Spatiotemporal Variability Assessment of Rainwater Quality in Oil and Gas Exploration Region of Nigeria

Christopher B. Afangideh [1], Udeme Udeme Udokpoh [1*]

[1] Department of Civil Engineering, Akwa Ibom State University, Ikot Akpaden, Nigeria

Abstract

In developing countries where the prevailing water supply systems are inadequate to meet the demands of their citizens, rainwater harvesting (RWH) has become an alternative source of water resources. Anthropogenic activities have led to the release of greenhouse gases (GHGs) into the atmosphere, which has an endangering impact on the quality of rainwater and also poses great risks to people who depend on this source of water supply. Therefore, this study was conducted to assess the physicochemical, bacteriological, and heavy metal parameters of direct harvested rainwater from six locations in Mkpat Enin, Ibeno, and Ikot Ekpene Local Government Areas of Akwa Ibom State between March to October, 2021. Eighteen (18) water quality parameters were considered and analysed in the laboratory in accordance with the WHO guidelines for drinking water quality. Results from the laboratory analysis show seasonal and spatial variation in the water quality parameters of the rainwater samples obtained within the six localities. The laboratory results were also compared with the permissible water quality parameters as recommended by WHO. The comparative analysis indicated that the concentration of pollutants in rainwater was not within the allowable limit except for Sulphate and Zinc.

Keywords: Environmental Pollution; Gas Flare; Oil Spillage; Physicochemical; Rainwater Harvesting; Water Quality.

1. Introduction

Water is used on a daily basis by humans for both potable and non-potable purposes, and it is necessary for the sustainability of life [1]. Drinking, washing, cooking, and other daily activities require clean water that is devoid of contaminants that might cause waterborne diseases. Access to clean water and safe treatment facilities are the most important measures taken to prevent certain waterborne illnesses [2]. Access to safe drinking water is a serious threat to many countries around the world, particularly developing countries like Nigeria [3]. However, the World Health Organization (WHO) estimates that over 5.2 billion people utilize clean water for hygiene [4]. In spite of the progress, more than a billion people around the globe, mostly in developing countries, lack access to safe drinking water and improved sanitation [4, 5]. Waterborne disease has claimed the lives of approximately 2.2 million people annually in developing countries [6]. Recent incidents of low water quality in Nigeria have had a substantial negative impact on the health of its citizens in various parts of the country [7]. Diarrhoea, vomiting, diabetes, cardiovascular disease, nausea, abdominal pain, and hypertension are just a few of the potentially dangerous health issues associated with consuming contaminated water [8-10]. Table 1 shows the pollutants present in water and their adverse health effects.

Table 1. Selected contaminants in water and their health impact

Parameter	Unit	Health Impact
Aluminum	mg/L	Potential Neuro-degenerative disorder
Arsenic	mg/L	Cancer
barium	mg/L	Hypertension
Cadmium	mg/L	Toxic to kidney
Chromium	mg/L	Cancer
Copper	mg/L	Gastrointestinal disorder
Lead	mg/L	Cancer, interference with vitamin D metabolism, affect metal development in infants, toxic to the central and peripheral nervous systems
E. coli	cfu/100 mL	Urinary tract infection, bacteraemia, meningitis, diarrhea, acute renal failure, haemolytic anaemia
Total coliform count	cfu/100 mL	Indication of faecal contamination
Trihalomethanes (Total)	mg/L	Carcinogenic

When the quality of these water sources deteriorates, it becomes more expensive to supply clean water to the people [12]. However, access to safe drinking water is a major challenge across the world, since the demand for fresh water is increasing more rapidly than the world's population. In Nigeria, the two broad categories of water resources accessible are fresh and saltwater. The former is made up of rainwater, surface water (streams, lakes, and rivers), and groundwater (boreholes and dug wells); it is ideally available to all populations [13]. Rainfall is one of Nigeria's main freshwater resources [14]. The majority of the rainfall events are intense, frequently convective storms with extremely high rain intensities and extreme spatial and temporal rainfall variability [15]. Rainfall to evaporation ratios are frequently inadequate. In dry to semi-arid regions, rainfall typically ranges from 200 to 600 mm/year [16]. Seasonal variability in rainwater distribution has increased the need for conserving public potable water supplies around the world, and rainwater harvesting is a valuable tool that can be used to meet this need. However, a lack of knowledge about the quality of harvested rainwater has prevented widespread use of this practice [17, 18].

1.1. Rainwater Harvesting

Rainwater harvesting (RWH) is a technique for collecting and storing rainwater that falls on a surface [19]. The first method of collecting rain runoff and storing it for domestic or other purposes was to collect RWH from building roofs or other surfaces [20]. In the field of water resource management, it is not a novel notion [21]. RWH is currently a widely used option for supplying and distributing both potable and non-potable water, particularly in developing nations where groundwater and surface water are insufficient to fulfill people's expanding requirements due to fast urbanization and population expansion [22]. Authorities in the water resources sector in Australia, Brazil, China, and India are actively encouraging RWH. In addition, including a RWH system in a building plan is required in order to obtain clearance from local building authorities in Chennai and New Delhi [23, 24]. When collected and stored in a properly designed and managed water catchment system, rainwater may be a valuable resource and potable [25]. Rainwater has been developed as the only source for collecting water in its purest state, devoid of minerals and most of the common pollutants found in ground and surface water sources. It happens spontaneously as a result of natural distillation [26, 27]. However, the quality of rainfall has been threatened due to environmental circumstances (such as contaminants in the atmosphere, bird litter, and overhanging vegetation), catchment material, and storage material. However, environmental elements are challenging to regulate since they are site-specific and independent of the RWH system's design [20]. Pollution from catchment surfaces (CSs) is caused by two major sources. These are particles that have accumulated on the catchment surfaces as a result of direct air deposition, rodent and bird litter, or overhanging vegetation. Furthermore, the catchment material itself degrades with time and can contribute both particulate matter and dissolved pollutants to runoff water. The former is mostly site-specific, whereas the latter is fairly constant across the board. The available CSs for direct rainwater collection for water delivery include building rooftops, hillsides, rock surfaces, or paved courtyards. Interestingly, building roof catchments appear to be the most prevalent CS for rainwater collection, because residents use their existing rooftops and incur no additional expenses. The amount and quality of rainwater collected, however, will be determined by the environment and the type of roof materials used. Aluminum, galvanized iron, corrugated iron sheets, corrugated plastic, asbestos-cement sheets, zinc, tiles, concrete, or clay are examples of roof materials that can be used alone or in combination. Roofs, if clean, provide an ideal collecting surface for rainwater harvesting. They can also be a significant source of non-point source pollution [28]. Materials such as metals, aluminum, and cement-asbestos are often associated with the leaching of trace elements, detected in the dissolved form in the runoff.

