with recharge waters derived from precipitation.

2) The mobility of the contaminant is assumed to be equal to that of the groundwater.

3) Attenuation processes are assumed to go on in the soil, Vadose zone and aquifer.

Scientific DRASTIC index was used here to estimate the sensitivity of the groundwater against pollution, but in order to make a vulnerability map some steps should be followed:

i) Divide the survey area into cells, each cell must be given a node, and coordinates.

ii) Translate aquifer rocks, unsaturated zone rocks, permeability, groundwater recharge, groundwater depth and topography (slope) into digital forms according to DRASTIC index rates.

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iii) Multiply the resulted numbers, which is related to every cell by the importance of the variety according to DRASTIC index equation.

iv) Gathering the results of the multiplication which comes from every cells, and so degree of sensitivity will be obtained, and classified according to DRASTIC index. Each parameter is subdivided into ranges and is assigned different ratings in a scale of 1 (least contamination potential) to 10 (highest contamination potential) based on importance of the parameter (Table 3.1). The weighting factors ranges from 1 (least significant) and 5 (most significant).

The DRASTIC model of evaluating aquifer vulnerability makes use of intrinsic factors (physical factors) without considering the impact of human activities on safety of the aquifer. The effects of population, industrialization, urbanization and land-use are not taken into account via DRASTIC model.

#### 2.7.7.1 DRASTICA MODEL

In this study, anthropogenic factor was added to compliment the DRASTIC method considering the effect the various human activities in the area may have on the aquifer system. This gave rise to DRASTICA model, an improved version of DRASTIC model. The linear additive combination of the above parameters with the ratings and weights was used to calculate the DRASTICA Vulnerability Index (DVI). Therefore chemical and bacteriological analyses of geomaterials are used in the determination of DRASTICA Vulnerability Index (DVI).

DVI = DrDw + RrRw + ArAw + SrSw + TrTw + IrIw + CrCw + ArAw

Where

Dr = Ratings to the depth to water table

- Dw = Weights assigned to the depth to water table.
- Rr = Ratings for ranges of aquifer recharge
- Rw = Weights for the aquifer recharge
- Ar = Ratings assigned to aquifer media
- Aw = Weights assigned to aquifer media
- Sr = Ratings for the soil media
- Sw = Weights for soil media
- Tr = Ratings for topography (slope)
- Tw = Weights assigned to topography
- Ir = Ratings assigned to vadose zone
- Iw = Weights assigned to vadose zone
- Cr = Ratings for rates of hydraulic conductivity
- Cw = Weights given to hydraulic conductivity
- Ar = Ratings for anthropogenic factor
- Aw = Weights assigned to anthropogenic factor

Components	Weight
Depth to water	5
Net recharge	4
Aquifer media	3
Soil media	2
Topography	1
Unsaturated zone media	5
Hydraulic conductivity	3
Anthropogenic factor	5

 Table 3.1: Weights of the different components in DRASTICA Model

Good knowledge of the geology and hydrogeology of the research area is a prerequisite to determine rating ranges of the parameter. The procedure for mapping the study area according to DRASICA index was clarified for every component. Dealing with a big data set calls for the use Surfer technique specifically Minimum Curvature gridding method, and GIS ARC-View to produce the vulnerability map of the area.

## (i) Depth to Water Table

The top of the saturated zone is called the water table. The water table rises and falls according to the season of the year and the amount of rain that occur. It is usually higher during the rainy season and lower in dry season. Heavy rainfall or drought conditions may cause fluctuations in the groundwater table. Water table depth determines the depth which a contaminant must travel before reaching the aquifer. Rates for groundwater depths are given in Table 3.2.

Water Table Depth (m)	DRASTICA Rating
0.00 - 1.23	10
1.23 - 4.58	9
4.58 - 9.15	7
9.15 - 15.25	5
15.25 - 22.88	3
22.88 - 30.50	2
>30.50	1

 Table 3.2: Ratings of water table depth

#### (ii) Vadose Zone

This is the zone above the water table which is unsaturated or discontinuously saturated. It determines the attenuation characteristics of the material below the typical soil horizon and above the water table. It is the region above the water table where pores and fractures are partially filled with water and partly by air. The pressure in the unsaturated zone is atmospheric. Conditions are usually highly oxidizing due to the presence of free oxygen from the air and highly reactive due to the presence of water. The unsaturated zone forms an important buffering zone for hazardous wastes before reaching the water table. Understanding the mechanisms and rates of movement of pollutants in rocks is an important step in the process of groundwater protection. It plays an important role in many modeling applications, e.g. for recharge estimation, surface-groundwater interaction and agricultural pollution. The unsaturated zone refers here to the mostly-unsaturated soil profile extending from the land surface down to the groundwater table. The profile is usually heterogeneous, consisting of horizons with distinct differences in the physical properties of the soil. The unsaturated zone is characterized by cyclic fluctuations in the soil moisture as water is replenished by rainfall and removed from the soil profile by evapo-transpiration and percolation. The geological map of the study area, and the available borehole data were used in defining this zone. Digitizing the different sub-zones and giving them the special rates using (Table 3.3) were carried out.

Unsaturated Zone Material	DRASTICA Rating
Confining layer	1
Silt/clay	3
Shale	3
Limestone	6
Sandstone	6
Bedded limestone, sandstone shale	6
Sand and gravel with significant silt and clay	6
Metamorphic/igneous	4
Sand and gravel	8
Basalt	9
Karst limestone	10

 Table 3.3: Ratings of the unsaturated zone material

## (iii) Aquifer Media

This refers to the consolidated or unconsolidated rocks serving as aquifers (sand and gravel or limestone). The route and path length which a contaminant must follow are governed by the flow system within the aquifer. The aquifer media also influences the amount of effective surface area materials which contaminants may come into contact with. The larger the grain size and the more fractures or openings within the aquifer, the higher the permeability and the lower the attenuation capacity of the aquifer media. The geological map of the study area and the wells data were used as the data source in specifying the media of the aquifer all over the study area. The rates were given for every media type depending on Table 3.4.

DRASTICA Rating
2
3
4
5
6
6
6
8
9
10

## Table 3.4: Ratings of the aquifer material

## (iv) Topography

This refers to the slope and slope variability of the land surface. It controls the likelihood that a pollutant will run off or remain on the surface long enough to infiltrate. Topography also influences soil development and has an effect on pollutant attenuation. Zero-two percent slope provides the greatest opportunity for a pollutant to infiltrate. Neither the

pollutant nor precipitation exits the area as runoff. On the other hand, 18+ percent slope provides a high runoff capacity and a lesser probability of contaminant infiltration (high erosion and contamination of surface water). A digital elevation model of the study area – 100 meter spacing- has been used in generating the slope. IDRISI (2000) was used in modeling the percent slope of the study area, and in converting the produced raster model into (X, Y, Z) type of data. The produced data was put in an ascending order, and the rates were given depending on Table 3.5. Rates were found to range from 1 to 10. The gridding method of Minimum Curvature was used.

Slope (%)	DRASTICA Rating
0-2	10
2-6	9
2-12	5
12-18	3
>18	1

 Table 3.5: Ratings of slope percent

## (v) Soil Material

This refers to the uppermost portion of the vadose zone characterized by significant biological activity. Soil has a significant impact on the amount of recharge which infiltrates into the ground. The presence of fine-textured material such as loam and clay loam can decrease soil permeability and restrict contaminant movement. The pollution potential of a soil is largely affected by the type of clay present, the shrink/swell potential of that clay and the grain size of the soil. The less clay shrinks and swells and the smaller the grain size, the

less pollution potential. The geological map of the study area, besides some sieve analyses results were used as the data source for the soil media in the study area. The produced different zones were grouped after the special rates as in Table 3.6.

Soil Material	<b>DRASTICA Rating</b>	
Thin or absent	10	
Gravel	10	
Sand	9	
Peat	8	
Shrinking and or aggregated clay	7	
Sandy loam	6	
Loam	5	
Silt loam	4	
Clay loam	3	
Muck	2	
Non-shrinking and non aggregated clay	3	

## Table 3.6: Ratings of soil material

#### (vi) Hydraulic Conductivity

This is the ability of the aquifer materials to transmit water. It controls the rate at which ground water will flow under a given hydraulic gradient. The rate at which the groundwater flows also controls the rate at which a contaminant moves away from the point it entered the aquifer. High conductivities are associated with higher pollution potential. Values for hydraulic conductivity are calculated and modeled from the pumping tests and permeameter tests carried out. Zones of hydraulic conductivity were defined and accordingly the special rates depending on Table 3.7.

Table 3.7: Ratings of hydraulic conductivity

Hydraulic Conductivity (m)	DRASTICA Rating
$0.50*10^{-6} - 0.50*10^{-4}$	1
$0.50*10^{-4} - 0.15*10^{-3}$	2
$0.15^{*}10^{-3} - 0.36^{*}10^{-3}$	4
$0.36^{*}10^{-3} - 0.51^{*}10^{-3}$	6
$0.51^{*}10^{-3} - 0.10^{*}10^{-2}$	8
>0.10*10-2	10

#### (vii) Aquifer Recharge

Precipitation is the primary source of groundwater because it infiltrates through the surface of the ground and percolates to the water table. Net recharge represents the amount of water per unit area of land which penetrates the land and reaches the water table. Recharge water is the principle vehicle for leaching and transporting contaminants vertically to the water table and horizontally within the aquifer. The greater the recharge, the greater the potential for ground water pollution (measured in mm/year). Other sources include irrigation, artificial recharge and wastewater application. No maps were found to represent the net natural recharge in eastern Niger Delta. However, rainfall and evaporation data for the area was obtained from the Federal Ministry of Environment while slope, soil media, vegetation cover and infiltration rates were studied to estimate the groundwater recharge values. Relative similarity of climate in eastern Niger Delta allowed the assumption that rainfall and evaporation amounts are virtually the same all over the area. Accordingly, soil and slope were the major factors to deduce a primary estimation of natural recharge values to the area taken from recharge rates of the aquifer due to DRASTICA model (Table 3.8).

Recharge (mm/year)	DRASTICA Rating
0.00 - 50.8	1
50.8 - 101.6	3
101.6 - 177.8	6
177.8 – 254.0	8
>254.0	9

Table 3.8: Ratings of groundwater recharge

#### (viii) Anthropogenic Factor

This refers to the various human activities that affect the hydrologic cycle. Such activities in the area includes petroleum exploration, exploitation, refining and marketing as well as gas flaring, oil spillage, sewage, soakaway, industrial and domestic waste. These human endeavours offer the greatest threat to aquifer and groundwater contamination and very expensive to ignore (Table 3.9).

Anthropogenic Factor	DRASTICA Rating
Oil spillage/gas flaring	10
Effluents/sewage/industrial waste (untreated)	9
Cementary/soakaway/pitlatrine (unlined)	8
Open dumpsites (non-sanitary landfill)	8
Effluents/sewage/industrial waste (treated)	7
Emissions from automobiles/generators	8
Domestic waste (organic/degradable)	7
Fertilizer application	7
Cementary/soakaway/pitlatrine (lined)	6
Sanitary landfill	5
Bush burning	4

 Table 3.9: Ratings of anthropogenic factor

## **3.8 Hydraulic Conductivity**

The hydraulic conductivity of the aquifer was calculated from the grain size distribution curve using the Hazen's method (1911). The method is applied to sandy sediment at exactly the effective grain size ( $d_{10}$ ), which is the size corresponding to the 10% line on the grain size distribution curve. The Hazen's formula is given as:

 $K = c[d_{10}]^2$ 

Where:

K = hydraulic conductivity (cm/sec)

 $d_{10}$  = the effective grain size (cm)

C = a coefficient based on the following table given below:

Very fine sand, poorly sorted	40 - 80
Fine sand with appreciable fine	40 - 80
Medium sand well sorted	80 - 120
Coarse sand, poorly sorted	80 - 120
Coarse sand, well sorted, clean	120 - 150

Depending on the dominant grainsize, the average of the range was used. In this study it falls within the coarse sand, poorly sorted, and 100 which is the average value (80 -120) was used in the calculation and the results obtained are tabulated in the next chapter.

#### **3.9 Transmissivity**

The method used to determine the transmissivity of the aquifer was the Cooper and Jacob's method (1946). The Cooper and Jacob's method was used because:

- The aquifer is unconfined,
- The aquifer has a very large area extent,
- The aquifer is homogenous and of approximately uniform thickness,
- Prior to pumping, the water table was horizontal over the area influenced by the pumping test,
- The aquifer is pumped at a constant rate,
- The borehole penetrates the aquifer and thus receives water from the saturated zone.

The Cooper and Jacob's method (1946) is a modification of Thesis method (1935) and given as:

$$T = \frac{2.3Q}{4\pi\Delta S}$$

Where:

T = transmissivity (m<sup>2</sup>/day) Q = Pumping rate (m<sup>3</sup>/day)  $\Delta s = Slope$ 

The values of Q was determined in the field as pumping was in progress while the values of  $\Delta s$  was determined from the slope along drawdown graph in the semi-log graph shown in chapter four.

## **3.10 Storativity**

Cooper-Jacob's method (1946) was used to determine the aquifer storativity in the area. The equation is given as and the results obtained are discussed in chapter four:

$$S = \frac{2.25KTt_o}{r^2}$$

where: r = radius of the well (mm),

t = time (Sec),

KD = hydraulic conductivity X aquifer thickness

 $T = Transmissivity (m^2/day),$ 

S = Storativity (dimensionless).

#### **CHAPTER FOUR**

4.0

## **RESULTS AND DISCUSSION**

The results of hydrogeological mapping, borehole logging, sieve analysis, geophysical investigation, pumping test and laboratory analyses are presented and discussed in this chapter.

## 4.1 Hydrogeological Mapping of parts of Eastern Niger Delta

The geological mapping carried out lead to the construction of the hydrogeological map of parts of Eastern Niger delta (Figure 2.3). The mapping exercise revealed that the area is underlain by thick sandy horizons belonging to the Benin Formation of Miocene to Recent age. The formation is composed of friable sands with intercalations of clay of varying depths and this was ascertained by borehole logs. Open surface logging carried out in the course of the fieldwork revealed three lithofacies associations: Horizontally Bedded Sandstone Facies (Plate II) and Wavy Bedded Sandstone Facies (Plates III) and logging of the lateritic overburden as shown in Figures 4.1a & b. The sands are coarse-grained, pebbly, poorly sorted and contain pods and lenses of fine-grained sands while the clay and shale occur as streak and discontinuous lenses and increases northwards. Borehole logs obtained from drilled boreholes across the study area also indicate a northwards increase in clay thickness away from the coastline. Recharge into the unconfined aquifer is through direct infiltration of precipitation (Uma, 1984).



Plate II: Horizontally Bedded Sandstone Facies



Plate III: Wavy Bedded Sandstone Facies

According to Onyeagocha (1980), petrographic study on several thin sections shows that quartz makes up more than 95% of all grains while Avbovbo (1978) indicated that greater percentage of other skeletal materials including feldspar. The general thickness of the Benin Formation is variable and ranges from less than 150 m at the northern portion where it is underlain by the lignite series of Ogwashi-Asaba Formation to about 2000 m at the southern portion. The Ogwashi-Asaba Formation consists predominantly of shale, mudstone and lignite. The studied areas are underlain by a thick unconfined aquifer of regional extent with four major rivers (Aba, Bonny, Imo and Kwa-Ibo) flowing in a northwest-southeast direction.



Figures (4.1a & b): Open Surface Lithologic Logs from the Eastern Niger Delta, Nigeria

#### 4.2 Pre-drilling Geophysical Survey

To compliment surface geological and hydrogeological mapping, ABEM SAS 1000 Terrameter was used to conduct vertical electrical sounding (VES). A total of 18 VES location strategically selected across the entire study area was carried out using Schlumberger Configuration. A total spread (L) of 700 m was covered at 350 m (L/2) on the right side of the gas flaring station and another 350 m (L/2) on the left towards the direction of Akpulu Community. Similar traverse was carried out in other VES locations. The traverse was straight and adequate for the measurement as all necessary precautions were taken, leading to the successful drilling of the 18 boreholes.

All field data (Appendix B) have been subjected to both manual and computer processing techniques using the Schlumberger automatic analysis package. A representative computer modelled curve is shown in figure 4.2. The remaining computer modelled VES curves are contained in Appendix C. The subsurface lithologic interpretation and geoelectric section are contained in Table 4.1 and figure 4.3a respectively. Five lithologic units were identified and the results show that sand is the dominant formation in the area with minor and discontinuous occurrences of clay, shale, silt and gravel. The finding conforms to the results of geological and hydrogeological investigations earlier discussed.



Figure 4.2: Computer Modelled Curve of Resistivity versus L/2

Table 4.1: Results of subsurface lithology from Eastern Niger Delta

Layer	Average Thickness (m)	Lithologic Description
1	0-6.2	Top Lateritic Sand
2	6.5 - 45.0	Silty Sand
3	46.0 - 103.0	Sand, Gravel bed, Clay intercalation
4	104.0 - 118.0	Sand, Gravel (Prolific)
5	120 – Below	Sandstone, Shaley



Figure 4.3a: Geoelectric Section from VES in Eastern Niger Delta, Nigeria

#### 4.3 Lithologs

The 18 drilled boreholes that fall within the study area were logged (Figure 4.3b) while a combined borehole casing tally and lithologs are shown figure 4.3c. Four boreholes were correlated along the North-South axis of the study area and illustrated in figure 4.4. A closer look at the borehole logs show that the subsurface geology is made up of fine to coarse grained sand with clay intercalations of variable thickness. The lithologies (Figure 4.3a-4.3c) gave a clear and concise lithostratigraphic profile of the formations that make up the subsurface geology of the southern part of the study area while the correlated litholog and casing tally (Figure 4.c) gives a true reflection of the subsurface geology of the northern part of the study area. The sample box obtained directly by borehole logging and from where strata-logs were prepared shows variation in the sandy formation in both colour and grain size, starting from the top fine brownish lateritic sand to the deeper white medium to coarse grained sand. These findings agree with the results of the open surface logging (Figures 4.1a & b) and the geoelectric sections (Figure 4.3a-4.3c).



