

# ASSESSMENT OF HYDROCARBON INDUCED GROUNDWATER POLLUTION AND IDENTIFICATION OF POLLUTANTS IN BARUWA COMMUNITY

By

# AGBEYEGBE EMMANUEL EYITUOYO

| 17CN022850 |

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SUPERVISOR: DR ROTIMI OLUWATOSIN

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# **DECLARATION**

I hereby declare that I worked on the work reported in this project in the Department of Petroleum Engineering, Covenant University, under the supervision of Dr Rotimi Oluwatosin. I also solemnly declare that to the best of my knowledge; no part of this report has been submitted here or elsewhere in a previous application for the award of a degree. All sources of knowledge used have been duly acknowledged.

# AGBEYEGBE EMMANUEL EYITUOYO

17CN022850

# **CERTIFICATION**

This is to certify that the project titled "Assessment of Hydrocarbon Induced Groundwater Pollution and Identification of Pollutants In Baruwa Community" by AGBEYEGBE EMMANUEL EYITUOYO, meets the requirements and regulations governing the award of the Bachelor of Engineering degree in Petroleum Engineering, Covenant University and is approved for its contribution to knowledge and literary presentation.

Agbeyegbe Emmanuel Eyituoyo	Date
(Student)	
Dr. Rotimi Oluwatosin	Date
(Supervisor)	
Professor Oyinkepreye David Orodu	Date
(Head of Department)	
External Examiner	Date

# **DEDICATION**

I dedicate this work first to God, my savior and ever-present help.

I dedicate this work to my family and friends also, for their unending love and support from the start of this journey through to finish.

Finally, I dedicate this work to my instructors in school for all their care, efforts in grooming me even until this point but most especially to my supervisor who saw me through even stage of this project.

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## ABSTRACT

Across the world today are communities where residents suffer from untold hardships getting about their mundane chores simply due to the level of hydrocarbon-induced pollution from spillage into water bodies, explosions etc. owing to ageing or vandalized pipelines running underneath and so on. Research has shown that a good number of communities in Lagos state are victims of hydrocarbon induced pollution and the focus has been on the conspicuous effects such as the damages from explosions. However, only a few articles have successfully described the underlying effects of hydrocarbon induced pollution in cases of groundwater pollution. This study aims at investigating the groundwater pollution in Baruwa community, Lagos state, providing more information about the extent of the pollution and identifying the hydrocarbon pollutants responsible. Based on a good number of literatures reviewed, two types of investigation approaches were utilized: geophysical survey and physicochemical analysis of contaminated water samples.

For the geophysical survey, the 2D ERT and VES investigations are done using Wenner and Schlumberger arrays respectively while analyses were done on 34 water samples to determine the concentration of BTEX and Total Petroleum Hydrocarbons (TPH). The results show that 38% of water sources contained concentrations of BTEX above-acceptable standard and 76% contained significant amounts of TPH. The results also revealed that the likely source of these pollutants is gasoline, kerosene, fuel oil and lubricating oil from pipelines in the area. On this basis, it is recommended that the areas with extremely high concentration of pollutants be advised to stop using these water sources. Also, more research is carried out to investigate how water with these identified pollutants can be treated and how long it takes for affected areas to be bioremediated.

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# **CHAPTER ONE: INTRODUCTION**

#### 1.1 History of Study

A significant contribution to global energy consumption and the economic boom of oil-producing countries is attributed to the exploration and development of petroleum resources (e.g., a case study is Nigeria) (Ite, 2016). Hydrocarbons are a vital commodity that might be called the cornerstone of today's global economy, and the oil and gas sector wield a significant amount of power across the world (Anejionu et al, 2015). Nigeria has been a member of an oil-producing group that comprises several of Africa's major oil producers since 1956 when commercial amounts of petroleum were found in Oloibiri (Bayelsa State) (Ite et al, 2018).

Every stage of hydrocarbon extraction, however, has a major environmental impact (from seismic survey to oil production and processing) (Anejionu et al, 2015). Crude oil, as well as its derivatives, are delivered from areas where oil is being produced to regions where oil is being consumed by ocean-going boats with large cargo capacity. Accidents involving the hulls of these boats being compromised and their contents overflowing have the potential to cause significant environmental harm. Incessant oil spills are documented to have wreaked havoc on the aquatic and terrestrial habitats on a regular basis (Adegbesan, 2019). The following are some of the repercussions of the accidental discharge of petroleum hydrocarbons into the environment: (i) Natural gas flaring and venting cause pollutants in the atmosphere, which is a contributor to global climate change (Ogri, 2001); (ii) Pollution of the maritime ecology, resulting in detrimental consequences on wildlife as well as fishing, tourism, etc.; (iii) Soil and water contamination (groundwater and surface water) (Yakubu, 2017), (iv) socio–economic challenges such as degradation of our history and culture (Ite, 2012), and (v) Polluted lands, food quality concerns, and a drop in agricultural output (Okwechime, 2018).

Oil wells, whether on land or offshore, have the potential to leak oil into the water. Unfortunately, spills have grown commonplace in certain regions of the country (Adegbesan, 2019).

#### Niger Delta and petroleum hydrocarbon pollution

Recently, the Niger Delta has become increasingly well-known because of intensified oil exploration and exploitation. The Niger Delta is largely covered by the OML and OPL, providing oil exploration businesses unfettered access to work on lands and waters in pursuit of crude oil (Anejionu et al, 2015). However, the region is also known for the perpetual vandalism of pipelines conveying petroleum and petroleum products, enormous tearing down of oil facilities by agitated youths, domestic and/or industrial accidents and oil bunkering (Adegbesan, 2019). These actions have resulted in oil spillage and the discharge of petroleum product into existing water bodies, all of which have contributed to a critical state of environmental degradation. Fishing and agriculture were the primary occupations of the people of Niger Delta before the days of crude oil. The Niger-Delta region had an extensive flora and fauna, as well as fertile terrain that could support a broad range of plants and a wide variety of freshwater fish species. The region's ecosystem had one of the greatest concentrations of biodiversity in the world. However, the negative effects of oil exploration and extraction have obliterated the region's incandescent pride in nature. The Niger-Delta people's livelihood has been harmed by the poisoned ecology. A people who took pleasure in fishing and rely on land for subsistence are now left with nothing. Environmental damage in the Niger-Delta resulting from oil and gas production has drawn the attention of environmentalists and other specialists who see the region in the light of globalization.

As a result, we can see that the region is just as well recognized for its environmental concerns as it is for oil and gas exploitation.

Apart from the employment of massive ocean-going boats with large capacity for transporting oil from oil-producing areas to oil-consuming areas, pipeline networks are also used. Pipelines are commonly used to transmit petroleum hydrocarbons across millions of kilometers throughout the world. The pipeline structures are made to withstand a variety of environmental loading conditions to ensure secure and reliable distribution from the location of production to the coast or distribution depot. Failure of pipelines can cause serious ecological catastrophes, and the loss of human lives. Oil spills and other kinds of hydrocarbon-induced pollution are well known in the Niger Delta, but because to the massive pipeline network crisscrossing the nation, they also exist in other regions of the country (Renner et al. 2008). The heavily populated metropolis of Lagos is included in this category of "other regions" of the country experiencing hydrocarbon-induced pollution.

#### Hydrocarbon-induced challenges in Lagos state

For more than two decades, the densely populated city of Lagos has been rocked by pipeline explosions that have resulted in the destruction of lives and properties, in most cases beyond repair or complete restoration. These incidents have occurred repeatedly and yet without warning, leaving the victims devastated, livelihood destroyed, buildings turned to dust. Yet one will think that with all attention these incidents of pipeline explosion bring to the scene adequate attention will be given to prevent them from reoccurring. However, the frequency of these incidents is proof that not much has been done so far. Between 1998 and 2013 about 9 pipeline incidents have taken place in the densely populated city of Lagos state as is seen in Table 1.1.

Table 1.1: Cases of pipeline vandalism/rupture in Lagos state from 1998 to 2013 and their attendant consequences.

DATE & LOCATION	CONSEQUENCES	
20 <sup>th</sup> February 2000.	At least three deaths were reported, as well as damage to	
	farmlands and canoes. (Onuoha, 2007)	
30 <sup>th</sup> November 2000.	At least 60 deaths were recoded and environmental pollution	
	(USATODAY, 2006)	
16 <sup>th</sup> September 2004. Ijegun.	Around 60 fatalities were recorded, as well as air and water	
	contamination. (Onuoha, 2007)	
December 2004. Imore.	500 deaths were recoded, and environmental pollution	
	(Onuoha, 2007)	
12 <sup>th</sup> May 2006. Ilado.	150 deaths and several injured, water and environmental	
	pollution (Onuoha, 2007)	
2 <sup>nd</sup> December 2006. Ijeododo.	1 fatality, ruined farmland, and contamination of the	
	environment (Onuoha, 2007)	
26 <sup>th</sup> December 2006. Abule Egba.	At least 500 lives were lost, 40 cars were burned, dozens of	
	residences, including a mosque and two churches, were	
	completely destroyed, and other businesses were damaged.	
	(Onuoha, 2007)	
16 <sup>th</sup> May 2008. Ijebu.	At least 100 deaths, and environmental pollution (Nnadi,	
	2007)	
17 <sup>th</sup> December 2012. Ojo.	unspecified death and environmental pollution (Agha, 2012)	

Nonetheless, there exist an even salient, yet silent menace brewing underground as opposed to that which is seen at the surface; this is the contamination of groundwater due to hydrocarbon leakages from pipelines, either naturally occurring or human induced. Underground spillage might result from rupture or corrosion of these hydrocarbon transporting pipelines which are buried in the earth. The spilled petroleum products then come in contact with the groundwater aquifers contaminating them, thus, making the water unfit for consumption (Öztürkoğlu & Lawal, 2016). Findings by E. Ite et al., (2013) reveal that soil and water pollution by petroleum hydrocarbon have been a source of crucial environmental concerns and human health risks in the last fifty-five years. This is due to the fact that several hydrocarbon compounds possess carcinogenic and mutagenic properties.