Table 2. Catchment type and impact on water quality [29]

Type	Impact on water quality
Galvanised iron sheet and aluminum	Excellent water quality
	Surfaces is smooth and high temperature help to sterilise the water (kill bacteria)
Tiles (glazed)	Good water quality
	Unglazed tiles can harbour mould
	Contamination can exist in tile joins
Asbestos-cement sheets	New sheets give good quality of water
	No evidence of carcinogenic effects from ingestion
	Slightly porous so reduced run-off coefficient
	Older roofs harbour moulds and even moss
Organic material	Poor water quality Little first-flush
	High turbidity due to dissolved organic material which does not settle

Van Metre & Mahler [30] discovered that galvanized metal roofs were a greater source of zinc and cadmium pollution in rainwater, whereas asphalt roofs were linked with higher amounts of mercury and lead. Mendez et al. [31] did a similar study in Texas and discovered that residential roofing materials had a negative influence on the quality of rainwater and that roof cleaning enhanced the quality. Certain types of paint covering on catchment surfaces, on the other hand, may leak harmful compounds (for example, lead, chromate, and bitumen) into rainwater storage tanks and should be tested for compatibility before use [32]. Various researchers have reported pollution of harvested rainwater as a result of environmental factors such as pollutants in the atmosphere [33-38]. Their findings found a significant concentration of physicochemical and microbial constituents in rainwater samples obtained, indicating that they are unsafe for human consumption. Because of large GHG emissions and the integration of these industries into urban areas and residential areas, there is a risk of air pollution. However, domestic gaseous wastes, emissions from gas flaring operations, crude oil exploration, automotive exhaust and exhaust from electricity generating sets, and particulate matter generation from a variety of anthropogenic activities are all causes of air pollution [39].

Crude oil and natural gas make for over half of the world's energy resources [40]. Nigeria is placed seventh and twelfth in the world in terms of crude oil exports and production [41]. According to reports, Nigeria contains 35 to 36.22 billion barrels of crude oil, 187 trillion standard cubic feet barrels of natural gas, and 31 billion barrels of oil equivalent of tar sand [42-45]. Nigeria is reported to generate around 6 billion standard cubic feet of gas per day [45], and 2.2 - 2.7 million barrels of crude oil per day [43, 45, 46]. However, the pace of production varies owing to a variety of reasons such as terrorist activity in Nigeria's oil-rich area, pipeline vandalism, sabotage, and oil spills, among others. Among these, the operations of militia in the region have had a considerable impact on Nigeria's output rate [47]. For example, insurgency and resource control actions reduced crude oil output considerably in the first half of 2016. Nigeria's crude oil and natural gas are found in the Niger Delta, which includes the states of Akwa Ibom, Rivers, Delta, Bayelsa, Ondo, Edo, Abia, and Imo. The region's crude oil and natural gas are found both offshore and onshore. Crude oil and natural gas are the two major products produced. Both have a negative impact on the environment. Crude oil spills into the environment and alters the properties of the receiving environment, such as soil and water quality [48-50].

Emissions from oil exploring platforms, as well as their environmental consequences, have continued to pique the interest of air pollution meteorologists and environmental specialists, among others [51-54]. The southern section of Nigeria is a region with active petroleum exploitation, exposing it to the danger of pollution from petroleum and other pollutants. Due to the lack of an adequate regulatory structure, inaccessibility to local and international markets, and limited financial resources, gas flaring appears to be unavoidable in developing countries such as Nigeria. Gas flaring is common in Nigeria because it is inexpensive and there is a lack of equipment to recover or re-inject gas [55]. Meanwhile, gaseous emissions and flaring into the atmosphere have been occurring since the beginning of petroleum extraction in the Niger Delta in 1956 [56]. According to Elvidge et al. [56], a total of 160 billion cubic meters (BCM) of gas was flared, with Nigeria flaring more than 14 percent, ranking second only to Russia among the top twenty gas flaring countries in 2004. A typical gas flare in a Nigerian oilfield is normally positioned at ground level, surrounded by dense vegetation and farmlands, with buildings and human occupants located between 20 and 30 metres from the heat source or flare [57]. For more than 40 years, oil exploration and extraction have been the predominant activity in the area. Meanwhile, the activities of Liquefied Natural Gas (LNG) companies have both beneficial and bad effects on the environment and society since they supply an essential commodity for residential and industrial usage [58, 59]. Flaring of related gas from oil and gas exploration and production processes has a number of environmental impacts. Crude and refined oil spillages and gas flares caused by the oil and gas industry, among other things, have had a detrimental influence on the air, arable land, and aquatic ecosystems, and there is substantial pollutant-atmosphere interaction.

Figure 1. Horizontal and vertical gas flaring in Niger Delta region

Recent study has looked into the effect of oil and gas exploration on the quality of rainwater. Ezenwaji et al. [60] investigates the geographical impacts of gas flaring on rainwater quality in Bayelsa State, Nigeria's Eastern Niger-Delta. Rainwater samples from eight different places were analysed to determine the physiochemical properties using appropriate techniques. The results demonstrate that all eight physicochemical components had values higher than the World Health Organisation's maximum permissible concentration limit, although at varied degrees, with NO_3^- being the highest. Seiyaboh et al. [47] also examines the effects of gas flaring on vegetation and water quality in Nigeria's Niger Delta region. The research found that gas flaring changes the concentration of water ions (particularly sulphate, carbonate, and nitrate), pH, conductivity, and heavy metals (such as lead and iron) in rainfall. It also has an impact on plants, resulting in decreased growth and production, most likely as a result of changes in soil quality characteristics. Similarly, Akintola et al. [61] developed a modelled approach for assessing the consequences of anthropogenic activities assumed to emanate from gas flaring on atmospheric quality using domestic roof-harvested rainwater (DRHRW) as an indicator. They looked at seven elements (Cu, Cd, Pb, Zn, Fe, Ca, and Mg) as well as six water quality indices (acidity, PO_4^{3-}, SO_4^{2-}, NO_3^-, Cl^-, and pH). These were employed as input parameters at 12 sampling points from gas-flaring environments (Port Harcourt, Nigeria), with Ibadan serving as a reference. Pb, and Cd were found to be the main pollutants of concern in the captured rainwater, according to their research.

There is evidence in literature that information on the quality of rainwater harvested for domestic water supply in the oil and gas exploration region of Nigeria is extremely limited. The few that are available are not adequately documented, making it difficult for authorities in water resource sector to have access to enough information to help them make decisions. As a result, it is crucial to assess the quality of rainwater in these locations in order to provide recommendations for corrective steps to the appropriate authorities. However, the notion that rainfall is clean and suited for potable uses has motivated many Nigerian homes, as well as those in other developing countries across the globe, to harvest it and channel it for potable uses. In this search, rainwater samples were collected directly from three locations in Mkpat Enin local government area (Ikot Akpaden, Ikot Ekong, and Ikot Enin communities) and two locations in Ibeno local government area (Ukpenekang and Iwuochang communities) between March and October in order to evaluate the level of pollution. A reference sample was also taken in Ikot Ekpene local government area, which has no industrial activities. The paper's findings will allow relevant government officials to assess the scope of the flaring in the region and ensure that the various regulations already in place to address the issue are adequately implemented.

