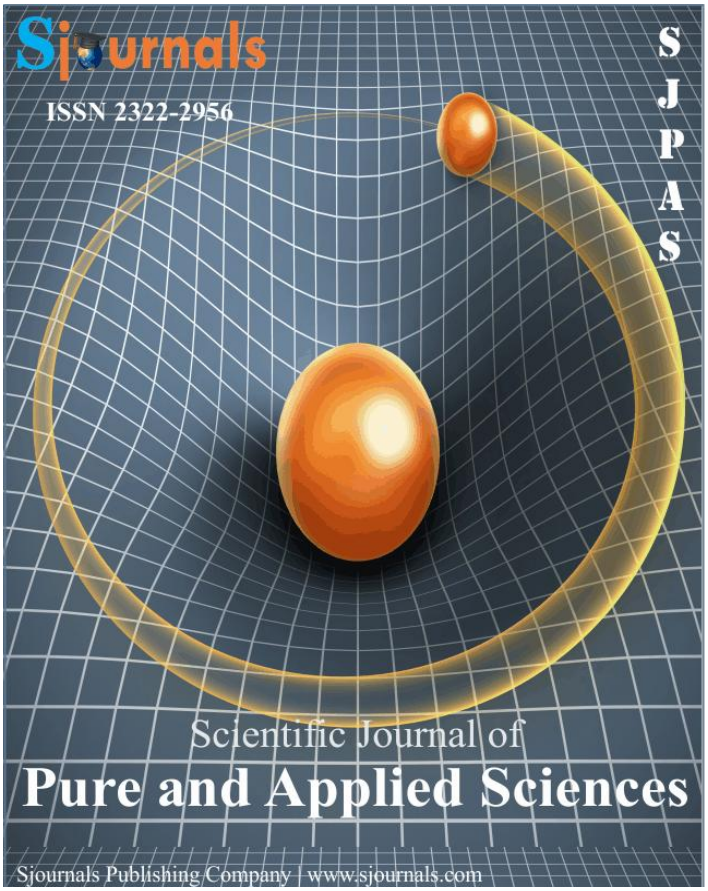
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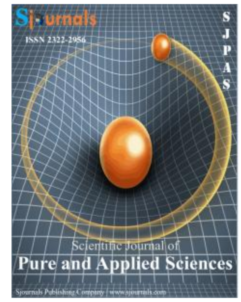


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**Original article**

# Quality characteristics of rainwater around an industrial area in Warri, Delta State, Nigeria

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Petroleum crude oil refining to generate useful products releases noxious gases such as sulphur (IV) oxide, nitrogen (IV) oxide and carbon (IV) oxide, which dissolve in rainwater to form acid rain. This research was to ascertain the impact of the refining process on the rainwater quality in a peri-urban area where residents depend on precipitation for domestic use, including cooking. Rainwater samples were collected from some locations in close proximity to a refinery in Warri and characterized in terms of physico-chemical parameters, and heavy metals proximal contents using methods recommended by America Public Health Association. For the period under study, results revealed that pH was relatively low in all the rainwater samples. Mean pH values obtained ranged from 4.20 ± 0.17 to 6.24 ± 0.04. Turbidity values ranged between 2.00 ± 0.20 NTU and 12.5 ± 0.83 NTU. Although the levels of heavy metals notably, lead, copper, cadmium and zinc were low, total iron was slightly significant in some samples. Water with low pH values and high heavy metal concentrations could adversely affect water bodies, aquatic life, soils, plants and cause lots of aesthetic damage to structures. Similarly, possible percolations into underground water aquifers can affect humans that use such water, including rainwater for most domestic uses.



## 1. Introduction

Water is the most abundant resources in nature. It is vital for all known forms of life and an essential constituent of all animal and plant matters. It forms about 75% of matter in the Earth's crust. Rainwater is an important source of freshwater especially for those who live in rural communities and cities where the growing demand for freshwater supply is very high. In many areas, rainwater is still considered safe and a suitable source of potable water, and it is commonly used as such (Okoli et al., 2005; Wondyfraw, 2014). Developments in science and technology have brought improved standard of living, but have also unwittingly introduced some pollution into our environment. As noted by Rim-Rukeh et al. (2005), the concentrations of pollutants in the environment correlates with industrial activities and these substances / chemicals are mostly odourless, colourless, tasteless and most importantly, hazardous to man, animals or plants, if present in relatively high concentration.

The water cycle (hydrologic cycle), describes the continuous movement of water on, above and below the surface of the Earth. Water could change states between liquid, vapour, and ice at various places in the water cycle. Water undergoes evaporation and transpiration (evapotranspiration), condensation, and precipitation, falling back to the Earth, pure and fresh (Nduka and Orisakwe, 2010). The sun, which drives the water cycle, heats water in oceans and seas. Water evaporates as water vapour into the air, while ice and snow could sublimate directly into water vapour. Evapotranspiration is water transpired from plants and evaporated from the soil. Rising air currents take the vapour up into the atmosphere where cooler temperatures cause it to condense into clouds. Air currents move water vapour around the globe, cloud particles collide, grow and fall out of the sky as precipitation (Rodhe et al., 2002; Panyakapo and Onchnag, 2008). Some precipitation falls as snow or hail, and could accumulate as ice caps and glaciers (frozen water). Most water falls back into the oceans or onto land as rain, where the water flows over the ground as surface runoff. Not all runoff flows into rivers, much of it soaks into the ground as infiltration. Some water infiltrates deep into the ground and replenishes aquifers, which store freshwater. Over time, the water returns to the ocean, where the water cycle started (USEPA, 2008).

Since rainwater evaporates from the sea as a result of extensive heat and it is produced by distillation process, it is considered the purest form of naturally occurring water; however, the rainwater in an area could become impure due to air pollution from anthropogenic activities. Acid rain has become a serious environmental problem in many industrialized area, especially where there are refineries (Rim-Rukeh et al., 2005; Wondyfraw, 2014). The petroleum refining is an industrial process where crude oil is processed and refined into useful petroleum products, such as liquefied petroleum gas, gasoline, kerosene, diesel, heating oil, asphalt / bitumen, etc. The crude refining process in the oil refinery releases noxious gases into the atmosphere which causes air pollution with notable odour associated with its operations (Omoniyi and Oluwadare, 2013).