Water is commonly acknowledged as a fundamental human need, and its provision is thought to be vital. Groundwater is underground water (Groundwater Foundation, 2012). Because pollutants are restricted in the soil profile, a reliable source of drinking water is from underground aquifers. Shallow, and permeable aquifers are, however, still vulnerable (Adejuwon & Mbuk, 2011). All water in the soil and fractures of rocks that originate from rainfall absorption, or rivers are referred to as groundwater (Saeed, 2014). Lagos derives its water supply from both surface and groundwater sources present in the state (Sharma et al., 2013). A people's health is strongly influenced by the quality of the water they drink (WHO, 2010). Groundwater is thought to be pure and accounts for 95% of all freshwater resources. As a result, water is the most vital and valuable natural resource, and groundwater is a major source. It is vital in all aspects of human life (Acharya, 2004). Groundwater is used excessively due to its ease of access, superior protection from pollutants, seasonal stability (UNESCO, 2004), and reduced production costs (Sharma, 2013). These advantages make groundwater a large-scale supply option (UNESCO, 2004).

A number of neighborhoods in Lagos are at risk of losing access to safe ground and surface water due to the presence of hydrocarbons from pipeline leakages. The Baruwa community in Lagos state is one of these impacted locations. The community is traversed by several NNPC/PPMC pipelines running underneath. NNPC PROW indicators can be seen around farms (Figure 1.4) and even residential buildings in the community (Figure 1.7). This hamlet was harmed by NNPC/PPMC pipeline ruptures between 1994 and 1996. For several weeks, the leaking of petroleum products from the community's pipeline remained undetected, contaminating subsurface water bodies, poisoning wells, and boreholes, and leaving the waters unfit for human consumption. The Baruwa neighborhood discovered in 1996 that over 180 wells had been contaminated by petroleum products (*WATER POLLUTION IN LAGOS, NIGERIA*, 2013). These products included gasoline, kerosene, diesel, and other residues (Ogunlesi & Okiei, 2009). Baruwa community, has experienced widespread release of refined petroleum hydrocarbons into the subsurface of the groundwater, which has rendered groundwater virtually unusable, and residents forced to endure a slew of hardships and costs just to carry out their regular household chores.

#### **1.2 Problem statement**

In the Baruwa community of Lagos state, there is the presence of contamination of their groundwater resulting from hydrocarbon seepages from pipelines either damaged from deterioration due to ageing or vandalized by residents who siphon them for cash. As a result of this, majority of the residents cannot use the water from their wells or boreholes. The contaminated water has a distinct brown coloration in their water tanks (Figure 1.6) as well as other containers used to hold water such as their cups and buckets. The distinct brown coloration is due to the presence of iron, copper, zinc, and other trace metals present in gasoline (Santos, et al., 2011). Furthermore, the people are exposed to pipeline explosions resulting from these damaged and/or exposed pipelines (Figure 1.5).

#### 1.3 Significance of Study

Many a times, the most salient issues are not addressed because they are not as conspicuous as others. The contamination of ground water is a rather salient hydrocarbon induced pollution that should be given adequate attention but perhaps because it is not as loud as the sound of an explosion, it has been swept under the rug for years whilst the effect is only evident to those directly affected by it.

If the goal of this study is achieved, the benefit would be a significant improvement on existing findings in the study area. With that, we hope to be able to draw the attention of international bodies such as the UNICEF and others who would take these issues seriously and intervene. The people of Baruwa would be rescued from the hardship and long-term health challenges that are brewing for those who use the contaminated water due to a lack of financial resources to purchase safe drinking water from vendors.

#### 1.4 Aim and Objectives

#### 1.4.1 Aim

The aim of this study was to assess the groundwater hydrocarbon-induced pollution of the affected environment and to characterize the groundwater pollutants responsible for the pollution.

#### 1.4.2 Objectives

The following are the objectives of this study:

- i. Creation of relevant base map(s) at scale 1:10,000.
- ii. Determining the depth of contamination within the sub-surface of the affected areas.
- Analysis of water samples from the study area for heavy metals, cations, and hydrocarbon content.

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iv. Identification and characterization of individual contaminants present in the hydrocarboncontaminated water.

#### **1.5 Scope of Study**

Baruwa Community serves as our case study. The community lies between latitude 06° 35' 12" North and 03° 16' 21" East. It is located in Iyana-Ipaja in Lagos State, Southwest of Nigeria (Figure 1.1), between the renowned Iyana-Ipaja Bus Stop and the Ikotun Area of Alimosho Local Government Council (Figure 1.2). Iyana-Ipaja Bus Terminal is approximately 2.5 kilometers away, and the community is bordered on the right and left by Gowon Estate and Abesan Estate, respectively. The area has a steeping topography (Figure 1.3) and is prone to erosion which leaves buried pipelines exposed as is seen in Figure 1.5.

This densely inhabited residential area, which is connected to Ipaja and Ayobo by a network of highways, is home to more than 100,000 people and is a major transportation hub. Its history may be traced back to the early twentieth century, but it only gained widespread recognition in the 1970s as a consequence of the population growth in Lagos, which led in the building of satellite villages in the surrounding area (Adekunte, 2008).



Figure 1.1: a. Map of Nigeria with Lagos highlighted in red. b. Map of Lagos showing all the LGAs



Figure 1.2: a. Map of Lagos showing all the LGAs. b. Map of Lagos showing Baruwa in Alimosho LGA



Figure 1.3: Photo showing the nature of the topography of Baruwa



Figure 1.4: NNPC ROW indicator just beside a farm in Baruwa



Figure 1.5: Exposed pipelines in Baruwa



Figure 1.6: Evident water contamination in water tanks



Figure 1.7: NNPC pipeline row indicator just beside a residential building in Baruwa

# **CHAPTER TWO: LITERATURE REVIEW**

#### 2.1 Groundwater assessment studies

The amount of gasoline, diesel, and lubricants utilized in modern civilization is quite large unlike other chemicals of environmental issues (Logeshwaran et al., 2018). However, according to Das and Chandran (2011), accidents, leaks, and spills resulting from the exploring, producing, transporting, and storing of petroleum leads to the discharge of petroleum-based compounds into the environment, which has negative impacts. Research done by Kvenvolden, and Cooper (2003) reveals that crude oil seepage pollutes aquatic and terrestrial ecosystems all across the world at a rate of around 600,000 tons annually, with a range of uncertainty of 200,000 metric tons annually. According to Ahmed and Fakhruddin (2018), pollution of the environment by petroleum hydrocarbon is one of the biggest problems of the modern world.

Water is commonly acknowledged as a basic human need, and its provision is thought to be vital. Famiglietti (2014) declared that groundwater remains the world's leading source of public water supply, with over 2 billion people relying on it as their major water source globally. Lagos also taps its water from surface as well as groundwater sources (Shiru et al., 2019). Nonetheless, because pollutants are restricted in the soil profile, groundwater is a reliable source of water. According to U. S Geological Survey (What Is Hydrology? | U. S. Geological Survey, 2019), compared to pollution in rivers and lakes, groundwater pollution is less obvious, but it is also more pervasive and challenging to clean up. All of these factors together with others demonstrate the need for quick assessment and remediation of petroleum hydrocarbon pollution of groundwater aquifers.

#### 2.2 Petroleum composition

Hydrocarbons in various states-gaseous, liquid, and solid-along with trace amounts of other substances including nitrogen, oxygen, and sulfur-are the main components of petroleum (Speight, 2014). The breakdown of a variety of precursors, including organic matter and fossils that have been buried for millions of years, results in the formation of crude oil. The physical and chemical makeup of petroleum oil varies considerably between regions as a result of the severe variances in the precursor components. The location, age, and depth of each individual oil well are other factors that affect these compositional differences. According to molecular analysis, petroleum oil is made up of diverse mixture of hydrocarbons (83%-87%), a small portion of organic components that contain hydrogen (about 10%–14%), oxygen (about 0.05%–1.5%), sulfur (about 0.05%-6.0%), and nitrogen (about 0.1%-2.0%), and a small percentage of metallic components (<1000 mg/L) that include copper, nickel, iron, and concerns (Logeshwaran et al., 2018). In addition, paraffins, cycloparaffins, and aromatics can be referred to as classes of the hydrocarbons found in petroleum. The Canadian Council of Ministers of the Environment (CCME, 2010) states that PH are split according to the precise fraction or ranges of equivalent carbon number for assessing their threat to humans and the environment. Volatile fractions are those with carbon numbers ranging from C6 to C10 (Fraction 1). Semi-volatiles make up fraction 2 and range in from C10 to C16. The equivalent carbon numbers in fraction 3 range from C16 to C34, and this fraction is known as a non-volatile fraction. Since fraction 4 has an equivalent carbon number greater than C35, it is regarded as the least volatile and soluble of all the other fractions.

According to Logeshwaran et al. (2018), PH infiltrate through soil layers and finally reach groundwater aquifers, polluting them due of the lower octanol-water coefficient Because soil PH pollution and its groundwater contamination both result from long-lasting PH residuals in soil, there is a clear connection between the two (Pawlak et al., 2008).