Figure 4.3b: Borehole Strata Log in Eastern Niger Delta, Nigeria



Figure 4.3c: Borehole Casing Tally and Strata-Log from Eastern Niger Delta

North

```
South
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Figure 4.4: Borehole correlation along North-South axis of the Eastern Niger

Delta

## **4.4 Sieve Analysis**

In order to determine the textural characteristics of the uppermost layer of the underlying lithologies which invariably influence infiltration rate of rainfall and leachate, soil and borehole samples were collected and subjected to sieve analysis. The particle size distribution curve (Figure 4.5) obtained from the sieve analysis shows that the formations were mainly sand and fine gravel and this conforms to the results of the geological, hydrogeological, geophysical and boreholes logging. This is in agreement with the findings of Uma, (1989); Ezeigbo and Aneke, (1993).



Figure 4.5: Particle Size Distribution Curves from Eastern Niger Delta

## **4.5 Permeability Test**

The results of the coefficient of permeability determined from Constant Head Permeameter test are contained in Table 4.2 and the values ranged from  $4.14 \times 10^{-5} \text{ cms}^{-1}$  to  $9.4 \times 10^{-5} \text{ cms}^{-1}$  with a mean value of  $6.8 \times 10^{-5} \text{ cms}^{-1}$ . By implication, it means that soil zone through which water infiltrate the underlying aquifer is of relatively high permeability. Due to the high permeability of the soils and rocks, coupled with the shallow water table, there is a possibility of chemical and bacteriological contamination of the groundwater in the area. Uma, (1989) gave the average linear groundwater flow in the area at about 400 m/yr and that leachate moves at about 6 km away from its source in every 15 years time interval. The porous and permeable nature of the sandy formation, coupled with the long-term effects of oil spillage, gas flaring, dumping of refuse on abandoned burrow-pits, river channels and other unhealthy sanitary practices may have the propensity to alter the groundwater quality in the area. The high concentration observed in most of the physical, chemical and bacteriological parameters analyzed may also be testimonies of poor unsanitary practices in the region.

Parameters	Minimum	Maximum	Mean
Coefficient of Permeability(K) Cms <sup>-1</sup>	9.4x10 <sup>-5</sup>	4.14x10 <sup>-5</sup>	6.8x10 <sup>-5</sup>
Elevation (m)	53.0	78.0	61.0
Depth (m)	1.2	3.6	2.4

Table 4.2: Summary of coefficient of permeability using Constant Head Permeameter

## 4.6 Pumping Test

The raw data of the pumping test carried out are contained in Appendix D while the drawdown, recovery and specific yield graphs are shown in Appendix E. The results were used to determine the aquifer discharge (Q), static water level (SWL), transmissivity (T), hydraulic conductivity (K), Storativity (S) and specific capacity (SC) contained in Table 4.3. The values of Q were determined in the field as pumping was in progress while the values of  $\Delta$ s were determined from the slope of the drawdown and recovery in a semi-log graph. The aquifer transmissivity and storativity were calculated from Cooper-Jacob's method.

Parameters	Minimum	Maximum	Mean	
Borehole depth (m)	46.0	310.0	124.0	
Discharge (m <sup>3</sup> /day)	1624.0	7216.0	3218.0	
Static water level (m)	3.0	28.0	11.0	
Transmissivity (m <sup>2</sup> /day)	152.0	2835.0	1026.0	
Hydraulic conductivity (m/day)	3.2	478.4	98.6	
Storativity (dimensionless)	9.5x10 <sup>-6</sup>	1.5x10 <sup>-4</sup>	5.8x10 <sup>-5</sup>	
Specific capacity (m <sup>2</sup> /day/m)	828.0	15314.0	6258.0	

 Table 4.3: Statistical summary of pumping test data from Eastern Niger Delta

#### **4.6.1 Hydraulic Conductivity**

The hydraulic conductivity of the aquifer was calculated from the grain size distribution curve using the Hazen's method (1911). The method is applied to sandy sediment at exactly the effective grain size (d<sub>10</sub>), which is the size corresponding to the 10% line on the grain size distribution curve. From the grain size distribution curves, over 85% fall within the coarse sand and poorly sorted. The average value of the two intervals (80 - 120) was used as the value for "C". The results of hydraulic conductivity are contained in Table 4.3, with values ranged between 3.2 m/day and 478.4 m/day and a mean value of 98.6 m/day. The result of hydraulic conductivity indicates high permeability rates. This implies that as soon as pollutants get to the water table via leachate, it is easily transported and dispersed from one point to another. Easy movement of leachate/pollutant leads to a multiplier effect, as a large number of people are liable to have access to flowing polluted surface or migrating groundwater. This is one characteristics of sandy aquifer and it is in concord with the findings obtained from the open surface logging, geoelectric section and borehole stratalog.

From the textural point of view, low hydraulic conductivity and hydraulic gradient implies angular or sub-angular grain shape meaning that the grains have not experienced any meaningful movement (Uma, 1989; Ibe *et al.*, 1992). On the other hand, high hydraulic conductivity values (high hydraulic gradient) suggests that the grains have witnessed appreciable transportation and as a result, are well-sorted and rounded, indicating high permeability. From environmental standpoint, areas with high hydraulic conductivity, permeability, and transmissivity are vulnerable to pollution. The aquiferous system in the area may have been undergoing some level of pollution arising from heavy anthropogenic activities going on in the area coupled with the nature of the local geology of the area.

## 4.6.2 Transmissivity

The values of the transmissivity ranged from 152.0 m<sup>2</sup>/day to 2835.0 m<sup>2</sup>/day with an average transmissivity value of 1026.0 m<sup>2</sup>/day (Table 4.3). The transmissivity values when compared with the standards postulated by Bouwer, (1978), Gheorge (1978) and Krasny, (1993) as tabulated in Tables 4.4 - 4.6, indicate a high groundwater potential typical of an unconfined, porous and permeable formation. The results obtained had shown a consistent dominance of medium to coarse grained sandy aquiferous system for the area.

## 4.6.3 Storativity

Transmissivity Dange

The values of the storativity ranged between  $9.5 \times 10^{-6}$  and  $1.5 \times 10^{-4}$  with a mean value of  $5.8 \times 10^{-5}$  and are contained in Table 4.4 while a representative drawdown and recovery curve plotted from the pumping test carried out in parts of Eastern Niger Delta is illustrated in figure 4.6.

Transmitting Dotontials

Transmissivity Kange	Transmitting Totentials
$T > 500 \text{ m}^2/\text{day}$	High potential
T between $50 - 500 \text{ m}^2/\text{day}$	Moderate potential
T between $5 - 50 \text{ m}^2/\text{day}$	Low potential
T between $0.5 - 5 \text{ m}^2/\text{day}$	Very low potential
$T < 0.5 \ m^2/day$	Negligible potential

 Table 4.4: Gheorge Standards for Transmissivity (T)

T (m2/day)	Designation of Transmissivity Magnitude	Groundwater supply potential
1000	Very high	Regional consumption
100	High	Local consumption
10	Intermediate	Community consumption
1	Low	Private consumption
0.1	Very low	Limited consumption
< 0.1	Imperceptible	Negligible consumption

# Table 4.5: Krasny's Transmissivity Standards

K-ranges	Materials
$10^{-8} - 10^{-2}$ m/day	Deep clay beds
0.001 - 0.1 m/day	Clay, sand and gravel mixes (till)
0.01 - 0.2  m/day	Clay soils (surface)
0.1 - 1  m/day 1 - 5 m/day	Example solis (surface)
5 - 20  m/day	Medium grained sand
5 – 100 m/day	Sand and gravel mixes
20 – 100 m/day	Coarse grained sand
100 – 1000 m/day	Gravel

Table 4.6: Bouwer Standard for Hydraulic Conductivity (K)



## Figure 4.6: Drawdown & Recovery Graph from Eastern Niger Delta, Nigeria

#### 4.7 Physico-chemical and Bacteriological Analysis

#### 4.7.1 Groundwater

The groundwater raw data analyzed are contained in Table 4.7 while the statistical summary is shown in Table 4.8. A cursory examination of Table 4.8 reveals that majority of the groundwater samples in the area are characterized by low pH (3.84 - 7.74), low concentration of carbonates (0.00) and high concentrations of salinity (10.00 - 820.00), silica (0.22 - 101.89), temperature (26.50 - 31.60), electrical conductivity (28.00 - 752.00), total dissolved solids (12.00 - 605.00), chloride (12.00 - 721.00), sulphate (0.10 - 250.40)and heavy metals in the decreasing order of: Fe > Ni > Cu > Zn > Mn > Cd > V > Co > Pb> Cr > As > Hg. Carbonate is normally low in natural water because CO<sub>3</sub> is insoluble, but reacts with H<sub>2</sub>O to form HCO<sub>3</sub> which is soluble and hence is normally high in natural waters. A close look at Table 4.7 also shows wide range with corresponding high mean, standard deviation and variance values for chloride, EC, salinity, silica, sulphate and TDS. This is an indication that there are substantial differences in the quality/composition of the groundwater system in the aquifer within the study area. The arithmetic means were determined in order to know what the central tendency for each physical, chemical and bacteriological properties concentration could be. The deviations in the aiming grade from a typical normal concentration were analyzed using kurtosis test. An evaluation of the symmetry in the value distribution applying the skewness test was carried out and majority of the hydrologic date are non-normal or positive skewed.

Location	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	L-9	L-10	L-11	L-12
Temp. ( <sup>0</sup> C)	27.20	26.91	27.02	28.33	26.51	29.03	26.35	27.67	29.03	29.64	28.28	27.19
pH	4.55	6.81	4.50	7.40	3.84	7.72	6.60	6.70	7.23	7.34	7.30	5.90
EC (µS/cm)	675.00	421.60	522.00	513.00	717.40	618.20	230.00	183.70	195.20	181.40	33.50	49.30
TDS (mg/l)	350.00	370.50	230.60	221.30	142.70	297.20	49.00	183.21	55.00	59.70	21.00	12.60
TSS (mg/l)	3.00	5.00	10.00	12.00	1.00	0.00	10.00	3.00	1.00	0.00	2.00	3.00
Hardness (mg/l)	38.00	8.43	14.50	20.40	14.00	36.00	10.40	70.00	142.00	8.00	6.00	7.00
Cl <sup>-</sup> (mg/l)	730.00	250.00	330.00	300.00	351.00	410.00	53.00	331.00	300.00	68.00	18.00	48.00
SO4 <sup>2-</sup> (mg/l)	10.80	6.57	22.45	75.00	19.30	90.10	69.13	82.55	96.32	38.31	87.15	75.80
Fe (mg/l)	1.60	0.40	0.56	0.40	0.02	0.10	0.20	0.30	0.20	0.40	0.50	0.80
Salinity (mg/l)	326.00	511.00	355.00	82.00	181.00	163.40	398.60	200.50	85.10	49.31	240.11	150.00
NO3 <sup>-</sup> (mg/l)	2.89	0.86	0.20	0.83	0.51	1.65	12.05	14.00	34.00	0.10	6.50	3.20
HCO <sub>3</sub> (mg/l)	32.40	21.80	6.70	10.32	21.01	54.01	11.00	39.23	3.00	8.19	12.11	15.30
$Ca^{2+}$ (mg/l)	3.460	4.444	7.633	4.111	2.000	6.123	8.100	11.234	5.000	4.121	5.395	7.523
Na <sup>+</sup> (mg/l)	2.756	3.000	1.022	0.834	0.666	3.400	1.400	1.776	1.822	0.310	0.433	1.764
$Mg^{2+}$ (mg/l)	2.222	2.981	0.826	4.500	2.757	0.445	0.233	2.080	1.000	3.221	0.310	0.278
$K^{+}$ (mg/l)	0.540	0.810	0.505	0.300	0.891	0.431	0.733	0.144	0.656	0.444	0.500	0.401
PO <sub>4</sub> <sup>3+</sup> (mg/l)	0.010	0.221	0.030	0.732	0.010	0.233	0.131	0.001	0.233	0.000	0.231	0.088
Mn (mg/l)	0.002	0.041	0.033	0.780	0.101	0.011	0.004	0.001	0.041	0.033	0.003	0.334
F- (mg/l)	1.900	2.200	2.310	0.800	1.300	0.411	0.330	0.500	0.510	1.631	0.010	2.100
SiO <sub>2</sub> (mg/l)	2.641	4.301	0.948	0.602	5.506	4.944	5.862	6.807	6.000	1.492	5.407	3.101
$Zn^{2+}$ (mg/l)	0.219	0.302	0.603	0.331	0.038	0.483	0.307	0.365	0.152	0.300	1.305	0.264
$Cu^{2+}$ (mg/l)	0.011	0.037	0.053	0.039	0.631	0.012	0.002	0.053	0.013	0.000	0.011	0.058
Pb (mg/l)	0.012	0.028	0.017	0.021	0.283	0.027	0.074	0.044	0.034	0.098	0.062	0.033

 Table 4.7a: Results of Groundwater analysis for location 1 to location 12 in Eastern Niger Delta

Locations	L-13	L-14	L-15	L-16	L-17	L-18	L-19	L-20	L-21	L-22	L-23	L-24
Temp. ( <sup>0</sup> C)	26.40	27.92	27.51	26.83	26.33	27.04	28.27	29.47	28.03	28.17	26.78	28.51
pН	5.81	6.23	5.90	7.11	6.02	5.83	5.31	5.44	5.93	6.01	6.82	6.76
EC (µS/cm)	28.00	429.30	350.60	560.00	527.00	150.00	160.00	50.00	35.00	56.00	32.00	49.42
TDS (mg/l)	20.00	241.00	122.70	401.00	270.00	255.00	218.00	25.00	25.00	59.00	39.30	65.60
TSS (mg/l)	1.00	35.00	3.00	7.00	8.00	4.00	14.00	2.00	3.00	4.00	1.00	3.00
Hardness (mg/l)	20.00	13.50	2.50	11.00	13.00	121.32	78.36	135.00	132.10	12.34	18.00	48.00
Cl <sup>-</sup> (mg/l)	38.00	250.00	115.00	103.50	132.00	401.00	390.50	12.00	35.00	38.00	19.00	23.00
SO4 <sup>2-</sup> (mg/l)	0.40	48.00	72.96	22.03	24.70	230.11	9.70	78.00	65.10	74.71	96.00	54.45
Fe (mg/l)	0.20	0.02	0.82	0.00	0.10	0.02	0.01	0.20	0.10	0.01	0.04	0.03
Salinity (mg/l)	50.00	113.21	210.32	63.70	25.00	15.60	62.10	95.30	26.40	62.10	672.75	60.24
NO <sub>3</sub> <sup>-</sup> (mg/l)	0.31	6.30	0.60	13.00	9.31	0.50	0.10	0.20	0.50	0.01	1.55	1.58
HCO <sub>3</sub> (mg/l)	58.04	15.51	30.00	7.11	9.50	15.21	20.71	8.08	10.35	11.00	13.40	10.36
Ca <sup>2+</sup> (mg/l)	12.210	4.223	3.000	8.234	9.200	6.322	18.300	4.250	2.478	13.788	5.333	6.781
Na <sup>+</sup> (mg/l)	2.433	2.321	1.443	2.320	1.000	2.303	1.820	2.211	0.213	0.241	1.444	2.300
$Mg^{2+}$ (mg/l)	0.823	1.789	5.677	2.111	4.577	8.900	7.000	2.821	0.332	4.300	2.781	4.000
$K^{+}$ (mg/l)	0.300	0.424	0.555	0.678	0.341	0.231	0.322	0.788	0.133	0.567	0.044	0.781
PO4 <sup>3+</sup> (mg/l)	0.001	0.232	0.221	0.781	0.210	0.200	0.020	0.231	0.777	0.200	0.000	0.233
Mn (mg/l)	0.100	0.230	0.727	0.030	0.004	0.003	0.010	0.782	0.605	0.200	0.210	0.002
F- (mg/l)	2.333	2.000	1.520	0.910	0.701	0.322	0.410	0.335	0.441	0.210	0.222	0.800
SiO <sub>2</sub> (mg/l)	4.445	0.801	4.558	6.701	9.134	5.000	0.565	0.751	0.383	4.133	9.000	2.152
Zn <sup>2+</sup> (mg/l)	0.528	0.152	0.147	0.432	0.211	0.778	0.281	0.217	0.367	0.182	0.159	0.653
$Cu^{2+}$ (mg/l)	0.032	0.026	0.035	0.012	0.059	0.066	0.068	0.012	0.062	0.067	0.093	0.021
Pb (mg/l)	0.000	0.018	0.045	0.032	0.024	0.033	0.034	0.100	0.031	0.049	0.033	0.012

 Table 4.7b: Results of Groundwater analysis for location 13 to location 24 in Eastern Niger Delta

Location	L-25	L-26	L-27	L-28	L-29	L-30	L-31	L-32	L-33	L-34	L-35
Temp. ( <sup>0</sup> C)	28.02	27.30	28.03	27.22	28.00	27.11	28.13	27.24	29.60	38.40	26.55
pH	4.69	7.71	6.50	4.75	6.83	5.73	4.28	4.80	6.34	6.40	3.82
EC (µS/cm)	36.73	30.21	74.01	33.00	45.00	250.13	519.40	250.20	281.40	174.01	687.40
TDS (mg/l)	140.54	33.60	36.00	33.00	35.72	150.10	381.31	301.50	219.60	136.00	202.70
TSS (mg/l)	1.00	2.00	1.00	3.00	4.00	1.00	2.00	3.00	2.00	2.00	1.00
Hardness (mg/l)	4.00	13.13	12.00	10.00	30.23	19.31	25.22	18.68	14.00	22.00	18.00
Cl <sup>-</sup> (mg/l)	41.00	30.80	50.51	32.00	16.10	28.00	215.00	84.36	88.00	56.51	320.00
SO4 <sup>2-</sup> (mg/l)	80.00	70.00	78.00	191.32	126.00	100.00	80.00	121.35	78.30	98.00	69.30
Fe (mg/l)	0.05	0.40	0.21	0.09	0.30	0.40	0.36	0.22	0.41	0.32	0.12
Salinity (mg/l)	130.30	220.50	120.12	50.00	10.33	15.11	12.00	25.00	48.30	900.12	381.00
NO3 <sup>-</sup> (mg/l)	2.00	5.32	0.40	0,33	0.62	0.66	0.37	0.86	0.41	0.41	0.516
HCO <sub>3</sub> (mg/l)	12.71	15.17	12.12	13.10	29.10	12.00	12.00	21.00	10.15	16.52	24.01
$Ca^{2+}$ (mg/l)	5.340	6.000	7.586	2.300	5.789	4.234	8.000	6.333	6.395	5.613	4.482
Na <sup>+</sup> (mg/l)	1.000	3.445	2.111	0.333	2.113	0.631	1.376	0.311	0.533	1.222	0.713
$Mg^{2+}$ (mg/l)	8.721	3.010	2.111	6.200	5.833	4.050	2.341	3.000	0.310	4.820	1.332
$K^{+}$ (mg/l)	0.233	0.457	0.543	0.789	0.233	0.540	0.220	0.567	0.400	0.555	0.323
PO <sub>4</sub> <sup>3+</sup> (mg/l)	0.440	0.788	0.421	0.210	0.780	0.788	0.220	0.221	0.238	0.130	0.567
Mn (mg/l)	0.033	0.450	0.333	0.210	0.200	0.021	0.030	0.456	0.203	0.333	0.614
F- (mg/l)	0.788	0.011	0.310	0.210	0.227	0.233	0.734	0.400	0.210	2.510	0.641
SiO <sub>2</sub> (mg/l)	101.891	4.089	2.641	60.020	2.752	0.571	0.554	0.573	15.400	10.944	7.384
$Zn^{2+}$ (mg/l)	0.701	0.458	0.433	0.356	10.091	0.400	0.247	1.000	1.401	0.800	0.456
Cu <sup>2+</sup> (mg/l)	0.022	0.757	0.036	0.023	0.011	0.051	0.300	0.089	0.312	0.255	0.169
Pb (mg/l)	0.012	1.099	0.043	0.064	0.012	0.067	0.067	0.023	0.067	0.113	0.099

 Table 4.7c: Results of Groundwater analysis for location 25 to location 35 in Eastern Niger Delta
Parameters	Range	Minimum	Maximum	Mean	St. Dev.	Variance	Skewness	Kurtosis
Arsenic	0.015	0.001	0.016	0.007	0.009	0.012	0.001	0.003
Bicarbonate	55.01	3.03	58.04	16.31	12.89	166.04	2.15	4.48
$CO_3^-$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BOD	5.03	3.20	8.23	5.60	6.85	32.46	1.23	2.10
Cadmium	0.12	0.07	0.19	0.14	0.09	0.15	0.03	0.06
Calcium	116.30	2.00	118.30	46.53	3.50	12.25	1.56	3.22
Cobalt	0.08	0.00	0.08	0.03	0.19	0.23	0.05	0.02
Chloride	709.00	12.00	721.00	275.20	171.25	29326.22	1.32	1.66
Chromium	0.09	0.02	0.11	0.07	0.05	0.08	0.06	0.10
Copper	1.15	0.03	1.15	0.08	0.17	0.03	3.35	10.83
COD	5.18	7.80	12.98	10.60	9.68	6.42	3.45	3.98
E.Cond(µs/cm)	726.00	28.00	752.00	254.00	231.50	53593.30	0.76	-0.78
EC(cfu/100ml)	18.00	0.00	18.00	6.00	0.42	0.68	0.36	0.74
Fluoride	2.32	0.01	2.33	0.85	0.74	0.55	0.94	-0.55
T. Hardness	139.50	2.50	142.00	54.31	41.49	1721.83	1.80	1.95
Iron	6.82	0.05	6.87	0.62	1.41	1.98	3.76	14.46
Lead	1.07	0.02	1.09	0.08	0.19	0.04	5.13	27.52
Mercury	0.002	0.002	0.004	0.003	0.001	0.023	0.001	0.002
Magnesium	88.67	0.23	88.90	33.16	2.35	5.52	0.87	0.36
Manganese	0.77	0.01	0.78	0.19	0.24	0.06	1.41	0.88
Nickel	0.03	0.01	0.40	0.28	0.21	0.18	0.15	0.13
Nitrate	63.97	0.03	64.00	17.82	6.68	44.62	3.35	13.53
pН	3.90	3.84	7.74	5.46	1.02	1.04	-0.51	-0.38
Phosphate	30.75	0.04	30.79	10.29	0.26	0.07	1.02	0.12
Potassium	60.85	0.04	60.89	20.47	0.22	0.05	0.04	-0.79
Salinity	810.00	10.00	820.00	265.47	193.98	37628.31	2.07	4.23
Silica	101.51	0.38	101.89	8.38	19.92	396.93	4.13	17.46
Sodium	153.23	0.22	153.45	61.59	0.94	0.88	0.18	-0.81
Strontium	3.59	0.91	4.50	3.02	1.14	1.31	-0.51	-1.01
Sulphate	250.30	0.10	250.40	98.62	52.53	2758.93	0.98	1.99
TDS	393.00	12.00	605.00	255.00	119.65	14315.07	0.64	-0.75
Temp.(°C)	4.90	26.50	31.60	28.70	0.89	0.79	0.45	-0.41
TSS	54.89	0.11	55.00	14.60	6.59	43.40	3.48	14.70
TC (cfu/ml)	48.00	0.00	48.00	15.00	11.80	40.36	2.82	5.62
Zinc	10.06	0.03	10.09	0.70	1.73	3.01	5.45	30.38

 Table 4.8: Statistical Summary of the Groundwater data from Eastern Niger Delta

BOD-biochemical oxygen demand; COD-chemical oxygen demand; TC-total coliform; E.Cond-Electrical Conductivity EC-Escherichia coli; TSS-total suspended solid

# **4.7.1.1 Physical Parameters of Groundwater**

#### pH and Temperature (°C)

The pH ranged between 3.84 and 7.74 with a mean value of 5.46 (Table 4.8). The pH is an important indicator of water quality and the extent of pollution. The mean pH of the groundwater falls below the acceptable range of 6.50-8.50 postulated by Nigerian Standard for Drinking Water Quality (NSDWQ, 2007). It could be attributed to the impact of acid rain witnessed in the area, which might have resulted from the accumulation effect of gas flaring in the area. The temperature of the groundwater ranged from 26.50 °C to 31.60 °C with an average value of 28.70 °C. These values were found to be within the maximum permissible limit (NSDWQ, 2007). The wide range in temperature values may be attributed to the heating effect of gas flaring on the region and subsequent acid rain formation which infiltrates into the shallow static water table.

The low pH as shown in the pH distribution map of the area (Figure 4.7), is an indication of acidity in the groundwater from the area and may be linked to acid-rain formation probably caused by continuous gas flaring-where the gas associated with oil extraction is burnt off into the atmosphere, a method adopted by oil companies operating in the area, as means of getting rid of associated gas in the course of oil exploitation. In developed countries such as United Kingdom and United States of America, 99% of associated gas is used or re-injected into the ground, but in Nigeria, 99% of associated gas is flared, thereby making Nigeria highest flare of gas in the world (World Bank, 2004). Temperature is a measure of the degree of hotness or coldness of a substance. It is an important water quality parameter which plays a major role in the distribution and abundance of organisms. Aquatic organism like other organisms is tolerant of certain ranges of temperature outside which they cannot

function (Larry, 1995). Many biological processes in water are known to be influenced by changes in environmental temperature and chemical substances dissolve more readily as temperature increases, unlike most gases which become less soluble as temperature rises (Wooten, 1992).



Figure 4.7: pH Map of Eastern Niger Delta, Nigeria

# **Total Dissolved Solids**

Total dissolved solids (TDS) indicate the general nature of water quality especially salinity. Its concentration in groundwater ranged between 12.00 mg/l and 605 mg/l and a mean concentration of 255.00 mg/l (Table 4.8). These values lie below the maximum permissible limit of 500.00 mg/l (NSDWQ, 2007).

#### **Total Suspended Solids**

The concentration of total suspended solids (TSS) varied from 0.11 to 55.00 mg/l and a mean value of 14.60 mg/l (Table 4.8). Suspended solids in water can fill pore spaces between gravels thereby reducing the rate of permeability/groundwater migration. The values here are low hence there is less influence on groundwater migration.

# **Electrical Conductivity**

The electrical conductivity (EC) is a valuable indicator of the amount of materials dissolved in water. Its value ranged between 28.00  $\mu$ s/cm and 752.00  $\mu$ s/cm with an average value of 254.00  $\mu$ s/cm (Table 4.7). The conductivity values are below the acceptable limit of 1000.00  $\mu$ s/cm for safe water (NSDWQ, 2007).

# **4.7.1.2 Bacteriological Parameters**

# **Escherichia Coli and Total Coliform Bacteria**

The concentration of Escherichia coli (E.coli) ranged between 0.00 and 18.00 cfu/100ml with an average value of 6.00 cfu/100ml while total coliform (TC) varied from 0.00 to 48.00 cfu/ml and a mean value of 15.00 cfu/ml (Table 4.8). Their presence in groundwater is an indication of faecal contamination. The practice of unlined pit-latrine and soakaway in shallow aquifer region like the eastern Niger Delta exposes the groundwater to faecal

contamination and good sanitary system is advocated for the area due to the vulnerability of its aquifer system. Faecal contamination causes water-borne diseases such as cholera, typhoid, meningitis and diarrhea as well as morbidity and mortality among children. It also causes acute renal failure and hemolytic anemia in adults (Khadse, Patni, Kelkar and Devotta, 2008; Juang, Lee and Hsueh, 2009).

#### **4.7.1.3 Chemical Parameters**

#### **Biochemical Oxygen Demand (BOD)**

This is a measure of the amount of oxygen required to oxidize organic matter by bacterial action. The study of BOD gives an idea of the oxidizable matter actually present in a water sample and allows pollution load evaluation to be established. The concentration of BOD ranged between 3.20 mg/l and 8.23 mg/l with a mean value of 5.60 mg/l (Table 4.8). These values are within the recommended limit of water for domestic use (WHO, 2006).

#### **Chemical Oxygen Demand (COD)**

Chemical oxygen demand (COD) measures the total organic carbon, with the exception of certain aromatics such as benzene, which are not completely oxidized in the reaction. Values of COD for the groundwater ranged between 7.80 mg/l and 12.98 mg/l with an average value of 10.60 mg/l. These values are within the permissible limit recommendation (WHO, 2006).

# Chloride

The concentration of chloride in the groundwater ranged between 12.00 mg/l and 721.00 mg/l and an average value of 275.00 mg/l (Table 4.8). These values in most locations exceed by far the maximum permissible limit of 250.00 mg/l (WHO, 2006; NSDWQ,

2007). High chloride concentration in groundwater may indicate pollutions by sewage, industrial waste or saline water intrusion (Bertram and Balance, 1998). The high concentration of chloride, conductivity and total dissolved solid is an indication that the groundwater may be in contact with water of marine origin and that there is a possibility of saltwater intrusion into the coastal aquifer system in the area. A saltwater/freshwater interface ranging between 5.0 m and 180.0 m and varying from coastline to mainland was obtained. This is in agreement with the findings Nwankwoala, (2011) and Oteze, (2003) as well as the results of geophysical investigation and borehole drilling. High chloride values may not constitute health hazard to human beings, but it does produce salty taste, corrode metal pipe and may harm non-halophytic plants (Lawal *et al.*, 1986). The chloride concentration map of the area is shown in Figure 4.8.



Figure 4.8: Chloride concentration map of the Eastern Niger Delta, Nigeria

# Sulphate

The concentration of sulphate varied from 0.10 to 250.40 mg/l with a mean value of 98.62 mg/l (Table 4.8). The concentration of sulphate exceeds the maximum allowable limit of 100.00 mg/l as recommended by (WHO, 2006; NSDWQ, 2007). The high sulphate values may be attributed to the reaction between  $SO_x$  released by gas flaring, industrial combustion and vehicular transportation and H<sub>2</sub>O molecules in the atmosphere leading to the formation of H<sub>2</sub>SO<sub>4</sub>, which falls as part of acid-rain. The aquifer in the area is largely unconfined, porous and permeable and these signatures enhance easy migration of the acid-rain into the shallow groundwater table and enriched the groundwater system with SO<sub>4</sub>.

### Nitrate

The concentration of nitrate ranged between 0.03 mg/l and 64.00 mg/l and a mean value of 17.82 mg/l (Table 4.8). Nitrate values in some locations were higher than the maximum permissible limit of 50.00 mg/l by (WHO, 2006; NSDWQ, 2007). High nitrate level in drinking water causes infant methaemoglobinaemia (blue-baby syndrome), gastric cancer, metabolic disorder and livestock poisoning. The sources of nitrate in the groundwater can be attributed to anthropogenic activities such as on-site sanitation, waste dumpsites and fertilizer application (Dan-Hassan *et al.*, 2012) as well as the reaction between NO<sub>x</sub> and H<sub>2</sub>0 in the atmosphere leading to the formation of H<sub>2</sub>NO<sub>3</sub> which falls as parts of acid-rain and infiltrates into the groundwater table.

# Phosphate

The concentration of phosphate ranged between 0.04 and 30.79 mg/l and an average value of 10.29 mg/l. Phosphate is an indicator of pollution arising from poor sanitation and manure/fertilizer application by farmers (Blaustein and Hamlyn, 1983; Dan-Hassan, 2012).

# Sodium

In this study, the sodium ion content ranged between 0.22 and 153.45 mg/l with a mean content of 61.59 mg/l (Table 4.8). This concentration is within the allowable limit of 200.00 mg/l based on guidelines set out for drinking water purposes by the World Health Organization (WHO, 2006) and Nigerian Standard for Drinking Water Quality (NSDWQ, 2007). Studies have considered Na as a major risk factor in drinking water (Calabrese and Tuthill, 1981; Blaustein and Hamlyn, 1983). In epidermiological studies, a direct correlation between hypertension and Na level in drinking water has been observed (Folosom, 1982) while the noxious effects of Na on blood vessels have been known for years (Dyckner and Wester, 1983). Though high Na content in water may not be harmful to living matter due to the non-toxic nature of the metal, balance among other nutrient elements may affect the soil used for agricultural purposes (Wardener and MacGregor, 1983).

#### Calcium

Calcium has values ranging from 2.00 mg/l to 118.30 mg/l and a mean value of 46.06 mg/l, which are within the permissible limit of 200.00 mg/l based on (WHO, 2006) and (NSDWQ, 2007) recommendations. Calcium is necessary in animals for the formation of strong tooth and its high in water does not have any negative impact on health.

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# Magnesium

Magnesium concentration in the groundwater ranged from 0.23 to 88.80 mg/l and an average of 33.16 mg/l. The values are within the recommended value of 200.00 mg/l on (WHO, 2006) and (NSDWQ, 2007). The importance of Mg in water is both quantitative and qualitative. Studies have shown that Mg in water is better and more quickly absorbed than dietary Mg. This particular availability might help to understand why an adequate water Mg level may determine a better state of health, even without any Mg deficiency. Epidemiological data in man and experimental data in rats have demonstrated that the intake of water containing sufficient amount Mg can prevent arterial hypertension and correlated ionic and nervous disturbances (Durlach *et al.*, 1985).

# Potassium

The concentration of K varied from 0.04 to 60.89 mg/l with a mean value of 20.47 mg/l (Table 4.8). High concentration of Na and K may indicate the leaching and dissolution of secondary salts in the pore spaces. The observed concentrations in the major anions and cations are signatures of the interaction of water with the aquifer formations.

#### Salinity Content

Salinity refers to the concept of saltiness of a body of water. Water is defined as saline if it contains 3 to 5 % salt by volume (wt/v). The ocean is naturally saline approximately 3.5 % salt (Nachtergaele, Van-Lynden, and Batjes, 2002). The technical term for ocean saltiness is halinity, from the fact that halides (chloride, specifically) are the most abundant anion in the mix of dissolved solids. In oceanography, it has been traditional to express salinity as concentration in parts per thousand (ppt), which is grams salt per liter of water (Por, 1972; Karbassi *et al.*, 2007; Akoto *et al.*, 2008). The salt content of most lakes, rivers, and

streams is so small that these waters are termed fresh water as salt content is a factor in water potability. Salinity influences the types of organisms that live in a water body, as well as the kinds of plants that grow either in the water body, or on land fed by groundwater. Plants adapted to saline conditions are called halophytes while animals and bacteria that can live in very salty conditions are termed extremophiles (Por, 1972; Gueu, Yao, Adouby and Ado, 2007; Vinodhini and Narayanan, 2008). The salinity content ranged from 10.00 to 820.00 with a mean value of 265.47 (Table 4.8). The average to high salinity value in the groundwater is an indication that the salt water intrudes into the aquifer system in the area thereby contaminating the fresh groundwater (Figure 4.9).

Apart from anthropogenic sources of groundwater pollution in the area arising from huge human activities domiciled in the area, salinity and high iron content constitutes the major natural sources of groundwater pollution in the area. Many boreholes in the Bonny, Degema and Port-Harcourt Metropolis have been abandoned either due to the problem of salt water intrusion or high iron content. The results of pre-drilling geophysical survey, borehole drilling and chemical analysis of borehole water samples indicate that salt water interface occur at depths ranged between 5m to 185m while iron-water occurs between 65-170 m depth. Boreholes greater than 200 m may not have these problems (saltwater and iron-water) but drilling such deeper wells in the area is challenging, since well collapse due to the friable nature of the sand is common in the area. A lot of bentonites are needed to hold the walls and this weakens with time.

The impact of salt intrusion is more on the southern part of the area than the northern part of the area while the reverse was the case for high iron content. The sea water from the Atlantic Ocean that bounds the southern portion of the area may be responsible for the problem of salt intrusion (Oteri, 2003; 2013).