2. Research Methodology

2.1. Sampling Site Description

Akwa Ibom State is one of Nigeria's 36 states. It is situated in the southern Niger Delta area between latitudes 4°32' N and 5°33' N and longitudes 7°25'E and 8°25'E in the country's coastline southern section. It is one of the six Nigerian states that form the country's south-south geopolitical zone, sharing borders with Cross Rivers State in the east, Rivers and Abia States in the west, and the Atlantic Ocean and the southernmost part of Cross River State in the south. The state has a population of approximately five (5) million people and covers an area of 6900 square kilometers, with the biggest cities being Uyo, Eket, and Ikot Ekpene. The state is drained by numerous rivers, including the Imo River, which is shared with Imo State, the Kwa Iboe River, which gives the state its name, the Cross River, which is shared with Cross River State, and the Azumini Blue River, which is shared with Abia State, as well as numerous streams that drain the state's hinterland. The entire state of Akwa Ibom is located in the tropical forest zone, with mangrove forest vegetation. The state of is often humid due to its location just north of the Equator and inside the humid tropics, as well as its closeness to the sea. Akwa Ibom State's climate may be defined as tropical wet, with abundant rainfall and very high temperatures, based on its geographical location. The state's mean annual temperature is between 26°C and 29°C, with 1,450 hours of sunlight per year and mean annual rainfall ranging from 2.000mm to 3.000mm, depending on the area. Naturally, the highest humidity is reported in July, while the lowest is observed in January. The thick cloud

cumulonimbus type is most prevalent from March to November. The yearly evaporation rate is considerable, with annual values ranging from 1500 mm to 1800 mm. Like the rest of Nigeria's coastal areas, the state experiences two distinct seasons: wet and dry. The wet or rainy season lasts eight to nine months, from mid-February to the end of November. The dry season starts in the last week of November or early December and lasts until the beginning of February. Rainfall is predicted every month of the year, despite seasonal changes, due to the nature and position of the state along the coast, which exposes it to hot maritime air masses.

The Niger Delta is rich in natural resources, particularly hydrocarbon reserves. Crude oil production and export from the area, estimated at two million barrels per day, dominates the Nigerian economy, accounting for more than 90 percent of total export revenues. Nigerian crude oil output grew to 1,663,000 BOPD in June 2017 from 1,494,000 BOPD in May 2017. From 1973 to 2017, crude oil production in Nigeria averaged 1892,300 BOPD, with an all-time high of 2,475,000 BOPD in November 2005 and a low of 675 BOPD in February 1983. Nigeria is projected to contain 37.2 billion barrels of proved oil reserves and 180 trillion cubic feet of natural gas reserves, ranking seventh in the world.

Akwa Ibom State is now Nigeria's largest oil and gas producing state, accounting for more than 60 percent of the country's daily output. It has the most offshore production and has produced more petroleum reserves offshore per acreage than any other oil producing state in the country. Oil and gas are commercially accessible in the state's Ibeno, Mbo, Etinan, Idu, Enwang, Mkpat Enin, and Onna local government areas. Mineral resources, notably petroleum hydrocarbon reserves, abound throughout the state. Akwa Ibom State, Nigeria's greatest oil producing state, recorded 504,000 barrels per day, accounting for 31.4 percent of total oil produced in Nigeria each day. The Akwa Ibom State Coastal Zone is blessed with a diverse range of minerals. Crude oil and its related gas are the most significant minerals currently mined. The coastal zone has been the site of several oil and gas discoveries. While Nigeria's present oil resources are estimated to be 21 billion barrels and its gas reserves to be 11 trillion cubic feet, it is worth noting that the large rise in crude oil and gas resources since 2012 is due to discoveries in Akwa Ibom State's deep offshore zone.
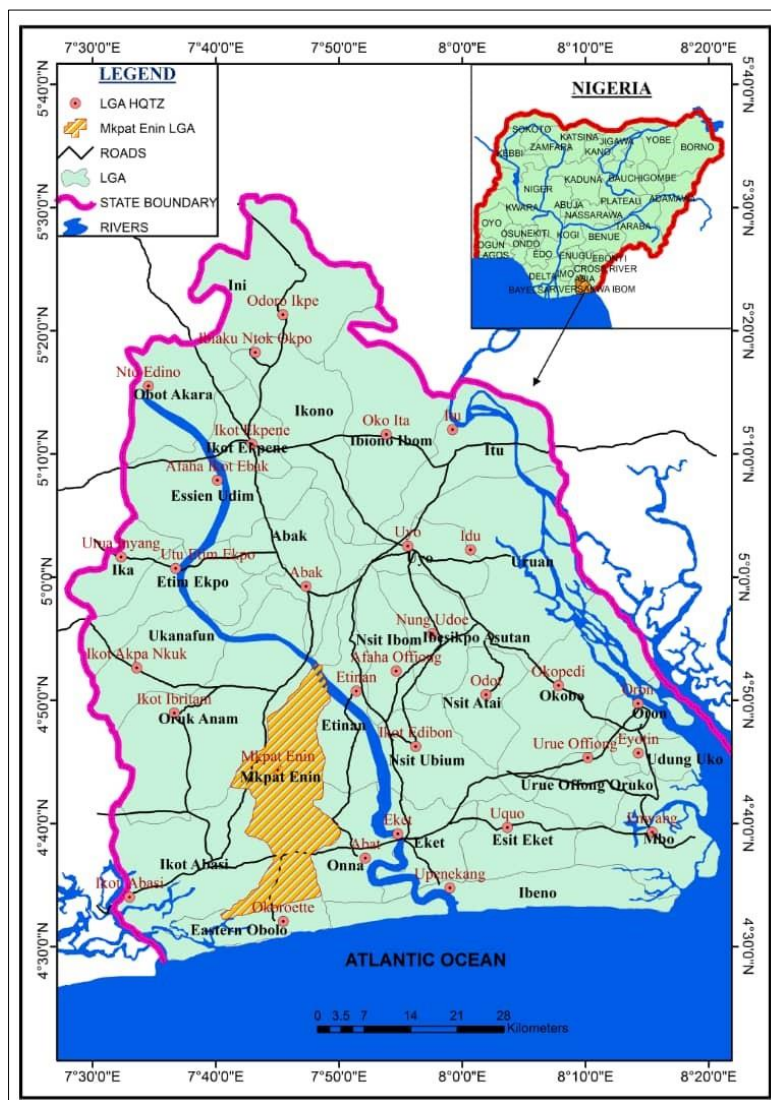

Figure 2. Map of sampling site

Table 3. General characteristics of sampling site-Data sampling

Parameter	Location		
	Mkpat Enin	Ibeno	Ikot Ekpene
Average rainfall (mm/yr)	2034	2102	1920
Evaporation (mm/yr)	1562	1497	1812
Average max. Temp.	28.5	28.3	29.2
Average min. temp.	24.7	24.2	26.8
Coordinates	4.732° N, 7.748°E	4.578° N, 8.156°E	5.174° N, 7.714E
Economic activity	Agriculture	Agriculture	Commercial
Population (×1000)	249.1	105.1	398
Area (km^2)	322.352	271.2	116.5
% of State's area	4.67	3.93	1.69

Water samples for this study were collected from rainwater at the start of the rainy season in the three local government areas of the state (Ibeno, Mkpat Enin, and Ikot Ekpene) between March and October 2021, as this was when gaseous impurities in the air reached their highest concentration, having not been optimally removed by the rainwater due to the dry season that lasted few months. Most of these places had their first significant rainfall between February and early March 2021, however our water samples were taken from the middle of March to enable toxins to be flushed away by the early rainfall. To avoid rain splashing, the water samples were collected using the approach described by Okoye et al. [62], in which free fall rainwater was collected with a rainfall collector positioned on a support 1.5 m above the ground. To filter out inserts and capture detritus, the collector's funnel was filled with fibre. Prior to analysis, the rainwater samples were transferred to 500 mL plastic bottles that were appropriately labeled and kept in the refrigerator for no more than 24 hours at a temperature of roughly 4°C. The containers used to collect samples were cleaned, and precautions were taken to prevent contamination. Three (3) samples were collected in each month on weekly basis within the communities for analysis and the average result captured.