Gas flaring is a major source of pollution, which could have tremendous effect on humans and the ecosystem due to noxious gases emitted into the atmosphere. During the refining process, the thick black smoke together with the flame seen protruding into the atmosphere at the tip of a refinery flare stack could be due to incomplete combustion. The flare only goes off when there is no production; it is shut down for maintenance, or develops a technical fault. The flare releases a myriad of substances such as volatile organics, oxides of carbon, nitrogen, sulphur, suspended particulate matter, some heavy metals and other toxins at levels that sometimes exceed both National and International standards (Ajugwo, 2013). Besides, compromising the quality of the atmosphere, the gas flare has local and regional effect such as acid rain (Edem, 2011; Ezenwaji et al., 2013).

Acid rain is water that precipitates on the surface of the earth in the form of rain drops, containing certain harmful solutes and gases that have been absorbed by water vapour during evaporation from water bodies and transpiration from the leaves of autotrophic plants. The pH of normal rain has traditionally been given a value of 5.6, and now with a slightly acidic pH range of 5.3-6.0. However, scientists now believe that the pH of rain may vary from 5.6 to a low of 4.5 with the average value of 5.0. Acid rain or acid snow is a direct result of the method that the atmosphere cleans itself (USEPA, 2008). The tiny droplets of water that make up clouds continuously capture suspended solid particles and gases in the atmosphere. The gases of sulphur oxides and nitrogen oxides are chemically converted into sulphuric and nitric acids. When enough of the tiny cloud droplets clump together to form a larger water drop, it may fall to the earth as wet acid precipitation including rain, snow, ice, sleet, or fog (Butnariu and Samfira, 2013). Acid rain is one of the largest contributors to an industrialized form of pollution and could also be formed when pollutants are released from the use of coal in the production of electricity, base-metal smelting and fuel combustion in vehicles besides, refining of crude oil.

The most important pollutants that contribute to the formation of acid rain include: nitrogen (IV) oxide, sulphur (IV) oxide and carbon (IV) oxide. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various chemical compounds. Once released into the air, these gaseous pollutants drift along with clouds until the rain eventually reacts and converts them intotrioxonitrate (V) acid ($HNO_3$), tetraoxosulphate (VI) acid ($H_2SO_4$) and trioxocarbonate (IV) acid ($H_2CO_3$) respectively (Seinfield and Pandis, 1998; USEPA, 2008). The ability of the trioxocarbonate (IV) acid ($H_2CO_3$) to release hydrogen ion ($H^+$) is what classifies it as an acid, thus lowering the pH of the rain.

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Similarly, nitrogen (II) oxide (NO) also contributes to the acidity of rain water. In air, NO is oxidized to nitrogen (IV) oxide ($NO_2$), which in turn reacts with water to give trioxonitrate (V) acid ($HNO_3$). This acid dissociate in water to yield hydrogen ions and trioxonitrate (V) ions ($NO_3^-$).

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$
$$3NO_{2(g)} + H_2O_{(g)} \rightarrow 2HNO_{3(aq)} + NO_{(g)}$$ (Butnariu and Samfira, 2013).

Similarly, the sulphur reacts with oxygen from the air to form sulphur (IV) oxide ($SO_2$). Sulphur (IV) oxide is further oxidized to sulphur (VI) oxide, which reacts with water to form tetraoxosulphate (VI) acid. Tetraoxosulphate (VI) acid accounts for 75% of the acidity of rain water and its presence causes the acidity of the rain to increase and thus, the pH of the rainwater drops to harmful levels.

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

Considering the detrimental damage likely to result from acid rain as evident in several studies, including works of Odilison (1999); Ogunkoya and Efe (2003); Olobaniyi and Efe (2007); Nduka et al. (2008); Nduka and Orisakwe (2010); Olowoyo (2011); Ezenwaji et al. (2013), it was necessary to ascertain the quality of rainwater and its subsequent effects around some close communities to the Warri Refining and Petrochemical Company (WRPC), Warri, Delta State, since some of the residents use the rainwater for various domestic purposes including cooking.

## 2. Materials and methods

### 2.1. The study area

The study location is in Ubeji community in Warri South Local Government area, which houses the Warri Refinery and Petrochemical Company (WRPC), Warri, Delta State with a coordinate of $5^o$ 32'N and $5^o$ 41'E. Areas spread around the refinery include: Jeddo, Ekpan, Jakpa, Bunkery road, Refinery road, Chinkelly, Niger cat and Effurun express road areas with Eboh road as the control location (Fig. 1, 2). The area is made up of fresh water with moderate temperature. Historical rainfall data from Nigeria Meterological Agency (NIMET) in the study area reported an annual rainfall of between 96.8 mm and 328 mm. The month of July has the highest rainfall with a monthly mean of 365.7 mm and less intense rainfall occurs in December and February with monthly mean of 19.8 mm and 50.1 mm respectively. When rainfall has surpassed 1.0 mm per day (24h), it is defined as a day with precipitation (WMO, 2013).

The natural vegetation is rainforest with swamp forest in some areas. However, in recent time, the once rich rainforest have started showing signs of declining timber, palm as well as fruit trees. Major activities in the area include: legal / illegal refining of petroleum crude oil, fishing, farming, trading, open dump waste disposal, waste incineration, waste composting, poor / wrong agricultural practices, uncontrolled use of pesticide including herbicides etc. Some of the residents, especially peasant farmers grow vegetables and other crops around the refinery and waste management facilities. States surrounding Delta State includes Edo, Ondo, Anambra, Rivers and Bayelsa (Ekeh, 2005).