Figure 4.9: Salinity Map of Eastern Niger Delta, Nigeria

Iron

The concentration of iron ranged from 0.05 to 6.87 mg/l with a mean value of 1.62 mg/l (Table 4.8) as against the maximum recommended value of 0.30 mg/l by WHO, (2006) and NSDWQ, (2007). Iron is an essential nutrient that is vital to the processes by which cells generate energy. Iron can also be damaging when it accumulates in the body. Some people simply don't eat enough iron containing foods to support their health optimally, while others have so much iron that it threatens their well-being. The principle that too little or too much of a nutrient is harmful seems particularly appropriate for iron. Iron has a knack of switching back and forth between two ionic states. In the reduced state, iron has lost two electrons, and therefore has a net positive charge of two. Iron in the reduced state is known as ferrous iron. In the oxidized state, iron has lost a third electron, has a net positive charge of three, and is known as ferric iron.

Because iron can exist in different ionic states, iron can serve as a cofactor to enzymes involved in oxidation-reduction reactions. In every cell, iron works with several of the electron-transport chain proteins that perform the final steps of the energy yielding pathways. There are so much of the body's iron is in the blood, as a result, iron losses are greatest whenever blood is lost. Bleeding from any site incurs iron losses. Active bleeding ulcers, menstruation, and injury result in iron losses. Women are especially prone to iron deficiency during their reproductive years because of repeated blood losses during menstruation (Shahtaheri, Abdollahi, Golbabaei, Rahimi-Froushani and Ghamari, 2008). Pregnancy places iron demands on women as well since iron is needed to support the added blood volume, the growth of the fetus and blood loss during childbirth. Infants and young children receive little iron from their high milk diets, yet extra iron is needed to support their rapid growth. The rapid growth of adolescence, especially for males, and the menstrual losses of teen females demand extra iron that a typical teen diet may not provide. Organs that may be most affected by iron are the pancreas, liver, kidneys, brain, heart, arteries, and joints (Nouri *et al.*, 2006). This is not so much because the mineral deposits there. In fact, more iron is in the liver than elsewhere, but so are many other minerals deposited there

The aquifer in the area is overlain by iron-stained lateritic formation of varying depth. Results of geophysical survey, sieve analysis and the rate of penetration during drilling confirmed that the laterite is sandy with little clay ratio. At the Owerri end of the study area, where the Benin Formation is underlie by the Ogwashi-Asaba Formation which is composed of shale, clay and lignite. Around Imo Concorde Hotel, Owerri, high iron content in the groundwater was traceable to the presence of marcasite in the shale and lignite horizons of the Ogwashi-Asaba Formation. The mineral marcasite is iron sulfide (FeS<sub>2</sub>) with orthorhombic crystal structure. It is physically and crystallographically distinct from pyrite, which is iron sulfide with cubic crystal structure. Marcasite is soluble and more brittle than pyrite and easily breaks up due to the unstable crystal structure and this explains its avaliable in the groundwater system in the area. Studies revealed that marcasite occurs in sedimentary rocks (shales and low grade coals horizons) as well as in highly acidic conditions. The marcasite is likelyfrom the shale and coal seams of the Ogwashi-Asaba Formation and low pH in the area enhances its enrichment in the groundwater system through high rate of infiltration due to heavy rainfall in the area.

# **Heavy Metals**

Heavy metals are metallic chemical elements that have a relatively high density and are toxic even at a very low concentration. It refers to chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water (Anderson, Todd, Ellen, Kruger and Coats, 1995).

#### Lead

Lead is defined by the United States Environmental Protection Agency (USEPA) as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms (USEPA, 1996). It is a gray-white, soft metal with a low melting point, a high resistance to corrosion, and poor electrical conducting capabilities. The lead concentration in the groundwater ranged between 0.02 and 1.09 mg/l with an average value of 0.08 mg/l (Table 4.7). The values were far higher the maximum permissible limit of 0.01 mg/l (WHO, 2006; NSDWQ, 2007). High concentration of lead in the groundwater may be attributed to the various anthropogenic activities domiciled in the area. Studies had shown that lead is naturally available in all environmental media (atmosphere, biosphere and hydrosphere) varying concentrations. From the atmosphere, lead is transferred to soil, water and vegetation by dry and wet deposition. It is carcinogenic and affects several organs of the human body, including the nervous system, the blood system, the kidney, the cardiovascular system and the reproductive system. Of most concern are the adverse effects of lead on the nervous system of young children: reducing intelligence and causing attention deficit, hyperactivity and behavioural abnormalities. These effects occur at relatively low blood lead levels without a known lower threshold (Schwartz, 1994; Ahmad *et al.*, 2010). Various studies have found a positive correlation between lead exposure and measured intelligence quotient (IQ) of school-age children (Bellinger, 1992; Bird *et al.*, 2003; Kraft *et al.*, 2006; Venugopal *et al.*, 2009). Reviews of studies concluded that a 10  $\mu$ g/l increase in blood lead can be associated with a 2.5 point decrease in IQ (WHO, 2006; Lee *et al.*, 2007). The negative impact of lead exposure is generally stronger on verbal IQ than on performance IQ (WHO, 2006; Kar *et al.*, 2008). Prenatal exposure of lead was also demonstrated to produce toxic effects in the human fetus, including reduced birth weight, disturbed mental development, spontaneous abortion and premature birth. Such risks were significantly greater at blood lead level of 15  $\mu$ g/l and more (WHO, 2006).

# Cadmium

The concentration of cadmium varied between 0.07 and 0.19 mg/l with a mean value of 0.14 mg/l as against the maximum allowable limit of 0.003 mg/l (NSDWQ, 2007). They observed high concentration of cadmium can be as a result of the heavy anthropogenic activities going-on in the area. Cadmium ingestion via food, especially plant-based foodstuff, is the major route by which cadmium enters the human body from the environment. The intake of cadmium dust through inhalation (absorbed by the lungs) is generally less than the intake via drinking water (Macklin *et al.*, 2003). The kidney, especially the renal tract, is the critical organ of intoxication after exposure to cadmium. Excretion is slow, and renal accumulation of cadmium may result in irreversible

impairment in the reabsorption capacity of renal tubules (Adams *et al.*, 2008). Several renal dysfunction and damage to the bone structure, a syndrome known as itai-itai disease, have been associated with long-term exposure to cadmium in food (mainly rice) and water in Japan (USEPA, 1997; WHO, 2006).

Deficiencies of iron, zinc and calcium in the human body generally facilitate cadmium absorption. Most crops, with the exception of rice have been found to contain zinc that inhibits the uptake of cadmium by animals and humans (Chaney, Sioco and Majam, 1995; Suthar and Singh, 2008). Acute and chronic exposure to cadmium dust and fumes as a result of working conditions or smoking can result in cadmium poisoning. Several studies have yielded sufficient evidence of cadmium carcinogenicity in animals (Hatje, Bidone and Maddock, 1998; Amman *et al.*, 2002; Kar *et al.*, 2008) while long term occupational exposure to cadmium causes prostate and lung cancer (Mohan *et al.*, 1996; Rim-Rukeh, Ikhifa and Okokoyo, 2006; WHO, 2006).

# Copper

Copper is one of several heavy metals that are essential to life despite being as inherently toxic as non-essential heavy metals exemplified by Pb and Hg (Scheinberg, 1998). The concentration of Cu ranged between 0.03 and 1.15 mg/l with an average concentration of 0.08 mg/l. Some locations have concentrations above the maximum recommended value of 1.00 mg/l (NSDWQ, 2007). The higher value in parts of the area indicates an anthropogenic addition from industrial effluents and dumpsites. Gastrointestinal disorder in human can be due to elevated copper concentration in drinking water (USEPA, 1997; NSDWQ, 2007).

# Nickel

Nickel values ranged between 0.01-0.04 mg/l with an average value of 0.28 mg/l (Table 4.8). The mean concentration of nickel is greater the maximum acceptable limit of 0.02 mg/l recommended by (NSDWQ, 2007). Nickel is a very abundant element in the environment, and is found primarily combined with oxygen (oxides) or sulfur (sulfides). Small nickel particles in the air via tobacco smoke, auto exhaust and gas flaring settle to the ground or are taken out of the air in rain. Leachate from dumpsites and industrial effluents can also enrich nickel concentration in the groundwater. The most common adverse health effect of nickel in humans is an allergic reaction. People can become sensitive to nickel when things containing it are in direct contact with the skin, when they eat nickel in food, drink it in water, or breathe dust containing it (Aktar et al., 2010). Once a person is sensitized to nickel, further contact with it will produce a reaction. The most common reaction is a skin rash at the site of contact. Less frequently, allergic people have asthma attacks following exposure to nickel. Lung effects, including chronic bronchitis and reduced lung function, have been observed in workers who breathed large amounts of nickel.

Acute toxic effects occur in two stages, *immediate* and *delayed*. Headache, dizziness, shortness of breath, vomiting, and nausea are the initial symptoms of overexposure to nickel; the delayed effects, consist of chest pain, coughing, shortness of breath, bluish discoloration of the skin, and in severe cases, delirium, convulsions, and death (Bird *et al.*, 2003; Kraft *et al.*, 2006). Recovery is protracted and characterized by fatigue on slight exertion. Repeated or prolonged exposure to nickel carbonyl has been associated with an increased incidence of cancer of the lungs and sinuses. Products of decomposition (nickel

oxide and carbon monoxide) are less toxic that nickel carbonyl itself (USEPA, 1997; Lohani, Singh, Rupainwar and Dhar, 2008).

### Zinc

The concentration of zinc varied from 0.03 mg/l to 10.09 mg/l and a mean value of 0.70 mg/l (Table 4.8). This values falls below the permissible limit of 3.00 mg/l (NSDWQ, 2007). Zinc is one of the commonest elements in the earth's crust. It's found in air, soil, and water, and is present in all foods. Pure zinc is a bluish-white shiny metal and has many commercial uses such as coating to prevent rust, in dry cell batteries, and mixed with other metals to make alloys like brass and bronze. Zinc compounds are widely used in industry to make paint, rubber, dye, wood preservatives, ointments, household utensils, castings and printing plates. Some zinc is released into the environment by natural processes, but most comes from activities of people like mining, steel production, gas burning, and wastes dumps. Rain and snow remove zinc dust particles from the air and moves it into the groundwater and into lakes, streams, and rivers. The WHO recommended dietary allowance of zinc is 15 milligrams a day for men (15 mg/day); 12 mg/day for women; 10 mg/day for children; and 5 mg/day for infants (WHO, 2006).

Zinc is an essential element in our diet. Too little zinc can cause health problems, but too much zinc is also harmful. Acute toxicity may result in sweet taste, throat dryness, cough, weakness, generalized aching, chills, fever, nausea and vomiting. Zinc chloride fumes have caused injury to mucous membranes and pale gray cyanosis. Ingestion of soluble salts may cause nausea, vomiting and purging. Breathing large amounts of zinc (as dust or fumes) can cause a specific short-term disease called metal fume fever (Lee *et al.*, 2007). Chronic

toxicity can cause stomach cramps, nausea, vomiting, anemia and pancreas damage (USEPA, 1997; Nouri, Mahvi, Jahed and Babaei, 2008).

# Chromium

The concentration of chromium ranged from 0.02 to 0.11 mg/l with a mean value of 0.07 mg/l (Table 4.8). The mean concentration is higher than the maximum permissible limit of 0.05 mg/l recommended by (WHO, 2006; NSDWQ, 2007). Chromium has three main forms chromium (0), chromium (III), and chromium (VI). Chromium (III) compounds are stable and occur naturally, in the environment. Chromium (0) does not occur naturally and chromium (VI) occurs only rarely. Chromium compounds have no taste or odor. Chromium (III) is an essential nutrient in our diet, but we need only a very small amount. Other forms of chromium are not needed by our bodies (Venugopal *et al.*, 2009).

Chromium is a naturally occurring element found in rocks, soil, plants, animals, and in volcanic dust and gases. In the beginning of life the mineral chromium is important from the very earliest stage of life. Conception of new life begins a process of rapid cell duplication by division (mitosis) over and over again. This requires lots of energy. Chromium is used in manufacturing chrome-steel or chrome-nickel-steel alloys (stainless steel) and other alloys, bricks in furnaces, and dyes and pigments, for greatly increasing resistance and durability of metals and chrome plating, leather tanning, and wood preserving. Chromium (III) helps insulin maintain normal glucose levels (Bellos and Swaidis, 2005).

All forms of chromium can be toxic at high levels, but chromium (VI) is more toxic than chromium (III). High chromium concentration can damage and irritate your nose, lungs,

stomach, and intestines (USEPA, 1997). People who are allergic to chromium may also have asthma attacks after breathing high levels of either chromium (VI) or (III). Long term exposures to high or moderate levels of chromium (VI) cause damage to the nose (bleeding, itching, sores) and lungs, and can increase your risk of non-cancer lung diseases. Ingesting very large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with liquids or solids containing chromium (VI) may lead to skin ulcers. Some people have allergic reactions including severe redness and swelling (USEPA, 1997; Juang *et al.*, 2009).

# Cobalt

Cobalt is is a steel-gray, shiny and hard metal which can enter into humans through water, soil or food. The concentration of cobalt in the groundwater ranged between 0.00 and 0.08mg/l with an average value of 0.03 mg/l (Table 4.8). Cobalt used in industry is imported or obtained by recycling scrap metal that contains cobalt. It is used to make alloys, paints, large appliances, and kitchen-wares. Cobalt has also been used as a treatment for anemia, as it causes red blood cell production (Mohanty, Misra and Nayak, 2001). Acute toxicity of cobalt may be observed as effects on the lungs, including asthma, pneumonia, and wheezing. Animal studies have found problems with the development of the fetus in animals exposed to high concentrations of cobalt during pregnancy. The International Agency for Research on Cancer has determined that cobalt is a possible carcinogen to humans. Studies in animals have shown that cobalt causes cancer when placed directly into the muscle or under the skin and did not cause cancer in animals that were exposed to it in the air, in food, or in drinking water (Bellos and Swaidis, 2005).

# Mercury

The value of mercury ranged from 0.001 to 0.004 mg/l and an average value of 0.003 mg/l (Table 4.8). This concentration of mercury was found to be higher than maximum permissible limit of 0.001 mg/l (WHO, 2006; NSDWQ, 2007). The metallic mercury is a shiny, silver-white, odourless liquid, but when heated gives a colourless and odourless gas. Mercury also combines with carbon to form organic mercury compounds. The most common organic mercury compound is methyl mercury, which is produced mainly by small organisms in the water and soil. The more mercury becomes available in the environment the more methyl mercury is produced by these small organisms that make them. Metallic mercury is used to produce chlorine gas and caustic soda and also in thermometers, amalgams (dental fillings) and batteries (Singh, Mondal, Kumar, Singh, Tewary and Sinha, 2008). Mercury salts are used in skin-lightening creams and as antiseptic creams and ointments.

Mercury is used in scientific and electrical equipment, in the electrolytic production of chlorine and sodium hydroxide; and as a catalyst in polyurethane foam production. It enters the water or soil from natural deposits, disposal of wastes, and the use of mercury-containing fungicides (Mohanty *et al.*, 2001). The acute toxicity of mercury varies significantly with the route of exposure. Inhalation of high concentrations of mercury causes severe respiratory irritation, central nervous system, digestive disturbances, developing fetus, brain and kidney damage. The World Health Organization (WHO, 2006) reported no evidence that inorganic mercury is carcinogenic.

# Arsenic

The concentration of arsenic ranged between 0.001 and 0.016 mg/l with a mean value of 0.007 mg/l (Table 4.8). Most arsenic compounds have no smell or special taste. When arsenic enters the environment, it does not evaporate, instead it can be absorbed in the soil, dissolve in groundwater or release in the atmosphere via burning of arsenic compounds (Karbassi *et al.*, 2008). Arsenic is the most common cause of acute heavy metal poisoning in adults and is released into the environment by the smelting process of copper, zinc, and lead, as well as by the manufacturing of chemicals and glasses (Sekabira, Oryem-Origa, Basamba, Mutumba and Kakudidi, 2010). Arsenic gas is a common by-product produced by the manufacturing of pesticides that contain arsenic. Arsenic may be also be found in water supplies worldwide, leading to exposure of shellfish, cod, and haddock. Other sources are paints, rat poisoning, fungicides, and wood preservatives. Target organs are the blood, kidneys, and central nervous, digestive, and skin systems (Khadse *et al.*, 2008).

## Manganese

The concentration of Mn ranged from 0.01 to 0.78 mg/l with an average value of 0.29 mg/l (Table 4.8). Some locations have values higher the WHO and NSDWQ acceptable limit of 0.2 mg/l. Decomposition and subsequent leaching industrial effluent are probable sources of groundwater enrichment in Mn. Manganese is essential for plants and animals, and are used in products such as batteries, glass and fireworks (Aboud and Nandini, 2009). Potassium permanganate is used as an oxidant for cleaning, bleaching and disinfection purposes. Other manganese compounds are used in fertilizer, fungicides and as livestock feeding supplements (Huang and Lin, 2003).

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# 4.7.2 Surface Water

Surface water in the area were sampled and analyzed for relevant physical, chemical and microbial analysis (Table 4.9) and the summary shown in Table 4.10. Some of the rivers in the area have witnessed various degree of pollution by oil spills and industrial effluent without any form of treatment. The results when compared with the Nigerian Standard for Drinking Water Quality (NSDWQ, 2007) and subjected to geostatistical technigues such as Water Quality Index (WQI), Heavy Metal Pollution Index (HMPI) and Factor Analysis (FA) shows that both the surface and groundwater in the area have experienced varying degree of pollution and and needs treatment before used for domestic purposes.

During the fieldwork, it was observed that the surface water, especially those in the creeks contains floating oil, ranging from thin sheen to thick dark oil. This has also led to the extinction of many species of fishes as well as destruction of fishing habitat, as fishermen in the area are stripped of their viable profession. In parts of Ogoniland and Eleme LGA, hydrocarbon was found in soils at depth of about 4.0 m and some public boreholes have been abandoned due to hydrocarbon pollution. Similar results were reported by the United Nations Environment Programme (UNEP, 2011).

Parameters (mg/l)	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	L-9	L-10	L-11	L-12	L-13
Temperature (°C)	32.00	32.00	32.00	33.00	33.00	33.00	32.00	32.00	32.00	32.00	33.00	32.00	33.00
Colour	24.00	18.00	17.00	11.00	22.00	4.00	3.00	5.00	2.00	6.00	18.00	15.00	4.00
pН	4.80	6.80	6.85	6.50	6.00	4.80	6.60	5.60	4.60	4.70	4.50	4.60	5.80
Conductivity (µs/cm)	13.00	36.00	28.00	10.00	11.00	8.00	37.00	9.00	88.00	42.00	17.00	28.0	11.00
TDS	7.30	23.00	18.00	3.30	5.20	7.20	24.00	6.00	57.00	27.00	11.00	19.00	7.20
Suspended solid	10.00	8.00	4.00	9.00	11.60	1.80	2.60	3.60	5.10	7.00	15.00	20.00	6.00
Bicarbonate	42.00	39.00	36.00	25.00	17.90	19.60	45.00	27.00	23.00	16.00	30.00	42.00	38.00
Carbonate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chloride	3.60	4.00	2.40	2.90	1.30	5.30	3.10	2.30	1.80	2.60	1.60	1.70	4.30
Manganese	0.10	0.50	1.50	0.10	0.05	0.05	1.00	0.01	0.03	0.03	0.05	0.30	0.90
Iron <sup>3+</sup>	0.71	0.23	0.18	0.60	0.56	0.37	0.14	0.15	0.24	0.19	0.12	0.10	0.43
Sulfate	17.00	4.00	5.00	2.00	4.00	15.00	3.00	3.50	2.00	1.00	3.00	5.00	2.00
Nitrate	32.00	25.00	22.00	30.00	28.20	19.70	16.30	24.00	18.00	19.40	34.00	29.00	40.00
Cal. Hardness	62.60	45.00	37.10	39.80	29.30	104.0	84.20	44.00	65.00	55.00	31.40	28.90	57.90
Total Solid	17.00	32.00	25.00	15.00	18.00	10.00	29.00	9.00	35.00	29.00	25.00	49.00	51.00
Magnesium	7.90	4.80	3.70	3.80	5.10	1.60	8.80	7.50	7.20	7.70	9.80	3.30	8.50
Calcium	24.00	26.00	21.00	22.00	18.00	16.00	49.00	30.00	39.00	32.00	26.00	17.00	34.00
Total Hardness	87.00	60.00	53.00	56.00	45.00	154.0	122.0	75.00	96.00	81.00	64.00	43.00	84.00
Potassium	6.50	0.63	1.60	1.40	0.41	3.60	0.20	1.10	2.30	0.56	0.30	1.80	2.40
Chlorine	0.06	0.15	0.18	0.10	0.02	0.17	0.13	0.11	0.60	0.03	0.12	0.10	0.14
Sodium	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
E.Coli	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Coliform	129.0	52.00	48.00	68.00	72.00	81.00	38.00	61.00	53.00	92.00	359.0	462.0	68.00

 Table 4.9a: Results of surface water analysis for location 1 to location 13 in Eastern Niger Delta

L-14	L-15	L-16	L-17	L-18	L-19	L-20	L-21	L-22	L-23	L-24	L-25	L-26	L-27	L-28
29.00	29.00	30.00	30.00	30.00	30.00	29.00	29.00	29.00	30.00	30.00	30.00	29.00	30.00	30.00
15.00	18.10	24.00	17.00	8.00	10.00	7.00	22.00	18.00	9.00	4.00	8.00	34.00	25.00	6.00
5.30	5.20	5.30	5.50	5.60	5.90	5.50	5.50	6.00	5.50	5.80	5.60	6.00	5.50	5.70
17.00	10.00	9.00	112.0	176.0	299.0	23.00	156.0	14.00	93.00	33.00	182.0	458.0	230.0	17.00
11.10	6.50	5.80	72.90	114.4	149.5	14.90	101.4	9.10	60.40	21.40	118.3	297.7	149.5	11.05
25.00	4.00	22.00	64.00	53.00	78.00	9.80	42.00	15.00	32.00	28.00	51.00	81.00	60.00	90.00
28.00	15.00	32.00	52.00	11.00	16.00	35.00	12.00	20.10	19.00	25.00	17.00	54.00	43.00	22.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18.00	24.50	9.00	1.50	12.00	17.00	15.00	30.00	17.50	21.00	10.00	21.50	37.50	12.00	7.50
0.20	0.15	0.02	0.10	0.30	0.14	0.01	0.17	0.21	0.01	0.02	0.02	0.01	0.03	0.01
0.10	0.20	0.17	0.09	0.06	0.31	0.16	0.10	0.23	0.11	0.27	0.30	0.28	0.19	0.35
6.00	3.00	8.00	9.60	4.00	13.00	10.00	5.00	5.80	6.00	4.70	2.00	6.00	3.00	2.00
11.30	7.60	5.60	8.70	15.30	17.00	28.00	22.00	9.90	10.30	29.00	25.00	31.10	19.00	6.00
21.00	22.70	36.70	31.90	57.90	58.00	77.00	47.00	15.00	11.70	32.00	19.00	83.00	38.00	43.00
42.00	24.00	31.00	213.0	168.0	227.0	35.00	160.0	26.00	90.00	58.00	169.0	378.0	210.0	32.00
1.60	2.80	3.70	2.37	5.60	7.70	8.90	3.50	2.10	1.70	3.00	3.90	9.80	3.29	6.30
8.40	9.10	14.00	12.70	23.00	23.30	30.80	18.80	6.00	4.70	12.80	7.60	33.20	14.40	17.20
28.00	35.00	51.30	42.00	82.00	91.00	115.0	62.00	24.00	19.00	45.00	36.00	125.0	52.00	70.00
17.00	3.30	5.80	15.00	10.20	27.00	16.00	9.00	8.00	25.00	22.00	10.60	31.00	38.00	6.70
0.18	0.14	0.01	0.05	0.20	0.21	0.02	0.34	0.03	0.28	0.60	0.06	0.16	0.20	0.05
0.00	0.00	1.20	1.78	0.14	0.80	0.30	0.00	0.00	0.20	0.00	0.73	0.00	0.00	0.26
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
117.0	48.00	72.00	275.0	410.0	310.0	54.00	150.0	65.00	38.00	91.00	160.0	280.0	510.0	715.0
	L-14 29.00 15.00 5.30 17.00 11.10 25.00 28.00 0.00 18.00 0.20 0.10 6.00 11.30 21.00 42.00 1.60 8.40 28.00 1.60 8.40 28.00 1.60 8.40 28.00 1.60 0.18 0.00 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 Table 4.9b: Results of surface water analysis for location 14 to location 28 in Eastern Niger Delta

Parameters (mg/l)	L-29	L-30	L-31	L-32	L-33	L-34	L-35	L-36	L-37	L-38	L-39	L-40	L-41	L-42	L-43
Temperature (°C)	30.00	29.00	29.30	29.70	28.60	28.80	27.60	28.90	30.60	30.40	25.00	25.00	25.00	28.30	27.60
Colour	1490	1390	1400	1330	1300	1450	1340	1410	1410	1420	1420	1320	484	1401	1524
pН	2950	2800	2790	2670	2500	2600	2580	2660	2940	2840	28.00	2640	100	2610	2890
Conductivity (µs/cm)	6.80	6.80	6.69	6.87	6.61	6.80	6.77	6.81	6.60	6.70	7.20	7.20	7.30	6.53	6.32
TDS	55.20	44.90	45.80	86.30	87.00	65.60	58.90	48.60	60.20	68.40	45.50	50.00	16.10	56.80	64.30
Suspended solid	1.50	1.40	1.40	1.40	1.50	1.40	1.60	1.50	1.40	1.50	1.50	1.40	0.50	1.50	1.40
Bicarbonate	5.70	6.90	4.10	6.60	5.90	4.60	6.50	6.40	4.30	8.40	6.40	6.20	8.80	4.80	5.20
Carbonate	3.30	1.20	2.00	2.00	1.00	4.00	5.60	2.70	2.10	1.90	2.50	3.40	2.40	2.20	3.40
Chloride	0.20	2.80	3.40	4.40	2.40	2.60	11.20	0.40	4.00	3.80	0.20	0.40	1.80	11.20	0.20
Manganese	16.50	0.42	0.59	0.45	0.42	1.54	0.50	6.75	0.53	0.50	12.50	8.50	1.33	0.20	17.00
Iron <sup>3+</sup>	158.6	170.8	152.8	512.4	189.1	207.4	195.2	219.6	219.6	219.6	91.5	91.50	109.8	91.50	79.30
Sulfate	0.98	1.41	0.84	0.98	1.05	1.05	1.12	1.69	1.62	1.34	1.12	3.65	1.69	0.56	0.56
Nitrate	0.38	1.39	1.06	1.17	1.02	3.51	4.97	2.27	1.02	1.75	1.32	1.61	6.58	1.10	2.05
Cal. Hardness	0.025	0.021	0.030	0.025	0.046	0.031	0.036	0.037	0.035	0.030	0.038	0.033	0.076	0.021	0.018
Total Solid	0.004	0.008	0.017	0.017	0.017	0.008	0.017	0.004	0.008	0.017	0.017	0.017	0.021	0.00	0.004
Magnesium	0.28	1.66	1.24	0.07	0.97	0.83	0.69	0.41	0.28	0.28	0.55	0.97	0.28	0.69	0.83
Calcium	1285	994.0	1207	1030	1314	1101	1207	994.0	1243	1172	213.0	178.0	142.0	107.0	178.0
Total Hardness	316.6	231.5	277.8	327.8	285.2	301.8	275.9	288.9	283.3	281.5	42.60	292.0	153.7	22.22	59.26
Potassium	24.41	20.79	23.50	22.15	23.05	25.31	19.44	19.89	26.22	20.34	10.40	20.79	16.72	7.23	12.20
Chlorine	25.65	20.04	22.44	22.44	25.65	21.64	20.04	18.44	24.05	19.24	7.21	16.83	8.02	4.01	3.21
Sodium	64.17	50.55	62.71	58.82	52.01	67.57	58.33	59.3	69.03	65.14	1.94	53.47	19.93	0.97	1.94
E.Coli	0.07	0.03	0.07	0.10	0.08	0.14	0.07	0.11	0.19	0.06	0.02	0.05	0.06	0.01	0.02
Total Coliform	0.01	0.01	0.01	0.04	0.01	0.02	0.01	0.04	0.03	0.01	0.01	0.01	0.01	0.01	0.01

 Table 4.9c: Results of surface water analysis for location 29 to location 43 in Eastern Niger Delta

Parameters	Soil (mg/kg)		Surface Water (mg/l)			
	Range Mean		Range	Mean		
pН	3.17-7.12	5.20	5.32-7.30	6.10		
Temp. (°C)	28.00-30.00	29.20	25.00-30.60	28.50		
TDS	10.80-78.50	46.50	484.00-1524.00	1340.20		
Conduct.(µs/cm)	17.00-187.00	120.70	28.00-2950.00	1410.00		
Na	146.30-398.10	265.60	22.32-328.60	230.40		
Ca	48.50-98.00	72.40	3.21-125.65	78.45		
Mg	8.60-110.80	48.60	0.98–168.34	82.18		
Κ	85.68-842.24	535.80	7.23–46.20	25.484		
PO <sub>4</sub>	2.46-97.66	39.28	5.60-68.00	31.04		
$SO_4$	0.25-35.00	17.84	1.70-86.25	41.25		
NO <sub>3</sub>	0.35-652.55	243.72	0.80-125.30	42.80		
Cl	24.00-400.00	160.50	107.00-1315.00	816.80		
Fe	20.33-252.72	232.40	0.01-2.46	0.92		
Mn	0.42 - 108.00	21.25	0.01 - 0.08	0.05		
Zn	1.62-20.94	10.98	0.02 - 0.80	0.45		
Cu	1.46-15.30	9.70	0.03-1.28	0.82		
Cr	0.06-1.86	0.88	0.02–0.14	0.76		
Cd	1.08-24.58	10.76	0.07-0.20	0.13		
Ni	0.50-18.24	11.62	0.01-0.15	0.82		
V	0.44-20.56	12.58	0.005-0.018	0.011		
Pb	0.32-1.86	0.78	0.01-0.14	0.06		
Hg	0.03-0.07	0.05	0.002-0.005	0.003		
As	0.01-0.07	0.03	0.001 - 0.004	0.002		
TOC	15.10-84.65	43.30	0.10-2.40	1.70		
THC	2.98-39.80	14.18	0.68-5.24	1.06		
BOD	1.56-38.90	17.64	1.00-5.80	3.78		
COD	4.25-51.05.	23.96	0.20-11.20	4.94		
TBC	$1.0 \times 10^{2} - 6.0 \times 10^{5}$	$2.5 \times 10^3$	0.00-715.00	60.00		

 Table 4.10: Statistical Summary of analyzed Soil and Surface Water parameters from

**Eastern Niger Delta** 

Total Bacteria Count: Soil (cfu/g), Water (cfu/l); THC- total hydrocarbon content; TOC- total organic carbon; BOD- biochemical oxygen demand; COD- chemical oxygen Demand

# **4.7.2.1 Physical Parameters**

#### pН

pH of aquatic systems is an indicator of the water quality and extent of pollution. The pH of a water body generally influences the fish population, the optimum value for fish growth ranged from 6.7 to 8.6 (Parker and Corbit, 1992; Yisa, 2002). Only small species of fishes are known to survive outside this range (Figure 4.10). Unpolluted rivers/streams show a near neutral or slightly alkaline pH. The pH of the surface water ranged between 5.32 to 7.30 with a mean value of 6.10 (Table 4.10). The pH values show acidic condition and may be attributed to the dumping of industrial and domestic wastes into the river system.

# Temperature

It is a measure of the degree/extent of hotness or coldness of a medium and it effects the various reactions that take place in the water body. It brings about reduction in solubility of gases and amplification of tastes and odours of water. The temperature values ranged from 25.00 to 30.60 °C and a mean temperature of 28.50 °C (Table 4.10). Water temperature is also a crucial aspect of aquatic habitat, as aquatic organisms are adapted to live within a certain temperature range. As the upper and lower temperature limits are approached, the organism becomes more susceptible to diseases. Also, fish that spend extra energy searching for cool areas may be at a disadvantage when competing for food (EPA, 1991).

рН	PH 6.5	<b>PH 6</b> .0	PH 5.5	PH 5.0	PH 4.5	PH 4.0
TROUT						
BASS						
PERCH						
FROGS						
SALAMANDERS						
CLAMS						
CRAYFISH						
SNAILS						
MAYFLY						

Figure 4.10: Correlation between survival of aquatic life and pH values

## **Total Dissolved Solids**

It is an indication of the general nature of water quality or salinity. Water samples containing more than 500 mg/l of TDS is considered undesirable for domestic use but unavoidable cases of 1500 mg/l is also allowed (WHO, 2006). In the present investigation (Figure 4.10), the TDS values varied from 484.00 to 1524.00 mg/l with a mean value of 1340.00 mg/l. The high TDS values may be a reflection of anthropogenic interference with the surface water body and an indicator of pollution. These solids can reduce visibility, making it difficult for fish to prey. It can also clog the gills of fish and suffocate macro invertebrates. Seawater intrusion may also be responsible for the high TDS values in the surface water.

# **Electrical Conductivity**

The electrical conductivity is a valuable indicator of the amount of material dissolved in water. Its value ranged between 20.00 and 2950  $\mu$ s/cm with an average value of 1410.00  $\mu$ s/cm (Table 4.10). The wide range of TDS and EC is a testimony that there are substantial differences in the quality/composition of the surface water within the study area.