#### 2.3 Groundwater hydrocarbon contamination

According to Nadim et al. (2000), shortly after a spill, since PH have a lower specific gravity than water, they tend to pool non-aqueous phase liquid (NAPL), part of which gradually dissolves in groundwater to produce a plume of hydrocarbons in the groundwater flowing in the subsurface.

As water is extracted at the surface from wells and other means, the groundwater flows causing the plume of hydrocarbons to spread over a wider area. The expanding border of the plume, called the plume edge, can contact water wells, making the water supplies unsuitable for consumption (Wikipedia contributors, 2003). All of this happens in the sub-surface, hence, residents of regions with these contaminated aquifers are unaware of the extent of groundwater pollution. This raises the need for the assessment of the aquifers in regions where the hydrocarbon pollution is described to have taken place.

#### 2.4 Delineation of contaminated groundwater aquifers

Geophysical methods have proven to be helpful in groundwater aquifer assessment especially in the mapping of areas of contaminated soil and groundwater (Nwankwo & Emujakporue, 2012). Geophysical research or surveys employ physics to make measurements in geographically constrained areas that are then used to figure out how physical attributes are distributed at depths that correspond to the regional subsurface geology (Kearey et al., 2002). Drilling boreholes is, of course, and alternative methods of subsurface geological assessment or investigation but according to Kearey et al. (2002), it is a relatively expensive method and the information provided by this method is restricted to discrete locations where the boreholes are dug. This is opposed to geophysical surveys which, when properly applied, optimizes exploration programmes by covering more ground (Kearey et al., 2002). Geophysical data interpretation can be fraught with ambiguities and uncertainties, but it is nonetheless a quick and affordable way to gather dispersed data on subsurface hydrogeology (Kearey et al., 2002). Several geophysical methods. The most commonly used geophysical methods can be found in Table 2.1.

Method	Measured parameter	Physicalpropertygoverning method
Electrical resistivity	Resistance of the Earth.	Electrical conductivity.
Magnetic	Spatial variations in thestrengthofthegeomagnetic field.	Magnetic susceptibility and remanence.
Induced polarization	Ground resistance that varies with frequency or polarization voltages	Electrical capacitance.
Seismic	Reflected or refracted seismic wave travel durations.	Density and elastic moduli, which governs velocity at which seismic waves are propagated.
Self-potential	Responsetoelectromagnetic radiation	Electrical conductivity.
Radar	Travel times of reflected radar pulses	Dielectric constant

Table 2.1: Various Geophysical methods and how they are applied (Kearey et al., 2002)

	The strength of the Earth's	
Gravity	gravitational field varying	Density
	spatially.	

Over the past 10 years, due to the rapid advancement of electronic technology and the creation of numerical simulation techniques, applying geophysical methods for mapping of groundwater resources and the assessment of water quality has grown tremendously (e.g., in Ndlovu et al., 2010). According to Muchingami et al. (2012), due to the ability to correlate hydrogeologic characteristics, such as porosity and permeability, to electrical resistivity values, electrical methods are specifically well suited for groundwater studies. The electrical approach has been successfully employed for groundwater since it is less complicated, more effective, and less harmful to execute when providing subsurface imaging than drilling boreholes (Dor et al. 2011).

#### 2.4.1 Geoelectrical methods

The main focus of geo-electrical approaches is the measuring of electrical resistivities of formations in the subsurface, which primarily offers details on the various geological formations, layers, and groundwater presence. In essence, electrical resistivity methods are used to map and measure the resistivity of materials in the subsurface. It also describes a survey that was conducted to display an image of the electrical characteristics of the subsurface by running an electrical current down numerous pathways and gauging the resulting voltage (Abidin et al., 2011).

Methods for measuring electrical resistivity are based on how the earth responds to the passage of electrical current. It is sensitive to changes in the sub-surface's electrical resistivity, as measured in Ohm meters (Riwayat et al., 2018).

When carrying out resistivity investigations, two current electrodes (C1 and C2) are used to induce electric current into the earth, and the resulting voltage at two potential electrodes (P1 and P2) is measured (see Figure 2.1).



Figure 2.1: Resistivity measurement set up consisting of four-electrodes two electrodes (C1 and C2) and two (P1 and P2) (Source: Adapted from Lech et al, 2020)

The apparent resistivity ( $\rho_a$ ) value can be calculated using the mathematical equation relating current (*I*) and voltage (*V*)(see  $\rho a = k \frac{V}{I}$  Equation 2.1).

$$\rho_a = k \frac{V}{I}$$
 Equation 2.1

"k" represented the geometric factor that is dependent on the configuration of the four electrodes. Electrical resistivity imaging depends on the electrode spacing. To investigate subsurface properties at greater depth the electrode spacing is increased. Greater imaging depth is also a function of the electrode array's overall length. The imaging depth is also influenced by the overall underlying resistivity, with highly resistant terrain often having a shallower depth after inversion.

Asides the use of electrical methods in groundwater presence detection they have also proven useful in the study of contaminated groundwater zones as well (Uchegbulam & Ayolabi, 2014). In accordance with Uchegbulam and Ayolabi (2014) hydrocarbon plumes may be delineated in subsurface aquifers using resistivity methods as hydrocarbons generally have a much low electrical conductivity compared to fresh water. The resistivity approach is particularly well suited for the delineation of hydrocarbon-contaminated aquifers as a result of this characteristic.

Sauck (1998) also found that fresh oil pollution has a high resistivity anomaly, whereas old oil pollution has a low resistivity anomaly. The low resistivity anomaly arises from instances where the hydrocarbons are being biodegraded. Biodegradation increases the total dissolved salts in groundwater (Sauck, 1998).

Electrical Resistivity Tomography (ERT), a recent advancement in resistivity sounding, takes small measurements along profiles for the 2D investigation of inhomogeneous media. A number of electrodes are either manually connected or automatically connected (Shevnin et al., 2003). Shevnin et al. (2003) also claims that the Vertical Electrical Sounding has also proven to be an effective technique as far as the delineation of hydrocarbon contaminated zones is concerned. The VES technique is carried out to evaluate vertical changes in electrical resistivity of the subsurface formations. The current and potential electrodes are kept in the same relative spacing in a straight line around a fixed central point. Similar to other electrical resistivity methods as the distance between current electrodes increases, the current penetrates deeper (Swapan, 2018).

#### 2.4.2 Relevant studies on groundwater assessment utilizing geoelectrical methods

In studies done by Shevnin et al. (2003) resistivity soundings were performed as ERT to detect the oil pollution in groundwater aquifers in Mexico. They used a two-sided dipole array with current electrode placements along the profile, a constant step between electrodes, and the same step between sounding stations in order to decrease geological noise. About 8 profiles were generated from different locations. The interpretation of all the profiles helped in the identification of the contaminated zones and this helped in the estimation of the pollution sources as well as the direction of the pollutant migration in the study area.

More recently, a study by Metwaly et al. (2013) employed transient electromagnetic (TEM) and 2D ERT technique in their investigation of groundwater pollution in Al-Quwy'yia. The results from the geoelectrical investigation were used to generate a profile for the contamination plumes. The TEM gave detailed information about the vertical extensions of the contamination while the ERT profiles demonstrated the lateral distribution.

Similar studies were carried out by Uchegbulam and Ayolabi (2014) where the 2D ERT technique was also applied in the investigation of hydrocarbon groundwater pollution in Sapele, a community in Delta state, Nigeria. They conducted their research using Wenner and Gradient arrays, which examined and showed resistivity variations along the survey lines in both the vertical and horizontal orientations. The electrode spacing on these arrays was at least 2 m.

The use of the Wenner and Gradient arrays took advantage of the good vertical resolution as well as lesser sensitivity to noise and better lateral coverage. The 2 m electrode spacing ensured that considerable details of any hydrocarbon plumes. Three traverses were taken to generate three ERT profiles which revealed the depths of possible hydrocarbon contaminants in the subsurface A lateral distance of 126 m was traversed by each traverse. For the first profile, the depths of potential 21

hydrocarbon plumes ranged from 0 to 18 meters, for the second, from 0.5 to 21 meters, and for the third, from 0.1-6 meters. However, the hydrocarbon pollution seemed to have migrated to 21 m below the surface for lateral distances of 20 to 70 m and 86 to 100 m. The investigation contributed to the discovery that the study area's shallow aquifers were contaminated. Since it was not the study's goal to go deeper than 30 meters, it was not pursued.

#### 2.5 Petroleum contaminants in groundwater

As previously discussed, according to Nadim et al. (2000), shortly after a spill, since PH have a lower specific gravity than water, they tend to pool non-aqueous phase liquid (NAPL), part of which gradually dissolves in groundwater to produce a plume of hydrocarbons in the groundwater flowing underground. Furthermore, a constant source of groundwater PH pollution are chemicals with a greater molecular weight and lower mobility, which are frequently held in pure liquid form in soil pores and are adsorbed onto clay (Nadim et al., 2000). Due to the heterogeneous composition of PH, higher molecular weight chemicals with less solubility are found closer to the plume's origin with less physical movement inside the plume, whereas lower molecular weight molecules with more solubility are found anterior to the plume (Logeshwaran et al., 2018). Anderson and Lovely (1999) discovered that the greatest concern come from the fact that due to the high-water solubility of some PH components such as low weight polycyclic aromatic hydrocarbons (PAH), these contaminants are more mobile in groundwater sources. According to Mojiri et al. (2019), PAHs are a class of toxic organic compounds made up of two or more benzene rings joined together in a cluster, linear, or angular pattern. Over 400 different types of PAHs have been found, and their effects have been studied (Pan et al., 2006). PAHs in soils are known to be rather recalcitrant (Ite, 2012), and several of these compounds have been classified as teratogens, mutagens, or carcinogens.