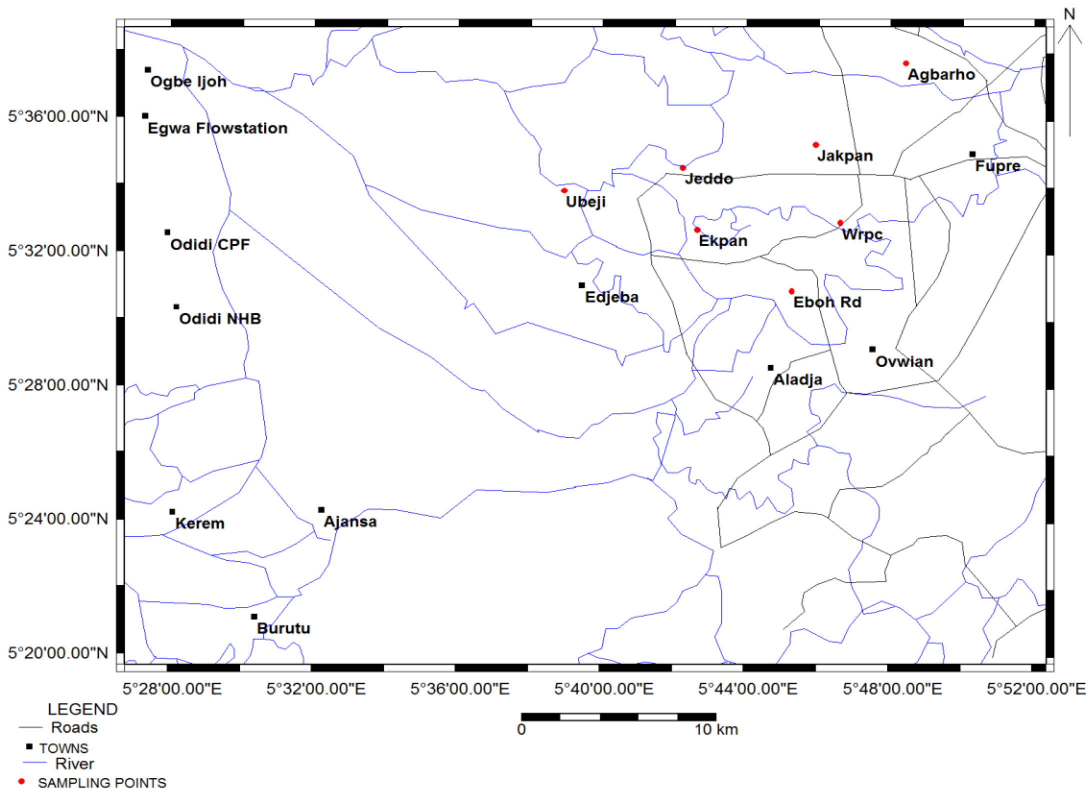


**Fig. 1.** Map of Delta State showing the study area in Warri, Delta State (Ministry of Lands and Housing, Delta State, Nigeria).

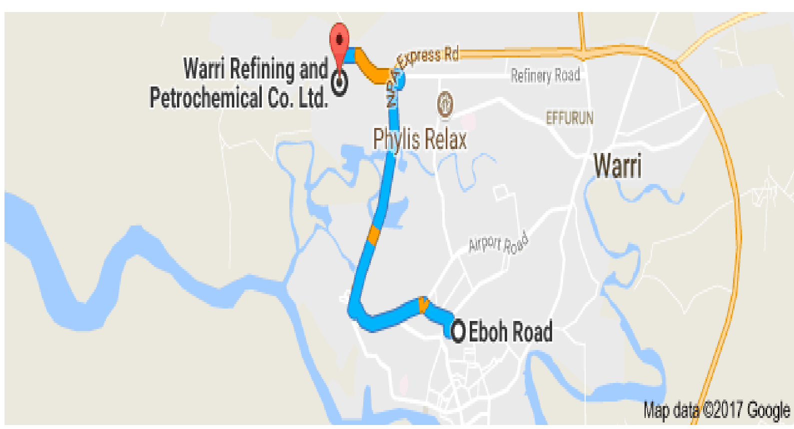


**Fig. 2.** Map showing the study area and control, Warri, Delta State (Google map).

### 2.2. Rainwater sampling

One hundred and eighty nine (189) rainwater samples were collected in triplicates during the rainy months of May to September for three years (2014, 2015 and 2016) and analyzed for physico-chemical parameters and heavy metals (Table 1). The samples within the refinery were collected from the WRPC (topping unit and wastewater unit areas) while those outside the refinery were collected from four communities in close proximity to the refinery namely Ubeji, Jakpa, Ekpan and Jeddo with Eboh as control (Fig. 2). The rainwater samples were stored in 1

Lpolyethylene bottles and were preserved by cooling at 4 $^{o}$C, while samples for metals analyses was preserved with 2 mL of 1:1 nitric acid (AR) (APHA, 2005). Nitric acid was added to the water samples for metal analysis because it would result in a drop in pH so that the loosely bonded ions could be released for determination.

**Table 1**
Specific parameters and methods used in this assessment.

| **Parameters** | **Analytical methods** |
|---|---|
| pH | pH, (APHA 4500 $H^{+}$) |
| Temperature $^{o}$C | Thermometer (APHA, 2550-B) |
| Electrical conductivity µS/cm | Conductivity (APHA 2510 B) |
| Total Dissolved Solids (TDS) mg/L | TDS (APHA 2540-C) |
| Salinity ($Cl^{-}$) mg/L | Mohr's Argentometric method (APHA 4500 Cl-B) |
| Sulphate mg/L | Turbidimetric, (APHA 4500-$SO_4^{2-}$-B) |
| Total Suspended Solids (TSS) mg/L | TSS (APHA 2540-C) |
| Nitrate, $NO_3$-N mg/L | APHA 4600-$NO_3$-B |
| Bicarbonate mg/L | Titrimetric method (API-RP 45) |
| Turbidity NTU | (Nephelometric method) APHA 2130 B |
| Metals (Total Fe, Pb, Cu, Cd, Zn) | Atomic Absorption Spectrophotometer (Shimazu6701 F model) |

### 2.3. Determination of metals in rainwater samples

The rainwater samples were digested using concentrated nitric acid (AR). The samples were mixed and 250 mL was transferred to a beaker to which 5 mL concentrated nitric acid was added and brought to a boil on a hot plate to the lowest volume possible (15 to 20 mL). Filtration was done after digestion. The filtrate was then diluted to volume with distilled water in a 50 mL volumetric flask (APHA, 2005). The concentration of heavy metals were analyzed using Atomic Absorption Spectrophotometer (AAS) by direct aspiration into a standardized computer interfaced Schimadzu AAS-6701F.