2.2. Data Analysis

The laboratory protocols for analyzing the water samples were similar to those used by [the American Public Health Association (APHA)]. The samples were analysed in the laboratory by the Quality Control Department of the Akwa Ibom State Ministry of Science and Technology. The pH and turbidity of the samples were determined using a pH meter with the model HACH SENSION 3 and a turbid meter with the model 2100P TURBIDIMETER. Before using the pH meter, it was warmed for around 15-20 minutes. Dissolve total the conductivity meter model HACH SENSION 5 was used to determine the solid. Dissolve oxygen (DO) was measured with a model JYD-IA dissolve oxygen meter. The heavy metal characteristics were determined using a spectrophotometer type DR 2010 HACHSENSONS. Excel was used to determine the Coefficient of Variation (CV), Correlation Coefficient, and ANOVA in the statistical study. Statistical techniques were used to establish relationship between water quality parameters and the level of pollution in the region, as well as to determine the variance in parameters by location. The findings of the various parameters were further compared to WHO guidelines from 2004 and 2011 to evaluate water suitability for portable and non-portable purposes.

3. Results and Discussion

3.1. Results

The quality of rainwater and the level of pollution were assessed using the quality standards proposed by ASTM based on WHO guidelines. Figures 3 to 8 present the finding of spatial-temporal variation in physiochemical, bacteriological, and heavy metal concentration in rainwater respectively, while Table 4 and Figure 9 show the comparison of pollutant concentration in rainwater within the sample locations and referenced to the permissible limit recommended by WHO. Tables 5 to 7 display the results of statistical analysis carried out to know the correlation between water quality parameters and the level of pollution in the study area, and also to determine the variance in parameters base location.