According to Mohamadi et al. (2015) the most common PH pollutants detected in groundwater, aside from PAHs, are volatile organic compounds (VOCs), including benzene, toluene, ethylbenzene, and xylenes (BTEX). VOCs comprises of organic compounds distinguished by their highly volatile behavior when present in the environment.

Due to their chemical properties, which include poor water solubility, high lipid solubility, semivolatility, and the capacity to pass through biological membranes and build up in fatty tissues, they are a major environmental problem (Chary & Fernandez-Alba, 2012).

Spills from petroleum products like gasoline, diesel, lubricating oil, and heating oil are among the most frequent sources of BTEX pollution in soil and groundwater (Doherty & Otitoloju, 2012). Both PAHs and VOCs, PH most common pollutants found in drinking water are reported to be introduced into the environment from the spillage of refined petroleum products such as gasoline, diesel etc. which are transported through pipelines. Since pipelines used to carry petroleum products are buried in the earth and could rupture or corrode, these pollutants then come into contact with the underground source of drinking water, contaminating it.

#### 2.5.1 Petroleum contaminant identification through geochemical analysis

Environmental water analysis is a challenging task owing to the complexity of the matrix they are present in as well as the diversity of analytes and the range of available concentrations. As a result, the kind of sample must be considered while selecting the best procedures for sample enrichment, determination, isolation, and quantification. **Error! Reference source not found.** lists many established analytical techniques and apparatus configurations for the forensic characterization of petroleum-related compounds released into the environment. Total petroleum hydrocarbons (TPH) is the total quantity of PH contained in an environmental matrix as determined by analytical procedures. Due to their specificity, the analytical techniques used for the detection, quantification, and monitoring of TPHs, and their metabolites vary greatly.

Techniques including gas chromatography-mass spectrometry (GC-MS), capillary GC with flameionization detection (FID), solid-phase microextraction, and headspace GC-MS are often used for the identification and analysis of TPHs in groundwater (see Figure 2.2). Primarily, three types of techniques are used for the identification of PAH: chromatographic, spectrometric and immunoassay (Adeniji et al., 2018).



Figure 2.2: Gas chromatography showing hydrocarbons present in different petroleum products (Source: Adapted from Senn and Johnson, 1985).

However, according to Poster et al. (2006), liquid and/or gas chromatography (LC and GC) are the most extensively used techniques for assessing PAHs in environmental media. These techniques have been established and widely deployed during the last few decades.
Substances	Technique
Hydrocarbon gases in the C1–C5 range	GC (FID)
n-Alkanes (C8 – C35)/particular branched-	GC/FID or GC/MS
chain alkanes.	
Significant volatile hydrocarbons found in	HP CC/FID or CC/MS
gasoline.	TIK GC/TID OF GC/MIS
BTEX	PD-GC or GC/MS
Oxygenated blending agents (alcohols &	T d CC/EID or CC/MS
ethers)	I-d-GC/FID OF GC/MS
Lead, organic lead, and trace metals (V / Ni) $$	ICPS
AB, ACH, PNAHC, PCSHC (steranes/	COMS
terpanes)	UC/IVIS

Table 2.2: Analytical methods used for the identification of petroleum related products (Kamal & Klein, 2010).

Furthermore, GC has been the method of choice and an efficient technique for the study of VOC occurrence and distribution in the environment (Chary & Fernandez-Alba, 2012). Combining GC with traditional detectors like the flame-ionization detector (FID), electron-capture detector (ECD), and photoionization detector (PID), as well as more contemporary detectors like the mass-selective detector (MSD), improved performance in the determination of VOCs in the majority of GC systems (Chary & Fernandez-Alba, 2012).

The combination of gas chromatography and mass spectrometry is a costly but more superior analytical approach for characterization in terms of identification and quantification of unidentified chromatographic components (Kamal & Klein, 2010).

#### 2.5.2 Related works on identification of petroleum contaminant in groundwater

In order to determine the TPHs in soil and groundwater samples collected from five communities in Nigeria's Rivers state where crude oil exploitation once took place, Alinnor and Nwachukwu conducted a study in 2013. The Agilent 6890N GC-FID instrument was used to separate and detect chemicals in soil and groundwater samples. The analysis's findings showed that soil samples from the first community were polluted with TPHs at values of 1320.00, 1516.66, and 1063.16 mg/kg, respectively. These samples were taken at depths of 1.0-2.0 m, 3.0-4.0 m, and 4.0-5.0 m. The outcome also revealed that the fifth community's soil sample exhibited high TPHs contents, measuring 1534.66, 1438.00, and 1651.00 mg/kg at the varying depths, respectively. The result of the analysis helped confirm that the groundwater at all the communities studied were contaminated with TPHs.

Similarly, Wang et al. (2002) confirmed the occurrence of gasoline and other petroleum pollutants in water samples retrieved at a case study site. The water samples were analyzed using GC–MS and capillary GC with FID, solid-phase microextraction and headspace GC–MS techniques. The result of the analysis showed the presence of hydrocarbons in the groundwater at shallow depths from the surface, 0-5 m, as well as the individual hydrocarbon component present which were of two types: gasoline and another heavy petroleum product. TPHs and BTEX concentrations were also determined to be 1070 and 155  $\mu$ g/kg of water for the sample (taken between 0 and 5 m), respectively. However, the degree of contamination appeared to reduce with increasing depth and the concentration of the TPH and BTEX of groundwater sample taken at the greatest depth (between 15 and 60 m) was 130 and 2.6  $\mu$ g/kg respectively. The presence of several volatile chlorinated compounds in the groundwater was also revealed by the analysis.

In 2010, Kamal and Klein employed GC–MS technique for the identification and quantification of BTEX in groundwater samples. Here are the findings of this study's sample analysis: (1) RT 3.9 m/z 78 (0.728 lg); (2) RT 6.7 m/z 91 (0.722 lg); (3) RT 8.65 m/z 91 (0.038 lg); (4) RT 8.75 m/z 91 (0.027 lg); (5) RT 8.86 m/z 91 (0.072 lg) and (6) RT 9.54 m/z 91 (0.065 lg).

In the spring and summer of 2012, Sobhanardakania et al. (2016) evaluated the degree of heavy metal contamination in the groundwater resources of the Asadabad plains, Iran. The levels of heavy metals were assessed for 30 critical groundwater sample sites in their analytical observational investigation. Using ICP-OES, the metal concentrations (As, Zn, Pb, Cd, and Cu) were analyzed. The analyses' findings enabled the researchers to assess the heavy metal evaluation index (HEI) and heavy metal pollution index (HPI). The findings show that the average As, Zn, Pb, Cd, and Cu contents in groundwater samples taken from Asadabad Plain in the spring season were as follows:  $52.53\pm13.62$ ,  $15.51\pm23.45$ ,  $10.10\pm2.80$ ,  $4.48\pm1.80$  and  $8.63\pm10.87 \mu g$  l–1, respectively and in summer season were  $57.60\pm16.90$ ,  $14.99\pm17.66$ ,  $9.28\pm2.46$ ,  $4.57\pm1.73$  and  $10.45\pm10.30 \mu g$  l–1, respectively. The results also demonstrated that there were considerable differences in the metal concentrations between sampling sites. However, because the concentrations of heavy metals were found to be within WHO acceptable range, the water samples were pronounced safe to drink.

Shevnin et al. (2005) carried out a characterization of an oil-contaminated site using geoelectrical methods in Tabasco, Mexico where an oil well used to be using the VES method on 2D resistivity imaging technology and 2D interpretation. It was an extensive geoelectrical investigation with over 246 VES points, along 11 profiles. About 50 electrodes were used along each profile with a

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constant interval of 2 m and the Schlumberger array was employed. However, only the geological structure in the study area's upper 10 m was explored in order to outline the oil-contaminated zones and assess the degree of pollution. The VES 2D interpretation was successful in delineating the contaminated and non-contaminated zones as well as in finding the optimal layer in the lower part of the vadose zone. The geoelectrical data was then correlated with water and soil resistivity measurements alongside geochemical studies where the TPH concentration of selected water samples were determined using the infrared spectroscopy in accordance to EPA418.1 (USEPA, 1983). The clay content and soil particle size distribution were also determined in accordance with Bouyoucos. The TPH concentration, clay content and soil particle distribution as well as the soil and water resistivity measurements helped to guide the interpretation of geoelectrical anomalies and to correlate the geochemical and geoelectrical data.

Also, whilst the geochemical investigations were done in a pit, the geoelectrical investigations spanned a wider area. The study was extensive and very detailed results were obtained and more accurate conclusions were made compared to studies by previous studies Shevnin et al. (2003) where only the geoelectrical methods were used. The study showed the efficiency and effectiveness of integrating geoelectrical methods with geochemical analysis in obtaining a more detailed and accurate assessment of hydrocarbon induced groundwater pollution in a given study area.

The methods used in this study employs the same; an integration of geoelectrical methods and geochemical studies in the assessment of the hydrocarbon induced groundwater pollution in Baruwa community of Lagos state, Nigeria.

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# **CHAPTER THREE: METHODOLOGY**

### **3.1 Introduction**

The rapid advancement of computer software and accompanying numerical modeling methods has boosted the use of geophysics for groundwater exploration and water quality analyses.