### 2.4. Statistical analysis

All data collected were subjected to descriptive statistics and analysis of variance (ANOVA) in Statistical Package for Social Science (SPSS) statistical software in Version 22.0. These were used to test the mean statistical difference between the controls and study data at significance levels of $P<0.05$. Column and line graphs were used for pictorial display of the various data.

## 3. Results and discussion

### 3.1. Rainwater quality

The results of physico-chemical and metal analysis for rainwater samples collected within and around the study area, including the control are given in Tables 2, 7 and shown in Figures 3, 5. The rainwater samples within the Refinery (RTUA and RWWA) showed lower pH values than the other locations while the control samples were slightly acidic. For the three years of the rainwater study, 2014, 2015 and 2016, the mean pH value was lowest at the Refinery topping unit area (RTUA) (4.32 ± 0.17, 4.42 ± 0.17 and 4.20 ± 0.17 respectively. However, besides the refinery area, the pH results from lowest to highest for 2014, 2015 and 2016 respectively were: 5.36 ± 0.02 (Jeddo) to 6.24 ± 0.01 (Eboh), 5.21 ± 0.03 (Jakpa) to 5.57 ± 0.01 (Eboh) and 4.95 ± 0.02 (Ubeji) to 6.24 ± 0.04 (Eboh), (Tables 2, 4). The pH values were correlated with the concentrations recorded for bicarbonate (<0.01 mg/L) in most of the rainwater samples except the control - Eboh area (10 km), which were quiet far from the refinery area with little or no industrial activities. Besides, the samples from the control area which were slightly acidic, all other samples had values that implied acid rain (pH = 5.6).

The rainwater samples showed relatively low levels of total dissolved solids (TDS) and electrical conductivity concentrations. The levels of total dissolved solids (TDS) in all the samples for the three years (2014, 2015 and 2016) varied from 4.49 ± 0.15 mg/L (Jakpa) to 20.15 ± 0.85 mg/L (RWWA). Electrical conductivity concentrations were in the range of 9.91 ± 0.03 µS/cm (Ubeji) to 39.80 ± 3.90 µS/cm (RWWA) for the respective period of sampling. The rainwater samples could be considered ''fresh'' as indicated in the concentration of salinity, which was within the freshwater range of <500 mg/L. Salinity concentrations for 2014, 2015 and 2016 ranged from 2.26 ± 0.30 mg/L in Eboh to 13.56 ± 0.10 mg/L in RWWA (Tables 2, 4). Sulphate and nitrate were in low concentrations and within the WHO stipulated limits of 400 mg/L and 10 mg/L respectively.

**Table 2**

Mean concentrations of physico-chemical parameters of rainwater in the study area (2014).

| Parameters | WHO limits | RTUA | RWWA | Ubeji | Jakpa | Ekpan | Jeddo | Eboh |
|---|---|---|---|---|---|---|---|---|
| pH | 5.5-6.5 | 4.32 ± 0.17 | 4.54 ± 0.06 | 5.48 ± 0.09 | 5.51 ± 0.03 | 5.57 ± 0.13 | 5.36 ± 0.02 | 6.24 ± 0.01 |
| Temperature $^{o}$C | N/A | 29.1 ± 0.1 | 30.1 ± 2.1 | 27.5 ± 0.2 | 27.5 ± 0.2 | 27.9 ± 0.20 | 27.5 ± 0.20 | 27.0 ± 0.10 |
| Electrical conductivity µS/cm | 400 | 31.7 ± 0.20 | 39.80 ± 3.9 | 9.91 ± 0.03 | 10.40 ± 0.09 | 12.0 ± 0.5 | 17.0 ± 0.5 | 13.0 ± 0.31 |
| Total Dissolved Solids (TDS) mg/L | N/A | 15.09 ± 0.10 | 20.15 ± 0.85 | 4.96 ± 0.08 | 4.49 ± 0.15 | 6.48 ± 0.07 | 8.90 ± 0.28 | 6.69 ± 0.26 |
| Salinity ($Cl^-$) mg/L | 600 | 8.56 ± 0.10 | 13.56 ± 0.10 | 2.61 ± 0.15 | 2.68 ± 0.07 | 3.26 ± 0.09 | 4.26 ± 0.09 | 3.46 ± 0.09 |
| Sulphate mg/L | 400 | 2.76 ± 0.06 | 1.28 ± 0.55 | 0.83 ± 0.12 | 0.86 ± 0.07 | 0.92 ± 0.01 | 1.99 ± 0.11 | 0.66 ± 0.04 |
| Nitrate, $NO_3$-N mg/L | 10 | 0.10 ± 0.01 | 0.12 ± 0.01 | 0.08 ± 0.02 | 0.07 ± 0.01 | 0.15 ± 0.02 | 0.18 ± 0.01 | 0.05 ± 0.02 |
| Bicarbonate mg/L | 500 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | 0.86 ± 0.05 |

Values are mean ± SD (standard deviation) of 3 replicates; N/A = Not available; RTUA = Refinery Topping unit area; RWWA = Refinery waste water treatment area; NTU = Nephelometric Turbidity Unit.