# **4.7.2.2 Bacteriological Parameters**

The bacteriological analyses result in Table 4.10 shows high bacteria count (total coliform) in the surface water in the range of 0.00 to 715.00 cfu/l with a mean value 60.00 cfu/l. This is an indication of urban water pollution which may be attributed to faecal contamination arising from animal and human faeces being in contact with surface water. Studies have revealed that water pollution through faecal contamination is responsible for most water borne diseases such as meningitis, cholera and diarrhea as well as morbidity and mortality

among children (Adekeye and Ishaku, 2004; Olasehinde and Amadi, 2009). It also causes acute renal failure and haemolytic anaemia in adults (WHO, 1998).

#### **4.7.2.3 Chemical Parameters**

# Chloride

The concentration of chloride ranged between 107.00 and 1315.00 mg/l with a mean value of 818.80 mg/l. The values by far exceed the maximum permissible limit of 250 mg/l (WHO, 2006). Seawater encroachment into the river system may be responsible for the high chloride concentration. High chloride values may not constitute health hazard to human beings, but it does produce salty taste, corrode metal pipes and harm non-halophytic plants (Lawal, Adewoye and Singh, 1986).

# Sulphide

The sulphide level in the surface water ranged between 1.70 and 86.25 mg/l with an average value of 41.25 mg/l (Table 4.10). The sulphide concentration is within the acceptable limits of 100.00 mg/l (NSDWQ, 2007). High concentration of sulphide can cause high fish mortality (Steven, 1983).

# **Biochemical Oxygen Demand (BOD)**

The BOD test determines the relative oxygen necessary for biological oxidation of waste waters, effluents and polluted waters. It is the only test available to determine the amount of oxygen required by bacterial while stabilizing decomposable organic matter. Biochemical oxygen demand (BOD) measures the biodegradable organic carbon and, under certain conditions, the oxidizable nitrogen present in a water sample. The study of BOD gives an idea of the oxidizable matter actually present in a water sample and this allows pollution

load evaluation to be established. The BOD values ranged from 1.00 to 5.80 mg/l with a mean value of 3.78 mg/l (Table 4.10). These values are within the health limits of World Health Organization.

#### **Chemical Oxygen Demand (COD)**

The chemical oxygen demand provides a measure of the oxygen equivalent of the portion of organic matter in a sample that is susceptible to oxidation by strong chemical oxidant. It determines the quantity of oxygen required for the oxidation of the inorganic and organic matter in a water sample under controlled condition of oxidizing, temperature and time. Chemical oxygen demand (COD) test measures the total organic carbon, with the exception of certain aromatics such as benzene, which are not completely oxidized in the reaction. Values of COD in the rivers varied between 0.20 and 11.20 mg/l with an average value of 4.94 mg/l (Table 4.10). The BOD and COD measure the water oxygen available for aquatic organisms.

# **Total Hydrocarbon Content (THC)**

The concentration of total hydrocarbon content (THC) in the surface water ranged between 0.10 and 2.40 mg/l with a mean value of 1.70 mg/l (Table 4.10). These values are higher than recommended maximum permissible value of 0.01 mg/l by Federal Ministry of Environment/Department of Petroleum Resources/World Health Organization.

# **Total Organic Carbon (TOC)**

The concentration of total organic carbon (TOC) varied from 0.68 and 5.24 mg/l with an average value of 1.06 mg/l as against the 5.0 mg/l maximum permissible limit recommended by Nigerian Standard for Drinking water Quality. Studies have shown that

high concentration of both THC and TOC are carcinogenic and an indication of water contamination by hydrocarbon.

# Sodium

Studies have shown a direct relationship between hypertension and high sodium level in drinking water. The noxious effects of sodium on blood vessels have also been observed (Meyer, 1983). The concentration of sodium varied from 22.32 and 328.60 mg/l with a mean value of 230.40 mg/l (Table 4.10). These values in some locations exceed the permissible limit of 250 mg/l by (WHO, 2006). Seawater intrusion might also be responsible the high concentration of sodium in the surface water.

# Calcium

Calcium ion content in the surface water ranged between 3.21 and 125.65 mg/l with a mean value of 78.45 mg/l (Table 4.10). This values falls within the allowable limits for a potable water. Calcium is needed by the body for good bone development.

# Magnesium

Magnesium in water is better absorbed than dietary magnesium. Epidemiological data in man and experimental data in rats have demonstrated that the intake of water containing sufficient amount of magnesium may prevent arterial hypertension and nervous disturbances (Durlach, Bara and Guiet-Bura, 2008). Magnesium concentration ranged from 0.98 and 168.34 mg/l with an average value of 82.18 mg/l (Table 4.10). These values are within the acceptable limits for a safe drinking water.

# Iron

The concentration of iron varied from 0.01 and 2.46 mg/l with a mean concentration of 0.92 mg/l as against the acceptable value of 0.30 mg/l by World Health Organization. The implication of the high iron content is that the water from the river may have taste, colour and other aesthetic problems such as hemochromatosis.

# Lead

The value of lead in surface water ranged between 0.01 and 0.14 mg/l with a mean value of 0.06 mg/l as against the permissible value of 0.01 mg/l (NSDWQ, 2007). Lead is potentially hazardous to most form of life and is considered toxic to organisms. Low lead concentration can affect fish by causing the formation of coagulated mucous over the gills and subsequently over the entire body and thus cause the death of fish due to suffocation. Lead is bio-accumulated by benthic foraminifera, freshwater plants, invertebrates and fish. The chronic effect of lead on man includes neurological disorders, especially in the foetus and in children, synthesis of hemoglobin, gastrointestinal tract, kidney diseases and impaired performance in IQ test. Lead is however used in batteries, petrol additives, alloys, cable sheathing, pigments, rolled and extruded products.

# Copper

Copper is an essential substance to human life, but in high concentration, it can cause anemia, liver and kidney damage, stomach and intestinal irritation. The concentration level for copper in the surface water ranged from 0.03 to 1.28 mg/l with an average value of 0.82 mg/l (Table 4.10). Copper normally occurs in drinking water from copper pipes, weathering of products made from copper as well as from additives used to control weed.

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# Zinc

Zinc concentration ranged from 0.02 to 0.80 mg/l and an average value of 0.45 mg/l (Table 4.10). High zinc concentration could be a problem in aquatic ecosystem. Zinc is unusual in that it has low toxicity to man, but relatively high toxicity in fish or livestock watering.

# Manganese

The concentration of manganese ranged 0.01 to 0.08 mg/l with a mean value of 0.05 mg/l (Table 4.10). High manganese concentration causes respiratory and neurological disorder in man.

# 4.7.3 Piper Diagram

This method was devised by Piper in 1944 to outline certain fundamental principles in a graphic procedure which appears to be an effective tool in interpreting analytical data for critical study with respect to sources of the dissolved constituents in water. The concentration of 8 major ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sup>-</sup><sub>3</sub> and SO<sub>4</sub><sup>2-</sup>) are represented on a trilinear diagram by grouping the K<sup>+</sup> with Na<sup>+</sup> and the CO<sub>3</sub><sup>2-</sup> with HCO<sup>-</sup><sub>3</sub>, thus reducing the number of parameters for plotting to 6. On the Piper diagram, the relative concentration of the cations and anions were plotted in the lower triangles, and the resulting two points are extended into the central field to represent the total ion concentrations. The degree of mixing between freshwater and saltwater can also be shown on the Piper diagram. The Piper diagram (Figure 4.11) was also used to classify the hydrochemical facies of the groundwater samples according to their dominant ions. The groundwater in the area is majorly Na-Cl-facies, followed by Ca-Mg-HCO<sub>3</sub>-facies in their order of dominance
respectively. This implies that the water in the area has some marine interference and the aquifer stained with iron.



Figure 4.11: Piper Diagram for Eastern Niger Delta, Nigeria

#### 4.7.4 Durov-Diagrams

Durov diagram was another means of categorizing the hydrochemical facies of both surface and groundwater. The Durov diagram plots the major ions as percentages of milliequivalents in two base triangles. The total cations and the total anions are set equal to 100% and the data points in the two triangles are projected onto a square grid which lies perpendicular to the third axis in each triangle. This plot reveals useful properties and relationships for large sample groups. The Durov diagram (Fig.4.12) shows clustering of data points and this indicate samples that have similar compositions. The clustering of the data points concentrated around the Na+K/Cl region indicating possible marine origin. The hydrochemical facies identified are: Na-Cl-facies, Ca-Mg- HCO<sub>3</sub>-facies, Mg-Ca- SO<sub>4</sub>facies, Ca-Mg-Cl-facies, Na-Fe-Cl-facies and Na-Fe-Cl-NO<sub>3</sub>-facies.



Figure 4.12: Durov diagram for Eastern Niger Delta, Nigeria

# 4.7.5 Schoeller-Plots

These semi-logarithmic diagrams were developed to represent major ion analyses in meq/l and to demonstrate different hydrochemical water types on the same diagram (Figure 4.13). This type of graphical representation has the advantage that, unlike the trilinear diagrams of both Piper and Durov, actual sample concentrations are displayed and compared. In addition to the major cations and anions, other parameters such as nitrate, iron and nickel whose concentration appreciably high were used in the classification.



Figure 4.13: Schoeller-Plot for Eastern Niger Delta, Nigeria

#### 4.7.6 Factor Analysis/Principal Component Analysis

The factor analysis (FA) and principal component analysis (PCA) have emerged as a useful tool for better understanding of the relationship among variables and for revealing groups (or clusters) that are mutually correlated within a data body (Amadi *et al.*, 2010). The correlation pattern between the different physical, chemical and bacteriological properties and the sampling sites were evaluated using factor/principal analysis. As could be seen in Table 4.11, factors explaining variance percentage lower than 6.08 percent have been rejected, aiming at interpreting the significance of the factors in an easier way. FA/PCA (raw matrix rotated) on the same standardized data were used with eigenvalues higher than one to generate six varifactors, accounting for 90.70 percent of the total variance.

**Factor-1** has the highest loading of 29.16% and the contributors include conductivity, total dissolved solid (TDS), electrical conductivity (EC), chloride, calcium, magnesium, total hardness (TH), sodium and salinity. These factors can be associated with the seawater intrusion which leached into the aquifer system, increasing the concentrations of these ions by its percolation and longer residence time. High tides and uncontrolled groundwater abstraction are the main factors that induce the infiltration of saltwater into the aquiferous zone.

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Arsenic	0.345	0.325	0.211	0.080	0.258	0.581
BOD	0.123	0.234	0.680	0.406	0.321	0.231
Bicarbonate	0.086	0.605	0.234	0.278	0.205	0.245
Cadmium	0.231	0.121	0.023	0.298	0.623	0.329
Calcium	0.789	0.458	0.219	0.308	0.067	0.244
Cobalt	0.141	0.010	0.377	0.074	0.148	0.511
Chloride	0.985	0.723	0.241	0.329	0.401	0.310
Chromium	0.235	0.333	0.219	0.102	0.644	0.090
COD	0.317	0.283	0.508	0.321	0.157	0.049
Copper	0.215	0.104	0.210	0.765	0.593	0.301
E.Cond. (µs/cm)	0.843	0.187	0.091	0.207	0.412	0.214
E.Coli (cfu/100ml)	0.156	0.309	0.792	0.214	0.321	0.109
Fluoride	0.200	0.098	0.190	0.526	0.239	0.198
T. Hardness	0.890	0.120	0.234	0.245	0.234	0.206
Iron	0.128	0.844	0.118	0.648	0.276	0.234
Lead	0.321	0.232	0.380	0.124	0.178	0.598
Mercury	0.139	0.081	0.212	0.005	0.080	0.506
Magnesium	0.612	0.219	0.204	0.112	0.198	0.256
Manganese	0.097	0.125	0.102	0.688	0.027	0.294
Nickel	0.129	0.183	0.310	0.129	0.623	0.023
Nitrate	0.218	0.390	0.588	0.213	0.069	0.216
pH	0.393	0.768	0.342	0.147	0.216	0.143
Phosphate	0.107	0.352	0.701	0.218	0.231	0.389
Potassium	0.315	0.576	0.215	0.109	0.068	0.291
Salinity	0.955	0.266	0.012	0.234	0.219	0.278
Silica	0.236	0.762	0.324	0.250	0.135	0.289
Sodium	0.928	0.215	0.248	0.235	0.089	0.215
Strontium	0.263	0.233	0.213	0.290	0.045	0.503
Sulphate	0.247	0.611	0.356	0.213	0.066	0.156
TDS	0.861	0.257	0.120	0.276	0.045	0.207
Temp.(°C)	0.312	0.089	0.621	0.258	0.071	0.135
TSS	0.234	0.619	0.126	0.223	0.009	0.087
T. Coli (cfu/ml)	0.109	0.103	0.625	0.412	0.224	0.231
Zinc	0.387	0.312	0.023	0.634	0.129	0.079
Eigenvalue	6.123	3.870	3.178	2.229	1.738	1.276
% of Variance	29.16	20.43	15.14	11.61	8.28	6.08
Cumulative %	29.16	49.59	64.73	76.34	84.62	90.70

 Table 4.11: Factor Analysis of Groundwater from Eastern Niger Delta

BOD-biochemical oxygen demand; COD-chemical oxygen demand; TC-total coliform;

E.Cond-Electrical Conductivity; EC-Escherichia coli; TSS-total suspended solid

**Factor-2** explains 20.43% and includes pH, silica, bicarbonate, chloride, iron, potassium, sulphate and total suspended solid (TSS). The TSS may be as a result of the partial dissolution of these ions (bicarbonate, chloride, iron, silica, potassium and sulphate) in the water either through natural means such as chemical weathering in the course of groundwater movement or anthropogenic interference and the processes are enhanced by a low pH condition. The iron content in the marcasite from the underlying shale and coal horizon of the Ogwashi-Asaba Formation is mobilized and leached into the shallow water table due to the porous and permeable nature of the aquiferous layer. Excessive iron in the body does not present any health hazard, only the turbidity, taste and appearance of the drinking water will usually be affected.

**Factor-3** has a high loading for temperature, biochemical oxygen demand (BOD), chemical oxygen demand (COD), E.coli, phosphate, nitrate and total coliform (TC) and it accounts for 15.14% of the total variance (Table 4.11). These may be attributed to urban groundwater pollution arising from faecal contamination (E.coli and TC), fertilizer application (nitrate and phosphate), oil spillage (BOD and COD) and gas flaring (temperature). The rate of dissolution of BOD, COD, E.coli, TC, phosphate and nitrate are temperature dependent. The poor sanitary situation in the area is responsible for the high E.coli and total coliform content in the water, as majority of the pit-latrine and soakaway in the area are unlined and poorly sited. After excretion, the faeces find their route into the shallow water-table. Also, due to lack of space, most private boreholes are sited close to the toilet system (pit-latrine and soakaway). During pumping of the well, water is discharged and the recharging water may be accompanied by plume from the nearby toilet system. Rampant oil spill occurrence in the area has depleted the oxygen content in the soil and

rivers/streams and this has contributed significantly to the death of wild and aquatic lives. Gas flaring has led to increase in temperature of the area as well as release of gases that have devastated the environment and health of the people in the area.

**Factor-4** accounts for 11.61% of the total variance (Table 4.11) with copper, fluoride, iron, manganese and zinc as the contributing factor. They are used in electroplating, alloys, roofing, cooking utensils, coins and paint manufacture (Pascual, Gold-Bouchot, Ceja-Moreno, del Ri'o-garc'a, 2004). Their enrichment in the groundwater may be related to the various activities taking place in the area as well as decomposition and leaching of materials that contain these metals. It could also arise from the impacts of oil spills, gas flaring and decomposition of drilling wastes. Iron could also come from leaching of the thick lateritic overburden via chemical weathering.

**Factor-5** has a moderate loading of 8.28% of the total variance (Table 4.11) and is attributed to cadmium, chromium, copper and nickel. These metals are raw material used in making alloys, batteries, electronics, plastics, glass and electrical wiring (Gorenc, Kostaschuk and Chen, 2004). When these products are damaged, they are discarded and during decomposition processes, these metals are leached away and they may finally come in contact with the aquifer system. They may also be attributed to oil spills and gas flaring activities taking place in the area as well as through indiscriminately dumped drilling wastes in the area.

**Factor-6** has the lowest loading of 6.08% with arsenic, cobalt, lead and mercury. These metals are carcinogenic at low concentration (Aboud and Nandini, 2009) and their presence

may be due to the discharge of industrial effluent from the industries domiciled in the area as well as gas flaring and oil spill activities in the area.

It is worthy of note that the masking (shielding) effect of chemically similar elements such as  $(Na^+ + K^+)$  and  $(HCO_3^- + CO_3^-)$  as obtained in Piper, Durov and Schoeller has been avoided by the use of these geostatistical techniques (principal component analysis, factor analysis, water quality index, metal pollution index, DRASTICA index, contamination factor and geo-accumulation index in this study. Also, physical and bacteriological parameters as well as heavy metals that were not part of facies classification in Piper diagram and others are now used in the geostatistical techniques thereby giving a comprehensive and precise reflection of the concentration/contribution of each parameter in the aquifer/groundwater pollution.

#### **4.7.6.1 Scree-plot and Factor Score Diagram**

The screen-plot is a graph of eigenvalues versus magnitude. It shows a distinct break between the steepness of the high eigenvalues and the gradual trailing off of the rest of the factors (Figure 4.14). In the present study, the 6 factors extracted (eigenvalues > 1) represent adequately the overall dimensionality of the data set and accounted for 90.70 % of the total variance, while the remaining 12 factors (eigenvalues < 1) accounted for only 9.30 % of the total variance.

Similarly, the high communalities indicate that most of the variance of each variable is explained by the extracted factors. Loadings (< 0.500) have negligible impact or effect in respect to groundwater contamination in the area and were therefore omitted from Table 4.8. Similarly, the factor scores accounted for the six extracted factors with (eigenvalues >

1) and factor loading (> 0.500), contributing about 90.70 % of the total pollution in the area. This procedure reduces overall dimensionality of the linearly correlated data by using a smaller number of new independent variables called varifactor, each of which is a linear combination of originally correlated variables (Figure 4.15.). The FA/PCA reduces the dataset into six major components representing the different sources of the contaminant. The usefulness of FA/PCA in interpreting the hydrogeochemical data as well as identifying and categorizing pollutants has been demonstrated in this study.



Figure: 4.14: Scree-plot of PCA/FA



Figure: 4.15: Factor Score diagram

# **4.7.7 Water Quality Index**

In addition to FA/PCA, water quality index (WQI) of the studied groundwater samples was performed in order to get an overall impression about the samples in a multidimensional space defined by the analyzed parameters. The water quality index (WQI) was calculated from the point view of suitability of the water for human consumption by using the weighted arithmetic index method. The quality rating scale for each parameter  $q_i$  was calculated by using this expression:

$$q_i = (C_i / S_i) \times 100$$

A quality rating scale  $(q_i)$  for each parameter is assigned by dividing its concentration  $(C_i)$ in each water sample by its respective Nigerian Standard for Drinking Water Quality  $(S_i)$ and the result multiplied by 100. The Relative weight  $(w_i)$  was obtained by a value inversely proportional to the recommended standard  $(S_i)$  of the corresponding parameter: The overall Water Quality Index (WQI) was calculated by aggregating the quality rating (q<sub>i</sub>) with unit weight (w<sub>i</sub>) linearly.

$$i = n$$
  
WQI = ( $\Sigma q_i w_i$ )

n = 1

Where:

q<sub>i</sub>: the quality of the ith parameter,

w<sub>i</sub>: the unit weight of the ith parameter and

n: the number of the parameter considered.

The overall water quality of an area is therefore obtained using the formular:

Overall WQI = 
$$\frac{\sum q_i w_i}{\sum w_i}$$

The physico-chemical and bacteriological parameters analyzed were used to calculate the WQI in accordance with the procedures explained above and contained in Table 4.12. The computed overall WQI value was 285.20 and this means that the groundwater in the area falls within the 'very poor quality' as illustrated in Table 4.13.

Overall WQI = 
$$\frac{\sum q_i w_i}{\sum w_i} = \frac{460442.528 = 285.20}{1614.45}$$

The high value of WQI obtained may be as a result of the high concentration of salinity, TDS, TH, EC, COD, nitrate, copper, iron, nickel, zinc, lead, chromium and coliform bacteria in the groundwater can be attributed to anthropogenic sources through the various human activities such as oil spill, gas flaring and indiscriminate dumping of waste in the area.

Parameters (mg/l)	Ci	Si	qi	Wi	qiWi
Arsenic	0.007	0.010	70.000	100.000	7000.000
BOD	5.600	6.000	93.333	0.167	15.587
Calcium	46.530	200.000	3.265	0.005	0.016
Chloride	175.200	250.000	64.480	0.004	0.258
Chromium	0.070	0.050	140.000	20.000	2800.000
Copper	0.080	1.000	8.000	1.000	8.000
Conductivity(µs/cm)	254.000	1000.000	25.138	0.001	0.025
COD	10.600	10.000	106.00	0.100	10.600
E.Coli (cfu/100ml)	22.000	0.000	0.000	0.000	0.000
Fluoride	0.850	1.500	56.667	0.667	37.797
Total Hardness	54.310	200.000	17.155	0.005	0.086
Iron	0.620	0.300	18.600	3.333	61.994
Lead	0.080	0.010	800.000	100.000	80000.000
Magnesium	33.160	150.000	2.107	0.007	0.015
Manganese	0.190	0.200	95.000	5.000	475.000
Mercury	0.003	0.001	300.000	1000.000	300000.000
Nickel	0.280	0.020	1400.000	50.000	70000.000
Nitrate	17.820	50.000	25.540	0.020	0.511
рН	5.460	6.500-8.500	82.267	0.133	10.942
Phosphate	10.290	5.000	5.800	0.200	1.160
Potassium	20.470	100.000	0.470	0.010	0.005
Sodium	61.590	200.000	0.795	0.005	0.004
Sulphate	98.620	100.000	69.980	0.010	0.699
TDS	155.000	500.000	29.098	0.002	0.058
T. Coli (cfu/ml)	15.000	10.000	120.000	0.100	12.000
TSS	14.600	500.000	0.926	0.002	0.002
Zinc	0.700	3.000	23.333	0.333	7.769

 Table 4.12: Computed WQI values for Eastern Niger Delta

BOD-biochemical oxygen demand; COD-chemical oxygen demand;

TC-total coliform; EC-Escherichia coli; TSS-total suspended solid

WQI value	Water quality	Water samples (%)	
<50	Excellent	09	
50-100	Good water	16	
100-200	Poor water	24	
200-300	Very poor water	31	
>300	Unsuitable for drinking	20	

 Table 4.13: Water Quality Classification Based on WQI Value

# 4.7.8 Metal Pollution Index

Heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. These metals cannot be degraded or destroyed and can enter our bodies through food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation is an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment.

Metal pollution index (MPI) is a method of rating that shows the composite influence of individual parameters on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance individual quality considerations. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the water (Amadi, 2011). It is also a combined physio-chemical and microbial index which makes it possible to compare the water quality of various water bodies (Tamasi and Cini, 2004; Prasad and Kumari, 2008). It has wide application and it is used as the indicator of the quality of sea (Filatov. *et al.*, 2005) and river water (Amadi, Olasehinde, Yisa, Okosun, Nwankwoala and Alkali, 2012a; Lylko *et al.*, 2001; Mohan *et al.*, 1996), as

well as drinking water (Nikoladis *et al.*, 2008; Amadi *et al.*, 2010). The MPI represents the sum of the ratio between the analyzed parameters and their corresponding national standard values as shown in Table 4.14 below:

$$MPI = \sum_{i=1}^{n} \left[ \frac{Ci}{(MAC)i} \right]$$

where:  $C_i$ : mean concentration

MAC: maximum allowable concentration

Water quality and its suitability for drinking purpose can be examined by determining the metal pollution index.

Parameters (mg/l)	Ci	MACi	MPI Value	Rating
Arsenic	0.007	0.01	0.70	Lightly polluted
Cadmium	0.11	0.02	5.50	Highly polluted
Cobalt	0.02	0.01	2.00	Moderately polluted
Chromium	0.07	0.05	1.40	Moderately polluted
Copper	0.8	1.00	1.90	Moderately polluted
Iron	0.62	0.30	2.10	Moderately polluted
Lead	0.08	0.01	8.00	Highly polluted
Manganese	0.19	0.20	0.95	Lightly polluted
Mercury	0.003	0.001	3.00	Moderately polluted
Nickel	0.28	0.02	14.00	Very highly polluted
Zinc	0.17	3.00	1.57	Moderately polluted

 Table 4.14: Calculated Metal Pollution Index for the Groundwater Samples

< 0.01= Very lightly polluted; 0.01-1.0= Lightly polluted; 1.0-5.0= Moderately polluted;

5.0-10.0 = Highly polluted; > 10.0 = Very highly polluted

# 4.7.9 Soil

Soil quality determines the sustainability and productivity of agro-ecosystems. The soils of the area are largely defined by their acidity (pH 3.17 - 7.12). The acidity is partly natural, being a characteristic of the soils of Sombriero–Deltaic sediment and partly anthropogenic due to prolonged effect of gas flaring in the region. The low nutritional status (organic matter content) of the soils with mean value of 5.20 (Table 4.10) is an important constraint on the capacity of the soils for agricultural use, hence the use of agro-chemical. The concentration of total hydrocarbon concentrations (THC), oil and grease, and heavy metal contents were found to be relatively high attributed to an oil spillage in the area. The excessive use of agro-chemical in intensive agriculture has led to the enrichment of soil in the area with heavy metal which has reduced the soil cohesiveness leading to an increase of erosion. Their enrichment is a function of soil pH, grain size, organic matter, cation exchange capacity (CEC) and hydraulic conductivity (Nachtergaele et al., 2002). The results of laboratory analysis of heavy metals in the soil and sieve analysis are illustrated in Table 4.15 while the statistical summary of the physico-chemical and bacteriological characteristics of the soil are contained in Table 4.10.

Location	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	L-9	L-10	L-11	L-12
Fe (mg/kg)	86.51	116.01	154.99	72.09	205.19	212.27	96.92	20.33	224.95	225.08	228.29	230.00
Mn (mg/kg)	0.87	3.68	2.81	4.76	2.17	4.29	4.11	2.17	1.73	0.43	1.95	1.96
Zn (mg/kg)	8.50	12.42	7.85	4.58	3.92	5.23	14.38	2.62	3.27	7.19	3.92	3.95
Cu (mg/kg)	10.35	9.78	10.21	9.49	10.11	11.59	9.94	10.01	9.70	12.38	10.90	10.90
Cr (mg/kg)	0.14	0.23	0.26	0.16	0.40	0.37	0.11	0.52	0.44	0.40	0.50	0.45
Cd (mg/kg)	1.84	1.98	4.57	1.87	3.42	3.50	3.61	2.53	2.08	3.60	3.38	3.32
Ni (mg/kg)	4.24	1.50	1.34	0.86	1.77	2.74	2.08	1.13	0.97	2.04	3.76	2.94
V (mg/kg)	0.88	20.40	1.40	1.00	1.60	0.92	0.96	2.00	0.76	2.04	0.64	0.68
Pb (mg/kg)	0.44	0.48	0.42	0.34	0.88	0.59	0.95	0.89	0.64	0.83	0.74	0.72
Hg (mg/kg)	0.05	0.04	0.07	0.04	0.04	0.04	0.06	0.03	0.05	0.03	0.04	0.04
THC (mg/kg)	0.80	0.50	0.60	14.30	0.80	1.90	1.00	0.70	0.90	50.50	11.40	10.00
% Clay	3.60	10.00	3.10	4.10	13.60	11.60	2.00	3.10	3.10	20.10	18.60	18.50
% Silt	4.40	3.00	2.40	4.90	8.40	7.40	1.00	0.40	0.90	10.90	12.90	13.40
% Sand	92.00	87.00	94.50	91.00	78.00	81.00	97.00	96.50	96.00	69.00	68.50	68.10

 Table 4.15a: Chemical and sieve analysis of soil samples for location 1 to location 12 in Eastern Niger Delta

Location	L-13	L-14	L-15	L-16	L-17	L-18	L-19	L-20	L-21	L-22	L-23	L-24
Fe (mg/kg)	226.42	206.26	213.33	252.72	201.18	233.76	196.38	236.80	207.33	217.07	204.79	230.02
Mn (mg/kg)	1.95	2.81	1.30	1.52	1.73	1.30	5.85	1.08	1.73	0.43	2.38	2.17
Zn (mg/kg)	6.45	8.50	7.19	5.88	5.23	4.58	6.54	6.54	20.92	10.46	11.77	17.00
Cu (mg/kg)	10.76	11.09	10.25	10.87	10.08	10.44	10.54	11.25	10.87	10.47	13.15	11.38
Cr (mg/kg)	0.38	0.40	0.34	0.48	0.47	0.34	0.36	0.27	0.47	0.41	0.85	0.37
Cd (mg/kg)	3.51	4.14	3.51	3.35	2.35	1.36	1.67	1.87	2.75	1.93	2.86	2.35
Ni (mg/kg)	1.56	2.15	2.31	1.99	2.58	2.09	1.77	2.58	2.20	2.25	2.90	2.09
V (mg/kg)	0.56	0.64	1.24	0.90	1.32	2.24	1.56	0.92	1.04	2.04	0.80	0.76
Pb (mg/kg)	0.65	0.69	0.80	0.94	1.11	0.84	0.58	0.85	1.76	0.78	0.89	0.77
Hg (mg/kg)	0.04	0.05	0.04	0.04	0.06	0.04	0.04	0.05	0.05	0.04	0.05	0.06
THC (mg/kg)	1.00	35.30	23.80	35.30	5.70	31.40	18.10	20.70	16.20	29.50	8.60	20.00
% Clay	18.10	2.00	0.00	16.60	20.60	22.60	21.60	23.60	17.10	23.10	22.60	21.10
% Silt	9.90	8.00	0.00	14.40	11.90	9.40	10.90	9.40	12.90	8.90	10.40	10.40
% Sand	72.00	90.00	100.00	69.00	67.50	68.00	67.50	67.00	70.00	68.00	67.00	68.50

 Table 4.15b: Chemical and sieve analysis of soil samples for location 13 to location 24 in Eastern Niger Delta

Location	L-25	L-26	L-27	L-28	L-29	L-30	L-31	L-32	L-33	L-34	L-35	L-36
Fe (mg/kg)	194.91	250.98	193.04	184.23	249.78	231.09	214.29	197.31	207.46	165.27	201.32	240.70
Mn (mg/kg)	1.95	2.17	3.46	0.87	1.08	1.02	1.08	0.87	1.02	6.50	3.46	1.30
Zn (mg/kg)	12.08	9.81	3.92	6.54	5.23	9.81	7.10	4.58	6.54	3.96	7.19	5.88
Cu (mg/kg)	11.66	11.71	10.64	10.09	10.54	10.30	10.76	10.18	10.68	10.68	10.30	11.63
Cr (mg/kg)	0.40	0.42	0.34	0.34	0.45	0.42	0.48	0.37	0.06	0.25	0.56	0.52
Cd (mg/kg)	2.41	3.15	2.33	2.32	2.32	2.26	3.70	4.58	1.08	4.05	1.75	1.88
Ni (mg/kg)	2.20	2.58	1.34	1.61	1.61	1.50	1.29	2.25	1.83	1.50	0.97	2.63
V (mg/kg)	0.56	0.44	0.72	0.64	0.96	0.96	1.12	0.68	1.20	2.28	2.72	0.84
Pb (mg/kg)	0.63	0.71	0.64	0.62	0.96	0.64	0.72	0.60	0.71	0.62	0.67	0.93
Hg (mg/kg)	0.03	0.04	0.04	0.04	0.04	0.03	0.05	0.07	0.05	0.05	0.06	0.04
THC(mg/kg)	8.60	57.20	28.60	0.08	3.80	0.60	0.70	0.50	25.70	0.60	57.20	41.00
% Clay	21.60	22.60	21.10	21.60	6.60	17.10	22.10	13.50	12.00	14.10	16.10	21.60
% Silt	10.90	10.40	10.40	10.40	8.40	12.90	11.40	8.50	5.50	11.40	12.90	10.90
% Sand	67.50	67.00	68.50	68.00	85.00	70.00	66.50	78.00	82.50	74.50	71.00	67.50

Table 4.15c: Chemical and sieve analysis of soil samples for location 25 to location 36 in Eastern Niger Delta

Location	L-37	L-38	L-39	L-40	L-41	L-42	L-43	L-44	L-45	L-46	L-47	L-48
Fe (mg/kg)	132.37	100.00	137.10	215.34	244.17	213.87	152.32	204.79	230.02	250.98	222.61	214.67
Mn (mg/kg)	1.73	0.65	1.95	1.02	0.43	2.17	3.03	2.38	2.17	2.17	2.71	3.03
Zn (mg/kg)	9.15	7.85	7.19	14.38	6.54	7.19	4.58	11.77	17.00	9.81	8.50	7.85
Cu (mg/kg)	9.99	10.30	10.78	9.58	10.40	10.78	9.58	13.15	11.38	11.71	12.02	13.91
Cr (mg/kg)	0.40	0.25	0.26	0.22	0.37	0.35	0.32	0.85	0.37	0.42	0.56	0.32
Cd (mg/kg)	2.59	2.89	2.79	1.98	2.39	2.57	2.61	2.86	2.35	3.15	2.59	2.08
Ni (mg/kg)	1.77	1.56	2.85	0.59	2.42	2.04	1.02	2.90	2.09	2.58	2.15	1.88
V (mg/kg)	0.44	0.96	1.40	1.64	1.32	0.72	1.04	0.80	0.76	0.44	0.64	0.72
Pb (mg/kg)	0.44	0.61	0.66	0.73	0.62	0.78	0.35	0.89	0.77	0.71	1.06	0.80
Hg (mg/kg)	0.04	0.05	0.05	0.03	0.06	0.05	0.04	0.05	0.06	0.04	0.05	0.05