The simplicity of the technology has made VES quite popular in groundwater prospecting. The electrical geophysical survey approach detects surface effects caused by underground electric current flow. Electrical approaches have been employed in mineral exploration, engineering, geothermal exploration, archeological research, permafrost mapping, and geological mapping.

# 3.2 Materials and Equipment utilized for ERT and VES survey

- a. Cable reels (Figure 3.1)
- b. Steel rod electrodes (Figure 3.7)
- c. 4 1000kg hammers ( Figure 3.2)
- d. Garmin GPSMAP 78 Handheld Marine GPS Device (Figure 3.3)
- e. ABEM (Signal Averaging System, SAS4000) Terrameter (Figure 3.4)
- f. Logix 12-volt battery (Figure 3.5)
- g. Surveyor measuring tape (Figure 3.6)



Figure 3.1: Cable reels



Figure 3.2: 1000kg hammer



Figure 3.3: Garmin GPSMAP 78 Handheld Marine GPS Device



Figure 3.4: ABEM SAS4000 Terrameter



Figure 3.5:12-volt Logix battery



Figure 3.6: Surveyor tape

# **3.3 Field investigation methods**

Two approaches were employed. These approaches include geo-electrical investigation/survey employing ERT and VES, and physiochemical analysis of water samples retrieved from water sources of local residents. The section below provides a thorough explanation of how the field investigation was conducted.

#### **3.3.1** Geo-electrical investigation

Due to the popularity of both the Schlumberger and Werner electrode configuration approaches for research such as these, a hybrid Werner–Schlumberger array (Loke, 2000) was adopted in this work. As earlier stated, two types of resistivity surveys were conducted during the field investigation, namely, the ERT and VES surveys.

For the ERT (Electrical Resistivity Tomography) surveys, the 2D Wenner array was employed. Four (4) distinct ERT traverse profiles were done along four (4) locations within the study area. These four locations include Road 1, Aduloju Street, Church Street, and Oguntayo Street of Baruwa community. The VES (Vertical Electrical Sounding) traverses were conducted perpendicular to that of the ERT traverses. A total of seven (7) VES traverses were taken along the same line using the roll-along method. The Schlumberger array was employed for the VES surveys.

#### Data Acquisition

The ABEM (Signal Averaging System, SAS4000) Terrameter is the primary equipment utilized in this survey. It was used to measure and record the resistance of the subsurface formations. Resistance values were shown on the digital screen of this equipment and then recorded in the field report book for each survey site. For each electrode arrangement, a sounding was performed, and the resistance R of the underlying subsurface formation was obtained. The apparent resistivity of the stated earth material was then calculated as the product of the configuration factors K and R. Four steel rod electrodes were used in conjunction with four cable reels of 500 meters of multiconductor wire, four 1000 kg hammers were used to put the electrode into the ground, and the entire electrical setup was powered by a Logix 12-volt battery. The coordinates of points along the VES and ERT traverses were determined using the Garmin GPSMAP 78 Handheld Marine GPS Device, and the distance of the traverse and every 5m along the traverse were measured using two 100 m surveyor tapes.

## ERT traverse 1:

The first ERT base station was located at N  $06^{\circ} 35' 46.7"$  and E  $003^{\circ} 16' 18.1"$  as shown in Figure 3.8: Base station set up for ERT Traverse 1 (Road 1) (with an elevation of 51 m) and ran through till N  $06^{\circ} 35' 49.1"$  and E  $003^{\circ} 16' 12.0"$  (with an elevation of 40 m). The traverse of 150 m was carried out along "Road 1" of the Baruwa community and the GPS readings for every 5 m along the traverse is shown in Table 3.1. Figure 3.7 shows a little distance of the entire ERT profile covered along this location.

S/N	Points (m)	Elevation (m)	S/N	Points (m)	Elevation (m)
1	0	51	17	80	47
2	5	52	18	85	53
3	10	47	19	90	41
4	15	50	20	95	41
5	20	55	21	100	44
6	25	56	22	105	42
7	30	50	23	110	42
8	35	50	24	115	45
9	40	48	25	120	46
10	45	46	26	125	44
11	50	44	27	130	45
12	55	48	28	135	46
13	60	49	29	140	45

Table 3.1: GPS elevation readings along ERT traverse profile 1

14	65	40	30	145	45
15	70	42	31	150	40
16	75	46			

## ERT traverse 2:

The second ERT base station was located at N 06° 35' 00.0" and E 003° 16' 21.5" as shown in Figure 3.10 (with an elevation of 45 m) and ran through till N 06° 35' 02.5" and E 003° 16' 15.8" (with an elevation of 47 m). A traverse of 200 m was carried out along "Aduloju Street" of the Baruwa community. Figure 3.9 shows the ERT profile along this traverse and the GPS readings for six (6) points along the traverse are presented in **Error! Reference source not found.** .

S/N	Points (m)	Elevation (m)
1	0	45
2	20	51
3	50	62
4	100	45
5	150	43
6	200	47

**Table 3.2:** GPS elevation readings along ERT traverse profile 2

### ERT traverse 3:

The third ERT base station was located at N  $06^{\circ} 35' 52.7"$  and E  $003^{\circ} 16' 20.7"$  as shown in Figure 3.12 (with an elevation of 53 m) and ran through till N  $06^{\circ} 35' 54.3"$  and E  $003^{\circ} 16' 14.6"$  (with an elevation of 40 m) as is captured in Figure 3.11. The traverse, spanning 200 m, was carried out along "Church Street" of the Baruwa community, with Figure 3.11 showing the ERT profile along the traverse and the GPS readings for every 5 m along the traverse is shown in Table 3.3.

S/N	Points (m)	Elevation (m)	S/N	Points (m)	Elevation (m)
1	0	53	22	105	50
2	5	46	23	110	48
3	10	49	24	115	51
4	15	50	25	120	47
5	20	55	26	125	46
6	25	43	27	130	49
7	30	45	28	135	55
8	35	44	29	140	48
9	40	49	30	145	51
10	45	46	31	150	45
11	50	50	32	155	45
12	55	51	33	160	41
13	60	45	34	165	50
14	65	43	35	170	50
15	70	48	36	175	49
16	75	40	37	180	42
17	80	43	38	185	48
18	85	41	39	190	48
19	90	50	40	195	47
20	95	57	41	200	43
21	100	52			

**Table 3.3:** GPS elevation readings along ERT traverse profile 3

# ERT traverse 4:

The fourth ERT base station was located at N  $06^{\circ} 35' 56.6"$  and E  $003^{\circ} 16' 21.0"$  (with an elevation of 45 m) and ran through till N  $06^{\circ} 35' 59.5"$  and E  $003^{\circ} 16' 15.8"$  (with an elevation of 47 m).

The traverse of 200 m was carried out along "Oguntayo Street" of the Baruwa community and the GPS readings for every 5 m along the traverse is arranged and presented in Table 3.4.

S/N	Points (m)	Elevation (m)	S/N	Points (m)	Elevation (m)
1	0	45	22	105	56
2	5	46	23	110	50
3	10	48	24	115	51
4	15	50	25	120	46
5	20	50	26	125	52
6	25	45	27	130	45
7	30	48	28	135	43
8	35	54	29	140	48
9	40	53	30	145	50
10	45	53	31	150	52
11	50	49	32	155	44
12	55	48	33	160	51
13	60	57	34	165	50
14	65	51	35	170	48
15	70	45	36	175	50
16	75	49	37	180	52
17	80	44	38	185	44
18	85	52	39	190	51
19	90	48	40	195	50
20	95	51	41	200	55
21	100	55			

**Table 3.4:** GPS elevation readings along ERT traverse profile 4



Figure 3.7: ERT traverse for Profile 1(steel electrode rod indicated by the red circle)



Figure 3.8: Base station set up for ERT Traverse 1 (Road 1)



Figure 3.9: ERT traverse for Profile 2



Figure 3.10: Base station set up for ERT traverse Profile 2 (Aduloju street)



Figure 3.11: ERT traverse for Profile 3



Figure 3.12: Base station set up for ERT traverse profile 3(Church Street)



Figure 3.13: Base station set up for VES survey

## **3.3.2** *Physicochemical analysis*

# Water Sample collection

Water samples were collected from water sources used by local residents which included taps and wells. A total of fifty (50) different locations were visited and a water sample was retrieved from each location, hence, a total of fifty (50) water samples were collected. Each sample was stored in a 946 ml glass jar with a plastic lid and sealed properly. Sample jars were adequately labelled according to the location where they were retrieved (see **Table 3.5** for GPS coordinates of each sample location).