**Table 3**

Mean concentrations of physico-chemical parameters of rainwater in the study area (2015).

| Parameters | WHO limits | RTUA | RWWA | Ubeji | Jakpa | Ekpan | Jeddo | Eboh |
|---|---|---|---|---|---|---|---|---|
| pH | 5.5-6.5 | 4.42 ± 0.17 | 4.35 ± 0.04 | 5.25 ± 0.04 | 5.21 ± 0.03 | 5.22 ± 0.06 | 5.48 ± 0.01 | 5.57 ± 0.01 |
| Temperature $^{o}$C | N/A | 28.1 ± 0.1 | 29.0 ± 0.1 | 30.0 ± 0.5 | 30.0 ± 0.5 | 29.9 ± 0.07 | 28.7 ± 0.20 | 29.0 ± 0.20 |
| Electrical conductivity µS/cm | 400 | 36.7 ± 1.20 | 28.80 ± 0.91 | 10.94 ± 0.65 | 37.40 ± 3.09 | 22.0 ± 1.0 | 18.0 ± 1.0 | 15.0 ± 0.28 |
| Total Dissolved Solids (TDS) mg/L | N/A | 18.09 ± 0.10 | 14.75 ± 1.46 | 5.89 ± 0.34 | 18.49 ± 2.85 | 12.5 ± 1.05 | 7.40 ± 0.67 | 7.90 ± 0.96 |
| Salinity ($Cl^-$) mg/L | 600 | 10.52 ± 0.15 | 6.68 ± 0.99 | 2.90 ± 0.16 | 7.20 ± 0.36 | 6.26 ± 0.22 | 3.26 ± 0.19 | 2.56 ± 0.39 |
| Sulphate mg/L | 400 | 2.50 ± 0.02 | 1.04 ± 0.13 | 1.28 ± 0.07 | 1.26 ± 0.34 | 1.92 ± 0.01 | 0.89 ± 0.01 | 0.86 ± 0.06 |
| Nitrate, $NO_3$-N mg/L | 10 | 0.14 ± 0.05 | 0.17 ± 0.05 | 0.10 ± 0.0 | 0.12 ± 0.05 | 0.26 ± 0.01 | 0.21 ± 0.01 | 0.07 ± 0.0 |
| Bicarbonate mg/L | 500 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | 0.98 ± 0.02 |

Moderate concentrations were recorded for total suspended solids (TSS) and turbidity in the rainwater for the three years sampled. However, black soot and suspended particles were observed in the rainwater samples collected especially within the refinery area and the immediate vicinity and these were correlated with the data recorded for turbidity and TSS. Results for TSS for the three years varied from 2.5 ± 0.16 mg/L (Eboh) to 15.0 ± 1.0 mg/L (RWWA). Similarly, within the refinery, turbidity values ranged between 7.50 ± 0.50 NTU (RWWA) and 11.5 ±

0.70 NTU (RWWA), while outside the refinery the values ranged between 2.00 ± 0.20 NTU (Eboh) and 12.5 ± 0.83 NTU (Ubeji) (Fig. 3). The results for turbidity were closely correlated with the values recorded for TSS in all the rainwater samples (Fig. 3, 4).

The black soot observed in the rainwater samples were also noticed on some cars packed within the premises in the refinery area, the communities mentioned above, and some structures with aesthetic values. Black soot was usually noticed whenever there was a fault in the refining processing unit thus leading to incomplete combustion as revealed in the flare stack emission. The values obtained for turbidity and TSS in a water body could often mean higher concentrations of bacteria, nutrients and metals in the water.

**Table 4**
Mean concentrations of physico-chemical parameters of rainwater in the study area (2016).

| Parameters | WHO limits | RTUA | RWWA | Ubeji | Jakpa | Ekpan | Jeddo | Eboh |
|---|---|---|---|---|---|---|---|---|
| pH | 5.5-6.5 | 4.20 ± 0.18 | 4.23 ± 0.07 | 4.95 ± 0.02 | 5.29 ± 0.01 | 5.48 ± 0.01 | 5.10 ± 0.01 | 6.24 ± 0.04 |
| Temperature $^{o}$C | N/A | 30.0 ± 0.51 | 30.0 ± 0.51 | 30.0 ± 0.5 | 30.5 ± 0.1 | 31.0 ± 0.15 | 30.7 ± 0.20 | 29.0 ± 0.20 |
| Electrical conductivity µS/cm | 400 | 26.7 ± 1.20 | 32.40 ± 2.39 | 11.24 ± 0.64 | 14.0 ± 1.49 | 16.0 ± 1.1 | 16.0 ± 1.1 | 14.0 ± 0.94 |
| Total Dissolved Solids (TDS) mg/L | N/A | 14.60 ± 0.14 | 17.87 ± 1.43 | 5.60 ± 0.10 | 7.80 ± 0.74 | 8.5 ± 1.05 | 8.80 ± 0.01 | 7.40 ± 0.86 |
| Salinity ($Cl^-$) mg/L | 600 | 7.42 ± 0.24 | 8.82 ± 0.85 | 2.24 ± 0.09 | 3.20 ± 0.15 | 3.94 ± 0.11 | 3.24 ± 0.02 | 2.26 ± 0.30 |
| Sulphate mg/L | 400 | 1.60 ± 0.12 | 2.0 ± 0.01 | 1.15 ± 0.24 | 0.96 ± 0.04 | 0.86 ± 0.04 | 0.80 ± 0.02 | 0.66 ± 0.13 |
| Nitrate, $NO_3$-N mg/L | 10 | 0.16 ± 0.0 | 0.19 ± 0.02 | 0.14 ± 0.0 | 0.10 ± 0.02 | 0.15 ± 0.01 | 0.11 ± 0.01 | 0.10 ± 0.03 |
| Bicarbonate mg/L | 500 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | <0.01 ± 0.0 | 0.86 ± 0.11 |