THC(mg/kg)	41.00	27.60	4.80	17.20	10.50	21.00	10.60	8.60	20.00	17.20	139.10	16.20
% Clay	20.60	19.10	21.10	17.30	12.10	10.60	19.10	22.60	21.10	22.60	19.60	19.60
% Silt	11.40	11.90	11.90	13.80	11.90	11.40	11.40	10.40	10.40	10.40	6.40	10.90
% Sand	68.00	69.00	67.00	68.90	76.00	78.00	69.50	67.00	68.50	67.00	74.00	69.50

Table 4.15d: Chemical and sieve analysis of soil samples for location 37 to location 48 in Eastern Niger Delta

Location	L-49	L-50	L-51	L-52	L-53	L-54	L-55	L-56	L-57	L-58	L-59	L-60	L-61
Fe (mg/kg)	229.22	254.45	221.08	228.69	242.44	236.96	252.32	192.77	241.64	239.10	249.51	232.42	235.80
Mn (mg/kg)	2.17	1.52	1.73	2.60	1.73	2.66	2.38	3.03	1.95	2.38	6.50	4.76	3.20
Zn (mg/kg)	3.27	1.96	5.23	6.54	8.50	6.54	7.19	6.54	9.81	15.69	13.08	5.88	6.40
Cu (mg/kg)	10.07	9.49	11.04	13.19	11.97	10.95	10.52	10.73	11.14	10.56	10.44	10.95	12.50
Cr (mg/kg)	0.34	0.39	0.55	0.42	0.35	0.29	0.63	0.56	0.49	0.50	0.56	0.54	0.40
Cd (mg/kg)	3.19	1.92	2.28	1.93	3.69	2.81	3.45	3.48	2.30	1.38	1.85	2.88	0.80
Ni (mg/kg)	1.45	2.58	0.75	0.97	1.50	1.50	1.40	1.45	2.04	1.72	2.15	3.97	3.55
V (mg/kg)	2.40	0.72	5.46	0.60	1.00	0.80	0.56	0.76	1.12	0.80	0.72	1.24	0.75
Pb (mg/kg)	0.99	0.43	0.41	0.89	0.95	8.85	0.76	0.85	0.88	0.83	1.21	0.85	0.85
Hg (mg/kg)	0.07	0.03	0.05	0.30	0.05	0.05	0.04	0.06	0.04	0.06	0.05	0.04	0.31
THC (mg/kg)	49.60	25.70	800.50	801.40	801.40	72.40	74.30	0.80	40.00	0.80	18.10	7.60	50.00
% Clay	15.60	10.60	19.60	21.60	14.60	4.60	16.10	15.10	11.60	12.60	15.10	19.10	21.10
% Silt	12.90	15.40	11.90	11.40	15.90	2.40	12.40	7.90	8.40	11.40	7.90	8.90	11.50
% Sand	71.50	74.00	68.50	67.00	69.50	93.00	71.50	77.00	80.00	76.00	77.00	72.00	67.40

 Table 4.15e: Chemical and sieve analysis of soil samples for location 49 to location 61 in Eastern Niger Delta

# 4.7.9.1 Physical Parameters

# pН

The soil pH ranged from 3.17 to 7.12 with a mean value of 5.20 (Table 4.12). The pH values signify an acidic soil condition, which might be attributed to the anthropogenic activities domiciled in the area. The soil pH influences the population of soil microbes and a useful indicator of the soil quality. It also affects the rate at which plants may absorb nutrient for growth and development. Studies have shown that soil pH influences the absorption of heavy metal such as Mn, Cu, Zn, Fe and Zn by plants as well as the cation exchange capacity (CEC). Micronutrient distribution and absorption by plants was studied in coastal plain soil and plants were found to grow better in quality and quantity within a pH range of 5.5 to 7.7. Soil buffering and liming were recommended for soil with pH values less than 5.5.

#### Temperature (°C)

The soil temperature varied from 28.00 to 30.00 °C and an average temperature of 29.20 °C (Table 4.10). It is on record that biological and chemical activities in soil are an energy expression and that these processes will not continue with the right intensity unless certain temperatures are maintained. This makes the temperature of the soil a major concern for seeds to germinate and plants to grow. The soil gets its energy for normal activity from the sun and the amount of energy entering the sun is contingent largely upon the colour, the slope and vegetation cover of the soil under consideration. Dark soils absorbs more energy from the sun than light coloured soils while red or yellow soils shows rapid temperature rise than white soils. Importantly, soil temperature can effects root development, nutrient

uptake and nutrient-use efficiencies in plants by counterbalancing mechanisms for meeting nutrient requirements for plant growth in each situation.

# **Total Dissolved Solid (TDS)**

The concentration of TDS ranged between 10.80 and 78.50 mg/l with an average value 46.50 mg/l (Table 4.10). Soil characteristics in terms of porosity, permeability and composition determine the concentration of TDS in soil.

## **Electrical Conductivity (EC)**

The electrical conductivity values ranged from 17.00 to 187.00 mg/l with a mean value of 120.70 mg/l (Table 4.10). The dissolution of minerals in soil makes the soil conductive.

# **4.7.9.2 Bacteriological Parameters**

The concentration of bacteria count ranged from  $1.0 \times 10^2$  to  $6.0 \times 10^5$  cfu/g with an average value of  $2.5 \times 10^3$  cfu/g (Table 4.10). The concentrations of total heterotrophic bacteria count (THBC), petroleum degrading bacteria count (PDBC) and total coliform count (TCC) were higher in crude oil contaminated soils with crude oil than in the control soils with no oil spillage. Also, the bacteria load of THBC, PDBC and TCC were lowest in soils close to gas flaring stations and increased away from the flare stations. The high temperature emanating at gas flaring stations may be responsible for the paucity of these bacteria in the surrounding soil.

#### 4.7.9.3 Chemical Parameters

#### **Heavy Metals**

They are metallic chemical elements that have relatively high densities and are toxic or poisonous even at low concentrations. Like all other chemical elements have distinguishing physical and chemical characteristics, properties such as density, valency, redox potentials and solubility makes them unique. From an environmental standpoint, the elements can looked at terms of their toxicity and health effects (Nikoladis *et al.*, 2008). In spite of some of these elements having physiological functions in plants and animal, they have been shown to be harmful beyond certain concentrations (USEPA, 1997). For the purpose of this study, twelve of these elements (Pb, Fe, Zn, Cu, Co, Cr, Cd, Mn, Ni, As, V and Hg) have been picked and the focus of this section is to give a brief run down on the physical, chemical as well as the toxic properties of these elements.

#### Arsenic

This element strictly speaking not a metal, but exists among a group of elements called metalloids which exhibits intermediate properties. A common form of arsenic is metallicgray, with a specific gravity of 5.7. This element, which is 52<sup>nd</sup> in natural abundance in rocks/soils, undergoes sublimation at 613 °C (Khadse, *et al.*, 2008). The concentration of arsenic ranged from 0.01 to 0.07 mg/kg with a mean concentration of 0.03 mg/kg (Table 4.10). Arsenic has a crustal abundance of 5.00 mg/kg (Prasad and Kumari, 2008). Studies have shown that soils overlying sulphide deposits and those in which pesticides have been applied can have arsenic concentration of over reported to level as high as 10,000 mg/kg and 500 mg/kg respectively. Anthropogenic source of arsenic in the environment include fertilizers, especially the phosphatic types; sewage sludge from metal processing industries and to a lesser extent agrochemicals (Amadi, Olasehinde, Okosun, Okoye, Okunlola, Alkali and Dan-Hassan, 2009).

Other sources include mine spoil-tip and tailing dams, gas flaring and possible arsenic wood treatment. Arsenic is a cumulative poison. Non-allergic contact dermatitis and conjunctivitis are common results of exposure to arsenic –containing dust (Cravotta, 2008). Continued inhalation of arsenic dust can lead to the perforation of the nasal septum. Acute exposure may result in severe illness such as the fall of blood pressure to shock levels.

## Cadmium

Cadmium concentration ranged between 1.08 to 24.58 mg/kg with an average concentration of 10.76 mg/kg (Table 4.12). This metal which melts and boils at 321 °C and 765 °C respectively has a specific gravity of 8.64 (Che, He and Lin, 2003). Cadmium is a relatively rare metal and is the 67<sup>th</sup> most abundant elements in the earth crust with crustal abundance of 0.15 mg/kg and 0.1-0.5 mg/kg in soils. The result of the analyses revealed that the soil in the area is contaminated with cadmium. The widely used phosphatic fertilizers are regarded as the most ubiquitous source of cadmium contamination of agricultural soils (Lambarkis, *et al.*, 2004; Amadi, Nwakwoala, Eze, Alkali and Waziri, 2012b).

Cadmium metal is used as an anticorrosive, electroplated on steel, Cadmium sulfide and selenide are commonly used as pigments in plastics, batteries and in various electronic components. It is also used with inorganic fertilizers produced from phosphate ores and when these products are no more servisable, they are thrown into the dump as waste. During decomposition, the Cd component is leached into the surrounding soil and over time gets accumulated in the soil. Cadmium is extremely toxic and the primary use of soil high in Cd in form of manure for the cultivation of vegetables and other food crops could cause

adverse health effect to consumers such as renal disease and cancer (Gorenc *et al.*, 2004). Moreover, when ingested by humans, cadmium causes pulmonary oedema, muscle cramps, acute inflammation of the kidney, mild liver damage, anaemia, proximal tubular disease and osteomalacia (Pascual *et al.*, 2004).

#### Chromium

Chromium is a transition metal with a relative density of 7.2. It melts at a temperature of 1851 °C and boils at 2672 °C (Lin, Teng and Chang, 2002). In terms of the natural abundance of elements within the crust, chromium occupies position 21<sup>st</sup> position with an average concentration of 122 mg/kg in rock and between 11 to 22 mg/kg in soils (Sundarary, 2009). The natural level of chromium in soils is generally low, except over serpentine deposits, which contain high concentration of chromium.

Chromium concentration ranged from 0.06 to 1.86 mg/kg with a mean value of 0.88 mg/kg (Table 4.10). Chromium is used in alloys, electroplating, pigments, paints manufacture, fungicides, photography, glass and leather tanning industries. Chromium is carcinogenic to animals and human especially  $Cr^{4+}$ . Other health effects of chromium include bronchitis, dermatitis and inflammation of the tissue (Aboud and Nandini, 2009).

# Copper

Copper is one of the metals that are widely used in the industry and it is an essential element in living organisms. It has a specific gravity of 8.9 and ranks 25<sup>th</sup> in the natural abundance of elements in the earth's crust. Its melting and boiling temperatures are 1089 °C and 2567 °C respectively. Crustal abundance value is 70 mg/kg and 30 mg/kg for soils. In terms of rock types, gabbro and basalt have the highest concentration while granodiorite and granite have the lowest copper contents. This therefore means that soils derived from

mafic rocks would have higher natural copper contents than those from felsic varieties (Pascual *et al.*, 2004).

Concentration in copper varied from 1.46 to 15.30 mg/kg with an average value of 9.70 mg/kg. Copper is widely used in electrical wiring, roofing, various alloys, pigments, cooking utensils, piping and in the chemical industries (Aboud and Nandini, 2009). Copper compounds are used in fungicides, algicides, insecticides, electricity wires, wood preservation, electroplating, dye manufacture, engraving, lithography, petroleum refining and pyrotechnics. It is also added to fertilizers and animal feeds as a nutrient to support plant and animal growth (Mielke, Adams, Chaney, Mielke and Ravikumar, 1991). Copper pollution in soils could result from weathering of copper products, gas flaring, discharge of sewage sludge on land and emission from metallurgical smelters to mention. Exposure to high concentration of copper can result in serious health consequences such as pulmonary oedema, lung carcinoma and transitory fever (Pascual *et al.*, 2004).

#### Lead

Lead is a metal with a specific gravity of 11.34 and melting and boiling temperature of 328 °C and 1740 °C respectively (McAllister, Smith, Baptista and Simpson, 2005). This element occurs in eight isotopic forms (4 stable and 4 radioactive) and is the 36<sup>th</sup> most abundant element in earth crust. The average abundance in the earth's crust is 13 mg/kg while in natural soils, background level ranged between 2.6 to 25.0 mg/kg. Lead has two stable oxidation states- Pb<sup>2+</sup> and Pb<sup>4+</sup>, but Pb<sup>2+</sup> species is the commonest from in the environmental (Sharma and Pervez, 2003). The main ore of this element is galena (PbS), but the Pb ion replaces potassium and calcium in carbonates and apatities. Studies showed that anthropogenic activities such as oil spill, gas flaring, lead mining and smelting, lead-

paint flakes, sewage, and application of lead bearing pesticides increases the averages crustal concentration of lead in soils (Aboud and Nandini, 2009).

The lead concentration in the soil ranged between 0.32 to 1.86 mg/kg with a mean concentration of 0.78 mg/kg (Table 4.12) and these concentrations are below its crustal abundance. Lead is non essential for plants and animals and is toxic by ingestion-being a cumulative poison (MacFarlane and Burchett, 2002). Lead toxicity leads to anaemia both by impairment of haemo-biosynthesis and acceleration of red blood cell destruction. In addition, Pb reduces sperm count, damages kidney, liver, blood vessels, nervous system and other tissues in human (Anglin-Brown, Armour and Lalor, 1995). Other uses of lead is in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, ammunition, glass and plastic stabilizers. Tetraethyl and tetramethyl lead are important due to their extensive use as antiknock compounds in petrol (Mielke *et al.*, 1991).

# Nickel

The transition metal nickel is the 24<sup>th</sup> most abundant element with crustal concentration of 80 mg/kg and specific gravity of 8.9. It melts and boils at 1455 °C and 2730 °C respectively but magnetic below 350 °C (Pascual *et al.*, 2004). The main anthropogenic route of entry of nickel into the environmental is through the disposal of metal rich solid wastes from metallurgical industries. Sewages sludge disposed on land is another major source of nickel contamination of soils. Other sources include phoshatic fertilizer, oil spill and gas flaring. Nickel has been shown to be carcinogenic at low concentration especially the carbonyl form (Ni(CO)4).

Nickel concentration ranged between 0.50 and 18.24 mg/kg with an average concentration of 11.62 mg/kg and these values are below the average crustal abundance of 80.00 mg/kg in an uncontaminated soil (Dineley, Hawkes, Hancock and Williams, 1976). Nickel is used mainly as alloys, which are characterized by their hardness, strength, and resistance to corrosion and heat. It is a major component in the production of stainless steels, non-ferrous alloys and super alloys. Other application of Ni includes electroplating, as catalysts, in nickel-cadmium batteries, coins, welding and electronic products (Pascual *et al.*, 2004).

## Zinc

Zinc is an essential element for both plants and animals, including human beings. This element which never occurs free in nature has a specific gravity of 7.14 with a melting and boiling points of 420 °C and 907 °C respectively (Alloway, 1990). The average zinc content of the lithosphere is 132 mg/kg. Zinc concentration in soil is a function of the composition of parent rock, as well as anthropogenic activities domiciled in the area. Zinc in the study ranged between 1.62 and 20.94 mg/kg and a mean value of 10.98 mg/kg (Table 4.10). With this values, the concentration of Zn in soils from the area are within the stipulated guideline limits for an uncontaminated soil (Preda and Cox, 2002). It is an essential growth element for plants and animals but can be toxic at elevated concentration. It is used in making alloys of brass and bronze, batteries, fungicides, pigments, pesticides, galvanizing steel and iron products. It is used in combination with some enzymes system which contributes to energy metabolism, transcription and translation (Anglin-Brown *et al.*, 1995). One main problem associated with high levels of zinc in the environment is its inhibitory effect to the uptake of copper, which is an essential element for plants. Excessive concentration of Zn in soil

leads to phyto-toxicity. Acute Zn intoxication leads to nausea, vomiting, severe anaemia and renal failure (Aboud and Nandini, 2009).

#### Manganese

Manganese in earth's crust is 1000 mg/kg and between 61-1060 mg/kg in soils. The concentration of Mn varied between 0.42 and 108.00 mg/l with an average value of 21.25 mg/kg (Table 4.10). Manganese is essential for plants and animals. Manganese dioxide and other manganese compounds are used in products such as batteries, glass, fertilizer, fungicides, livestock feeding supplements and fireworks. Potassium permanganate is used as an oxidant for cleaning, bleaching, and disinfection purposes. Manganese greensands are used in for potable water treatment. Manganese can be adsorbed onto soil, the extent of adsorption depending on the organic content and cation exchange capacity of the soil.

# Vanadium

The average vanadium abundance in earth's crust is 150 mg/kg and for soils, it ranged between 2.0-70.0 mg/kg. Vanadium concentration ranged from 0.44 to 20.56 mg/kg with a mean value of 12.58 mg/kg (Table 4.10). Vanadium is widely used in engraving, lithography, petroleum refining and pyrotechnics.

#### Iron

Iron is a common constituent in soils and readily participates in subsurface redox reactions. The average crustal abundance of iron is 50,000. The iron content of soils ranged between 20.33 to 252.55 mg/kg with an average value of 232.40 mg/kg (Table 4.10). The concentration of iron in soils is dependent upon the source rocks from which the soil was derived, transport mechanisms, and overall geochemical history. This is particularly true in

soil and groundwater systems that have been environmentally impacted with hydrocarbons. Iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron  $(Fe^{+2})$  or oxidized insoluble trivalent ferric iron  $(Fe^{+3})$ . It has been observed that the high iron value in the groundwater system from the area is due to the infiltration of iron contained in the thick lateritic soil into the shallow water table.

#### **Biochemical Oxygen Demand (BOD)**

Biochemical Oxygen Demand (BOD) test measures the biodegradable organic carbon and, under certain conditions, the oxidizable nitrogen present in a water sample. A critical study of the BOD gives an idea of the oxidizable matter actually present in a waste sample and allows pollution load evaluation to be established. The results of the analyses as could be seen in Table 4.10 shows that the soil BOD values ranged between 1.56 and 38.90 mg/kg with a mean value of 17.64 mg/kg while COD concentration varied from 4.25-51.05 mg/kg and an average concentration of 23.96 mg/kg. The World Health Organization (2006) maximum permissible limit for BOD and COD are 100 mg/kg and 40 mg/kg respectively. The concentration of BOD in the soil samples collected is below the World Health Organization allowable limit while the COD in few locations have values higher the World Health Organization maximum permissible value. Field observation revealed that locations with high COD values is either close to an oil spill or near a gas flow station, which implies that the high COD values in the soil are anthropogenically induced.

# Total Organic Carbon (TOC) and Total Hydrocarbon Content (THC)

The concentration of total organic carbon (TOC) in the soil samples ranged between 15.10 and 84.65 mg/kg with an average value of 43.30 mg/kg while the values of total hydrocarbon content (THC) varied between 2.98 and 39.80 mg/kg with a mean value of

14.18 mg/kg (Table 4.10). Some of these values are above the Department of Petroleum Resources (DPR) maximum permissible limit of 50.0 mg/kg and 1.0 mg/kg for TOC and THC respectively. The enrichment of the soil with TOC and THC may be attributed mainly to incidence of oil spillage in the area.

#### **4.7.9.4** Contamination Factor and Geo-Accumulation Index

Contamination factor (CF) and geo-accumulation index (GeoI) are quantitative check used to describe concentration trend of metals in soils. Contamination factor (CF) is a quantifier of the degree of contamination relative to either the average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area (Tijani et al., 2004). It is expressed as:

$$CF = C_m / B_m$$

Where  $C_m$  is the mean concentration of metal m in soil and  $B_m$  is the background concentration (value) of metal m, either taken from the literature (average crustal abundance) or directly determined from a geologically similar material.

Geo-accumulation index (GeoI) as proposed by Mueller (1979) and cited by Lokeshwari and Chandrappa (2006) have been widely used to evaluate the degree of heavy metal contamination in terrestrial and aquatic environments as expressed:

GeoI =  $\ln [C_m / 1.5 * B_m]$ 

Where  $C_m$  and  $B_m$  are as defined above, while 1.5 is a factor for possible variation in the background concentration due to lithologic differences. GeoI is classified into seven descriptive classes as follows: <0 = practically uncontaminated; 0 – 1.9 uncontaminated to slightly contaminated, 2.0 – 3.9 = moderately to highly contaminated, 4.0 – 5.9 = highly to very strongly contaminated, 6.0 and above = very strongly contaminated (Table 4.16). The

latter is an open-end class that is indicative of all values greater than 5, and a GeoI of 6 is said to be indicative of 100-fold enrichment of a metal with respect to the baseline value (Mueller, 1979).

Parameters	Cm	Bm	CF	GeoI	Overall summary of contamination level
Cd	1.40	0.15	9.33	1.828	Moderately contaminated
Mn	48.12	1000	0.048	-3.442	Uncontaminated
Cu	12.86	70	0.184	1.596	Moderately contaminated
Cr	1.34	12.2	0.011	2.920	Highly contaminated
Ni	2.94	80	0.037	3.709	Highly contaminated
Pb	1.08	1.6	0.068	3.101	Highly contaminated
As	0.05	3.0	0.010	1.007	Slightly contaminated
Zn	16.04	132	0.122	0.913	Slightly contaminated
Co	10.58	23	0.460	1.181	Slightly contaminated

Table 4.16: Metal Contamination Factor and Geo-accumulation Index of Metals inSoil from Eastern Niger Delta

CF- contamination factor;

GeoI- geo-accumulation index;

C<sub>m</sub>- mean concentration of the metal in the soil;

B<sub>m</sub>- average crustal abundance (background value) in an uncontaminated soil, adopted from (Dineley *et al.*, 1976).

The concentration of cadmium ranges from 0.18-2.60 mg/kg with a mean concentration of 1.40 mg/kg. The values of Cd obtained in this study are higher than the average crustal abundance of 0.15 ppm in an uncontaminated soil. The calculated geo-accumulation index (GeoI) for cadmium indicates that the soils around the dumpsite are moderately contaminated and Cd showed moderately positive correlation with Cobalt and organic matter.

Cadmium metal is used as an anticorrosive, electroplated on steel, Cadmium sulfide and selenide are commonly used as pigments in plastics, batteries and in various electronic components. It is also used with inorganic fertilizers produced from phosphate ores and when these products are no more serviceable, they are thrown into the dump as waste. During decomposition, the Cd component is leached into the surrounding soil and over time gets accumulated in the soil. Cadmium is extremely toxic and the primary use of soil high in Cd in form of manure for the cultivation of vegetables and other food crops could cause adverse health effect to consumers such as renal disease and cancer (Che *et al.*, 2003; Gorenc *et al.*, 2004). Moreover, when ingested by humans, cadmium accumulates in the intestine, liver and kidney and chronic exposure of Cd causes proximal tubular disease and osteomalacia (Pascual *et al.*, 2004). Therefore, the soils from this dumpsite are not suitable for agricultural purposes.

Manganese ranged 0.30-92.10 mg/kg. The mean was 48.12 mg/kg. Abbasi, Abbasi and Soni, (1998) gave an accepted value of 1000 mg/kg for manganese in an uncontaminated soil and the calculated GeoI value gave a value that indicates uncontaminated. Manganese is essential for plants and animals. Manganese dioxide and other manganese compounds are used in products such as batteries, glass and fireworks (Huang and Lin, 2003; Aboud and

Nandini, 2009). Potassium permanganate is used as an oxidant for cleaning, bleaching and disinfection purposes. Other manganese compounds are used in fertilizer, fungicides and as livestock feeding supplements. It can be adsorbed onto soil depending on organic content, pH, grain-size and cation exchange capacity (CEC) of the soil and this can be exemplified by the strong positive correlation with organic matter (<0.01 level). Concentration in copper varied from 1.06-15.98 mg/kg with an average value of 12.86 mg/kg. A moderately high positive correlation with lead and Zinc was established (Table 4.17). Copper is widely used in electrical wiring, roofing, various alloys, pigments, cooking utensils, piping and in the chemical industries (Aboud and Nandini, 2009). Copper compounds are used in fungicides, algicides, insecticides, wood preservation, electroplating, dye manufacture, engraving, lithography, petroleum refining and pyrotechnics. It is also added to fertilizers and animal feeds as a nutrient to support plant and animal growth (Mielke *et al.*, 1991; Pascual *et al.*, 2004). The Cu concentration in GeoI indicates a moderate contamination.

Chromium concentration ranges from 0.02-2.78 mg/kg with a mean value of 1.34 mg/kg (Table 4.10). No correlation was found with other metals and its concentration falls within the range of uncontaminated level. It is used in alloys, electroplating, pigments, paints manufacture, fungicides, photography, glass and leather tanning industries. Chromium is carcinogenic by inhalation and corrosive to tissue (Lin *et al.*, 2002; Aboud and Nandini, 2009). Nickel measured concentrations are below the average crustal abundance in an uncontaminated soil. A moderate positive correlation with Zn was noted at <0.05 level (Table 4.17). Nickel is used mainly as alloys, which are characterized by their hardness, strength, and resistance to corrosion and heat. It is a major component in the production of stainless steels, non-ferrous alloys and super alloys. Other application of Ni includes

electroplating, as catalysts, in nickel-cadmium batteries, coins, welding and electronic products (Pascual *et al.*, 2004).

The results show that lead concentration deposited at the dumpsite ranged 0.24-2.15 mg/kgwith a mean concentration of 1.08 mg/kg. Though there was an observed strong correlation with Cu (<0.01 level), its concentration is within the level of uncontaminated soil. Lead is non essential for plants and animals and is toxic by ingestion-being a cumulative poison (MacFarlane and Burchett, 2002; Sharma and Pervez, 2003). Lead toxicity leads to anaemia both by impairment of haemo-biosynthesis and acceleration of red blood cell destruction. In addition, Pb reduces sperm count, damages kidney, liver, blood vessels, nervous system and other tissues in human (Anglin-Brown et al., 1995). Other uses of lead is in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, ammunition, glass and plastic stabilizers. Tetraethyl and tetramethyl lead are important due to their extensive use as antiknock compounds in petrol (Mielke et al., 1991; McAllister et al., 2005). Arsenic concentration varied between 0.01 mg/kg and 0.08 mg/kg with an average concentration of 0.05 mg/kg. These values are found to be low the critical value of 16 mg/kg (average crustal abundance) for an uncontaminated soil. The GeoI concentration lies below the range for uncontaminated soil. Arsenic is highly carcinogenic has no nutritional value for plant and animal (Amadi et al., 2010).

Zinc in the study ranged 2.40-28.50 mg/kg. The mean value was 16.04 mg/kg. With this values, the concentration of Zn in soils from the dumpsite are slightly above the stipulated guideline limits. Zinc had very strong positive correlation with Cu and Pb (<0.01 level) and moderately positive correlation with Ni (<0.05 level; Table 4.17). It is an essential growth element for plants and animals but can be toxic at elevated concentration. Zinc is used in
making alloys of brass and bronze, batteries, fungicides, pigments, pesticides, galvanizing steel and iron products. It is used in combination with some enzymes system which contributes to energy metabolism, transcription and translation (Anglin-Brown *et al.*, 1995). Excessive concentration of Zn in soil leads to phyto-toxicity as it is a weed killer (Preda and Cox, 2002; Aboud and Nandini, 2009).

Cobalt concentration ranged 0.20-17.90 mg/kg with a mean value of 10.57 mg/kg. The measured concentrations of Co are acceptable range for an uncontaminated soil. Cobalt is widely used as alloys for steels, electroplating, fertilizer, porcelain and glass making. It is essential for the growth of algae and bacteria but required in trace concentration for higher plants and animals (Mielke *et al.*, 1991; Rayment and Higginson, 1992; Aboud and Nandini, 2009).

	Cd	Mn	Cu	Cr	Ni	Pb	Ar	Zn	Со	рН	ОМ	<b>C</b> + <b>S</b>
Cd	1.000											
Mn	0.109	1.000										
Cu	0.065	-0.112	1.000									
Cr	0.252	0.041	0.141	1.000								
Ni	0.354	0.678**	0.101	0.093	1.000							
Pb	0.327	-0.113	0.818**	0.008	0.334	1.000						
As	0.080	0.199	0.249	0.118	-0.333	0.090	1.000					
Zn	0.153	0.205	0.788**	-0.044	0.534*	0.637**	0.110	1.000				
Co	0.433*	0.084	0.211	0.208	0.360*	0.016	0.186	0.127	1.000			
pН	0.106	-0.112	0.024	0.091	0.119	0.095	0.112	0.085	0.101	1.000		
OM	0.598*	0.724**	0.028	0.284	0.284	0.195	0.220	0.054	0.066	0.841*	1.000	
C + S	0.045	0.293	0.123	0.031	-0.023	0.545*	0.151	0.049	0.137	0.521	-0.192	1.000

Table 4.17: Pearson Correlation Coefficient Matrix for Heavy Metals in Soils from Eastern Niger Delta

\*\*: Correlation is significant at the 0.01 level (2-tailed); \*: Correlation is significant at the 0.05 level (2-tailed); OM: Organic Matter; C + S: Clay + Silt.

## **4.8 Rainwater Sample**

Both direct rainwater (12 samples) and roof-top collected rainwater (10 samples) were collected twice a year for a period of 4 years (2008-2011) and analyzed for relevant physico-chemical parameters with emphasis on pH, carbonate, nitrate, sulphate and heavy metal. The concentration of the heavy metal in the direct rainwater and roof-top collected rainwater samples are contained in Tables 18 and 19 respectively while the statistical summary of the physic-chemical parameters are shown in Table 20. The incidence of rusting of corrugated iron sheets was the driving force behind the determination of carbonate, nitrate and sulphate content in rainwater considering the impact of gas flaring on the precipitation around the area. This is because certain air pollutant, including a variety of dust particles, smokes and acid droplets can influence the development of clouds and precipitation within an area, especially as these pollutants are hygroscopic and can serve as nuclei for cloud droplets, thereby accelerating condensation (Moran, Morgan and Wiesma, 1986).

Location	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	L-8	L-9	L-10	L-11	L-12	L-13
Fe	0.786	0.742	0.842	0.635	0.646	0.631	0.598	0.582	0.713	0.696	0.677	0.671	0.704	0.814
Zn	0.638	0.549	0.743	0.784	0.713	0.715	0.722	0.731	0.694	0.708	0.719	0.810	0.801	0.746
Cu	0.196	0.209	0.218	0.226	0.214	0.208	0.217	0.209	0.224	0.215	0.209	0.213	0.228	0.231
Mn	0.112	0.090	0.086	0.093	0.115	0.113	0.087	0.092	0.088	0.096	0.118	0.093	0.096	0.086
Ni	0.219	0.211	0.196	0.220	0.214	0.213	0.206	0.227	0.217	0.208	0.194	0.186	0.213	0.193
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cr	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
V	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.101	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.301