Figure 3.14: Water sample being collected from local resident's tap



Figure 3.15: Water sample being labelled according to our sample location numbering



Figure 3.16: Water samples being brought together to be sent to the lab for physiochemical analysis

Sample	GPS	Elevation	Sample	GPS	Elevation
Number	Coordinates	(m)	Number	Coordinates	(m)
1	N 06° 35' 47.1"	55	18	N 06° 35' 57.1"	49
	E 003° 16' 18.7"			E 003° 16' 20.3"	
2	N 06° 35' 44.3"	54	19	N 06° 35' 58.6"	46
	E 003° 16' 17.8"			E 003° 16' 18.2"	
3	N 06° 35' 40.6"	44	20	N 06° 35' 59.4"	42
	E 003° 16' 14.1"			E 003° 16' 18.3"	
4	N 06° 35' 39.8"	45	5 21 N 06° 35' 59.6" 46		46
	E 003° 16' 10.4"			E 003° 16' 18.5"	
5	N 06° 35' 38.1"	44	22	N 06° 35' 02.8"	58
	E 003° 16' 17.5"			E 003° 16' 16.3"	
6	N 06° 35' 45.3"	52	23	N 06° 35' 55.7"	50
	E 003° 16' 18.1"			E 003° 16' 10.9"	
7	N 06° 35' 52.1"	45	24	N 06° 35' 54.8"	40
	E 003° 16' 20.1"			E 003° 16' 11.6"	

Table 3.5: GPS readings	s for water sample source	S
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8	N 06° 35' 53.7"	43	25	N 06° 35' 50.6"	42
	E 003° 16' 17.2"			E 003° 16' 16.4"	
9	N 06° 35' 52.6"	42	26	N 06° 36' 005"	49
	E 003° 16' 17.5"			E 003° 16' 20.7"	
10	N 06° 35' 52.9"	46	27	N 06° 36' 002"	50
	E 003° 16' 15.9"			E 003° 16' 19.7"	
11	N 06° 35' 57.6"	44	28	N 06° 36' 59.6"	55
	E 003° 16' 13.1"			E 003° 16' 18.0"	
12	N 06° 35' 56.9"	42	29	N 06° 36' 02.4"	57
	E 003° 16' 12.3"			E 003° 16' 12.1"	
13	N 06° 35' 56.9"	56	30	N 06° 36' 01.9"	41
	E 003° 16' 13.0"			E 003° 16' 17.1"	
14	N 06° 35' 56.1"	51	31	N 06° 36' 03.2"	44
	E 003° 16' 11.4"			E 003° 16' 16.7"	
15	N 06° 35' 50.1"	45	32	N 06° 36' 03.8"	47
	E 003° 16' 13.8"			E 003° 16' 21.7"	
16	N 06° 35' 52.1"	41	33	N 06° 36' 08.2"	51
	E 003° 16' 15.7"			E 003° 16' 22.4"	
17	N 06° 35' 56.6"	46	34	N 06° 35' 50.6"	42
	E 003° 16' 20.9"			E 003° 16' 22.4"	

# Physicochemical laboratory analysis of water samples

The samples of water retrieved from the study area were analyzed for different physio-chemical properties. Three types of analysis were carried out on each sample to determine the contaminants present. They include:

- i. VOC (Volatile Organic Compounds)
- ii. TPH (Total Petroleum Hydrocarbons)

## **VOCs (Volatile Organic Chemicals)**

The details of how this physicochemical analysis was carried out is described in the section below:

Method Type: Instrumental

Method Code: MTH008

Instrument Used: Agilent 8860 GC-FID Coupled With 7697a Headspace Sampler (Figure 3.17).



Figure 3.17: AGILENT 8860 GC-FID Coupled with 7697A Headspace Sampler

### Analysis Procedure

The samples were introduced into the GC by means of a Headspace sampler. Vial pressurization gas used was Nitrogen gas and Helium was used as the carrier gas. Oven temperature was set at 80 0C, loop temperature was set at 85°C while the transfer line temperature was set at 120°C. Vial equilibration duration was set at 10 minutes, and the fill pressure was set at 15psi. 10ml of each sample was transferred into 20ml headspace vials and then placed into the 7697A carousel for analysis.

The Agilent 8860 GC-FID fitted with an HP-5 capillary column coated with 5% phenyl methyl siloxane (30m length x 0.32mm diameter x 0.25 µm film thickness), was used to examine the samples. At an injection temperature of 250 °C, a pressure of 4.227 psi, and a total flow of 0.6 mL/min, the samples were injected in split-less mode. Oven was originally set to 50 °C for two minutes, then ramped up to 300 °C at a rate of 10 °C/min. FID temperature with hydrogen was 300 °C: 300 mL/min of air were moved at 30 mL/min, and 18 mL/min of nitrogen was used as a makeup gas.

### **Calibration Procedure**

VOCs standard, 2000ppm (Catalog Number: M-502A-R-10X) containing 54 VOCs components was purchased from AccuStandard (USA). Three (4) point serial dilution calibration standards (0.1, 0.034, 0.019, 0.012ppm) was prepared from the stock and used to calibrate the GC.

### **TPH (Total Petroleum Hydrocarbons)**

The details of how this physicochemical analysis was carried out is described in the section below:

Method Type: Instrumental

Method Code: MTH003

**Instrument Used:** Agilent 8860 Gc-Fid (Figure 3.18)

Calibration Standards: Accustandard Hydrocarbon Window Defining Standard, 500mg/L (Catalog Number: Drh-008s-R2).



Figure 3.18: AGILENT 8860 GC-FID

# Analysis Procedure

The Agilent 8860A GC-FID fitted with a HP5 capillary column coated with 5% Phenyl Methyl Siloxane (30m length x 0.32mm diameter x 0.25µm film thickness) was used to analyze each sample (J&W).

 $1\mu$ L of the samples were injected using an Agilent 7693 Automatic Liquid Sampler (ALS) and in split-less mode at an injection temperature of 250°C. The inlet pressure was set at 10.296 psi and a total flow of 45.2 mL/min. Purge flow to split vent was set at 40 mL/min at 0.5 min. Helium was used as carrier gas with a constant column flow of 1 mL/minute.

The GC oven was initially set at 50 °C (0.5 min) then ramped at 10 °C/min to 300 °C (10 min). The temperature of the FID was set at 300 °C with Hydrogen: Air flow at 20 mL/min: 300 mL/min.

# **Calibration Procedure**

A working solution of 75mg/L was prepared from the stock solution procured from Accustandard (US). Calibration solutions of 0.06mg/L, 3mg/L, 6mg/L, 12mg/L and 75mg/L were prepared by a 5-point serial dilution of the working solution and used to calibrate the responses of the GC-FID.

# **CHAPTER FOUR: RESULTS AND DISCUSSION**

### **4.1 Geoelectrical Results**

#### 4.1.1 2D ERT

#### **Profile 1:**

The results of the 2D electrical resistivity imaging (Figure 4.1) depict the distribution of resistivity over a lateral span of 150 m from the surface to a depth of around 40 m below the surface. The 2D section revealed an anomalously high resistivity (1000 - 2300  $\Omega$ ·m) structure within a lateral distance of 72-107 m at a depth of 3-15 m. The resistivity for this profile appears to be highest between the lateral distances of 85 and 95 m, which could be explained by the presence of a hydrocarbon plume from a more recent spill in the subsurface. This spill may have resulted from leaks from underground pipelines in the study area or possibly from vandalism. The resistivity values around this anomalously high resistivity subsurface structure (a potential hydrocarbon plume from a recent spill) equally have high resistivity values indicative of mature or diffused hydrocarbon pollution in the region.



Figure 4.1: ERT profile for Road 1

The 2D ERT result reveal the possible contaminant plumes to be within the depth of 3-15 m. The ERT profile also supports the earlier claim that the study area has an undulating topography.

#### **Profile 2:**

The Wenner array 2D resistivity of the subsurface structure in the investigated region is shown in Figure 4.2. The results of the 2D electrical resistivity imaging show the distribution of resistivity over a lateral extent of 200 m and to a depth of about 40 m below the surface. The depth at which the highest anomalous resistivity values ( $\geq$ 39,000  $\Omega$ ·m) are recorded is between 0-10 m, which indicates the presence of possible hydrocarbon plumes from a recent oil spill. From this near-surface depth where this extremely anomalously high resistivity value is recorded, the resistivity values appear to reduce slowly between the lateral distance of 0-115 m and at depth 25 - 40 m which reveals the possible spreading of the hydrocarbon contaminant over a wider surface area perhaps due to the flowing groundwater. Thus, the groundwater in this part of the study area is likely to be situated at depth 25 - 40 m and flows from east to west underground.



Figure 4.2: ERT profile for Adeloju Street

## **Profile 3:**

Figure 4.3 shows the Wenner array 2D resistivity of the subsurface structure in the investigated region. The 2D electrical resistivity imaging result show the resistivity distribution over a lateral distance of 200 m and to a depth of about 40 m from the surface. Between the lateral distance of 140-165 m, and at a depth of 0-10 m anomalously high resistivity values ( $\geq 1500 \ \Omega \cdot m$ ) are noticed which indicates the likely presence of hydrocarbon plume. However, this is the only region along the profile with these resistivity values. This indicates that it is either the subsurface structures show low permeabilities or the spill is very recent and as such has not percolated through the soil columns to greater depths.



Figure 4.3: ERT profile for Church Street

## **Profile 4:**

Figure 4.4 shows the Wenner array 2D resistivity of the subsurface structure in the investigated region. The 2D electrical resistivity imaging result show the resistivity distribution over a lateral distance of 200 m and to a depth of about 40 m from the surface. At a lateral distance of 25 – 60 m, anomalously high resistivity values ( $1500 - 4000 \ \Omega \cdot m$ ) are recorded. The highest resistivity value occurs at a lateral distance of 38 - 50 m at a depth of 2 - 20 m beneath the surface. This is the depth at which the possible hydrocarbon plume is located. At a lateral distance of 25 - 60 m anomalously high resistivity values are still being recorded at depths between 20 - 40 m which indicates the likely spread of the hydrocarbon plume through the soil columns due to its permeability or the presence of flowing groundwater from an aquifer.



Figure 4.4: ERT profile for Oguntayo Street

### 4.1.2 VES Results

This section shows the results from the VES traverses carried out in the study area. All seven (7) traverses were done on a straight line and provides information about the geology of each traverse.