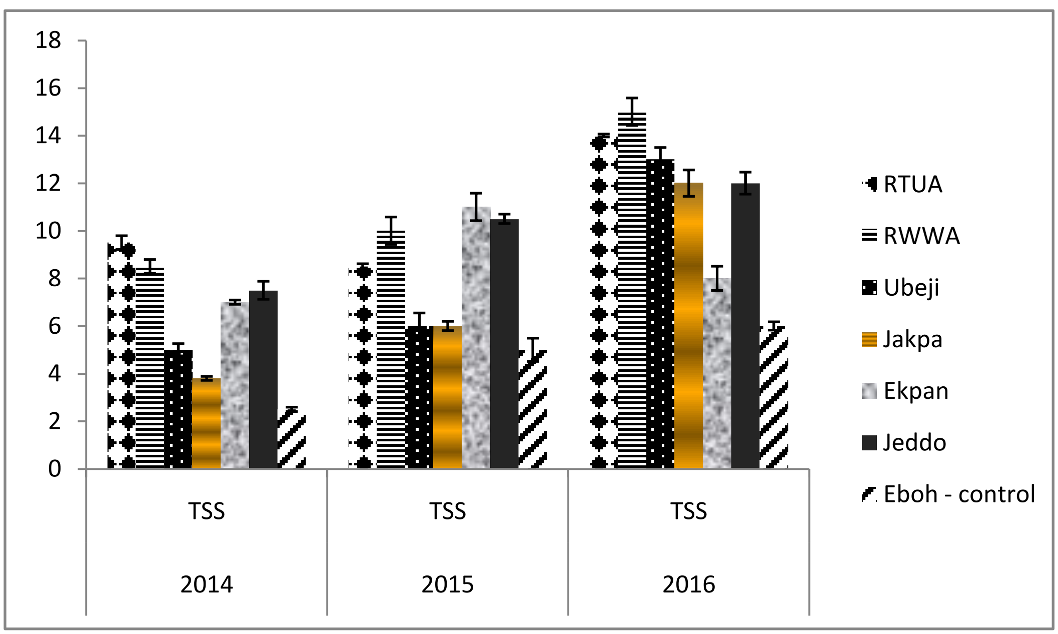


**Fig. 3.** Mean ± SE values for TSS in rainwater samples for 2014, 2015 and 2016.

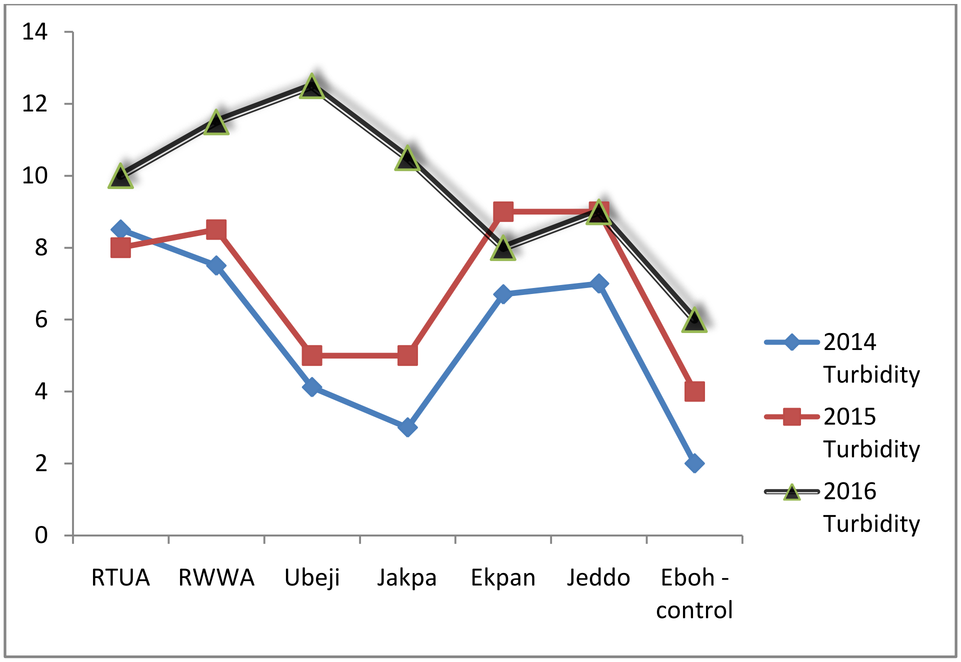


**Fig. 4.** Mean values for Turbidity in rainwater samples for 2014, 2015 and 2016.

Five heavy metals namely zinc, copper, total iron, lead and cadmium were analyzed in the rainwater samples. The concentration of iron ranged from 0.049 ± 0.001 mg/L (Eboh, 2014) to 1.309 ± 0.002 mg/L (Ubeji, 2016). Iron concentration for Ubeji in 2016 was higher than the set WHO limit of 1.00 mg/L. However, values observed in the control were relatively low and within the recommended limit (Fig. 5). Iron impacts taste, causes discolouration and increases the turbidity of water. As little as 0.3 mg/L can cause water to turn reddish brown in colour. However, iron is not considered hazardous to health. In fact, iron is essential for good health because it transports oxygen in the blood, but it is considered a secondary or aesthetic contaminant since it impacts turbidity to water. Similarly, at extremely high concentration, it could interfere with lipid tissues, leading to bioaccumulation, causing detrimental effects in living organisms. This is because the metal does not biodegrade and so tend to bioaccumulate (Duffus, 2002; Tawari-Fufeyin and Ekaye, 2007).