 Table 4.18a: Heavy metal concentration in direct rain-water samples for location 1 to location 13 in Eastern Niger Delta

Location	L-14	L-15	L-16	L-17	L-18	L-19	L-20	L-21	L-22	L-23	L-24	L-25	L-26
Fe	0.698	0.684	0.699	0.702	0.664	0.679	0.704	0.711	0.646	0.673	0.683	0.642	0.666
Zn	0.639	0.724	0.806	0.632	0.416	0.514	0.608	0.513	0.499	0.508	0.516	0.601	0.499
Cu	0.228	0.217	0.218	0.204	0.560	0.473	0.394	0.508	0.499	0.308	0.297	0.284	0.432
Mn	0.089	0.092	0.110	0.113	0.092	0.086	0.099	0.114	0.093	0.094	0.098	0.112	0.111
Ni	0.219	0.211	0.202	0.216	0.208	0.220	0.704	0.711	0.646	0.673	0.211	0.191	0.200
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cr	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
V	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.031	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.18b: Heavy metal concentration in direct rain-water samples for location 14 to location 26 in Eastern Niger Delta

Location	L-27	L-28	L-29	L-30	L-31	L-32	L-33	L-34	L-35	L-36	L-37	L-38	L-39
Fe	0.619	0.604	0.613	0.704	0.650	0.641	2.470	0.634	0.613	0.642	0.642	0.643	2.780
Zn	0.506	0.333	0.324	0.801	0.384	0.376	0.407	0.315	0.418	0.329	0.314	0.528	0.475
Cu	0.417	0.413	0.401	0.228	0.189	0.166	0.159	0.184	0.157	0.188	0.174	0.149	0.168
Mn	0.097	0.097	0.092	0.096	0.278	0.266	0.249	0.238	0.261	0.271	0.214	0.246	0.222
Ni	0.213	0.239	0.247	0.213	0.048	0.034	0.031	0.056	0.035	0.041	0.029	0.036	0.046
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cr	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
V	0.201	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.18c: Heavy metal concentration in direct rain-water samples for location 27 to location 39 in Eastern Niger Delta

Location	L-40	L-41	L-42	L-43	L-44	L-45	L-46	L-47	L-48	L-49	L-50	L-51	L-52
Fe	0.671	0.742	0.861	3.050	0.946	14.580	3.010	2.940	1.050	0.843	0.956	0.657	0.650
Zn	0.511	0.634	0.538	0.829	0.419	0.508	0.466	0.475	0.424	0.415	0.398	0.666	0.417
Cu	0.184	0.179	0.153	0.184	0.194	0.183	0.175	0.170	0.164	0.154	0.183	0.197	0.154
Mn	0.271	0.218	0.228	0.275	0.249	0.254	0.253	0.241	0.254	0.258	0.262	0.262	0.252
Ni	0.039	0.052	0.037	0.081	0.034	0.054	0.043	0.048	0.039	0.041	0.035	0.037	0.032
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cr	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
V	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.18d: Heavy metal concentration in direct rain-water samples for location 40 to location 52 in Eastern Niger Delta

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Location	L-53	L-54	L-55	L-56	L-57	L-58	L-59	L-60	L-61	L-62	L-63	L-64	L-65
Fe	0.753	0.687	0.541	0.633	0.786	0.546	0.604	0.609	0.563	0.594	0.686	0.714	0.814
Zn	0.538	0.241	0.542	0.511	0.638	0.475	0.638	0.878	0.714	0.604	0.718	0.719	0.804
Cu	0.216	0.290	0.214	0.223	0.196	0.246	0.251	0.223	0.222	0.228	0.234	0.239	0.209
Mn	0.084	0.087	0.081	0.092	0.112	0.096	0.091	0.115	0.089	0.086	0.110	0.094	0.098
Ni	0.208	0.223	0.197	0.214	0.219	0.226	0.231	0.204	0.204	0.217	0.216	0.222	0.248
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cr	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
V	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.18e: Heavy metal concentration in direct rain-water samples for location 53 to location 65 in Eastern Niger Delta

Location	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	L-9	L-10	L-11	L-12	L-13
HCO <sub>3</sub> -	10.25	1.22	0.98	0.98	1.71	1.46	1.71	1.22	1.46	1.22	1.46	3.17	24.40
CO3 <sup>2-</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
<b>SO</b> <sub>4</sub> <sup>2-</sup>	< 0.01	1.09	2.52	2.86	2.52	2.27	2.02	3.53	3.03	2.27	3.28	< 0.01	3.19
PO4 <sup>3-</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cl	6.23	6.23	6.23	6.23	3.12	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23
NO <sub>3</sub> -	4.60	5.80	5.80	5.60	5.60	5.80	4.60	4.90	4.60	5.60	4.80	4.80	5.60
$Ca^{2+}$	2.400	0.800	0.800	0.800	0.800	1.600	0.800	0.800	0.800	0.800	2.400	0.800	5.610
$Mg^{2+}$	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	< 0.01
$\mathbf{K}^+$	0.518	0.736	0.812	0.614	0.515	0.618	0.714	0.524	0.663	0.486	0.514	0.502	0.611
$Na^+$	6.40	7.55	9.43	6.38	7.59	6.64	8.34	7.94	8.26	8.12	7.52	6.39	8.33
Mn	0.184	0.157	0.188	0.174	0.149	0.168	0.184	0.179	0.153	0.184	0.194	0.183	0.175
Zn	0.315	0.418	0.329	0.314	0.528	0.475	0.511	0.634	0.538	0.829	0.419	0.508	0.466
Cr	0.238	0.261	0.271	0.214	0.246	0.222	0.271	0.218	0.228	0.275	0.249	0.254	0.253
Fe	0.634	0.613	0.642	0.642	0.643	2.780	0.671	0.742	0.861	3.050	0.946	14.580	3.010
Ni	0.056	0.035	0.041	0.029	0.036	0.046	0.039	0.052	0.037	0.081	0.034	0.054	0.043
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.19a: Chemical analysis of roof-top collected rainwater for location 1 to location 13 in Eastern Niger Delta

Location	L-14	L-15	L-16	L-17	L-18	L-19	L-20	L-21	L-22	L-23	L-24	L-25	L-26
HCO <sub>3</sub> -	0.11	1.22	0.98	1.22	2.79	2.39	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
CO3 <sup>2-</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
<b>SO</b> <sub>4</sub> <sup>2-</sup>	2.27	1.18	2.69	1.43	6.22	5.38	4.37	4.03	3.78	3.78	3.61	0.42	7.32
PO <sub>4</sub> <sup>3-</sup>	< 0.01	< 0.01	< 0.01	0.020	0.080	0.020	0.050	0.020	0.050	< 0.01	0.014	0.012	0.700
Cl	6.23	6.23	6.23	6.23	3.33	3.33	6.66	3.33	10.00	10.00	3.33	3.33	3.33
NO <sub>3</sub> -	5.80	5.60	5.20	5.60	0.88	0.88	0.88	4.40	10.10	18.00	3.52	18.90	8.80
Ca <sup>2+</sup>	0.800	0.800	1.600	0.800	1.600	1.600	4.896	1.600	3.210	1.600	3.210	3.210	1.600
$Mg^{2+}$	0.480	0.480	0.480	0.480	< 0.001	< 0.001	1.452	< 0.001	< 0.001	< 0.001	< 0.001	0.970	< 0.001
$\mathbf{K}^+$	0.816	0.519	0.602	0.553	0.842	0.741	0.663	0.761	0.824	0.719	0.643	0.698	0.708
Na <sup>+</sup>	7.53	9.46	8.42	10.06	5.63	4.84	4.98	5.06	5.11	6.41	5.93	5.86	5.54
Mn	0.170	0.164	0.154	0.183	0.246	0.251	0.223	0.222	0.228	0.234	0.239	0.209	0.216
Zn	0.475	0.424	0.415	0.398	0.475	0.638	0.878	0.714	0.604	0.718	0.719	0.804	0.538
Cr	0.241	0.254	0.258	0.262	0.096	0.091	0.115	0.089	0.086	0.110	0.094	0.098	0.084
Fe	2.940	1.050	0.843	0.956	0.546	0.604	0.609	0.563	0.594	0.686	0.714	0.814	0.753
Ni	0.048	0.039	0.041	0.035	0.226	0.231	0.204	0.204	0.217	0.216	0.222	0.248	0.208
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.19b: Chemical analysis of roof-top collected rainwater for location 14 to location 26 in Eastern Niger Delta

Location	L-27	L-28	L-29	L-30	L-31	L-32	L-33	L-34	L-35	L-36	L-37	L-38	L-39
HCO <sub>3</sub> -	< 0.01	0.99	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.19	< 0.01	< 0.01	< 0.01	< 0.01
CO3 <sup>2-</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
<b>SO</b> <sub>4</sub> <sup>2-</sup>	2.35	9.41	3.78	2.94	15.38	10.08	4.54	3.76	2.31	4.29	3.70	3.45	2.52
PO4 <sup>3-</sup>	0.700	< 0.01	0.024	0.040	0.024	< 0.01	0.004	0.070	< 0.01	0.093	< 0.01	0.010	0.131
Cl	3.33	6.66	3.33	6.66	6.66	209.90	3.33	3.33	6.66	6.66	3.33	3.33	3.33
$NO_3^-$	7.92	26.40	45.80	35.60	8.36	16.06	20.68	16.70	0.88	0.88	2.20	2.64	32.60
$Ca^{2+}$	3.210	4.810	6.410	6.410	6.410	0.400	3.210	3.210	3.210	2.405	3.210	1.600	6.410
$Mg^{2+}$	< 0.001	< 0.001	0.970	0.970	0.970	0.300	< 0.001	< 0.001	< 0.001	0.484	< 0.001	< 0.001	0.970
$\mathbf{K}^+$	0.640	0.598	0.613	0.814	0.866	0.713	0.728	0.646	0.659	0.708	0.719	0.548	0.599
$Na^+$	5.66	6.04	7.13	5.49	5.53	5.86	6.15	6.22	5.94	5.88	6.13	6.44	7.06
Mn	0.290	0.214	0.223	0.196	0.209	0.218	0.226	0.214	0.208	0.217	0.209	0.224	0.215
Zn	0.241	0.542	0.511	0.638	0.549	0.743	0.784	0.713	0.715	0.722	0.731	0.694	0.708
Cr	0.087	0.081	0.092	0.112	0.090	0.086	0.093	0.115	0.113	0.087	0.092	0.088	0.096
Fe	0.687	0.541	0.633	0.786	0.742	0.842	0.635	0.646	0.631	0.598	0.582	0.713	0.696
Ni	0.223	0.197	0.214	0.219	0.211	0.196	0.220	0.214	0.213	0.206	0.227	0.217	0.208
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.19c: Chemical analysis of roof-top collected rainwater for location 27 to location 39 in Eastern Niger Delta

Location	L-40	L-41	L-42	L-43	L-44	L-45	L-46	L-47	L-48	L-49	L-50	L-51
HCO <sub>3</sub> -	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
CO3 <sup>2-</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
$SO_4^{2-}$	7.98	2.86	10.13	3.78	1.85	1.68	1.43	4.20	2.18	2.35	3.76	2.94
PO <sub>4</sub> <sup>3-</sup>	< 0.01	0.050	0.030	0.010	0.080	0.004	0.251	0.013	< 0.01	< 0.01	< 0.01	< 0.01
Cl	6.66	6.66	6.66	16.66	3.33	3.33	3.33	39.90	6.66	3.33	3.33	10.00
NO <sub>3</sub> -	22.00	42.70	34.80	30.40	27.70	40.50	54.60	81.40	42.70	39.20	2.20	17.60
$Ca^{2+}$	6.410	2.405	7.214	4.010	4.810	6.410	14.430	6.713	5.611	3.210	0.200	3.210
$Mg^{2+}$	0.970	2.904	0.484	2.920	0.970	0.970	5.810	1.452	0.968	< 0.001	0.600	0.97
$\mathbf{K}^+$	0.611	0.634	0.708	0.719	0.804	0.806	0.596	0.604	0.598	0.614	0.619	0.718
$Na^+$	6.36	6.42	5.99	5.86	5.91	6.31	6.38	6.48	6.24	5.94	5.99	6.18
Mn	0.209	0.213	0.228	0.231	0.228	0.217	0.218	0.204	0.560	0.473	0.394	0.508
Zn	0.719	0.810	0.801	0.746	0.639	0.724	0.806	0.632	0.416	0.514	0.608	0.513
Cr	0.118	0.093	0.096	0.086	0.089	0.092	0.110	0.113	0.092	0.086	0.099	0.114
Fe	0.677	0.671	0.704	0.814	0.698	0.684	0.699	0.702	0.664	0.679	0.704	0.711
Ni	0.194	0.186	0.213	0.193	0.219	0.211	0.202	0.216	0.208	0.220	0.704	0.711
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.19d: Chemical analysis of roof-top collected rainwater for location 40 to location 53 in Eastern Niger Delta

Location	L-52	L-53	L-54	L-55	L-56	L-57	L-58	L-59	L-60	L-61	L-62	L-63
HCO <sub>3</sub> -	48.99	< 0.01	4.88	4.64	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.61	< 0.01
CO3 <sup>2-</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
$SO_4^{2-}$	3.78	3.78	< 0.01	1.09	9.33	3.87	3.36	4.03	7.06	3.15	1.60	8.66
PO <sub>4</sub> <sup>3-</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cl	3.33	6.66	3.12	6.23	16.66	16.66	3.33	3.33	6.66	3.33	6.23	4.50
NO <sub>3</sub> -	1.32	1.32	5.86	5.20	25.10	31.70	50.20	23.80	46.20	71.30	4.80	28.60
$Ca^{2+}$	17.640	3.210	0.800	0.800	1.600	2.405	5.611	4.810	6.410	1.200	0.800	14.930
$Mg^{2+}$	< 0.001	< 0.001	1.940	0.480	1.940	0.968	0.968	< 0.001	0.970	0.200	< 0.01	0.970
$\mathbf{K}^+$	0.649	0.704	0.570	0.742	0.693	0.646	0.682	0.673	0.66	0.594	0.650	0.589
$Na^+$	7.04	7.04	8.41	7.52	6.39	6.17	6.26	6.41	6.33	5.83	4.54	5.93
Mn	0.499	0.308	0.197	0.154	0.297	0.284	0.432	0.417	0.413	0.401	0.186	0.476
Zn	0.499	0.508	0.666	0.417	0.516	0.601	0.499	0.506	0.333	0.324	0.392	0.318
Cr	0.093	0.094	0.262	0.252	0.098	0.112	0.111	0.097	0.097	0.092	0.270	0.109
Fe	0.646	0.673	0.657	0.650	0.683	0.642	0.666	0.619	0.604	0.613	2.550	0.702
Ni	0.646	0.673	0.037	0.032	0.211	0.191	0.205	0.213	0.239	0.247	0.053	0.305
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.19e: Chemical analysis of roof-top collected rainwater for location 52 to location 63 in Eastern Niger Delta

Location	L-64	L-65	L-66	L-67	L-68	L-69	L-70	L-71	L-72	L-73	L-74	L-75
HCO <sub>3</sub> -	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.19	< 0.01	5.37	1.95	2.44
$CO_{3}^{2-}$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
$SO_4^{2-}$	13.28	17.39	3.61	1.68	3.61	3.03	4.87	3.24	4.28	1.85	1.77	2.19
PO4 <sup>3-</sup>	0.774	5.550	< 0.01	< 0.01	3.910	7.810	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01
Cl	3.33	3.33	3.33	3.33	3.33	26.70	19.65	8.95	6.78	6.23	6.23	6.23
NO <sub>3</sub> -	4.40	0.88	0.88	7.04	4.40	5.28	36.40	0.97	0.92	4.70	4.90	5.70
Ca <sup>2+</sup>	32.060	33.670	0.802	3.210	1.603	240.480	10.405	6.254	87.168	0.800	0.800	0.800
$Mg^{2+}$	5.810	3.870	0.484	< 0.001	1.952	20.34	0.918	< 0.001	0.884	0.480	0.480	0.480
$\mathbf{K}^+$	0.592	0.606	0.619	0.608	0.601	0.648	0.846	0.754	0.625	0.546	0.663	0.575
Na <sup>+</sup>	5.49	5.37	6.13	6.24	6.46	6.54	8.12	6.54	6.51	6.47	5.93	8.33
Mn	0.386	0.347	0.193	0.201	0.433	0.050	0.384	0.414	0.390	0.189	0.166	0.159
Zn	0.331	0.071	0.134	0.468	0.537	0.879	0.705	0.755	0.484	0.384	0.376	0.407
Cr	0.112	0.116	0.114	0.120	0.125	0.123	0.211	0.089	0.214	0.278	0.266	0.249
Fe	0.712	0.694	0.682	0.664	0.619	3.250	0.846	0.705	0.819	0.650	0.641	2.470
Ni	0.258	0.311	0.308	0.315	0.317	0.245	0.290	0.243	0.528	0.048	0.034	0.031
Cd	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
As	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

 Table 4.19f: Chemical analysis of roof-top collected rainwater for location 64 to location 75 in Eastern Niger Delta

The results of the laboratory analyses indicate a drop in carbonate, nitrate and sulphate content in the direct rainwater compared to the top-roof collected rainwater (Table 4.20). This may be attributed to the reactions between  $HCO_3$ ,  $HNO_3$  and  $H_2SO_4$  and the zinc/iron in the roofing materials according to the equations below:

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$$

Carbonic acid forms naturally in the atmosphere due to the reaction of water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) as shown above while gas flaring and burning of other organics adds nitrous oxides (NO<sub>x</sub>) and sulfurous oxides (SO<sub>x</sub>) to the atmosphere where they react with water molecules to form nitrous acid and nitric acid as well as sulfur trioxide and sulfate which are highly corrosive as illustrated below:

$$2NO_{2(g)} + H_2O_{(1)} \rightarrow HNO_{2(aq)} + HNO_{3(aq)}$$
  
 $2SO_{2(g)} + 2H_2O_{(1)} \rightarrow H_2SO_{3(aq)} + H_2SO_{4(aq)}$ 

The oxides of Carbon (CO<sub>x</sub>), nitrogen (NO<sub>x</sub>) and sulfur (SO<sub>x</sub>), are the three main sources of acid rain in the study area. These reactions are believed to be responsible for the accelerated rusting and caving-in of roofing sheets/materials in the area. The study further reveals that carbonate, nitrate and sulphate concentration in the rainwater are highest in the peak of dry season (December to February) when the rainfall frequency and intensity is low and drastically reduces as rainfall intensifies. It therefore means that the acidity and hence the carbonate, nitrate and sulphate contents of rainwater in the area is a function of the frequency and intensity of the rainfall. The precipitation is richer in carbonate, nitrate and sulphate when the interval between one rainfall and the other is longer. It is evident from the results that the very set of rain brings down all the NO<sub>x</sub>, CO<sub>x</sub> and SO<sub>x</sub> suspended in the air and the longer the rain falls, the more diluted the concentrations and hence the acidity. It has been established from the present study that the smaller the volume of rain that brings

down the acid droplets and suspended particles, the more acidic the rain water. In practice, strongly acid and corrosive moisture is more to be expected when mist condenses these acid droplets and bring them down as dew on corrugated iron roofs, a possibility in humid tropical condition like the Niger Delta. Though not determined, the acidity of such dews is likely to be more concentrated and hence corrosive than that of the rains.

Vehicular transportation is also a major source of the oxides ( $CO_x$ ,  $NO_x$  and  $SO_x$ ). Acid precipitation (acid rain) has the potential to liberate heavy metal from soil, which can infiltrate into the water table and may contaminate groundwater or are carried as run-off through which the surface water system may be polluted.

Parameters	RTCR	DR
pН	5.70	5.75
Conductivity	370.00	220.00
TDS	260.00	190.00
Chlorine	62.10	42.00
Phosphate	38.46	21.24
Sulphate	61.73	46.54
Nitrate	52.98	42.30
Sodium	90.10	78.12
Magnesium	65.40	47.33
Calcium	76.52	51.88
Potassium	58.06	45.20
Lead	0.84	0.52
Nickel	1.05	0.83
Zinc	0.53	0.35
Iron	1.09	0.76
Copper	0.98	0.45
Chromium	0.07	0.04

 

 Table 4.20: Mean Concentration of Direct Rainwater and Roof-Top Collected Rainwater Samples

RTCR- Roof-top collected rainwater; DR- Direct rainwater

## 4.8.1 Effects of Acid Rain

Acid-rain is a form of pollution that can cause a lot of damage to natural ecosystem, to man-made objects as well as harm human health. Acid-rain or more accurately acid precipitation is the term used for describing rainfall with a pH level lower than 5.6 (Moran *et al.*, 1986). This type of pollution is a matter of great debate currently due to its potential to cause environmental damages all across the world. For the last decade acid rain has caused destruction to hundreds of lakes and streams in many parts of the world, including the US, Canada, and Europe and is currently causing serious havoc in the Niger Delta region of Nigeria.

The ecological effects of acid rain are most clearly seen in the aquatic, or water, environments, such as streams, lakes, and marshes. Acid rain flows into streams, lakes, and marshes after falling on forests, fields, buildings, and roads. Acid rain primarily affects sensitive bodies of water, which are located in watersheds whose soils have a limited ability to neutralize acidic compounds called (buffering capacity). Lakes and streams become acidic (that is the pH value goes down) when the water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams; aluminum is highly toxic to many species of aquatic organisms

Acid rain causes a cascade of effects that harm or kill individual fish, reduce fish population numbers, completely eliminate fish species from a water body, and decrease biodiversity in fishes. As acid rain flows through soils in a watershed, aluminum is released from soils into the lakes and streams located in that watershed. So, as pH in a lake or stream decreases, aluminum levels increase. Both low pH and increased aluminum levels are

directly toxic to fish. In addition, low pH and increased aluminum levels cause chronic stress that may not kill individual fish, but leads to lower body weight and smaller size and makes fish less able to compete for food and habitat. Some types of plants and animals are able to tolerate acidic waters. Others, however, are acid-sensitive and will be lost as the pH declines. Generally, the young of most species are more sensitive to environmental conditions than adults. At pH 5, most fish eggs cannot hatch. At lower pH levels, both aquatic and wild lives die (Appendix A) and this has drastically affected peoples' cultural and socio-economic activities especially fishing. Accelerated rusting and caving-in of roofing sheets/materials and devastation of natural vegetation in the area are other confirmed signatures of acid rain (Appendix A).

The plants and animals living within an ecosystem are highly interdependent. Because of the connections between the fishes, plants, and other organisms living in an aquatic ecosystem, changes in pH or aluminum levels affect biodiversity as well. Thus, as lakes and streams become more acidic, the numbers and types of fish and other aquatic plants and animals that live in these waters decrease.

According to the National Oceanic and Atmospheric Administration (NOAA) report, these conditions are common in many of our nation's coastal ecosystems. These ecological changes impact human populations by changing the availability of seafood and creating a risk of consuming contaminated fish or shellfish, reducing our ability to use and enjoy our coastal ecosystems, and causing economic impact on people who rely on healthy coastal ecosystems, such as fishermen and those who cater to tourists. Both natural vegetation and crops are affected by acid rain. The roots are damaged by acidic rainfall, causing the growth of the plant to be stunted, or even in its death. Nutrients present in the soil, are

destroyed by the acidity. Useful micro organisms which release nutrients from decaying organic matter, into the soil are killed off, resulting in less nutrients being available for the plants. The acid rain, falling on the plants damages the waxy layer on the leaves and makes the plant vulnerable to diseases.

The cumulative effect means that even if the plant survives it will be very weak and unable to survive climatic conditions like strong winds, heavy rainfall, or a short dry period. Plant germination and reproduction is also inhibited by the effects of acid rain. All living organisms are interdependent on each other. If a lower life form is killed, other species that depended on it will also be affected. Every animal up the food chain will be affected. Animals and birds, like waterfowl or beavers, which depended on the water for food sources or as a habitat, also begin to die. Due to the effects of acid rain, animals which depended on plants for their food also begin to suffer. Tree dwelling birds and animals also begin to languish due to loss of habitat.

Mankind depends upon plants and animals for food. Due to acid rain the entire fish stocks in certain lakes have been wiped out. The economic livelihood of people who depended on fish and other aquatic life suffers as a result. Eating fish which may have been contaminated by mercury can cause serious health problems. In addition to loss of plant and animal life as food sources, acid rain gets into the food we eat, the water we drink, as well as the air we breathe. Due to this asthmatic people and children are directly affected. Urban drinking water supplies are generally treated to neutralise some of the effects of acid rain and therefore city dwellers may not directly suffer due to acidified drinking water. But out in the rural areas, those depending upon lakes, rivers, and wells will feel the effects of acid rain on their health. The acidic water moving through pipes causes harmful elements like lead and copper to be leached into the water. Aluminium which dissolves more easily in acid rain as compared to pure rainfall has been linked to Alzheimer's disease. The treatment of urban water supplies may not include removal of elements like Aluminium, and so is a serious problem in cities too. All living things, whether plants or animals, whether living on land or in the water or trees, are affected either directly or indirectly by acid rain. Even buildings, bridges and other structures are affected. In cities, paint from buildings has peeled off and colours of cars have faded due to the effects of acid rain. From the Taj Mahal in India to the Washington Monument great buildings all over the world have been affected by the acid rainfall which causes corrosion, fracturing, and discoloration in the structures.

In Europe, structures like The Acropolis in Greece and Renaissance buildings in Italy, as well as several churches and cathedrals have suffered visible damage. In the Yucatan peninsula in Mexico, and in places in South America, ancient Mayan Pyramids are being destroyed by the acid rain. Temples, murals, and ancient inscriptions which had previously survived for centuries are now showing severe signs of corrosion. Even books, manuscripts, paintings, and sculpture are being affected in museums and libraries, where the ventilation system cannot eliminate the acid particles from the air which circulates in the building. In some parts of Poland, trains are required to run slowly, as the tracks are badly damaged due to corrosion caused by acid rainfall.

In Niger Delta area of Nigeria, the problem of acid-rain is evidenced in the rusting and caving-in of corrugated iron sheet and in the decay of other building materials. The devastation of the vegetation, death of aquatic and wildlife are some signatures of acid-rain in the area (Figure 4.16).



Figure 4.16: Conceptual Model of the Environmental and Socio-economic impact of Acid-rain

These metals find their way into the atmosphere through gas flaring where they react with water molecules in the atmosphere and fall as precipitation. Depending on the prevalent climatic and geological conditions, oil spill either infiltrates in the water table through the soil or moves into the stream/rivers via surface run-off. Through any of these means, these heavy metals from the crude can enter absorbed by plants root and when animals/human eat these plants, they bio-accumulate and cause serious health problem especially carcinogenous diseases, skin diseases, respiratory illnesses, asthma attacks as well as other water borne diseases. The information obtained from Federal Medical Centre Owerri and other government hospitals from Aba and Port-Harcourt revealed that most premature deaths recorded in the region can be linked to cancer, water borne diseases, respiratory disorder, asthma and skin problem.

Results of chemical analysis from selected oil spill sites in the Eastern Niger delta have revealed that depending on the nature of the environment, heavy metals from the crude oil are introduced into the soil, surface water, leading to their bio-accumulation and subsequent deaths of fishes and other aquatic plants and animals in the river as well as degrading the vegetation. Through infiltration, the shallow groundwater table are also contaminated through a complex process as summarized in figure 4.17



Figure 4.17: Conceptual Model of the Impact of Crude Oil Spill on the Environment (Adapted from United Nations Environment Programme, 2011)

The present study has revealed that hydrocarbon pollution in the study area is widespread and worrisome as soil, groundwater, surface water and rainwater have varying degree of pollution arising from benzene, a known carcinogen and a major component of the hydrocarbon (Achi, 2003). Diseases such as respiratory disorder, asthma and skin problem are the footprint of long term exposure to gas flaring in the area. It has also been ascertained from the study that the environmental, socio-economic and health problems ravaging the host communities is due to pollution arising from hydrocarbon exploration, exploitation, refining and marketing.

Apart from the high concentration of benzene already established, crude oil also contains toluene, ethylbenzene and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). These compounds are known carcinogens and therefore dangerous to health (Achi, 2003). The negligence by the authorities concerned in cleaning up oil spill enables rainfall to wash the oil away into neighbouring farmlands and rivers while some infiltrates into the groundwater system. This explains why we have high concentration of total hydrocarbon content (THC) in the soil, groundwater, surface water and rainwater samples analyzed. The study has also confirmed that the heavy metals in the crude oil are the major sources of heavy metal pollution in the environment (soil, groundwater, surface water and rainwater).

Hydrocarbon pollution is more pronounced in the southern part (Port-Harcourt area) than the northern part (Owerri area) because the southern portion has more creeks, oil wells, flow station, oil pipeline and gas flaring point than the northern portion (Amadi and Nwankwoala, 2013). Geologically, the southern part is composed of mainly friable sand with minor clay intercalation that is not continuous while in the northern part, the clay layers are continuous due to overlapping of Benin Formation by the Ogwashi-Asaba Formation, which are composed clay and lignite horizons. The hydraulic conductivity, transmissivity and rate of infiltration pollutant is higher at the southern part but decreases northwards. This explains why in some locations at Eleme, around the NNPC pipeline, it was observed that refined petroleum product were floating on the water level in some public wells. The community may have been drinking water from these polluted wells for decades and the number of people that might have died or suffering from various sicknesses relating to water pollution is better imagined. Hydrogeologically, the groundwater flows in a NE-SW direction (Figures 4. 18a and 4.18b), and contaminants are moved south-wards in response to the natural flow of the groundwater.

Since the water level in the study area is shallow and natural attenuation mechanism such as advection, adsorption and dispersion are entirely absent due the local geology (porous and permeable formation) by implication, the soil and groundwater in the area are in serious danger once there is pollution such as oil spill, as it will easily infiltrate downward. The Department of Petroleum Resources of Nigerian National Petroleum Cooperation (NNPC) estimated 1.89 million barrels of petroleum were spilled into the Niger Delta between 1976 and 1996 out of a total of 2.4 million barrels spilled in 4,835 incidents (Daily Trust, 2008). The United Nations Development Programme (UNDP), report states that there have been a total of 6,817 oil spills between 1976 and 2001, which account for a loss of three million barrels of oil, of which more than 70% was not recovered (Daily Trust, 2008).



Figure 4.18a: Groundwater flow direction of parts of Eastern Niger Delta



Figure 4.18b: Digital terrain model (DTM), groundwater flownet and VES point.

However, because this amount does not take into account "minor" spills, the World Bank argues that the true quantity of petroleum spilled into the environment could be as much as 10 times the officially claimed amount (Tell Magazine, 2008). Amund (2000) reported that between 9 million and 13 million barrels of crude oil have been spilled in the Niger Delta since 1958.

By multiplying this number by over 50 years of oil exploration in the region, it can be imagined what the host environment may look like. The accumulation effect is what has left crude oil in soil at greater depth while it freely floats in wells in the area. Surface water and vegetation also had their own share as the heavy rainfall lead to oil spill been washed away into the farmlands and rivers. When oil reaches the root zone, the crops and other plants begin to experience stress and later die, while those that survive has very low yield unlike the non-impacted farmlands and this has become a routine observation in the study area. This problem is further compounded by the use of aquifers and rivers in the area as a repository for human and industrial waste and this lead to the generating a contamination plume map for the area (Figure 4.19).

The UNEP (2011) investigation of parts of the area revealed that all air samples analyzed, benzene was found with concentration ranging from 0.156 to 48.3  $\mu$ g/m<sup>3</sup> and this is about 10 times higher than the maximum permissible limit of World Health Organization (WHO, 2006) and the United States Environmental Protection Agency (USEPA, 1998) and attributed the cancer epidemic in the area to the accumulated effect of long term exposure to benzene.

The findings underline that the people of Eastern Niger Delta, especially host communities to oil installations are exposed hydrocarbon pollution either in the air through long term non-stop gas flaring, in drinking water through oil spill and acid rain, or through direct contact with contaminated soil, sediments, fishes, plants and surface water. Since oil exploration and exploitation has been going on in the area for the past 50 years, it is a possibility that many people from the host communities have lived with chronic oil pollution throughout their lives.



Figure 4.19: Contamination plume map of parts of Eastern Niger Delta

## 4.9 Groundwater Vulnerability Map for Eastern Niger Delta

The knowledge of the geology and hydrogeology of the area, coupled with the information obtained through geophysical survey, borehole logging, sieve analysis, permeability test, pumping test and laboratory analysis, employed in this study were used to develop the vulnerability map for the aquifer system in the area (Figure 4.20). The entire area was categorized into three region based on pollutant dominance: areas of high vulnerability, moderate vulnerability and low vulnerability. The high vulnerability area are domiciled by high profile anthropogenic activities and have witnessed long term environmental degradation arising from gas flaring, oil spills, open dumpsites, urbanization and industrialization. The local geology of the southern portion might be also a contributing factor. The low vulnerability area is dominated by farming and industrial activities are quite minimal. The medium/moderate vulnerability region shares the characteristics of both high and low vulnerability region.