Figure 3. Temporal variation of rainwater quality in Ikot Akpaden samples

Figure 4. Temporal variation of rainwater quality in Ikot Ekong samples

Figure 5. Temporal variation of rainwater quality in Ikot Enin samples

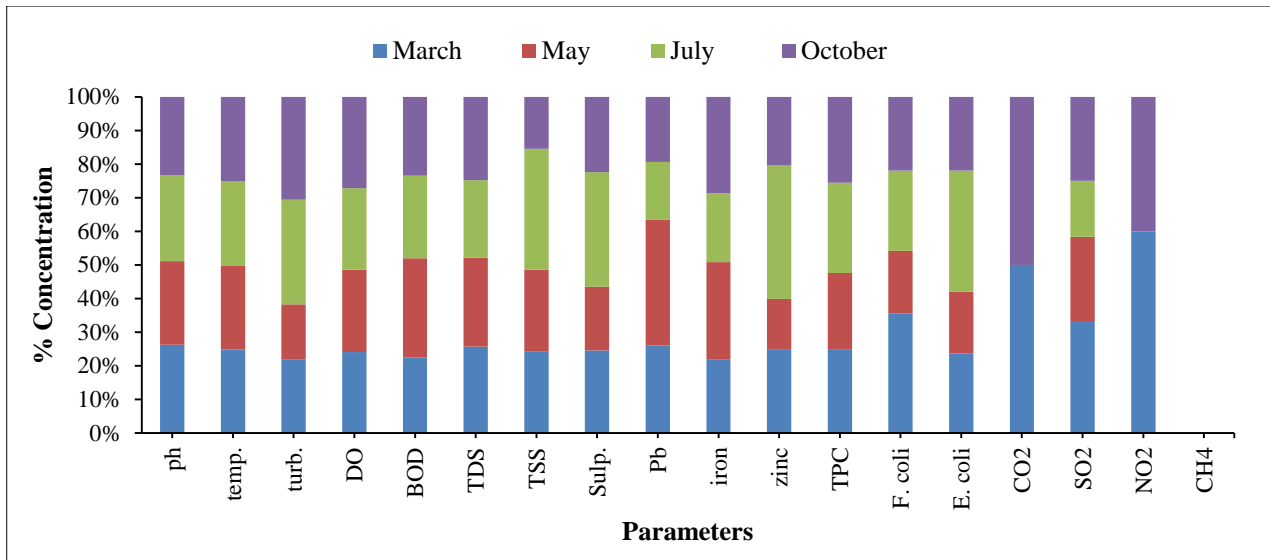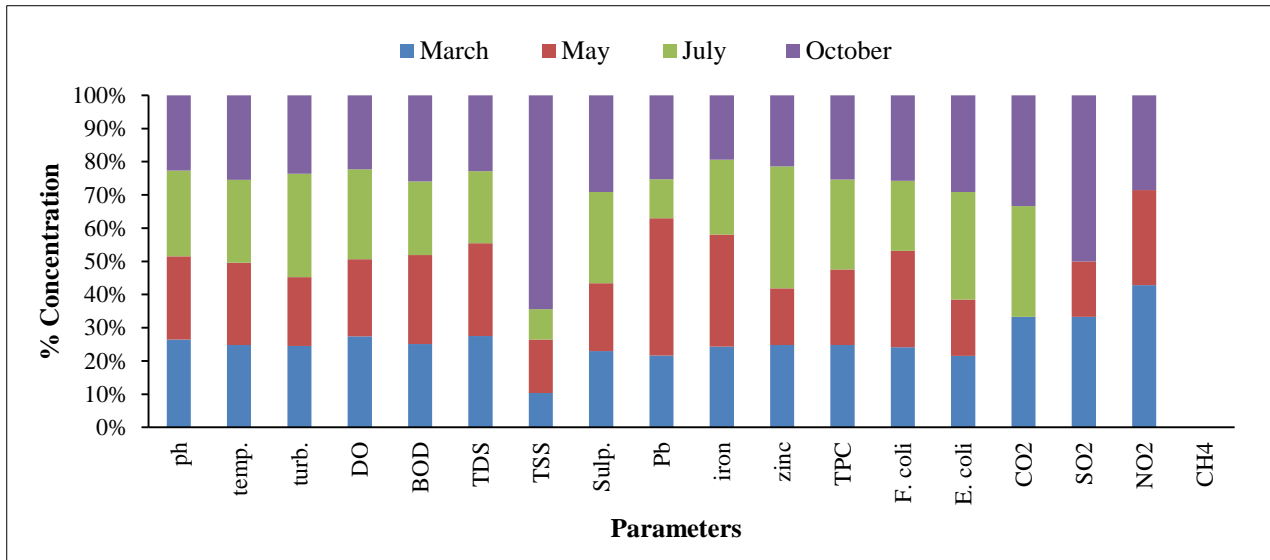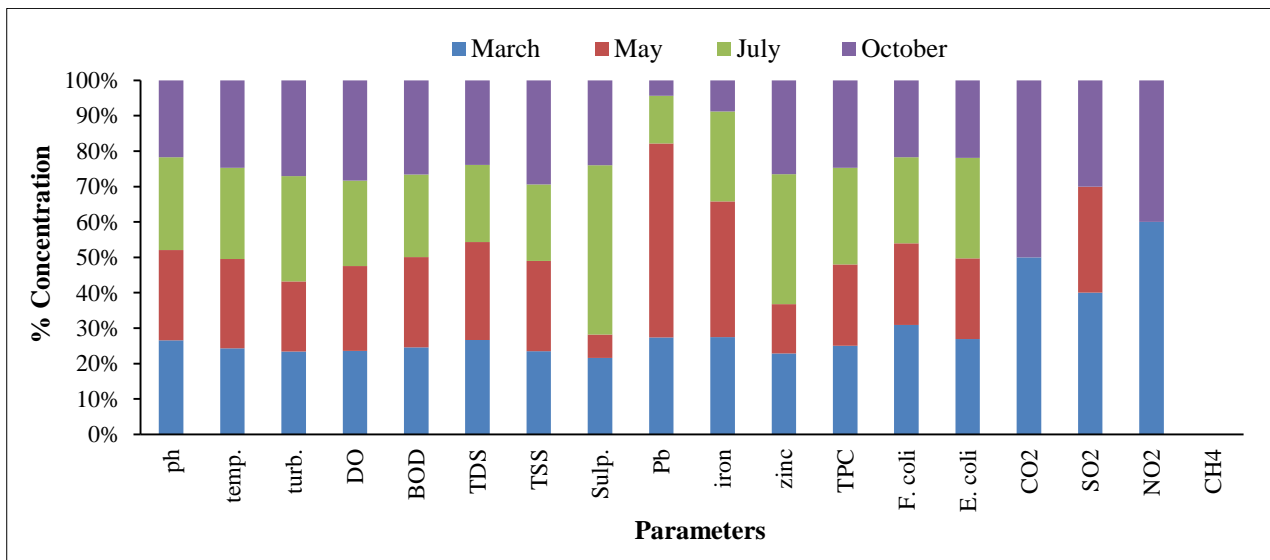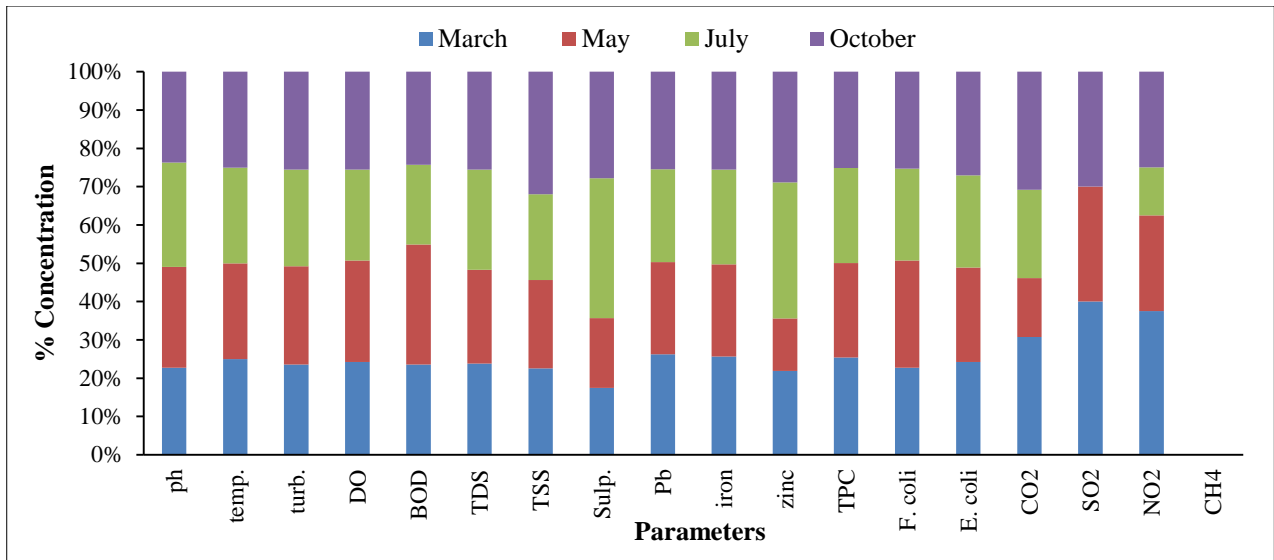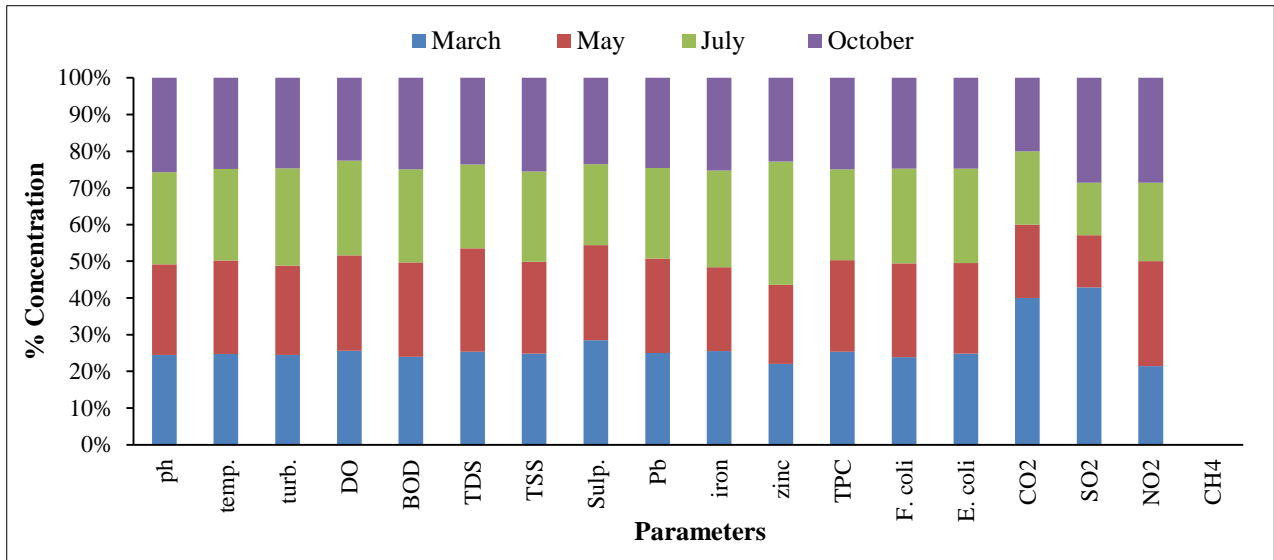**Figure 6. Temporal variation of rainwater quality in Ukpenekang samples**