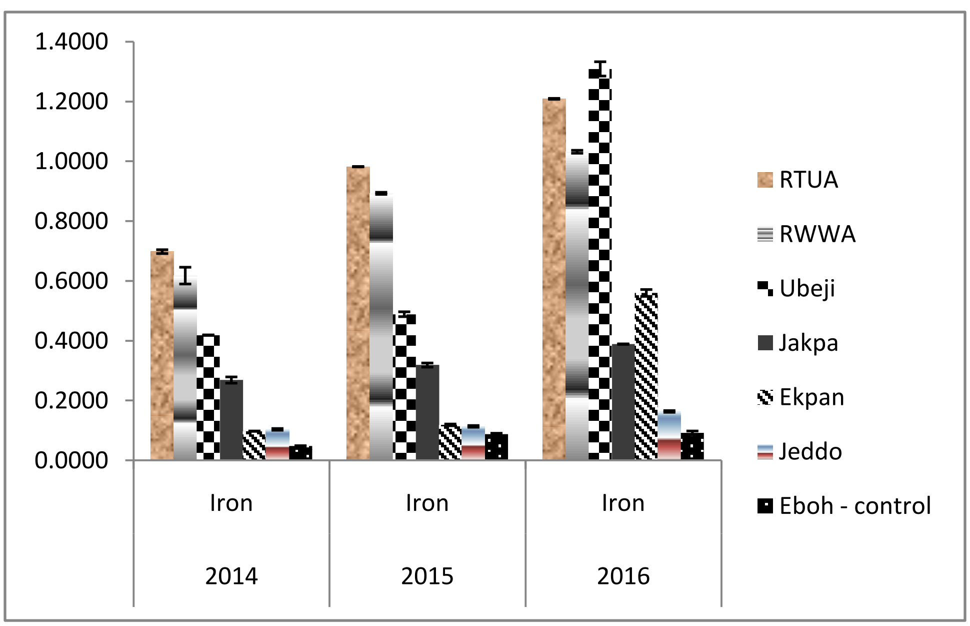


**Fig. 5.** Mean ± SE values for total iron in rainwater samples for 2014, 2015 and 2016.

Besides, the refinery area which had low concentrations for lead and cadmium, the results from the other locations were less than the minimum detection limit of the measuring instrument in the rainwater samples (Tables 5, 7). Apart from iron, which exceeded the WHO limit of 1.00 mg/L in some locations, all other heavy metals had concentrations that were within the recommended limits for both local and International standards.

**Table 5**
Mean concentrations of heavy metals (mg/L) in rainwater in the study area (2014).

| Conc., mg/L | WHO limits | RTUA | RWWA | Ubeji | Jakpa | Ekpan | Jeddo | Eboh |
|---|---|---|---|---|---|---|---|---|
| Zinc | 3.0 | 0.134 ± 0.006 | 0.165 ± 0.015 | 0.005 ± 0.001 | 0.013 ± 0.004 | 0.016 ± 0.001 | 0.019 ± 0.002 | 0.004 ± 0.001 |
| Copper | 2.0 | 0.039 ± 0.010 | 0.025 ± 0.007 | 0.019 ± 0.002 | 0.018 ± 0.003 | 0.201 ± 0.004 | 0.027 ± 0.003 | 0.011 ± 0.003 |
| Lead | 0.01 | 0.005 ± 0.001 | 0.002 ± 0.001 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| Cadmium | 0.003 | 0.002 ± 0.001 | 0.002 ± 0.001 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |

**Table 6**
Mean concentrations of heavy metals (mg/L) in rainwater in the study area (2015).

| Conc., mg/L | WHO limits | RTUA | RWWA | Ubeji | Jakpa | Ekpan | Jeddo | Eboh |
|---|---|---|---|---|---|---|---|---|
| Zinc | 3.0 | 0.104 ± 0.001 | 0.135 ± 0.001 | 0.004 ± 0.001 | 0.005 ± 0.002 | 0.021 ± 0.006 | 0.029 ± 0.003 | 0.002 ± 0.000 |
| Copper | 2.0 | 0.032 ± 0.007 | 0.029 ± 0.006 | 0.025 ± 0.002 | 0.011 ± 0.001 | 0.227 ± 0.013 | 0.031 ± 0.009 | 0.003 ± 0.001 |
| Lead | 0.01 | 0.005 ± 0.002 | 0.002 ± 0.001 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| Cadmium | 0.003 | 0.003 ± 0.001 | 0.001 ± 0.0 | 0.001 ± 0.0 | 0.0 ± 0.0 | 0.001 ± 0.0 | 0.001 ± 0.0 | 0.0 ± 0.0 |

**Table 7**
Mean concentrations of heavy metals (mg/L) in rainwater in the study area (2016).

| Conc., mg/L | WHO limits | RTUA | RWWA | Ubeji | Jakpa | Ekpan | Jeddo | Eboh |
|---|---|---|---|---|---|---|---|---|
| Zinc | 3.0 | 0.124 ± 0.010 | 0.125 ± 0,001 | 0.008 ± 0.002 | 0.002 ± 0.001 | 0.016 ± 0.001 | 0.019 ± 0.002 | 0.001 ± 0.0 |
| Copper | 2.0 | 0.039 ± 0.006 | 0.012 ± 0.004 | 0.001 ± 0.0 | 0.004 ± 0.002 | 0.202 ± 0.015 | 0.036 ± 0.002 | 0.001 ± 0.0 |
| Lead | 0.01 | 0.003 ± 0.001 | 0.001 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| Cadmium | 0.003 | 0.003 ± 0.001 | 0.001 ± 0.0 | 0.001 ± 0.0 | 0.0 ± 0.0 | 0.001 ± 0.0 | 0.001 ± 0.0 | 0.0 ± 0.0 |

### 3.2. Rainwater quality

As a result of failure of public water supply system in most part of Delta State, residents have resorted to using rainwater to augment for most domestic activities, including washing and sometimes cooking. Rainwater is one of the cleanest water because it falls freely from the atmosphere and the natural water cycle is very efficient in screening out contaminants that are normally found in the ground water and other sources. Since rainwater does not come in contact with the soil, it may not contain contaminant such as bacteria, dissolved salts and minerals. However, rainwater could be contaminated because it could absorb gases such as carbon dioxide, oxygen, nitrogen dioxide, and sulphur dioxide from the atmosphere and also capture soot and other particulate matters from a myriad of anthropogenic activities as it falls (Odilison, 1999; Ogunkoya and Efe, 2003).