Figure 4.20: Groundwater Vulnerability Map of part of Eastern Niger Delta

## 4.10 Landfill Design Options for Aquifer/Groundwater Protection for the Area

The choice of a suitable landfill system depends on the geological, hydrogeological and environmental settings of the area. The nature of the geology of the area and the need to protect aquifer from contamination through various human activities in the area engineered the design of a modern sanitary landfill for the area. The technique will ensure that the aquifer is not polluted by leachate from landfills as currently experienced in the area. The design of the modern sanitary landfill should incorporate leachate collection chambers made of geomaterials such as clay liners or geotextiles material which are capable of impeding the downward migration of leachate.

The plan and section of the proposed modern sanitary landfill for medium and high vulnerability area are shown in figures 4.21 and 4.22 respectively. The fully designed modern sanitary landfills for medium and high vulnerability are displayed in figures 4.23 and 4.24 respectively. Deposited waste should be compacted to enhance its density and stability and covered to prevent the activities of flies and rodents. Gas extraction systems are installed to extract the landfill gas which can be used to generate electricity.



Figure 4.21: Section AA<sup>I</sup> for the designed Modern Sanitary Landfill (Amadi, 2012)



Figure 4.22: Plan of the Modern Sanitary Landfill for Medium/High Vulnerability Area (Amadi, 2012)



Figure 4.23: Modern Sanitary Landfill with Two Clay Liners Proposed for High Vulnerability Area (Amadi, 2012)



Figure 4.24: A Modern Sanitary Landfill with One Clay Liner Proposed for Moderate Vulnerability Area (Amadi, 2012)
## 4.11 Bioremediation

Bioremediation is the branch of biotechnology that uses biological process to solve environmental problems. It provides an innovative, cost effective and natural means of removing contaminants from contaminated soils and water. It is the use of biological agents, such as bacteria and fungi, to remove or neutralize contaminants, as in polluted soil or water (Figure 4.25). Bacteria and fungi generally work by breaking down contaminants such as petroleum into less harmful substances. Bioremediation technology exploits various naturally occurring mitigation processes such as: natural attenuation, biostimulation and bioaugmentation.

Bioremediation which occurs without any form of human intervention except monitoring is called natural attenuation. This natural attenuation relies solely on natural conditions and behavior of soil microorganisms that are indigenous to the soil. Biostimulation utilizes indigenous microbial populations to remediate contaminated soils, with the addition of nutrients and other substances to soil in order to catalyze the attenuation processes. Bioaugmentation involves introduction of exogenic microorganisms (microorganisms sourced from outside the soil environment) which has the potentials of detoxifying the contaminant. Genetically altered microorganisms are majorly used in bioaugmentation (Biobasics, 2006).

During bioremediation, microbes utilize chemical contaminants in the soil as an energy source and, through oxidation-reduction reactions, they metabolize the target contaminant into useable energy for microbes. By-products (metabolites) released back into the environment are in a less toxic form than the parent contaminants.

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Figure 4.25: An illustration of bioremediation technique (Yisa, 2002)

For instance, soil or water contaminated with crude oil (benzene, toluene, xylene and polycyclic aromatic hydrocarbon) can be degraded by microorganisms in the presence of oxygen through aerobic respiration. The hydrocarbon loses electrons and is oxidized while oxygen gains electrons and is reduced. The result is formation of carbon dioxide and water (Nester, Denise, Evans, Nancy and Martha, 2001). When oxygen is limited in supply or absent, as in saturated soils or river sediment, biodegradation occurs through anaerobic respiration. Inorganic compounds such as nitrate, sulfate, iron, manganese, or carbon dioxide serve as terminal electron acceptors to facilitate biodegradation (Department of Environmental Quality, Mississippi, 1998).

Three primary ingredients for bioremediation are presence of a contaminant, an electron acceptor and presence of microorganisms that are capable of degrading the specific contaminant. Studies have revealed that a contaminant is more easily and quickly degraded if it is a naturally occurring compound in the environment, or chemically similar to a naturally occurring compound, because microorganisms capable of its biodegradation are more likely to have evolved (Yisa, 2002). Petroleum are naturally occurring chemicals, therefore, microorganisms which are capable of attenuating or degrading hydrocarbons exist in the environment. Development of biodegradation technologies of synthetic chemicals such DDT is dependent on outcomes of research that searches for natural or genetically improved strains of microorganisms to degrade such contaminants into less toxic forms.

Microorganisms have limits of tolerance for particular environmental conditions, as well as optimal conditions for optimal performance. Factors that affect success and rate of microbial biodegradation are nutrient availability, moisture content, pH, and temperature of the soil matrix. Inorganic nutrients including, but not limited to, nitrogen and phosphorus are necessary for microbial activity and cell growth. Research has shown that treating petroleum-contaminated soil with nitrogen can increase cell growth rate, decrease the microbial lag phase, help to maintain microbial populations at high activity levels, and increase the rate of hydrocarbon degradation (Walworth, Andrew, Ian, John, Susan and Paul, 2005). However, it has also been shown that excessive amounts of nitrogen in soil cause microbial inhibition. Walworth *et al.*, (2005) suggest maintaining nitrogen levels below 1800 mg nitrogen/kg H<sub>2</sub>O for optimal biodegradation of hydrocarbons. Addition of phosphorus has benefits similar to that of nitrogen, but also results in similar limitations when applied in excess (Walworth *et al.*, 2005).

All soil microorganisms require moisture for cell growth and function. Availability of water affects diffusion of water and soluble nutrients in and out of microorganism cells. However, excess moisture, such as in saturated soil, is undesirable because it reduces the amount of available oxygen for aerobic respiration. Anaerobic respiration, which produces less energy for microorganisms (than aerobic respiration) and slows the rate of biodegradation, becomes the predominant process. Soil moisture content ranged between 45 and 85 percent of the water-holding capacity of the soil (or about 12 percent to 30 percent by weight) is optimal for hydrocarbon degradation (US EPA, 2006).

Soil pH is important because most microbial species can survive only within a certain pH range. Furthermore, soil pH can affect availability of nutrients. Biodegradation of hydrocarbons is optimal at a pH 7 (neutral), however, the acceptable pH range of 6 - 8 has been recommended (US EPA, 2006). Temperature influences rate of biodegradation by controlling rate of enzymatic reactions within microorganisms. The speed of enzymatic

reactions in the cell approximately doubles for each 10°C rise in temperature (Nester *et al.*, 2001). Most bacteria found in soil, including many fungi that degrade hydrocarbons, are mesophiles which have an optimum temperature ranged between 25°C to 45°C (Nester *et al.*, 2001). Thermophilic bacteria (those which survive and thrive at very high temperatures) degrade hydrocarbons with an increase in temperature to 60°C (Perfumo, Ibrahim, Roger and Luigi, 2007).

Contaminants can adsorb to soil particles, rendering some contaminants unavailable to microorganisms for biodegradation. Thus, in some circumstances, bioavailability of contaminants depends not only on the nature of the contaminant but also on soil type. Hydrophobic contaminants, such as hydrocarbons, have low solubility in water and tend to adsorb strongly in soil with high organic matter content. In such cases, surfactants are utilized as part of the bioremediation process to increase solubility and mobility of these contaminants (Department of Environmental Quality, Mississippi, 1998). Contaminants adsorbed to soil particles are mobilized and their solubility, biodegradation and bioavailability are enhanced at higher temperatures (Perfumo *et al.*, 2007).

Soil type is an important consideration when determining the best suited bioremediation approach to a particular situation. In-situ bioremediation refers to treatment of soil in place. In-situ biostimulation treatments usually involve bioventing, in which oxygen and/or nutrients are pumped through injection wells into the soil. It is imperative that oxygen and nutrients are distributed evenly throughout the contaminated soil. Soil texture directly affects the utility of bioventing, in as much as permeability of soil to air and water is a function of soil texture. Fine-textured soils like clays have low permeability, which prevents biovented oxygen and nutrients from dispersing throughout the soil. It is also difficult to control moisture content in fine textured soils because their smaller pores and high surface area allow it to retain water. Fine textured soils are slow to drain from watersaturated soil conditions, thus preventing oxygen from reaching the soil microbes throughout the contaminated area (US EPA, 2006). Bioventing is well-suited for welldrained, medium to coarse grained soils.

Ex-situ bioremediation, in which contaminated soil is excavated and treated elsewhere, is an alternative. Ex-situ bioremediation approaches include use of bioreactors, land-farming and biopiles. In the use of a bioreactor, contaminated soil is mixed with water and nutrients and the mixture is agitated by a mechanical bioreactor to stimulate action of microorganisms. This method is better-suited to clay soils than other methods and is generally a quick process (US EPA, 2006). Land-farming involves spreading contaminated soil over a collection system and stimulating microbial activity by allowing good aeration and by monitoring nutrient availability (US EPA, 2006). Biopiles are mounds of contaminated soils that are kept aerated by pumping air into piles of soil through an injection system (US EPA, 2006).

In each of these methods, conditions need to be monitored and adjusted regularly for optimal biodegradation. Use of land-farming and biopiles also present the issue of monitoring and containing volatilization of contaminants. Like in-situ methods, ex-situ bioremediation techniques are generally cost effective and use natural methods. Bioremediation has potential to provide a low cost, non-intrusive, natural method to render toxic substances in soil or water to less harmful or harmless over time especially hydrocarbon contamination. The effectiveness of bioremediation in the clean-up of hydrocarbon contaminated soils and water has been demonstrated in other coastal regions of the world with similar geology as the Niger Delta. However, it is a new technology in Nigeria.

### 4.12 Phytoremediation

Phytoremediation is defined as the use of living plants to remediate contaminated soil or water through removal, degradation or containment of the pollutants (Figure 4.26). It is a technique that is gaining more and more acceptance in bio-hydrogeology. Although phytoremediation has been employed in field of botany for many years, it is an emerging technique in the field of hydrobiology. Plants and large trees have been used for centuries to drain swamps, absorb heavy metals and organics (Hansen, 2000). Plants, like indian mustard, are used to extract heavy metals from contaminated sites. Phytoremediation techniques includes: phytoextraction, hyperaccumulation, rhizofiltration, rhizodegradation, phytovolatilization and phytostabalization.

### **4.12.1** Phytoextraction

In phytoextraction, also called phytoaccumulation, plants such as Indian mustard are used to extract heavy metals from contaminated sites. These plants can then be harvested and dried or incinerated. The ashes or residue are then vitrified or stabilized and then placed in landfills. According to the EPA, nickel, zinc, and copper are the best candidates for this method (US EPA, 1996). The primary objective of phytoextraction research has been to maximize the transfer of metallic contaminants to plants.



Figure 4.26: Phytoremediation Technique Proposed for Low Vulnerability Area (Modified from Fetter, 2007)

### **4.12.2 Hyperaccumulators**

The term hyperaccumulators refers to plants which tend to absorb very high levels of nutrient metals and accumulate them as nutrient in their plant mass. Because these plants are unable to distinguish between nutrient metals and heavy contaminating metals, they are good candidates for cleaning up heavy metal contamination. A great deal of research has been conducted to find which plants are the best for cleaning up different types of metal contamination. Plants such as barley, oat, indian mustard and several types of grasses have been studied extensively and found to be useful. Researchers have found that some of these plants become chlorotic as a result of the uptake of heavy metals, while others seem unaffected (Ebbs and Kochian, 1998). Cattails and salt marsh bulrush have been found to be successful in removing selenium from contaminated sites (DeSouza, Pilon-smits and Terry, 2000). Poplar trees have been used with success to remove the pesticide atrazine from soil (Black, 1995). In efforts to clean some of the metal and radioactive contamination near Chernobyl, sunflowers and Indian mustard plants were used with success to remove heavy metals such as strontium and cesium from ponds near the disaster site (Johnson, 1999).

## 4.12.3 Rhizofiltration

While phytoextraction is used primarily to clean contaminated soils, a similar process called rhizofiltration has been developed using the same principles to extract heavy metals from groundwater. In this process, the plants such as sunflowers and hybrid poplar are raised in a greenhouse. When they have developed an extensive root system, water from the waste site is provided to acclimate them to the metallic environment. Then the plants are transplanted to the contaminated site and, as before, are harvested after they reach their peak metal concentration showing pale yellowish colour. As a slight variation, the plants can be hydroponically grown in water pumped from a contaminated aquifer (US EPA, 1996).

### 4.12.4 Rhizodegradation

In a process called rhizodegradation (or enhanced rhizosphere biodegradation), the microorganisms present in the area immediately adjacent to the root, called the rhizosphere, are used to break down or metabolize organic contaminants. These microorganisms have also been found to be able to volatilize heavy metals such as selenium (DeSouza *et al*, 2000). Rhizodegradation addresses the major drawbacks of bioremediation, which include low microbial populations and high microbial inactivity. In bioremediation, indigenous microorganisms often need to be stimulated by adjusting soil temperature, oxygen availability and nutrient content of the soil. But, this stimulation can often be effected by the addition of carefully selected plants. When these plants are added to the site, they can create an environment conducive to active populations of bacteria, fungi, yeast and algae. This is accomplished through the secretion of sugars, alcohols and acids as food for the microorganisms and the loosening of the soil to bring oxygen and water to the microbial populations.

A group of scientists in southern Mexico studied the use of marsh plants to remediate petroleum contamination (Hansen, 2000). The authors cited other researches that had found a native plant, *Cyperus* sp., capable of growing and thriving in an environment with hydrocarbon concentrations as high as 450,000 ppm. *Cyperus* sp. was tested in a hydrocarbon concentration of 200,000 ppm and found to be a useful plant in removing this contamination. These scientists also tested the rhizosphere for microorganisms and found

unusually high contents of actinomycetes, yeasts, molds and bacteria and concluded that these organisms helped metabolize the hydrocarbons.

Another study, by Anderson *et al* (1995), suggested the use of rhizodegradation at retail agrochemical dealer sites. These sites often have high herbicide contamination and so plants must be chosen which are highly tolerant to herbicide. Anderson recommended plants such as kochia, barnyard grass or pigweed and cited research showing a high rate of metabolism in rhizosphere microorganisms.

### 4.12.5 Phytovolatilization

In another phytoremediation technique, plants absorb contaminants from the soil or groundwater and then release them to the air through transpiration. Sometimes these compounds can be metabolized or changed to a less harmful form, but often they are released unchanged in gaseous form. The rate of volatilization depends on several factors, including temperature, contaminant concentration and type, transpiring plant and other environmental factors. A large amount of research has been done using poplar trees to volatilize tetrachloroethylene (TCE). The EPA claims that poplars can remove 90% of the TCE in a contamination plume (US EPA, 1996).

Volatilization can also be used in tandem with other phytoremediation techniques described in this section. In tests (DeSouza *et al.*, 2000) on selenium removal, 10 -30% of the selenium removed by the plants was volatilized. The rest built up in the plant biomass and was disposed of after the harvesting of the plant. DeSouza *et al* (2000) found that most of the volatilized selenium was released in the form of dimethyl selenium (DMSe) which is 500-600 times less toxic than its inorganic forms. They concluded that the rhizosphere microbial populations volatilized some of the selenium before it entered the plant. The level of microbial volatilization was proved when an antibiotic was added to the soil. Under these conditions, selenium uptake by Indian mustard was reduced by 77-88%. It was further concluded that volatilized forms of selenium (which are nutrients to humans and animals at low concentrations but become toxic at high levels) are diluted and dispersed away from the polluted site and deposited in areas of selenium deficiency.

### 4.12.6 Phytostabalization

Another use of plants in groundwater and soil remediation is called phytostabalization and involves the use of plants to prevent migration or spreading of contaminants. The addition of plants, especially grasses and small plants with fine roots, helps prevent wind or water erosion of surficial contamination. Larger plants and trees can be used as natural hydraulic pumps to prevent vertical migration to ground water or lateral movement. Poplar trees are successful pumps since they extract and transpire 50-300 gallons of water per day (USEPA, 1996). Two significant uses of phytostabalization are buffer strips and riparian corridors. Buffer strips are lines of trees placed around the perimeter of a landfill to prevent runoff from reaching the waste and to prevent leachate from reaching the groundwater. Riparian corridors are lines of trees planted along streams or rivers to prevent contamination from reaching the water. Although the EPA separates these two applications of phytostabalization, the terms are also used interchangeably or together and called riparian buffer zones. They are especially useful for stopping agricultural runoff from entering water sources.

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# 4.13 Summary of Findings

The study has identified natural phenomena of salt intrusion and high iron content compounded by anthropogenic activities of acid-rain, hydrocarbon pollution, use of agrochemicals, industrial effluents and poor sanitation as factors contributing to soil and water deterioration in the Eastern Niger Delta region of Nigeria.

The work-done in Eastern Niger Delta can be summarized as follows:

- 1. Geological mapping
- 2. Hydrogeological investigation
- 3. Pre-drilling geophysical survey
- 4. Litholog
- 5. Sieve analysis
- 6. Permeability test
- 7. Pumping test
- 8. Laboratory analysis

#### **4.13.1 Geological Mapping**

The geology of parts of Eastern Niger Delta was studied on a scale of 1:55 km. The formation is composed of sandy horizons belonging to the Benin Formation of Miocene to Recent age.. The sand is mostly coarse-grained, pebbly, poorly sorted and contains pods and lenses of fine-grained sands while clays occur as streak and discontinuous lenses.

# 4.13.2 Hydrogeological Mapping

The study area is underlain by a thick unconfined aquifer of regional extent although localized confined aquifers occur. The formation is made up of fresh water bearing continental sand with clay intercalation. Recharge into the unconfined aquifer is through direct infiltration of antecedent rain water with an annual rainfall of about 2500 mm. The depth to the water table is generally low (< 18 m), flowing in a NE-SW direction, obeying the regional flow direction of Niger Delta. The area is drained by Imo, kwa-Ibo, Aba and Bonny Rivers and their tributaries.

#### 4.13.3 Pre-drilling Geophysical Survey

The result of the geophysical investigation as evidenced in the geoelectric section indicates that the subsurface geology in the study area is dominated by sandy formation with minor occurrences of clay of variable depth. The results of the field curve matching and the interpretation of the computer modelled curve revealed that the VES curves in the area can be categorized into KH, AK and HA curve types. About 68% of the curves falls under KH-curve type where  $\rho_1 < \rho_2 > \rho_3 < \rho_4$ , followed by AK-curve type, which consists about 21% of the total curves in which  $\rho_1 < \rho_2 < \rho_3 > \rho_4$  and HA-curve type with about 11% dominance of the total curve types in which  $\rho_1 > \rho_2 < \rho_3 < \rho_4$ .

### 4.13.4 Litholog

The lithologs were prepared from the drilling cuttings collected at 3 m interval from each of the boreholes drilled. They were thoroughly washed, dried and described sequentially. The lithologs gave a good lithostratigraphic profile of the subsurface geology from north to south of the study area. The results of the lithologs revealed that the area is predominantly sandy formation, which is in line with the geological, hydrogeological and geophysical findings.

### 4.13.5 Sieve Analysis

The sieve analysis was carried out on borehole cuttings and soil samples to further ascertain the dominance lithology in the study area. The particle size distribution curves obtained shows that the about 92% of the curve falls within the sand portion. The hydraulic conductivity 'k' was obtained from the grain size distribution curve using Hazen's Formula. The values ranged between 3.2 m/d and 478.4 m/d with a mean value of 98.6 m/d. This result indicates a porous and permeable sandy formation which is in conformity to the findings obtained from lithological logging, geophysical, hydrogeological and geological mapping.

### 4.13.6 Permeability Test

The results of the coefficient of permeability determined from Constant Head Permeameter test ranged between  $9.5 \times 10^{-5}$  cm/s and  $4.2 \times 10^{-5}$  cm/s and an average value of  $6.8 \times 10^{-5}$  cm/s. These values indicate the soil horizon through which fluid migrates to the underlying aquifer is of relatively high permeability and this is in support with the earlier discussions and findings. By implication, the high permeability of the formation and the shallow water table makes the soil, aquifer and groundwater system in the area vulnerable, as pollutant can be transported with little resistance into the groundwater table.

### 4.13.7 Pumping Test

Pumping test was conducted from the drilled boreholes in order to ascertain the hydraulic properties of the aquifer which will determine the size of the submersible pump to be installed for optimum performance of the well. The information obtained from the pumping test (Table 4.3) show that the rocks in the area has high transmissivity and specific capacity with low static water level. The properties of the subsurface formation make it possible for

contaminant to migrate into the groundwater system overtime, giving the average linear groundwater velocity in the area ranged between 40 m/yr and 400 m/yr (Uma, 1986). It is on record that oil exploration and exploitation has been ongoing in the area for the past 50 years while some oil spill, flow stations, gas flaring point and dumpsites has been active for the past 35 years.

#### 4.13.8 Laboratory Analyses

Laboratory analyses were carried out on soil, surface water, groundwater and rainwater (direct rainwater and roof-top collected rainwater). The results of the analyzed relevant parameters were compared with the Nigerian Standard for Drinking Water Quality (NSDWQ, 2007) and World Health Organization (WHO, 2006) recommended maximum permissible limit. A cursory examination of the results shows a wide range of standard deviation and variance which implies a substantial difference in the soil and water quality. The Piper, Durov and Schoeller interpretation of the groundwater in the area revealed six hydro-facies/water types. Similarly, the application of multivariate geostatistical techniques on the groundwater identified six factors and this suggests six possible sources of pollution in the area, which can be categorized into both natural and anthropogenic sources.

The pH concentration is generally low and it could be attributed to acid rain arising from the long term non-stop gas flaring and indiscriminate oil spills that have characterized the area. Heavy metal concentrations are in the order of: Fe > Ni > Cu > Zn > Mn > Cd > V >Co > Pb > Cr > As > Hg and this similar trend were observed in the geologic materials analyzed. It has been established from this study that the heavy metal pollution is more on soil, followed by rainwater, groundwater and surface water respectively based on their concentration trend (Figure 4.27). Similar trend was observed in the vicinity of dumpsites in the area. It is believed that crude oil activities and leachate from dumpsite are the possible sources of these pollutants in the aquifer and groundwater system in the area. Solution of these gases in the rainwater under relatively high partial pressure of the gases raises the concentration of the bicarbonate and sulphate ions in the antecedent rainwater that subsequently recharges the groundwater.

The general pattern of distribution of the geochemical constituents with high values in the vicinity of gas flaring and flow stations and low values at distances away from the stations (Figure 4.28) clearly indicate that the enrichment of the ions are associated with the envisaged anthropogenic activities domiciled in the area. Hydrocarbon exploration, exploitation, refining and marketing has brought high class environmental degradation to the area and the footprint are shown by the hydrocarbon pollution of soil, sediments, air, groundwater, surface water and rainwater in the area. Fishing, farming and other socio-economic activities in the area have been crippled by same hydrocarbon pollution while the natural mangroves and vegetation have also been destroyed by the same culprit. The field observations and scientific investigation found that hydrocarbon pollution in the study area is widespread and multi-dimensional in nature as many components of the environments such as land, air and water are polluted and this has had its own share on the health of the people.



Figure 4.27: Relationship between Heavy Metal Concentration in Soil, Groundwater, Surface Water and Rainwater



Figure 4.28: Concentration of pH, Moisture Content (MC), Bacteria Count (BC), Temperature, Heavy Metals (HM) and Total Hydrocarbon (TH) in Soil with Distance (km) from a Gas Flaring Station

### **CHAPTER FIVE**

5.0 CONCLUSION AND RECOMMENDATIONS

# 5.1 Conclusion

This study has clearly established that gas flaring, oil spill and indiscriminate dumping of wastes constitute a major source of soil and water pollution in the oil producing region of Eastern Niger Delta, Nigeria. It is remarkable to note that concentration of the ions consistently decreased away from the gas flaring points, flow stations and dumpsites. The results revealed that the impact is heaviest on soil, followed by rainwater, groundwater and surface water. This is because the soil is directly in contact with the oil spill while rainwater is in contact with CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>2</sub> from the burning gas. It has also been confirmed that the concentration of heavy metals in soil and rainwater are higher dry season than in rainy season while the reverse is true for groundwater and surface water. These may be attributed to the possibility of heavy metals being lost through surface run-off in the rivers or by infiltration through the permeable formation into the groundwater table. The metals decrease in the order of: Fe > Ni > Cu > Zn > Mn > Cd > V > Co > Pb > Cr > As > Hg and this trend is applicable to soil, rainwater, groundwater and surface water.

Among significant variables that control the distribution and enrichment of heavy metals in soils are pH of soil, grain size of the soil, amount of organic matter in the soil and the cation exchange capacity of the soil (Lin *et al.*, 2002). The soil pH is generally low, signifying acidic soil while loamy soil characterize the top soil at the flow stations and dumpsites and these condition enhances the precipitation and bio-accumulation of heavy metals in soil. Heavy metals have a strong affinity for organic content, clay, silt and sandy fraction because of their high cation exchange capacity (Huang and Lin, 2003). The top-soil

from the area comprises of organic content, clay-silt and sandy fraction. The study has revealed that the various anthropogenic activities domiciled in the area have constituted serious soil and water quality problems which have resulted to classic environmental and health challenges in their host communities.

Apart from anthropogenic interference in the groundwater system in the area due the huge human activities going on in the area, salinity and high iron content constitutes the major natural sources of groundwater pollution in the area. Many boreholes in the area have been abandoned solely due to the problem of salt water intrusion and or high iron content. The impact of salt intrusion is more on the southern part of the area than the northern part of the area while the reverse was the case for high iron content. The sea water from the Atlantic Ocean that bounds the southern portion of the area may be responsible for the problem of salt intrusion while the leaching of thick porous and permeable lateritic overburden in the northern part of the may be attributed to the high iron content of the groundwater from the area.