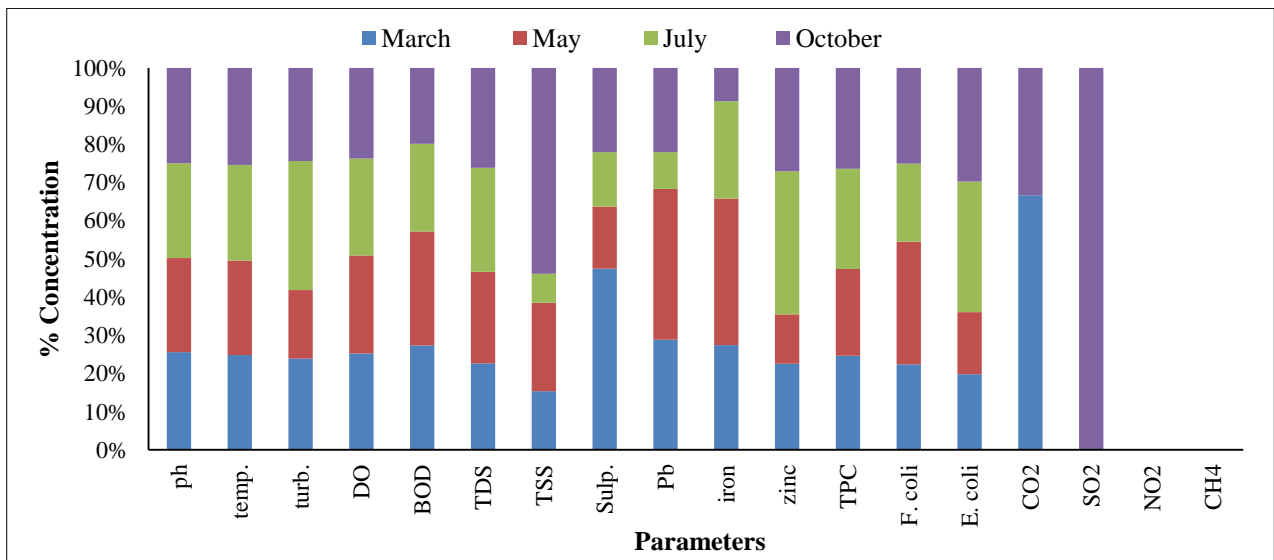**Figure 7. Temporal variation of rainwater quality in Iwuochang samples**

Figure 8. Temporal variation of rainwater quality in Ikot Ekpene samples

Table 4. Comparison of rainwater quality with WHO allowable limits

Parameters	Units	I. AK	I. EK	I. EN	UKP	IWU	I. EKP	WHO [65]
pH	-	6.078	6.073	5.82	4.813	5.398	6.355	6.5-8.5
Temperature	^{o}C	29.17	28.77	28.77	29.95	29.40	29.06	12-25
Turbidity	NUT	1.17	1.653	1.73	5.428	5.425	1.045	5.0
DO	mgL^{-1}	7.28	7.364	7.498	8.333	7.73	5.965	1.0-5.0
BOD	mgL^{-1}	3.27	3.010	2.90	3.855	3.365	2.375	3.0
TDS	mgL^{-1}	3.6	2.788	2.998	4.418	3.203	2.428	5.0
TSS	mgL^{-1}	0.21	0.022	0.013	0.117	0.104	0.003	5.0
Sulphate (SO_4)	mgL^{-1}	1.204	2.589	0.439	1.259	2.085	0.148	250
Lead (Pb)	mgL^{-1}	0.118	0.081	0.058	1.584	1.558	0.055	0.01
Iron (Fe^{+2})	mgL^{-1}	1.306	1.006	0.856	1.889	0.920	0.856	0.3
Zinc (Zn)	mgL^{-1}	1.202	1.504	1.302	1.323	1.348	1.208	3
TPC	1/100 CFU3	30.65	29.57	29.30	102.1	98.55	28.67	0
Fecal coliform	1/100 CFU3	1.88	2.763	2.163	11.95	13.06	1.566	0
E. Coli	1/100 CFU3	1.425	1.623	1.243	7.72	13.18	1.388	0
CO_2	ppm	0.002	0.002	0.002	0.003	0.003	0.002	-
SO_2	ppm	0.003	0.002	0.003	0.003	0.002	<0.001	-
NO_2	ppm	0.003	0.002	0.003	0.002	0.004	<0.001	-
CH_4	NUT	0.001	0.001	0.001	0.001	0.001	<0.001	-

I. AK- Ikot Akpaden; I. EK- Ikot Ekong; I. EN- Ikot Enin; UKP- Ukpenekang IWU- Iwuochang; I. EKP- Ikot Ekpene; WHO- World Health Organisation
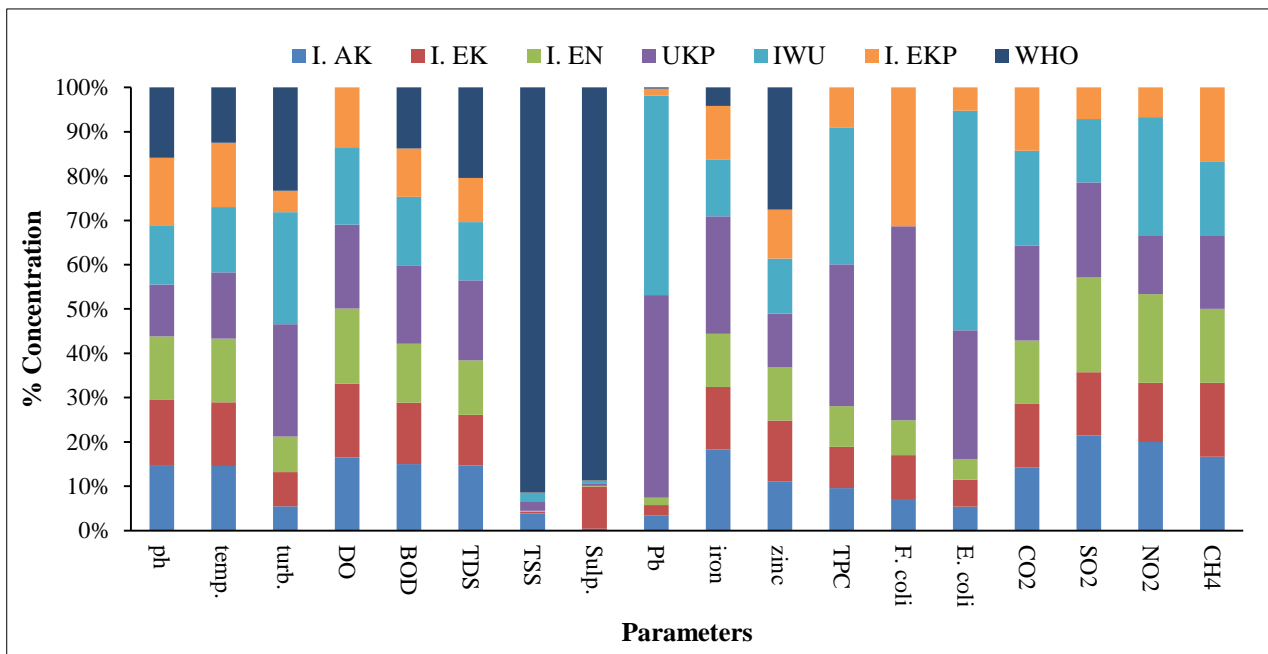