The results obtained showed relatively low pH values obtained in all the water samples. The acidic nature of waters in Warri, Delta State area may be connected with the anthropogenic activities including the refinery / petroleum industry activities. It has been known that intake of water with low pH values could cause some environmental and severe health implications. Thus, organisms in the environment would not be spared from the adverse effect of low pH level. Fish and most aquatic species cannot tolerate acidic environment and similarly, plants and soil dwelling biota may not be able to survive in extreme acidic conditions, most may become inactive or completely immobilized or used as feed for predators and eventually would die or go extinct (Wondyfraw, 2014). The Niger Delta ecological zone is one of the world's most threatened biodiversity zones and a lot of species usually found in the environment are no longer in existence (Ezenwaji et al., 2013). Acidic waters draw out soil toxins like aluminum and as such, trees take in the poisonous substances, and runoff dumps it in lakes, rivers and streams. Acid rain also dissolves helpful minerals and nutrients like calcium, magnesium and potassium before the trees can absorb them. Acid rain may stunt plant growth through years of soil degradation (Efe, 2003).

Similarly, acidic deposition degrades water quality by lowering pH levels (i.e. increasing acidity); decreasing acid-neutralizing capacity (ANC) and increasing aluminum concentration, which causes a damaging effects on the aquatic life, including micro-organisms, plants, and animals living in the lakes and seas (USEPA, 2008). Soil biology and chemistry could be seriously damaged by such quality of acid rain in the study area since some microbes are unable to tolerate changes to low pH and are killed. Similarly, the enzymes of these microbes could be denatured (changed in shape so they no longer function) by this acidic condition. The hydronium ions of acid rain also mobilize toxins such as aluminium, and leach away essential nutrients and minerals such as magnesium (Rodhe et al., 2002). The soil chemistry could also dramatically change when base cations, such as calcium and magnesium, are leached by acid rain thereby affecting sensitive soil dwelling species.

$$2\,H^{+}_{(aq)} + Mg^{2+}_{(clay)} \leftrightarrows 2\,H^{+}_{(clay)} + Mg^{2+}_{(aq)}$$

The decrease in water clarity caused by turbidity and TSS could affect the ability of fish to see and catch food. Suspended particles can also clog fish gills, reduce growth rates, decrease resistance to disease, and prevent egg and larval development. High turbidity and TSS in rainwater could lead to a high concentration in a water body, which can often mean higher concentrations of bacteria, nutrients, and metals in such waters (Ogunkoya and Efe, 2003). Any water may be safe to drink if it complies with certain regulatory standards for both physico-chemical and microbial parameters. The guidelines / rules should be that values / concentrations should not exceed the required limits for it to be adjudged fit for human consumption (DPR, 2002). Acid rain has some indirect effects on human health. Indirect effects involve damage to humans by contact with materials that have themselves been affected by acidification such as food and water supplies. Sulphur (IV) oxide is toxic to human health and even more toxic when it combines with aerosols, mists and smoke to form a mixture. This is because the mixture forms fine suspensions that penetrate the lungs more than the individual gas $SO_2$ (Olobaniyi and Efe, 2007; Tawari and Abowei, 2012).

Indirect effect of acid rain on human health involves toxic heavy metals because they are liberated from the soil when it gets acidified. The most common heavy metals include: Cd, Zn, Pb, Hg, Mn and Fe. These mobilized contaminants are dissolved in soil, water and transported to the groundwater that is consumed by humans and contaminates food (fish, meat and vegetables) eaten by humans (Pabian et al., 2012). In organisms, the level of metals retained in the body could cause alteration in the entire body structure since metals are known to reside in lipid tissues and this effect could result in the bioaccumulation of the toxicant in the organisms leaving the higher organisms that would feed on them at a high risk from a myriad of environmental and health related issues. These heavy metals when bioaccumulated in the body could result in various health problems, including dry coughs, asthma, headache, eye, nose throat irritations, cancer, etc. Polluted rainfall is especially harmful to those who suffer from asthma or breathing defect. However, even healthy people could have their lungs damaged by acid air pollutants.

The effect of acid rain could be felt miles away from the source of pollution (refinery). Acid rain could damage buildings, historic monuments, statues or sculptures, especially those made of limestone and marble that contain large amounts of calcium carbonate due to the corrosive effects of acids in the rain. It had been well established that either wet or dry deposition of sulphur dioxide significantly increases the rate of corrosion on limestone, sandstone and marble. Black soot could be observed on buckets, drums, clothes on cloth lines and even on food items, especially those hawking or displaying their wares and products for sales around the study area. The fate and effects of pollutants as well as drift of particulates could have been responsible for the movement and settlement of these pollutants in the receiving location (Nduka et al., 2008; Uge, 2009; Ajugwo, 2013; Butnariu and Samfira, 2013). The results from this study indicated that the rainwater quality was impaired as evident in some water quality parameters analyzed. The data reported for this research compared favourably with works of Ogunkoya and Efe (2003); Rim-Rukeh et al. (2005); Nduka et al. (2008); Olowoyo (2011); Ezenwaji et al. (2013) and Akpan (2016).

## 4. Conclusion

Water is a basic component of all forms of survival on earth and since rainwater is useful as an additional means of obtaining freshwater, it would be proper to ensure that the rainwater quality is such that it is not acidic since acid rain causes a myriad of environmental and health issues. Based on the data from this study, the rainwater quality in the study area had been impaired and as such should not be used for certain domestic purposes such as cooking due to the level of acidity. The combustion of fossil fuels is still one of the major ways by which electricity is generated; however, alternative renewable sources of energy such as biomass, wind and solar energy should be used to reduce the dependence on fossil fuels and hence reduce the consequences of acid rain. Similarly, for forests and aquatic ecosystems, the addition of lime into the soil or rivers and lakes can help neutralize the acidity and prevent the effects of acid rain. This study was with the view to safeguarding the ecosystem, humans and structures from the deleterious effects of contaminated rainwater from refinery zone.

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