### **Profile 1**

The traverse reveals a resistivity distribution ranging between 267.2  $\Omega$  and 1955.4  $\Omega$  (see Figure 4.5. Figure 4.5 also reveals the number of layers present in the subsurface as well as the resistivity, thickness, and depth of each layer. Six (6) layers were discovered, and the fifth layer was mapped out to be at a depth of 38.2 m. The type of curve for this profile is Type K.



Figure 4.5: VES 1 Profile (Geoelectric-section for VES 1)

# **Profile 2**

The traverse reveals a resistivity distribution ranging between 240.9  $\Omega$  and 797.4  $\Omega$  (see Figure 4.6). Figure 4.6 also reveals the number of layers present in the subsurface as well as the resistivity, thickness, and depth of each layer. Six (6) layers were discovered, and the fifth layer was mapped out to be at a depth of 46.0 m. The type of curve for this profile is Type K.



Figure 4.6: VES 2 Profile (Geoelectric-section for VES 2)

The traverse reveals a resistivity distribution ranging between 180.2  $\Omega$  and 623.5  $\Omega$  (see

Figure 4.7).

Figure 4.7 also reveals the number of layers present in the subsurface as well as the resistivity, thickness, and depth of each layer. Six (6) layers were discovered, and the fifth layer was mapped out to be at a depth of 66.4 m. The type of curve for this profile is Type Q.



Figure 4.7: VES 3 Profile (Geoelectric-section for VES 3)

The traverse reveals a resistivity distribution ranging between 151.0  $\Omega$  and 1116.0  $\Omega$  (see Figure 4.8). Figure 4.8 also reveals the number of layers present in the subsurface as well as the resistivity, thickness, and depth of each layer. Six (6) layers were discovered, and the fifth layer was mapped out to be at a depth of 82.1 m. The type of curve for this profile is Type Q.



Figure 4.8: VES 4 Profile (Geoelectric-section for VES 4)

The traverse reveals a resistivity distribution ranging between 76.7  $\Omega$  and 614.4  $\Omega$  (see Figure 4.9). Figure 4.9 also reveals the number of layers present in the subsurface as well as the resistivity, thickness, and depth of each layer. Six (6) layers were discovered, and the fifth layer was mapped out to be at a depth of 123.8 m. The type of curve for this profile is Type Q.



Figure 4.9: VES 5 Profile (Geoelectric-section for VES 5)

# **Profile 6**

The traverse reveals a resistivity distribution ranging between 460.0  $\Omega$  and 2016.0  $\Omega$  (see Figure 4.10). Figure 4.10 also reveals the number of layers present in the subsurface as well as the resistivity, thickness, and depth of each layer. Six (6) layers were discovered, and the fifth layer was mapped out to be at a depth of 48.0 m. The type of curve for this profile is Type A.



Figure 4.10: VES 6 Profile (Geoelectric-section for VES 6)

The traverse reveals a resistivity distribution ranging between 473.8  $\Omega$  and 2879.6  $\Omega$  (see Figure 4.11). Figure 4.11 also reveals the number of layers present in the subsurface as well as the resistivity, thickness, and depth of each layer. Six (6) layers were discovered, and the fifth layer was mapped out to be at a depth of 22.6 m. The type of curve for this profile is Type A.



Figure 4.11: VES 7 Profile (Geoelectric-section for VES 7)

## **VES** Interpretation

The geological section of the study area (see Figure 4.12) consists of the topsoil, sandy clay, lateritic clay, the main aquifer, and the confining bed. The results from seven (7) VES profiles are presented in Table 4.1. The depth of the first layer ranges from 1.5 - 3.0 m from the surface. The second layer is revealed to be located at a depth 4.0 - 12.0 m from the surface. The depth of the third layer ranges from 12 - 67.0 m and that of the fourth overlaps the third to a depth of 106 m. The depth of the main aquifer in the study area ranges between the depth of 20 m to 124 m.

This knowledge helps to guide the anomalies from the ERT results. From the ERT profiles 1 and 3 (see Figure 4.1 and Figure 4.3), the anomalously high resistivity values which indicate possible hydrocarbon contaminant plume occurred at the first three layers: top soil, sandy clay and lateritic clay. This is perhaps either because the hydrocarbon contaminant plume is from a recent spill, or it was quickly absorbed by the clay particles in the second and third layers where no free water exists. This would also explain why the plume does not advance into layers at deeper depths.



Figure 4.12: Geological section of the study area

Figure 4.2 and Figure 4.4 show the dispersal of the hydrocarbon contaminant plume, especially at depths between 25 - 40 m and correlating that with the geological section (see Figure 4.12), this dispersal or spreading of the contaminant plume is possibly due to the presence of flowing water from the main aquifer in the study area. This would mean that for wells located at the near surface depths (0 – 10 m), the concentration of the contaminant plumes will be higher than wells at greater depths where the plumes have dispersed to.

However, wells drilled to depths of 20 m, or more are likely to still contain the hydrocarbon contaminants at a lesser concentration but due to the movement of the groundwater, majority of the wells at this depth are vulnerable to contamination. The transportation of contaminants in wells at near surface are therefore slower and the tendencies are lower.

VES Profile No/	Layer Number	1	2	3	4	5	6
Curve type	Lithology	Topsoil	Sandy Clay	Laterit	Lateritic Clay		Confining Bed
	Resistivity	267.2	511.7	896.4	1955.4	1168.2	530.6
1/K	Thickness	1.5	2.6	5.0	9.9	19.2	-
	Depth	1.5	4.1	9.1	19.0	38.2	-
	Resistivity	240.9	420.6	609.1	757.8	797.4	358.8
2/K	Thickness	2.0	3.0	6.0	10.0	25.1	-
	Depth	2.0	5.0	10.9	20.9	46.0	-
	Resistivity	490.7	538.6	623.5	297.6	279.0	180.2
3/Q	Thickness	2.0	2.0	6.9	15.3	40.2	-
	Depth	2.0	4.0	10.8	26.2	66.4	-
	Resistivity	391.0	1116.0	632.0	248.0	333.0	151.0
4/Q	Thickness	1.6	1.5	9.0	11.0	59.0	-
	Depth	1.6	3.1	12.1	23.1	82.1	-
	Resistivity	319.5	14.4	235.6	178.8	260.8	76.7
5/Q	Thickness	1.5	10.5	54.7	39.0	18.1	-
	Depth	1.5	12.0	66.7	105.7	123.8	-

Table 4.1: VES profile data summary
	Resistivity	662.0	460.0	1033.0	1283.0	2272.0	2016.0
6/A	Thickness	2.0	10.0	9.0	8.0	19.0	-
	Depth	2.0	12.0	21.0	29.0	48.0	-
	Resistivity	473.8	448.7	664.7	972.7	1362.3	2879.6
7/A	Thickness	3.0	5.6	4.5	3.7	5.4	-
	Depth	3.0	8.6	13.1	16.8	22.2	-

### 4.2 Physicochemical Analysis

#### 4.2.1 VOCs Results

The analysis of the 34 samples of water retrieved from the sources utilized by local residents in the study area showed the concentration of Volatile Organic Compounds likely to have been introduced into the water sources from spillage of refined petroleum products being transported in the pipelines running through the subsurface. For samples labelled 3, 4, 5, 11, 12, 14, 17, 18, 21, 30, and 34 the concentration of VOC was 0 mg/L. However, for some samples the VOC concentrations were well above acceptable values. These samples include sample number 13, 25, 16, 24, 8, 19, 20, 31, 33, 9, 29, 27, and 28. The VOC concentrations of these samples are shown in Table 4.2. Samples 1, 2, 6, 7, 10, 15, 22, 23, 26, and 32 all contained trace amounts of VOCs.

1 ubio 1.2. 111gli VOC concentrations of anterent water samples from stady area	Table 4.2: F	ligh VOC	concentrations	of different	water sam	ples from	1 study area
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SAMPLE					CO	NCENTRATIO	N OF VOCs	(mg/L)		
S/N N	NUMBER	Benzene	Toluene	Chlorobenzene	Ethylbenzene	m, p Xylene	O-Xylene	1,2 Dichlorobenzene	1,3 Dichlorobenzene	1,4 Dichlorobenzene
1	13	0.71017	-	-	3.22168	-	-	2.60204	4.36423	-
2	25	-	1.42542	10.14694	1.45902	0.58048	1.20410	-	-	-
3	16	0.70392	2.67961	-	3.93224	-	-	4.82825	3.20571	-
4	24	-	3.04773	7.81666	2.91934	-	5.05546	-	-	2.39913
5	8	0.78001	-	-	6.31800	-	-	4.20813	7.82048	-
6	19	-	5.80951	6.41968	2.50573	0.70592	5.20897	-	-	1.84877
7	20	0.63513	4.47245	8.41356	3.15092	2.87837	3.97175	-	-	1.89568
8	31	-	8.76629	5.12130	3.20765	3.30459	5.92549	-	-	1.97638
9	33	-	3.89117	17.97577	2.20027	2.53266	5.15014	1.72560	-	2.01756
10	9	0.73665	-	-	20.40644	-	-	8.03964	11.61170	-
11	29	-	14.62319	11.85898	4.21176	7.72005	8.77731	1.31508	-	2.93631
12	27	-	41.79555	10.95109	1.24169	12.24197	14.53817	-	-	4.02815
13	28	-	67.19385	17.54362	2.32374	18.42648	22.10542	1.80389	-	5.76270

### Table 4.3: US EPA drinking water standard for BTEX compounds (Adapted from Fayemiwo et

al.,	201	7)
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Compound	MCLG (mg/L)	MCL (mg/L)
Benzene	0	0.005
Toluene	1	1
Ethylbenzene	0.7	0.7
Xylenes	10	10

MCLG-Maximum Contaminant Level Goal; MCL-Maximum Contaminant Level

Compound	MCLG (mg/L)	MCL (mg/L)
Benzene	0	0.01
Toluene	1	0.7
Ethylbenzene	0.3	0.3
Xylenes	0.5	0.5

Table 4.4: WHO guidelines for drinking water standard for BTEX compounds (WHO, 2021)

MCLG-Maximum Contaminant Level Goal; MCL-Maximum Contaminant Level

### Benzene

The concentration of Benzene in all the samples analyzed ranged between 0-0.78 mg/L. Sample 8 had the highest concentration of Benzene 0.78, followed by Sample 9, Sample 13, 16 and 20 (see Figure 4.13). The result of the analysis also showed that majority of the water sources in the study area had concentration levels of Benzene that exceed the acceptable limits of WHO (0.01 mg/L) (see Table 4.4) and US EPA (0.005 mg/L) (see Table 4.3) and as such residents are exposed to certain health risks. Short term exposure to concentration levels of Benzene that exceed acceptable limits are known to cause irritation of the eyes, skin, and upper respiratory as well as blisters on the skin. While a longer exposure may result in blood diseases, reproductive and developmental problems, and cancer (Garang Kuch & Bavumiragira, 2019).