Figure 9. Comparison of rainwater quality with WHO standard

Table 5. Correlation coefficients of rainwater quality parameters

	pH	Temp.	Turb.	DO	BOD	TDS	TSS	Sulp.	Pb	Iron	Zinc	TPC	F.coli	E.coli	CO$_2$	SO$_2$	NO$_2$	CH$_4$
pH	1.000																	
Temp.	-0.830	1.000																
Terub.	-0.921	0.802	1.000															
DO	-0.857	0.537	0.726	1.000														
BOD	-0.874	0.759	0.769	0.928	1.000													
TDS	-0.825	0.818/	0.630	0.806	0.931	1.000												
TSS	-0.307	0.518	0.262	0.420	0.650	0.690	1.000											
Sulp.	-0.226	0.049	0.365	0.481	0.455	0.138	0.201	1.000										
Pb	-0.830	0.779	0.977	0.621	0.700	0.545	0.320	0.371	1.000									
Iron	-0.708	0.810	0.490	0.627	0.806	0.928/	0.570	0.095	0.386	1.0000								
Zinc	-0.190	-0.183	0.238	0.409	0.215	-0.072	-0.348	0.802	0.154	-0.049	1.000							
TPC	-0.909	0.864	0.991	0.678	0.769	0.659	0.328	0.317	0.981	0.539	0.144	1.000						
F. coli	-0.647	0.771	0.829	0.230	0.374	0.312	0.055	0.081	0.867	0.292	-0.030	0.866	1.000					
E. Coli	-0.724	0.663	0.930	0.538	0.599	0.402	0.275	0.416	0.982	0.217	.178	0.926	0.843	1.000				
CO$_2$	-0.980	0.839	0.882	0.893	0.940	0.887	0.409	0.333	0.787	0.799	0.243	0.876	0.571	0.670	1.000			
SO$_2$	-0.495	0.238	0.167	0.717	0.624	0.7222	0.425	-0.069	0.032	0.579	-0.038	0.137	-0.300	-0.084	0.532	1.000		
NO$_2$	-0.358	0.051	0.478	0.623	0.506	0.235	0.390	0.608	0.524	-0.090	0.347	0.414	0.079	0.601	0.356	0.269	1.000	
CH$_4$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	10.000

Table 6. Coefficient of variation for rainwater quality parameters

Variable	Mean	SE Mean	S.D	Variance	C.V	Min	Max
pH	5.753	0.432	0.559	0.312	9.715	4.813	6.335
Temp.	29.186	0.325	0.444	0.197	1.522	28.768	29.945
Teurb.	2.742	1.790	2.096	4.395	76.461	1.045	5.428
DO	7.362	0.492	0.781	0.611	10.615	5.965	8.333
BOD	3.128	0.367	0.497	0.247	15.896	2.375	3.855
TDS	3.239	0.513	0.699	0.488	21.575	2.428	4.418
TSS	0.078	0.066	0.081	0.007	130.364	0.003	0.210
Sulp	1.287	0.700	0.933	0.871	72.514	0.148	2.589
Pb	0.6601	0.776	0.914	0.836	138.628	0.055	2.063
Fe	1.139	0.306	0.404	0.163	35.460	0.856	1.889
Zn	1.314	0.077	0.111	0.012	8.425	1.202	1.504
TPC	53.135	31.450	36.564	1336.919	68.813	28.673	102.075
F. Coli.	6.728	4.460	5.113	26.142	75.995	1.880	13.058
E. Coli.	4.430	4.014	4.974	24.743	112.296	1.243	13.180
CO_2	0.002	0.000	0.001	0.000	27.186	0.002	0.003
SO_2	0.002	0.001	0.001	0.000	40.112	0.001	0.003
NO_2	0.002	0.001	0.001	0.000	35.242	0.001	0.004
CH_4	0.001	0.000	0.000	0.000	0.000	0.001	0.001

Table 7. Analysis of variance for % concentration and spatial distribution

Source of Variation	SS	df	MS	F	P-value	F crit
parameters	18346.6	17	1079.212	14.623	1.6E-18	1.744299
locations	706.5218	5	141.3044	1.914633	0.100272	2.321812
Error	6273.198	85	73.80233			
Total	25326.32	107				

The pH of rainwater in the study area ranged from 4.813 to 6.335, with samples from Ikot Enin, Iwuochang and Ukpenekang communities having pH values that are less than 6.0 which are not within the permitted limit recommended by WHO. Rainwater samples obtained in all the six (6) locations had an average temperature values ranging from 28.77°C to 29.95°C, with samples from Ukpenekang recording the highest temperature of 29.95°C and closely followed with samples from Iwuochang (29.40 °C). Turbidity level in water sample from Ikot Akpaden, Ikot Ekong, Ikot Enin and Ikot Ekpene were less than 5.0 NTU. Rainwater samples from Ukpenekang and Iwuochang recorded the highest level of turbidity concentration of 5.425 and 5.428 NTU which are slightly above the WHO recommended limit in drinking water. The dissolved oxygen levels in all the water samples varied from 5.965 to 8.333, which was all above WHO standard of 5.0. Almost all of the water samples had BOD levels that were above the allowable limit for drinking water. BOD in water samples from Ikot Akpaden, Ikot Ekong, Ukpenekang and Iwuochang exceeded the allowed limit, whereas samples from Ikot Enin and Ikot Ekpene were within the acceptable range. TDS levels in all the water samples collected in the study area ranged from 2.428 to 4.418 mg/L and were within desirable limit of 5mg/L. TSS levels were generally satisfactory, ranging from 0.001 to 0.009 mg/L.

Sulphate found in all water samples were less than the allowable limit of 250mg/L. The values ranges from 0.148 to 2.589 mg/L with a higher concentration level observed in samples from Ikot Ekong and Iwuochang. The concentration of lead in the water samples ranged from 0.055 to 1.584mg/L, with all the samples exhibiting greater concentrations above the WHO tolerable limit of 0.01mg/L Pb in drinking water. The iron concentration in drinking water samples varied from 0.856.1 to 1.889mg/L, with all the values greater than the desired limit of 0.3mg/L. Zinc concentrations in all samples ranged from 1.202 to 1.348mg/L and well within the WHO standards of 3.0mg/L. The total plate count (TPC) values for all of the water show significant levels of pollution and were above the allowable limit in portable water. The concentration levels in samples from Ukpenekang and Iwuochang were far higher than in other samples. The results of faecal coliform reveals higher concentration in water samples from Iwuochang and Ukpenekang. The concentrations ranged from 1.566 to 13.06 CUF which are significantly above the WHO standards of zero in drinking water. The analysis results also show higher concentration of E. coli in all the water samples in the study area and varied from 1388 to 13.18 CUF which are above the permissible limit in drinking water. The results also reveal trace of CO_2, SO_2, NO_2 and CH_4 in all the water samples analysed in the study area.

Table 5 show the findings of the correlation in rainwater quality parameters. In the samples, there was a strong positive correlation between Turb. and TPC (0.991), Pb and TPC (0.981), Turb. and Pb (0.977), CO_2 and BOD (0.940), BOD and TDS (0.931), Turb. and E. coli (0.930), DO and BOD (0.928), TDS and Iron (0.928) and TPC and E. coli (0.926), indicating that their distribution was highly associated, r>0.5. There was a strong negative correlation coefficient between pH and CO_2 (-0.980), pH and Turb. (-0.921), TPC and pH (-0.909), and BOD and pH (-0.874). Pb (138.6282 %), E coli. (112.296 %), TSS (103.364 %), Turb. (76.461 %), F coli. (75.995 %), and Sulp. (72.514 %) had higher coefficients of variation, whereas Temp. (1.522 %), Zn (8.425 %), DO (10.615), BOD (15.896 %), and TDS (21.575 %) had low and narrow coefficients.