# **5.2 Recommendations**

The following recommendations are suggested:

- i. The government should without any further delay, put an end to gas flaring and artisanal crude oil refining.
- With respect to the degree and extent of hydrocarbon pollution in the area, a multi-purpose approach, aimed at cleaning up the polluted top soil, surface water and replanting of the vegetation as a way of restoration is advocated.

- iii. The use of all drinking water wells where crude oil has been detected should be discontinued and the community informed on the health implications associated with drinking water polluted with hydrocarbon.
- iv. Host communities where the surface water is polluted with hydrocarbon should be cautioned on the danger of fishing, swimming, bathing and drinking such water.
- v. Use of bioremediation and phytoremediation in degrading soils and water polluted with hydrocarbon is advocated, since they provide a cost effective, non-intrusive and natural method to render toxic substances in soil or water to less harmful or harmless.
- vi. People living near gas flaring stations and flow station where the rainwater is polluted should be advised not to consume or wash with such water. Alternative water supply should be arranged for such communities.
- vii. All government agencies saddled with the responsibility of cleaning up oil spill and other environmental challenges should be monitored to ensure compliance.
- viii. Public lectures, workshops and seminars should be organized to create the awareness on the danger of hydrocarbon pollution on the environment and how to minimize it.
- ix. Oil companies should henceforth ensure industry best practices are employed in their operations in the region
- x. Periodic environmental assessment by all stake holders in the oil sector (Government, oil companies and host communities) should be constituted to ensure no future abuse of the ecosystem.

- xi. Sequential evaluation of the soil and water from the area should be carried out to ensure that the water and soil from the area are free any form of pollution.
- xii. Over-exploitation of groundwater that propels salt water intrusion should be adequately controlled in the area.
- xiii. The use of waste hierarchy/pyramid (Figure 5.1), starting from prevention, minimisation, reuse, recycling, energy recovery to disposal is highly recommended.



Figure 5.1: Waste management hierarchy

# 5.3 Areas of further studies

Due the financial constrains, fishes, plants and sediments from the creeks and rivers were not analyzed. It is my opinion based on the hydraulic connection between soil and plant, that the root, stem and leaves of plants from the area be analyzed in order to ascertain the level of pollution in terms of hydrocarbon content and heavy metals, since some plant are known to absorb metal and organic compounds such as benzene and toluene. It will also be good if sediments from the polluted creeks and rivers were also analyzed so as to correlate their degree of pollution. Such studies will enable one to ascertain whether heavy metals are more concentrated on the sediment (bottom) than on the water (surface) and vice versa. Furthermore, it would have been good also if fish from the polluted creeks and rivers were analyzed and it concentration of heavy metals and benzene determined. This would have enabled one to know the different pollution source in the area either by land (oil spills), by water (drinking polluted groundwater, surface water and rainwater), by air (inhaling gases flared), or by food (eating polluted plants and fish). Pollution by hydrocarbon on land and water in the area has been investigated in the present study while air pollution by benzene in the area was confirmed (UNEP, 2011). The remaining challenge is to ascertain the degree of hydrocarbon pollution by food items such as plants, vegetables and fishes.

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#### **APPENDIX A**

# **Existing Environmental Situations in Esatern Niger Delta**



An overview of Afam flow station in the study area



Crude oil pipelines in Eleme, Rivers State



Villagers using heat from the gas flares to dry their food products



Overview of Enyimba dumpsite, Aba, Abia State



Death of craps, crayfish and fishes due to hydrocarbon pollution of the surface water



Cluster of zinc roofs with various degree of rusting/caving-in



Devastation of the Vegetation in the area due to acid rain



Crude oil spill on soil from the area (visible top-soil caked in dried crude oil)



Visible Hydrocarbon Pollution on Surface Water in Eleme



Degradation of land/vegetation due to leakage from crude oil pipeline

#### **APPENDIX B**

# Vertical Electrical Sounding (VES) field data

Reading	AB/2	MN/2	KS	R	<mark>Р</mark> а
1	1.5		6.28	.994	6.24
2	2.0		11.78	1.01	11.98
3	2.5		18.84	.644	12.13
4	3.5		37.68	.430	16.20
5	4.5		62.8	.406	24.49
6	6.0	0.5	112.3	.386	43.34
7	8.0		200.0	.419	83.80
8	10.0		313.21	.343	107.43
9	15.0		705.71	.381	268.87
10	10.0		39.36	6.26	246.39
11	15.0		95.43	3.11	296.78
12	20.0		173.98	1.83	318.38
13	25.0	3.5	274.86	1.17	321.58
14	35		544	.503	273.73
15	45		908.36	.223	202.56
16	55		1352	.119	160.88
17	45		205.1	1.14	233.81
18	55		317	.558	176.88
19	75	14.0	608.82	.359	218.56
20	95		991	.257	254.68
21	125		1730	.053	91.69
22	165		3030	.093	283.60
23	215		5161	.067	350.43

# **Result of Vertical Electrical Sounding for location 1**

Reading	AB/2	MN/2	KS	R	pa
1	1.5		6.28	28.19	177.03
2	2.0		11.78	18.10	213.21
3	2.5		18.84	13.40	252.45
4	3.5		37.68	8.97	337.98
5	4.5		62.8	6.50	408.20
6	6.0	0.5	112.3	44.29	481.76
7	8.0		200.0	2.92	584.00
8	10.0		313.21	2.22	695.32
9	15.0		705.71	1.41	995.05
10	10.0		39.36	14.34	564.42
11	15.0		95.43	8.88	847.41
12	20.0		173.98	6.10	106.22
13	25.0	3.5	274.86	4.15	1140.67
14	35		544	2.23	1213.12
15	45		908.36	1.26	1144.53
16	55		1352	.821	1109.99
17	45		205.1	5.02	1029.66
18	55		317	3.10	982.7
19	75	14.0	608.82	1.69	1028.90
20	95		991	1.01	1000.91
21	125		1730	.545	942.85
22	165		3030	34	1021.08

**Result of Vertical Electrical Sounding for location 2** 

Reading	AB/2	MN/2	KS	R	pa
1	1.5		6.28	29.72	186.64
2	2.0		11.78	19.18	225.94
3	2.5		18.84	11.45	215.71
4	3.5		37.68	8.91	335.72
5	4.5		62.8	6.75	423.91
6	6.0	0.5	112.3	4.91	551.31
7	8.0		200.0	3.35	670.00
8	10.0		313.21	2.45	767.36
9	15.0		705.71	1.43	1009.16
10	10.0		39.36	16.62	630.54
11	15.0		95.43	9.43	899.90
12	20.0		173.98	6.29	1003.89
13	25.0	3.5	274.86	4.44	1220.37
14	35		544	2.62	1425.28
15	45		908.36	1.66	1507.87
16	55		1352	1.27	1717.04
17	45		205.1	6.41	1314.69
18	55		317	4.76	1508.92
19	75	14.0	608.82	2.74	1528.13
20	95		991	1.83	1476.59
21	125		1730	1.21	1261.12
22	165		3030	0.49	1605.90

**Result of Vertical Electrical Sounding for location 3** 

Reading	AB/2	MN/2	KS	R	pa
1	1.5		6.28	15.92	99.99
2	2.0		11.78	8.67	102.13
3	2.5		18.84	5.78	109.08
4	3.5		37.68	3.17	119.44
5	4.5		62.8	.146	9.16
6	6.0	0.5	112.3	.163	18.30
7	8.0		200.0	.853	170.60
8	10.0		313.21	.511	160.11
9	15.0		705.71	.404	285.10
10	10.0		39.36	-1.21	123.20
11	15.0		95.43	.043	4.10
12	20.0		173.98	.08	21.80
13	25.0	3.5	274.86	.003	1.07
14	35		544	.455	247.52
15	45		908.36	1.09	992.83
16	55		1352	.286	386.67
17	45		205.1	1.165	238.94
18	55		317	.465	147.40
19	75	14.0	608.82	.026	15.82
20	95		991	.609	603.52
21	125		1730	2.0	290.43
22	165		3030	-65	183.42

**Result of Vertical Electrical Sounding for location 4** 

Reading	<b>AB/2</b>	MN/2	KS	R	ра
1	1.5		6.28	50.01	314.06
2	2.0		11.78	30.32	357.16
3	2.5		18.84	21.12	397.90
4	3.5		37.68	13.47	507.54
5	4.5		62.8	9.18	577.13
6	6.0	0.5	112.3	5.72	642.35
7	8.0		200.0	3.69	738.00
8	10.0		313.21	2.58	808.08
9	15.0		705.71	1.40	957.99
10	10.0		39.36	17.13	674.23
11	15.0		95.43	8.56	816
12	20.0		173.98	5.53	962.10
13	25.0	3.5	274.86	3.86	1060.95
14	35		544	2.22	1207.68
15	45		908.36	1.50	1362.54
16	55		1352	1.06	1433.12
17	45		205.1	6.60	1353.16
18	55		317	4.61	1451.37
19	75	14.0	608.82	2.74	1668.16
20	95		991	2.83	1613.53
21	125		1730	1.21	883.30
22	165		3030	0.490	1484.00

**Result of Vertical Electrical Sounding for location 5** 

Reading	AB/2	MN/2	KS	R	pa
1	1.5		6.28	111.36	699.46
2	2.0		11.78	74.72	880.20
3	2.5		18.84	51.19	964.41
4	3.5		37.68	29.80	1122.86
5	4.5		62.8	18.89	1183.15
6	6.0	0.5	112.3	11.20	1257.76
7	8.0		200.0	6.12	1224.00
8	10.0		313.21	3.89	1218.38
9	15.0		705.71	1.80	1270.27
10	10.0		39.36	37.32	1468.91
11	15.0		95.43	17.25	1646.16
12	20.0		173.98	10.45	1818.09
13	25.0	3.5	274.86	6.95	1910.27
14	35		544	3.47	1887.68
15	45		908.36	2.02	1880.30
16	55		1352	1.34	1865.76
17	45		205.1	11.41	2340.19
18	55		317	8.27	2621.59
19	75	14.0	608.82	4.83	2940.68
20	95		991	3.10	3072.10
21	125		1730	1.67	2889.10
22	165		3030	1.01	3060.31

**Result of Vertical Electrical Sounding for location 6** 

Reading	AB/2	MN/2	KS	R	Pa
1	1.5		6.28	18.32	115.04
2	2.0		11.78	10.30	121.33
3	2.5		18.84	6.81	128.30
4	3.5		37.68	4.54	171.06
5	4.5		62.8	3.04	190.91
6	6.0	0.5	112.3	2.02	226.84
7	8.0		200.0	1.40	280.00
8	10.0		313.21	1.01	316.34
9	15.0		705.71	.526	371.20
10	10.0		39.36	5.30	247.96
11	15.0		95.43	3.22	307.28
12	20.0		173.98	1.99	346.22
13	25.0	3.5	274.86	1.28	350.72
14	35		544	.628	341.63
15	45		908.36	.313	284.31
16	55		1352	.194	262.28
17	45		205.1	1.44	295.34
18	55		317	.838	265.64
19	75	14.0	608.82	.037	230.13
20	95		991	.205	203.15
21	125		1730	.121	209.33
22	165		3030	.084	256.64

**Result of Vertical Electrical Sounding for location 7** 

Reading	<b>AB/ 2</b>	<b>MN/2</b>	KS	R	pa
1	1.5		6.28	71.81	450.96
2	2.0		11.78	42.50	500.65
3	2.5		18.84	31.06	585.17
4	3.5		37.68	18.01	678.61
5	4.5		62.8	12.84	1131.02
6	6.0	0.5	112.3	8.53	957.91
7	8.0		200.0	5.50	1100.89
8	10.0		313.21	3.61	1130.68
9	15.0		705.71	1.40	987.99
10	10.0		39.36	28.71	1130.02
11	15.0		95.43	11.03	1052.59
12	20.0		173.98	4.91	854.24
13	25.0	3.5	274.86	2.57	689.89
14	35		544	1.00	544.00
15	45		908.36	.609	553.19
16	55		1352	.418	565.13
17	45		205.1	2.83	580.13
18	55		317	1.80	570.60
19	75	14.0	608.82	.785	477.92
20	95		991	708	701.62
21	125		1730	1.08	1868.43
22	165		3030	2.05	1358.21

**Result of Vertical Electrical Sounding for location 8** 

Reading	AB/ 2	MN/ 2	KS	R	pa
1	1.5		6.28	12.30	77.24
2	2.0		11.78	8.01	94.35
3	2.5		18.84	5.91	111.34
4	3.5		37.68	3.98	526.76
5	4.5		62.8	2.83	177.72
6	6.0	0.5	112.3	1.61	180.80
7	8.0		200.0	1.19	238.00
8	10.0		313.21	.790	247.43
9	15.0		705.71	.576	406.48
10	10.0		39.36	6.79	267.25
11	15.0		95.43	3.72	354.99
12	20.0		173.98	2.74	476.70
13	25.0	3.5	274.86	2.18	599.19
14	35		544	1.42	772.48
15	45		908.36	.992	901.09
16	55		1352	.735	993.72
17	45		205.1	4.26	873.72
18	55		317	3.12	989.04
19	75	14.0	608.82	1.804	1098.31
20	95		991	1.16	1149.56
21	125		1730	.630	1089.90
22	165		3030	.328	993.84

**Result of Vertical Electrical Sounding for location 9** 

Reading	<b>AB/2</b>	MN/2	KS	R	ра
1	1.5		6.28	27.15	170.50
2	2.0		11.78	13.56	159.73
3	2.5		18.84	8.55	161.08
4	3.5		37.68	4.43	166.92
5	4.5		62.8	3.29	206.61
6	6.0	0.5	112.3	2.12	238.07
7	8.0		200.0	1.67	324.00
8	10.0		313.21	1.23	385.24
9	15.0		705.71	.651	459.41
10	10.0		39.36	8.47	333.37
11	15.0		95.43	5.00	477.15
12	20.0		173.98	3.91	680.26
13	25.0	3.5	274.86	3.03	832.82
14	35		544	2.10	1142.40
15	45		908.36	1.58	1435.20
16	55		1352	1.58	1435.20
17	45		205.1	6.72	1378.27
18	55		317	5.38	1705.46
19	75	14.0	608.82	2.30	1400.28
20	95		991	1.93	1912.63
21	125		1730	1.50	2595.00
22	165		3030	1.49	4514.70

**Result of Vertical Electrical Sounding for location 10** 

Reading	<b>AB/ 2</b>	MN/2	KS	R	pa
1	1.5		6.28	95.16	597.60
2	2.0		11.78	56.08	660.62
3	2.5		18.84	40.57	764.33
4	3.5		37.68	24.65	928.81
5	4.5		62.8	16.82	206.61
6	6.0	0.5	112.3	11.91	1337.49
7	8.0		200.0	7.63	1526.20
8	10.0		313.21	5.43	1700.73
9	15.0		705.71	2.76	1947.25
10	10.0		39.36	42.31	1665.32
11	15.0		95.43	20.44	1950.58
12	20.0		173.98	12.25	2131.25
13	25.0	3.5	274.86	7.88	2165.89
14	35		544	4.22	2295.68
15	45		908.36	2.05	1871.22
16	55		1352	1.92	2595.84
17	45		205.1	13.83	2836.53
18	55		317	9.23	2925.91
19	75	14.0	608.82	5.37	3269.36
20	95		991	2.39	2368.49
21	125		1730	1.16	2006.80
22	165		3030	.558	1690.74

**Result of Vertical Electrical Sounding for location 11** 

Dooding	AB/2	MN/2	KS	D	00
1	1.5		6.28	37.96	238.38
2	2.0		11.78	25.44	311.46
3	2.5		18.84	18.82	354.56
4	3.5		37.68	11.54	434.82
5	4.5		62.8	8.50	533.80
6	6.0	0.5	112.3	8.96	669.31
7	8.0		200.0	4.04	808.00
8	10.0		313.21	2.85	892.64
9	15.0		705.71	1.51	1065.62
10	10.0		39.36	19.39	763.19
11	15.0		95.43	9.86	940.43
12	20.0		173.98	6.00	1043.88
13	25.0	3.5	274.86	3.99	1096.64
14	35		544	2.17	1180.48
15	45		908.36	1.30	1180.86
16	55		1352	.905	1223.56
17	45		205.1	6.82	1398.78
18	55		317	4.66	1477.22
19	75	14.0	608.82	3.04	1850.81
20	95		991	1.98	1962.18
21	125		1730	1.11	1920.30
22	165		3030	.359	1077.77

**Result of Vertical Electrical Sounding for location 12** 

Reading	<b>AB/ 2</b>	MN/2	KS	R	pa
1	1.5		6.28	58.29	366.06
2	2.0		11.78	35.24	415.12
3	2.5		18.84	23.85	449.33
4	3.5		37.68	13.04	491.34
5	4.5		62.8	8.06	506.16
6	6.0	0.5	112.3	4.76	534.54
7	8.0		200.0	3.53	706.00
8	10.0		313.21	2.36	739.17
9	15.0		705.71	1.45	1023.27
10	10.0		39.36	15.32	602.99
11	15.0		95.43	8.21	783.48
12	20.0		173.98	5.96	1036.92
13	25.0	3.5	274.86	4.41	1212.13
14	35		544	3.13	1702.72
15	45		908.36	2.57	2334.48
16	55		1352	1.77	2393.04
17	45		205.1	9.88	2026.38
18	55		317	6.86	2174.62
19	75	14.0	608.82	4.05	2465.72
20	95		991	2.86	2834.26
21	125		1730	1.47	2543.10
22	165		3030	.871	2439.13

**Result of Vertical Electrical Sounding for location 13** 

Reading	AB/ 2	MN/ 2	KS	R	ра
1	1.5		6.28	56.49	354.75
2	2.0		11.78	36.31	427.73
3	2.5		18.84	24.10	454.04
4	3.5		37.68	14.04	529.02
5	4.5		62.8	8.98	563.94
6	6.0	0.5	112.3	4.07	457.06
7	8.0		200.0	3.37	674.00
8	10.0		313.21	2.28	714.11
9	15.0		705.71	1.27	896.25
10	10.0		39.36	18.61	732.48
11	15.0		95.43	9.76	931.39
12	20.0		173.98	5.90	1026.48
13	25.0	3.5	274.86	4.41	1212.13
14	35		544	2.52	1370.88
15	45		908.36	1.63	1480.62
16	55		1352	1.45	1960.40
17	45		205.1	8.26	1694.12
18	55		317	5.92	1876.64
19	75	14.0	608.82	3.51	2136.95
20	95		991	1.89	1872.99
21	125		1730	.388	671.24
22	165		3030	.796	2411.88

**Result of Vertical Electrical Sounding for location 14** 

	Depth (m)	Resistivity (Ohm-m)	Lithology
	0-0.7	6.4	Lateritic sand
VES 1	0.7-12.2	1004.4	Fine sand
	12.2-57.7	89.3	Sand
	>57.7	528.6	Coarse sand
	0-1.1	171.3	Top soil
VES 2	1.1-13.3	586.6	Fine sand
	13.3-56.3	4035.4	Very coarse sand
	>56.3	646.8	Coarse sand
	0-1.4	160.1	Laterite
VES 3	1.4-4.3	1288.5	Fine sand
	4.3-33.6	2173.7	Coarse sand
	33.6-116.2	831.2	Sand with clay lenses
	>116.2	14786.7	Very Coarse sand
	0-3.9	88.1	Top soil
VES 4	3.9-10	8.2	Sand
	10-48.4	1365.8	Fine-medium sand
	>48.4	1223.4	Coarse sand
	0-2.8	366.1	Lateritic fine sand
VES 5	2.8-35.9	1555.1	Very coarse sand
	35.9-80.2	1208.7	Coarse sand
	>80.2	1216.3	Coarse sand
	0-1.8	799.9	Lateritic soil
VES 6	1.8-9.2	1624.8	Fine sand
	9.2-48	2385.4	Coarse sand
	>48	4159.5	Very coarse sand
	0-2.0	111.2	Laterite
VES 7	2.0-12.9	547.7	Medium grained sand
	12.9-53.8	175.1	Sand
	>53.8	254.3	Coarse sand

Interpreted Vertical Electrical Sounding data for location 1 to location 14

	0-1.3	406.1	Lateritic topsoil
VES 8	1.3-6.1	2035.6	Laterite
	6.1-30.1	346.7	Sand
	30.1-61.1	1183.4	Coarse Sand
	>61.1	3317.2	Very coarse sand
	0-1.9	95.4	Laterite
VES 9	1.9-12.7	784.5	Fine sand
	12.7-23.0	1536.6	Very coarse sand
	>23.0	1290.0	Coarse sand
	0-2.9	150.1	Laterite
VES10	2.9-8.3	786.1	Fine sand
	8.3-30.1	2680.3	Coarse sand
	>30.1	8481.5	Very coarse sand
	0-3.1	575.3	Laterite
VES11	3.1-13.9	4936.6	Very coarse sand
	13.9-93.8	2146.8	Coarse sand
	>93.8	1201.3	Coarse sand
	0-1.6	250.3	Sand
VES12	1.6-10.9	1313.2	Medium sand
	10.9-43.3	1720.9	Coarse sand
	43.3-106.2	1736.9	Coarse sand
	>106.2	896.8	Fine sand
	0-3.6	414.5	Laterite
VES13	3.6-9.6	1055.3	Fine sand
	9.6-39.8	4454.6	Very coarse sand
	>39.8	2508.7	Coarse sand
	0-3.6	412.6	Fine sand
VES14	3.6-10.2	1722.3	Coarse sand
	10.2-54.3	1676.3	Coarse sand

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#### **APPENDIX C**

#### **Computer Modelled Curves from the VES data**



**Computer Modelled Curves from the VES-2** 



#### **Computer Modelled Curves from the VES-3**



**Computer Modelled Curves from the VES 4** 



**Computer Modelled Curves from the VES 5** 



**Computer Modelled Curves from the VES 6** 



**Computer Modelled Curves from the VES 7** 



**Computer Modelled Curves from the VES 8** 



**Computer Modelled Curves from the VES 9** 



**Computer Modelled Curves from the VES 10** 



**Computer Modelled Curves from the VES 11** 



**Computer Modelled Curves from the VES 12** 



**Computer Modelled Curves from the VES 13** 



**Computer Modelled Curves from the VES 14** 

# **APPENDIX D**

# Pumping test field data (Drawdown and Recovery tests)

			Water			
D	<b>T</b> .	Discharge	Level	Drawdown		Specific
Day 1	Time 8.08	l/sec	<u>(m)</u>	<u>(m)</u>	<u>Min</u>	Yield
Day – I	0.00	1.52	57.5	0	0.00	
	8.09	1.52	61.7	2.2	0.50	0.69
	8.10	1.52	61.9	2.4	1.00	0.63
	8.15	1.52	62.1	2.6	6.00	0.58
	8.25	1.52	62.5	3	11.00	0.51
	8.45	1.52	62.6	3.1	36.00	0.49
	9.15	1.52	62.8	3.3	66.00	0.46
	10.15	1.52	62.9	3.4	126.00	0.45
	11.15	1.52	62.9	3.4	186.00	0.45
	12.15	1.52	62.9	3.4	246.00	0.45
	13.15	1.52	62.9	3.4	306.00	0.45
	14.15	1.52	62.9	3.4	366.00	0.45
	15.15	1.52	62.9	3.4	426.00	0.45
	16.15	1.52	62.9	3.4	486.00	0.45
	17.15	1.52	62.9	3.4	546.00	0.45
	18.15	1.52	62.9	3.4	606.00	0.45
	19.15	1.52	62.9	3.4	666.00	0.45
	20.15	1.52	62.9	3.4	726.00	0.45

# Drawdown data at Obigbo

	21.15	1.52	62.9	3.4	786.00	0.45
	22.15	1.52	62.9	3.4	846.00	0.45
	23.15	1.52	62.9	3.4	906.00	0.45
	24.15	1.52	62.9	3.4	966.00	0.45
	1.15	1.52	62.9	3.4	1026.0	0.45
	2.15	1.52	62.9	3.4	1086.0	0.45
	3.15	1.52	62.9	3.4	1146.0	0.45
	4.15	1.52	62.9	3.4	1206.0	0.45
	5.15	1.52	62.9	3.4	1266.0	0.45
	6.15	1.52	62.9	3.4	1326.0	0.45
	7.15	1.52	62.9	3.4	1386.0	0.45
Day – 2	8.15	3.92	65.7	6.2	1446.0	0.63
	9.15	3.92	65.9	6.4	1506.0	0.61
	10.15	3.92	66.1	6.6	1566.0	0.59
	11.15	3.92	66.4	6.9	1626.0	0.57
	12.15	3.92	66.4	6.9	1686.0	0.57
	13.15	3.92	66.4	6.9	1746.0	0.57
	14.15	3.92	66.4	6.9	1806.0	0.57
	15.15	3.92	66.4	6.9	1866.0	0.57
	16.15	3.92	66.4	6.9	1926.0	0.57
	17.15	3.92	66.4	6.9	1986.0	0.57
	18.15	3.92	66.4	6.9	2046.0	0.57
	19.15	3.92	66.4	6.9	2106.0	0.57

	20.15	3.92	66.4	6.9	2166.0	0.57
	21.15	3.92	66.4	6.9	2226.0	0.57
	22.15	3.92	66.4	6.9	2286.0	0.57
	23.15	3.92	66.4	6.9	2346.0	0.57
	24.15	3.92	66.4	6.9	2406.0	0.57
	1.15	3.92	66.4	6.9	2466.0	0.57
	2.15	3.92	66.4	6.9	2526.0	0.57
	3.15	3.92	66.4	6.9	2586.0	0.57
	4.15	3.92	66.4	6.9	2646.0	0.57
	5.15	3.92	66.4	6.9	2706.0	0.57
	6.15	3.92	66.4	6.9	2766.0	0.57
	7.15	3.92	66.4	6.9	2826.0	0.57
Day – 3	8.15	6.95	70.2	10.7	2886.0	0.65
	9.15	6.95	70.5	11	2946.0	0.63
	10.15	6.95	70.6	11.1	3006.0	0.63
	11.15	6.95	70.8	11.3	3066.0	0.62
	12.15	6.95	70.9	11.4	3126.0	0.61
	13.15	6.95	70.9	11.4	3186.0	0.61
	14.15	6.95	70.9	11.4	3246.0	0.61
	15.15	6.95	70.9	11.4	3306.0	0.61
	16.15	6.95	70.9	11.4	3366.0	0.61
	17.15	6.95	70.9	11.4	3426.0	0.61
	18.15	6.95	70.9	11.4	3486.0	0.61

19.15	6.95	70.9	11.4	3546.0	0.61
20.15	6.95	70.9	11.4	3606.0	0.61
21.15	6.95	70.9	11.4	3666.0	0.61
22.15	6.95	70.9	11.4	3726.0	0.61
23.15	6.95	70.9	11.4	3786.0	0.61
24.15	6.95	70.9	11.4	3846.0	0.61
1.15	6.95	70.9	11.4	3906.0	0.61
2.15	6.95	70.9	11.4	3966.0	0.61
3.15	6.95	70.9	11.4	4026.0	0.61
4.15	6.95	70.9	11.4	4086.0	0.61
5.15	6.95	70.9	11.4	4146.0	0.61
6.15	6.95	70.9	11.4	4206.0	0.61
7.15	6.95	70.9	11.4	4266.0	0.61

	Water				
Time	Level	Drawdown	ť'	t	t'/t
7.20	66.6	7.1	0	4266	0
7.30	65.9	6.4	10	4276	0.002339
7.50	62.5	3.0	30	4306	0.006967
8.20	61.8	2.3	60	4366	0.013743
9.20	60.7	1.2	120	4486	0.02675
10.20	59.8	0.3	180	4666	0.038577
11.20	59.8	0.3	240	4906	0.04892
12.20	59.8	0.3	300	5206	0.057626
13.20	59.8	0.3	360	5566	0.064678
14.20	59.8	0.3	420	5986	0.070164
15.20	59.8	0.3	480	6466	0.074234

# Recovery test data at Obigbo
Dav	Time	Discharge m <sup>3</sup> /h	Water Level	Drawdown (m)	Min	Specific yield (m <sup>2</sup> /h)
Day – 1	6.00	60	12.5	0	0.00	0.00
	6.01	60	12.73	0.23	1.00	0.00
	6.02	60	12.95	0.45	2.00	0.01
	6.03	60	13.2	0.7	3.00	0.01
	6.04	60	13.46	0.96	4.00	0.02
	6.05	60	13.76	1.26	5.00	0.02
	6.06	60	13.96	1.46	6.00	0.02
	6.07	60	14.32	1.82	7.00	0.03
	6.08	60	14.55	2.05	8.00	0.03
	6.10	60	14.76	2.26	10.00	0.04
	6.12	60	14.97	2.47	12.00	0.04
	6.15	60	15.21	2.71	15.00	0.05
	6.18	60	15.45	2.95	18.00	0.05
	6.20	60	15.65	3.15	20.00	0.05
	6.25	60	15.84	3.34	25.00	0.06
	6.30	60	16.14	3.64	30.00	0.06
	6.45	60	16.37	3.87	45.00	0.06
	7.00	60	16.54	4.04	60.00	0.07
	7.10	60	16.76	4.26	70.00	0.07
	7.15	60	16.96	4.46	75.00	0.07
	7.20	60	17.22	4.72	80.00	0.08
	7.30	60	17.54	5.04	90	0.08
	7.45	60	17.78	5.28	105	0.09
	8.00	60	17.94	5.44	120.00	0.09
	9.00	60	18.22	5.72	180.00	0.10

### Drawdown data at Eziobodo

	10.00	60	18.47	5.97	240.00	0.10	
	12.00	60	19.36	6.86	360.00	0.11	
	14.00	60	19.37	6.87	480.00	0.11	
	16.00	60	19.37	6.87	600.00	0.11	
	18.00	60	19.37	6.87	720.00	0.11	
	20.00	60	19.37	6.87	840.00	0.11	
	24.00	60	19.37	6.87	1080.00	0.11	
	3.00	60	19.37	6.87	1260.00	0.11	
Day-2	6.00	60	19.37	6.87	1440.00	0.11	
	6.01	64	19.48	6.98	1441.00	0.11	
	6.02	64	19.66	7.16	1442.00	0.11	
	6.03	64	19.88	7.38	1443.00	0.12	
	6.05	64	20.21	7.71	1445.00	0.12	
	6.07	64	20.43	7.93	1447.00	0.12	
	6.10	64	20.65	8.15	1450.00	0.13	
	6.15	64	20.88	8.38	1455.00	0.13	
	6.30	64	20.99	8.49	1470.00	0.13	
	6.45	64	21.2	8.7	1485.00	0.14	
	7.00	64	21.43	8.93	1500.00	0.14	
	7.15	64	21.72	9.22	1515.00	0.14	
	7.30	64	21.95	9.45	1530.00	0.15	
	7.45	64	22.2	9.7	1545.00	0.15	
	8.00	64	22.54	10.04	1560.00	0.16	
	9.00	64	22.73	10.23	1620.00	0.16	
	10.00	64	22.94	10.44	1680.00	0.16	
	12.00	64	23.2	10.7	1800.00	0.17	
	15.00	64	23.31	10.81	1980.00	0.17	
	20.00	64	23.34	10.84	2280.00	0.17	

	24.00	64	23.34	10.84	2520.00	0.17
	4.00	64	23.34	10.84	2760.00	0.17
Day-3	6.00	64	23.34	10.84	2880.00	0.17
	6.01	67	23.52	11.02	2881	0.16
	6.03	67	23.75	11.25	2883	0.17
	6.05	67	23.92	11.42	2885	0.17
	6.07	67	24.21	11.71	2887	0.17
	6.10	67	24.46	11.96	2890	0.18
	6.20	67	24.78	12.28	2900	0.18
	6.30	67	25.02	12.52	2910	0.19
	6.45	67	25.25	12.75	2925	0.19
	7.00	67	25.55	13.05	2940.00	0.19
	7.15	67	25.78	13.28	2955	0.20
	7.30	67	25.98	13.48	2970	0.20
	7.45	67	26.23	13.73	2985	0.20
	9.00	67	26.55	14.05	3060.00	0.21
	10.00	67	26.62	14.12	3120.00	0.21
	12.00	67	26.66	14.16	3240.00	0.21
	14.00	67	26.67	14.17	3360.00	0.21
	16.00	67	26.68	14.18	3480.00	0.21
	18.00	67	26.68	14.18	3600.00	0.21
	20.00	67	26.68	14.18	3720.00	0.21
	22.00	67	26.68	14.18	3840.00	0.21
	24.00	67	26.68	14.18	3960.00	0.21
	2.00	67	26.68	14.18	4080.00	0.21
	4.00	67	26.68	14.18	4200.00	0.21
	6.00	67	26.68	14.18	4320.00	0.21

	Water				
Time	Level	Drawdown	<u>t'</u>	t	<u>t'/t</u>
9.00	26.68	14.18	0	4320	0
9.01	26.1	13.6	1	4321	0.000231
9.02	25.52	13.02	2	4322	0.000463
9.03	25.05	12.55	3	4323	0.000694
9.05	24.72	12.22	5	4325	0.001156
9.10	24.25	11.75	10	4330	0.002309
9.15	23.74	11.24	15	4335	0.00346
9.30	23.15	10.65	30	4350	0.006897
9.45	22.5	10	45	4365	0.010309
10.00	22.1	9.6	60	4380	0.013699
11.00	21.2	8.7	120	4440	0.027027
12.00	20.45	7.95	180	4500	0.04
13.00	19.82	7.32	240	4560	0.052632
14.00	18.91	6.41	300	4620	0.064935
15.00	17.2	4.7	360	4680	0.076923
16.00	16.33	3.83	420	4740	0.088608
17.00	14.02	1.52	480	4800	0.1
18.00	13.55	1.05	540	4860	0.111111
19.00	12.9	0.4	600	4920	0.121951
20.00	12.73	0.23	660	4980	0.13253

# Recovery test data at Eziobodo

DAY	Time	Discharge l/sec	Water Level (m)	Drawdown (m)	Min	Specific vield
Day – 1	8.00	6.3	15.5	0	0.00	
	8.00	6.3	15.8	0.3	0.50	21.00
	8.01	6.3	16	0.5	1.00	12.60
	8.02	6.3	16.1	0.6	2.00	10.50
	8.03	6.3	16.1	0.6	3.00	10.50
	8.04	6.3	16.4	0.9	4.00	7.00
	8.05	6.3	16.4	0.9	5.00	7.00
	8.10	6.3	16.6	1.1	10.00	5.73
	8.20	6.3	16.6	1.1	20.00	5.73
	8.30	6.3	16.8	1.3	30.00	4.85
	9.00	6.3	17.1	1.6	60.00	3.94
	10.00	6.3	17.1	1.6	120.00	3.94
	11.00	6.3	17.4	1.9	180.00	3.32
	12.00	6.3	17.4	1.9	240.00	3.32
	13.00	6.3	17.4	1.9	300.00	3.32
	14.00	6.3	17.4	1.9	360.00	3.32
	15.00	6.3	17.5	2	420.00	3.15
	16.00	6.3	17.5	2	480.00	3.15
	17.00	6.3	17.5	2	540.00	3.15
	18.00	6.3	17.5	2	600.00	3.15
	19.00	6.3	17.5	2	660.00	3.15
	20.00	6.3	17.5	2	720.00	3.15
	21.00	6.3	17.5	2	780.00	3.15
	22.00	6.3	17.5	2	840.00	3.15
	23.00	6.3	17.5	2	900.00	3.15

# Drawdown data at Owerri

	24.00	6.3	17.5	2	960.00	3.15
	1.00	6.3	17.5	2	1020.00	3.15
	2.00	6.3	17.5	2	1080.00	3.15
	3.00	11.9	17.7	2.2	1140.00	5.41
	4.00	11.9	17.8	2.3	1200.00	5.17
	5.00	11.9	17.8	2.3	1260.00	5.17
	6.00	11.9	17.8	2.3	1320.00	5.17
	7.00	11.9	17.8	2.3	1380.00	5.17
Day – 2	8.00	11.9	17.9	2.4	1440.00	4.96
	8.15	11.9	17.9	2.4	1455.00	4.96
	9.00	11.9	17.9	2.4	1500.00	4.96
	10.00	11.9	18.1	2.6	1560.00	4.58
	11.00	11.9	18.1	2.6	1620.00	4.58
	12.00	11.9	18.2	2.7	1680.00	4.41
	13.00	11.9	18.2	2.7	1740.00	4.41
	14.00	11.9	18.2	2.7	1800.00	4.41
	15.00	11.9	18.2	2.7	1860.00	4.41
	16.00	11.9	18.2	2.7	1920.00	4.41
	17.00	11.9	18.2	2.7	1980.00	4.41
	18.00	11.9	18.2	2.7	2040.00	4.41
	19.00	11.9	18.2	2.7	2100.00	4.41
	20.00	11.9	18.2	2.7	2160.00	4.41
	21.00	11.9	18.2	2.7	2220.00	4.41
	22.00	11.9	18.2	2.7	2280.00	4.41
	23.00	11.9	18.2	2.7	2340.00	4.41
	24.00	11.9	18.2	2.7	2400.00	4.41
	1.00	18.9	18.5	3	2460.00	6.30
	2.00	18.9	18.6	3.1	2520.00	6.10

	3.00	18.9	18.6	3.1	2580.00	6.10
	4.00	18.9	18.6	3.1	2640.00	6.10
	5.00	18.9	18.6	3.1	2700.00	6.10
	6.00	18.9	18.6	3.1	2760.00	6.10
	7.00	18.9	18.6	3.1	2820.00	6.10
Day – 3	8.00	18.9	18.6	3.1	2880.00	6.10
	8.15	18.9	18.8	3.3	2895.00	5.73
	9.00	18.9	18.8	3.3	2940.00	5.73
	10.00	18.9	18.8	3.3	3000.00	5.73
	11.00	18.9	18.8	3.3	3060.00	5.73
	12.00	18.9	18.9	3.4	3120.00	5.56
	13.00	18.9	19.1	3.6	3180.00	5.25
	14.00	18.9	19.1	3.6	3240.00	5.25
	15.00	18.9	19.1	3.6	3300.00	5.25
	16.00	18.9	19.1	3.6	3360.00	5.25
	17.00	18.9	19.1	3.6	3420.00	5.25
	18.00	18.9	19.1	3.6	3480.00	5.25
	19.00	18.9	19.1	3.6	3540.00	5.25
	20.00	18.9	19.1	3.6	3600.00	5.25
	21.00	18.9	19.1	3.6	3660.00	5.25
	22.00	18.9	19.1	3.6	3720.00	5.25
	23.00	18.9	19.1	3.6	3780.00	5.25
	24.00	18.9	19.1	3.6	3840.00	5.25

	Water				
Time	Level	Drawdown	ť'	t	t'/t
6.00	19.1	3.6	0	3840	0
6.05	18.6	3.1	5	3845	0.0013
6.10	18.4	2.9	10	3855	0.002594
6.20	18.1	2.6	20	3875	0.005161
6.30	17.9	2.4	30	3905	0.007682
7.00	17.5	2	60	3965	0.015132
8.00	17.4	1.9	120	4085	0.029376
9.00	17.1	1.6	180	4265	0.042204
10.00	16.4	0.9	240	4505	0.053274
11.00	16.1	0.6	300	4805	0.062435
12.00	15.8	0.3	360	5165	0.0697
13.00	15.8	0.3	420	5585	0.075201
14.00	15.8	0.3	480	6065	0.079143

# Recovery test data at Owerri

			Water	
	Time	Min	Level	Drawdown
Day – 1	10.05	0	148.5	
		0.5	154.9	6.4
		1	155.4	6.9
		2	155.4	6.9
		3	156.2	7.7
		4	156	7.5
		5	156.7	8.2
		10	157.7	9.2
		15	158.6	10.1
		30	161.2	12.7
	11.05	60	162.3	13.8
	12.05	120	162.55	14.05
	13.05	180	162.9	14.4
	14.05	240	163	14.5
	15.05	300	163.1	14.6
	16.05	360	163.2	14.7
	17.05	420	163.24	14.74
	18.05	480	163.33	14.83
	19.05	540	163.35	14.85
	20.05	600	163.4	14.9
	21.05	660	163.41	14.91
	22.05	720	163.42	14.92
	23.05	780	163.42	14.92
	24.05	840	163.42	14.92
	1.05	900	163.47	14.97
	2.05	960	163.47	14.97

#### Drawdown data at Etche

	3.05	1020	163.47	14.97
	4.05	1080	163.47	14.97
	5.05	1140	163.47	14.97
	6.05	1200	163.47	14.97
	7.05	1260	163.47	14.97
	8.05	1320	163.47	14.97
	9.05	1380	163.42	14.92
Day – 2	10.05	1440	163.47	14.97
	11.05	1500	163.42	14.92
	12.05	1560	163.47	14.97
	13.05	1620	163.42	14.92
	14.05	1680	163.35	14.85
	15.05	1740	163.42	14.92
	16.05	1800	163.47	14.97
	17.05	1860	163.47	14.97
	18.05	1920	163.47	14.97
	19.05	1980	163.42	14.92
	20.05	2040	163.42	14.92
	21.05	2100	163.42	14.92
	22.05	2160	163.42	14.92
	23.05	2220	163.42	14.92

Dav	Time	Discharge	Water Level	Drawdown (m)	Min	Specific Vield
Day Day – 1	8.00	7.7	<u>61.6</u>	0	0.00	1 Ieiu
	8.00	7.7	61.8	0.2	0.50	38.50
	8.01	7.7	62.4	0.8	1.00	9.63
	8.02	7.7	62.8	1.2	2.00	6.42
	8.03	7.7	63	1.4	3.00	5.50
	8.04	7.7	63	1.4	4.00	5.50
	8.05	7.7	63.4	1.8	5.00	4.28
	8.10	7.7	64.1	2.5	10.00	3.08
	8.20	7.7	64.3	2.7	20.00	2.85
	8.30	7.7	64.5	2.9	30.00	2.66
	9.00	7.7	64.7	3.1	60.00	2.48
	10.00	7.7	64.8	3.2	120.00	2.41
	11.00	7.7	64.8	3.2	180.00	2.41
	12.00	7.7	65	3.4	240.00	2.26
	13.00	7.7	65.1	3.5	300.00	2.20
	14.00	7.7	65.2	3.6	360.00	2.14
	15.00	7.7	65.2	3.6	420.00	2.14
	16.00	7.7	65.6	4	480.00	1.93
	17.00	7.7	66	4.4	540.00	1.75
	18.00	7.7	66	4.4	600.00	1.75
	19.00	7.7	66.2	4.6	660.00	1.67
	20.00	7.7	66.4	4.8	720.00	1.60
	21.00	7.7	66.4	4.8	780.00	1.60
	22.00	7.7	66.5	4.9	840.00	1.57
	23.00	7.7	66.7	5.1	900.00	1.51

### Drawdown data at Port Harcourt

	24.00	7.7	66.9	5.3	960.00	1.45
	1.00	7.7	67.1	5.5	1020.00	1.40
	2.00	7.7	67.3	5.7	1080.00	1.35
	3.00	7.7	67.5	5.9	1140.00	1.31
	4.00	10.6	68	6.4	1200.00	1.66
	5.00	10.6	68.2	6.6	1260.00	1.61
	6.00	10.6	68.5	6.9	1320.00	1.54
	7.00	10.6	68.7	7.1	1380.00	1.49
Day – 2	8.00	10.6	68.9	7.3	1440.00	1.45
	9.00	10.6	68.9	7.3	1500.00	1.45
	10.00	10.6	69.1	7.5	1560.00	1.41
	11.00	10.6	69.2	7.6	1620.00	1.39
	12.00	10.6	69.2	7.6	1680.00	1.39
	13.00	10.6	69.5	7.9	1740.00	1.34
	14.00	10.6	69.9	8.3	1800.00	1.28
	15.00	10.6	70.2	8.6	1860.00	1.23
	16.00	10.6	70.2	8.6	1920.00	1.23
	17.00	10.6	70.5	8.9	1980.00	1.19
	18.00	10.6	70.5	8.9	2040.00	1.19
	19.00	10.6	70.8	9.2	2100.00	1.15
	20.00	10.6	70.8	9.2	2160.00	1.15
	21.00	10.6	71	9.4	2220.00	1.13
	22.00	10.6	71	9.4	2280.00	1.13
	23.00	10.6	71	9.4	2340.00	1.13
	24.00	10.6	71	9.4	2400.00	1.13
	1.00	10.6	71.3	9.7	2460.00	1.09
	2.00	17.7	74	12.4	2520.00	1.43
	3.00	17.7	74.5	12.9	2580.00	1.37

-		4.00	17.7	75.1	13.5	2640.00	1.31
		5.00	17.7	75.1	13.5	2700.00	1.31
		6.00	17.7	75.4	13.8	2760.00	1.28
		7.00	17.7	75.4	13.8	2820.00	1.28
		8.00	17.7	75.4	13.8	2880.00	1.28
	Day – 3	9.00	17.7	75.5	13.9	2940.00	1.27
		10.00	17.7	75.5	13.9	3000.00	1.27
		11.00	17.7	75.7	14.1	3060.00	1.26
		12.00	17.7	75.7	14.1	3120.00	1.26
		13.00	17.7	76.1	14.5	3180.00	1.22
		14.00	17.7	76.2	14.6	3240.00	1.21
		15.00	17.7	76.2	14.6	3300.00	1.21
		16.00	17.7	76.2	14.6	3360.00	1.21
		17.00	17.7	76.2	14.6	3420.00	1.21
		18.00	17.7	76.2	14.6	3480.00	1.21
		19.00	17.7	76.2	14.6	3540.00	1.21
		20.00	17.7	76.2	14.6	3600.00	1.21
		21.00	17.7	76.2	14.6	3660.00	1.21
		22.00	17.7	76.2	14.6	3720.00	1.21
		23.00	17.7	76.2	14.6	3780.00	1.21

	Water				
Time	Level	Drawdown	ť'	t	t'/t
0.00	76.2	14.6	0	3780	
5.00	75.5	13.9	5	3785	0.001321
10.00	71.3	9.7	10.00	3790	0.002639
20.00	70.2	8.6	20.00	3800	0.005263
30.00	67.1	5.5	30.00	3810	0.007874
60.00	64	2.4	60.00	3840	0.015625
120.00	62.5	0.9	120.00	3900	0.030769
180.00	62	0.4	180.00	3960	0.045455
240.00	62	0.4	240.00	4020	0.059701
300.00	62	0.4	300.00	4080	0.073529
360.00	62	0.4	360.00	4140	0.086957

# Recovery test data at Port Harcourt

# APPENDIX E Graphs of pumping test data





Graphy of Specific yield versus time at Obigbo



Graphy of Specific yield versus time at Ulakwo



Graph of Specific yield versus drawdown at Ngor Okpala



Graph of Specific yield versus drawdown at Nekede



Graphy of drawdown versus Specific yield at Port Harcourt



Graph of Specific yield versus yield at Aba



Graph of Specific yield versus discharge at Owerri







#### Graph of step by step drawdown versus time at Aba





Graph of drawdown versus time at Ngor Okpala

Graph of drawdown versus time at Ulakwo







Graph of recovery versus time at Eleme











#### Graph of drawdown versus recovery at Eche



#### TIME (minutes)

Graph of drawdown versus recovery at Ikwere



Graph of drawdown versus recovery at Umudim



Graph of drawdown versus recovery at Iheagwa