Figure 4.13: Concentration of Benzene for certain water samples

### Toluene

The concentration of Toluene in all the samples analyzed ranged between 0-67.19 mg/L. Sample 28 had the highest concentration (67.19 mg/L), followed by Sample 27 and Sample 29 (see Figure 4.14). Figure 4.14 also reveals that the water samples had a Toluene concentration that exceeds the WHO (see Table 4.4) and US EPA (see Table 4.3) standard that should be found in drinking water. Consuming water with such levels of Toluene may have an impact on the nerve system, irritate the skin, eyes, and respiratory tract, and result in birth defects, headaches, dizziness, and difficulties sleeping (Garang Kuch & Bavumiragira, 2019).



Figure 4.14: Concentration of Toluene for certain water samples

### Ethylbenzene

The concentration of Ethylbenzene in all the samples analyzed ranged between 0-20.41 mg/L. Particularly, for the 13 samples with high concentration of BTEX, sample 9 had the highest Ethylbenzene concentration (20.41 mg/L) and was 1,543.44% higher than Sample 27, which had the lowest Ethylbenzene at 1.24 mg/L (see Figure 4.15). As Figure 4.15 reveals, the water samples contain concentration levels of Ethylbenzene that lie above the acceptable limits to be found in drinking water by the WHO (Table 4.4) and US EPA (see Table 4.3). The implication of this includes throat and eye irritation, dizziness, chest constriction and may even result in blood disorder if consumption continues over time (Garang Kuch & Bavumiragira, 2019).



Figure 4.15: Concentration of Ethylbenzene for certain water samples

#### Xylenes (m, p-Xylene, and O-Xylene)

The concentration of Xylenes in the analyzed water samples ranged between 0 and 18.43 mg/L (m, p Xylene) and 22.11 mg/L (O-Xylene). In Figure 4.16, the concentrations of m, p Xylene and O-Xylene are shown for the 13 water samples with high BTEX concentrations. Sample 28 showed the highest concentration of both m, p Xylene and O-Xylene (see Figure 4.16). A good number of the water samples were discovered to have Xylene concentrations beyond the acceptable limits by WHO (see Table 4.4) and US EPA (see Table 4.3). Exposure to high concentrations of xylenes over a short period of time may result in neurological symptoms, nausea, vomiting, stomach irritation, moderate transitory ocular irritation, and effects on the nose and throat. The neurological system may be harmed by prolonged exposure to high doses of xylene (Garang Kuch & Bavumiragira, 2019).



m,p Xylene and O-Xylene by Sample No.

Figure 4.16: Concentration of m, p Xylene, and O-Xylene for certain water samples

### BTEX concentration levels in analyzed samples

Across the 13 water samples with showed significantly high concentrations of BTEX, Toluene appeared to be the compound with the highest concentration (Sample 28) followed by O-Xylene (Sample 28), then Ethylbenzene (Sample 9), and m, p Xylene (Sample 28). Benzene has the lowest concentration throughout all the samples analyzed (see Figure 4.17). However, seeing that the maximum concentration level for Benzene accepted in drinking water is rather low (0.005 mg/L by US EPA and 0.01 by WHO) most of the water sources are considered very harmful to the health of residents. Water sources from which Samples 8, 9, 13, 16, 20, 28, 27, and 29 are particularly very harmful to residents who utilize them as the concentration of BTEX in them are found to be the highest out of all 34 samples analyzed.



Figure 4.17: Chart showing BTEX concentration levels in analyzed water samples

### 4.2.2 TPH Results

The analysis for TPH in the water samples showed zero concentration levels in some, trace amounts in some, mild to high concentration in others. Precisely, samples 3, 5, 11, 14, 17, 21, 30 and 34 contained no amount of TPH. Samples 2, 4, 6, 7, 10, 12, 13, 15, 18, 22, 23, 26, and 32 had TPH concentrations ranging from 0.51 - 28.23652 mg/L. Samples 8, 16, 19, 24 and 25 showed TPH concentrations of 30.55964 - 38.90100 mg/L. However, samples 9, 20, 27, 28, 29, 31 and 33 showed TPH values as high as 98.74392 mg/L. Eight water samples with the highest TPH concentration levels were further visualized as see in Figure 4.18-Figure 4.21 using Microsoft Power BI. The visualization revealed that of the eight samples, for C8-C14, the compound with the highest concentration was C9 in Sample 33, (9.09266 mg/L) (see Figure 4.18). Also, very high concentration of C9 is noticed in Samples 9 and 31.

The second compound with the highest concentration levels was C10 (Sample 19) followed by C8 (Sample 29).



Figure 4.18: Concentration levels of C8-C14 in analyzed water samples

Figure 4.19 reveals the concentration levels for C15-C2 in which C16 had the highest concentration (6.35250 mg/L in Sample 9). This is followed by the concentration of C18 and C17 in Sample 20.



Figure 4.19: Concentration levels of C15-C21 in analyzed water samples

Moreover, C28 is the compound with the highest concentration level across all the petroleumrelated hydrocarbons analyzed in the water samples with a concentration level of 86.39102 mg/L in Sample 28 (see Figure 4.20). High concentration levels of C28 are also noticed in Sample 29 (Figure 4.20).



Figure 4.20: Concentration levels of C22-C28 in analyzed water samples

For Carbon fractions ranging between C29-C37, C29 had the highest concentration level of 43.40090 mg/L in Sample 27, followed by C30 with concentration levels of 42.30175 mg/L still found in Sample 27 (see Figure 4.21).





The result of the GC-MS as shown in Figure 4.18-Figure 4.21, reveals that the hydrocarbons present in the water samples are C8-C30. However, the more predominant hydrocarbons were C8-C10, C16-C18 and C27-C30. Figure 2.2 indicates that the likely source of these hydrocarbons include gasoline, Kerosene, fuel oil and lubricating oils. Corroborating the results from the VOC analysis (see Figure 4.13-Figure 4.17) and the TPH analysis (Figure 4.18-Figure 4.21) indicates that the presence of BTEX chemical components, precisely Toluene, is likely to be from gasoline. The significant presence of C16-C18 will be from Kerosene and C27-C30 from fuel oil and lubricating oils. Thus, the groundwater aquifers in the study area are contaminated with significant concentration levels of BTEX as well as hydrocarbons components from Kerosene, fuel oil and lubricating oils.

# **CHAPTER FIVE: CONCLUSION**

Groundwater contamination by petroleum hydrocarbons from ageing or vandalized pipelines are particularly of great concern due to the fact that the effect of the contamination is often times not known with certainty. This is due to the fact that the affected area is primarily not accessible as with surface water contamination. Also, even with the results of physicochemical analysis proving the presence of hazardous chemicals such as BTEX, some of which are environmentally mobile one cannot say with certainty just how much of these chemicals have been consumed over time. The constant consumption of these contaminated waters will result in biomagnification which will have adverse effects on the health of local residents. Howbeit, there is no known way to quantify the amount of the contaminant already consumed by local residents and how much more is still being consumed. Hence, the assessment of the health implication of this pollution cannot be well defined.

The groundwater contamination in the study area is largely due to the leakages from pipelines that crisscross the community. This study showed investigation of the subsurface structures howbeit to a limited depth of about 40 m. And with time, depending on the porosity and permeability of the structures, the contamination is likely to percolate through the soil columns to greater depths where there accumulate. There is therefore that need to utilize remote sensing devices to provide prompt warnings of possible leakages.

With regards to immediate actions that can be taken, there is the need for residents in locations that showed high level of contamination to put a stop to the usage of the water from the affected water sources. Also, seeing that the individual contaminants have been identified, possible remedial compositions can be formulated to make the water suitable for use, or the use of specially suited well filters can be employed.

These remedial compositions will be tailored toward mitigating against specific contaminants predominant in the various locations.

It is also recommended that when wells are to be drilled, they can be drilled to much deeper depths beyond which the contaminated zone exist. Also, the concept of well casing may be applied to isolate contaminated zones from polluting the water got from these new wells. Public and private organizations can provide good and safe water sources within the Baruwa community that will serve the needs of those in the regions most affected by the contamination. More studies in the regard of bioremediation are also encouraged as well so as to gain more insight on how fast polluted regions in the subsurface can be bioremediated.

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