In order to ascertain that the variation in the water quality parameters obtained from various geographical locations are significant and not merely by chance, the results were subjected to analysis of variance (ANOVA). The calculated F-value at 0.05 level of significance water quality parameters is 4.623 which is much greater than the critical F value of 1.744 (Table 7). This confirms that the variation in the water quality parameters is significant. On the contrary, the calculated F-value for variation in water quality parameters due to geographical location is 1.915 which is less than the critical F-value of 2.232. This shows that water quality parameters are independent of geographical location. The quality of rainwater in any location depends on both the anthropogenic and non-anthropogenic activities in the area.

3.2. Discussion

The results of the pH test demonstrates that the pH levels of rainwater in all sample sites are below the regulatory organizations' permissible limits in drinking water. Drinking water pH should be between 6.5 and 8.5 [63]. The pH values of the collected samples are found to be relatively low, reflecting acidic precipitation in the immediate surroundings natural gas processing plant [64]. Furthermore, the increased acidity of rain water in the gas flaring areas (Ukpenekang and Iwuochang) may be responsible for the low pH, given that control samples obtained farther from gas flaring communities show higher pH values. Rainwater samples from Ukpenekang and Iwuochang had higher turbidity than rainwater samples from other places. However, the turbidity values in these two communities are above the permissible limit of 5 NTU for drinking water [65]. Because oxygen (O_2) is involved in practically all chemical and biological activities in watercourses, dissolved oxygen (DO) analysis is used to determine the amount of gaseous oxygen dissolved in water, which is vital for all kinds of life [66]. The highest level of DO concentration was observed in all of the water samples, which were all above the WHO permissible limits. Sulphate concentrations in all water samples were within permissible levels, posing no hazard to rainfall as a source of drinking water. TDS concentrations in water samples from Ukpenekang and Iwuochang were higher than in other places, although all were below permitted limits. TDS concentrations in rainwater samples collected in the research region were attributed to particulate matter emissions from oil and gas plants. A high TDS reading indicates that the water is highly mineralized. TDS levels in water are normally not harmful to people, while high amounts may have an influence on persons with renal and cardiac disorders [64].

Iron concentrations were greater in all of the water samples, which were generally beyond the maximum allowable limit set by international regulatory authorities. This indicates that iron (Fe) dissolved in the atmosphere and washed down during rain. It might be connected to the consequences of gas flaring. Anemia can be caused by an iron deficiency in human blood, whereas excess iron can bring free radicals into the system, hastening the aging process [67]. The investigation also found that trace metals (Pb and Zn) were present in substantial proportions in the study region's rainwater. Metal traces are common in water and are normally not harmful to our health. Drinking water with high levels of Pb or Zn may be hazardous to one's health [64]. The average Pb concentrations in the assessed water samples were all found to be higher than the acceptable level set by international regulatory organization. Meanwhile, Zn levels in all of the water samples were below acceptable ranges. This indicates a satisfactory heavy metal remediation installation at crude oil processing facilities run by oil giants in the research region. Zinc has no detrimental health or environmental implications at this concentrations [68]. Even though the zinc concentration measured may appear to be insignificant, the long-term influence on health may be negative. Long-term lead exposure, such as over-dependence on water sources, may result in decreased performance in some tests measuring nervous system functions, weakness in fingers and wrists, the appearance of wrinkles, small increases in blood pressure and anemia, whereas high levels of lead exposure may result in severe brain and kidney damage, spontaneous abortion and death.

The total coliform group has been designated as the primary indicator bacteria for microorganisms in drinking water. It is a significant indicator of water's suitability for human consumption. If a vast number of coliforms are found in water, it is quite possible that there are other dangerous bacteria or organisms present. The WHO drinking water recommendations stipulate the absence of coliform in domestic drinking water sources. Faecal coliform and E. coli bacteria were discovered in considerable amounts in all of the water samples tested in this study. Based on the laboratory findings, all of the water samples failed to meet the WHO standard for faecal coliform and E. coli. Carbonates, nitrates, and sulfates are the acids found in rainfall. These acids are secondary pollutants formed in the atmosphere as a result of chemical interactions between main pollutants CO_2, NO_2, and SO_2 emitted during the combustion process [69-71]. The rising CO_2 level in the atmosphere raises the pH of rainfall to 5.6. SO2 is found in low amounts in the atmosphere, but it has a high dissociation constant and a high water solubility [70, 72]. Acid rain is caused by NO_2 and

SO_2. The study results show traces of CO_2, SO_2, NO_2, and CH_4 in water samples, with the greatest concentrations found in water samples from Ukpenekang and Iwuochang.

The findings of the spatiotemporal analysis indicated that rainwater collected during the dry season was more polluted than rainwater collected during the rainy season. This means that the concentration of gaseous pollutants in the atmosphere surged during the dry season and was washed away during the wet season. The investigation also revealed that the concentration of pollutants decreases with increasing distance from oil and gas facilities, indicating that oil and gas operations have a significant influence on the quality of water surrounding them. However, the quality of water used as a control sample was somewhat polluted and was taken around 88 kilometers away from these facilities. This might be attributable to increased commercial activity in the area, which could be caused by automobile or particulate matter emissions.

4. Conclusion

This study clearly shows that oil and exploration activities (such as gas flaring and pollutant emissions) are a major source of water pollution in the oil producing area. The research findings also clearly reveal that the quality of rainfall in Nigeria's oil and gas exploration zone is unsuitable for domestic use. The concentration levels of the eighteen (18) water quality criteria tested from samples collected near oil and gas facilities are not typically within the WHO approved range. The high concentration of these elements in rainwater from the area might be linked to the area's substantial industrial presence. Nonetheless, because rainwater is the most readily available source of portable water in the region, and to guarantee that the rainfall captured in these places meets health requirements for consumption, all harvested rainwater should be treated in some way. Conversely, the region's water resources would continue to deteriorate unless gas flaring and oil spillage are stopped, and hazardous air pollutants (HAPs) are properly treated before disposal. However, in order to have comprehensive baseline information on the impact of improper oil and gas exploration on the environment, an evaluation of the impact of improper oil and gas exploration (gas flaring, oil spillage, and HAPs emission) on the air, water bodies, plants, and soil should be undertaken in the area.

5. Declarations

5.1. Author Contributions

Conceptualization, C.B.A. and U.U.U.; methodology, C.B.A. and U.U.U.; formal analysis, C.B.A. and U.U.U.; investigation, C.B.A. and U.U.U.; resources, C.B.A. and U.U.U.; data curation, C.B.A. and U.U.U.; writing—original draft preparation, C.B.A. and U.U.U.; writing—review and editing, C.B.A. and U.U.U. All authors have read and agreed to the published version of the manuscript.

5.2. Data Availability Statement

The data presented in this study are available on request from the corresponding author.

5.3. Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

5.4. Declaration of Competing Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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