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Analysis of some physicochemical parameters of rainwater from an industrial area in Port Harcourt, Rivers State, Nigeria

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Abstract Rainwater is an important component of rural water usage in rural communities all over the world. Its composition and fitness for consumption and other uses in the face of utmost scarcity is therefore very important to humans. Its contents also reveal the underlying poor conditions of the atmosphere in the area and therefore needed to be examined. Borokiri is an industrial area within Port Harcourt metropolis and Rainwater samples were collected from the place as the experimental site and Igbo Etche as the control. The samples were examined for physicochemical parameters using standard methods. The parameters examined were; temperature, colour, conductivity, turbidity, pH, residual chlorine, chlorides, free CO_2, total acidity, total alkalinity, calcium, magnesium, potassium, sodium and nitrates. The mean levels of the examined parameters for the study and control sites were; Temperature (28.5792 ^{o}C, and 28.8350 ^{o}C), colour (20.2083 hazen units and 6.375 hazen units), conductivity (0.1238 µS/cm and 0.0625 µS/cm), turbidity (0.3150 NTU) and 0.108 NTU), pH (6.355 and 6.985), residual chlorine (0.1967 mg/L and 0.100 mg/L) , chloride (14.6167 mg/L and 18.8800 mg/L), free CO_2 (45.505 mg/L and 26.3700 mg/L), total acidity 21.5116 mg/L and 14.6900 mg/L), total alkalinity (28.4400 mg/L and 34.0600 mg/L), calcium (21.0333 mg/L and 15.2350 mg/L), magnesium (65.1033 mg/L and 32.66 mg/L), potassium (12.5333 mg/L and 11.3500 mg/L), sodium (33.4916 mg/L and 27.5850 mg/L) and nitrate (32.9150 mg/L and 16.2450 mg/L). All the parameters examined from the study sites showed higher levels compared to those of the control except pH and chlorides. Results obtained from the investigated parameters of the rainwater were within the acceptable limits for drinking water. However, since the results from the rainwater showed signs of increase in the levels from the study sites than the control, caution should be taken in the use of the rainwater for domestic and any other purpose as there might be increase in the levels of these parameters depending on the nature of the activities carried out in the environment.

Keywords parameters, rainwater, analysis, physicochemical, study sites, control sites, industrial, port Harcourt, environment etc

Introduction

Rainwater is an important source of fresh water especially for those who live in rural areas, where water use is limited due to scarcity or where surface and underground water quality is poor. In many areas, rainwater is still considered as a safe and suitable source of potable water, and it is commonly used as such [1]. Rain acts as a powerful mechanism to remove pollutants from the atmosphere. Precipitation chemistry is the result of a series of in-cloud and below-cloud atmospheric chemical reactions and a complex interaction between microphysical processes and cloud dynamics [2]. Rainwater composition is important in evaluating the role of transport of soluble material and the contribution of different sources of atmospheric pollutants.

Aerosols and gases released into the atmosphere can be transported over long distance from their sources, and can be removed by dry or wet deposition [3]. Man is primarily responsible for the enrichment of many trace elements in the atmosphere caused by the combustion of fossil fuels, including such additives as lead in gasoline, processing of crustal materials for manufacturing cements, roasting of ores for refining metals, and burning of waste materials [4]. Many industrial processes produce large quantities of oxides of sulfur and nitrogen which are emitted to the atmosphere, and these gases are being converted into strong acids, which lead to many areas experiencing precipitation of very low pH values [5-6]. Composition of rainwater varies from site to site and it is difficult to control as it is influenced by both natural and anthropogenic sources. If the source is influenced by manmade activities more, it will contribute to acidic gases like NOx and SOx due to which rainwater become acidic [7-8]. Environmental adverse effects of acid rain include changes in the leaching rates of nutrients from plant foliage and soil nutrients, acidification of lakes and rivers, effects on metabolism of organisms and corrosion of structures [9-10]. In addition to that, acid rain is also responsible for reduction of visibility and deterioration of historical structures especially by damaging the details on historic places or sculptures [11]. Precipitation composition thus is an indispensable measurement and helps to understand the comparative importance of the different sources of these materials. Because of this concern, precipitation chemistry in both rural and urban areas has been the subject of intense research in the last two decades [12-13]. Currently, there are more than 1000 stations conducting precipitation chemistry study/ measurements around the world. All these working stations may be categorized into global, regional and local networks.

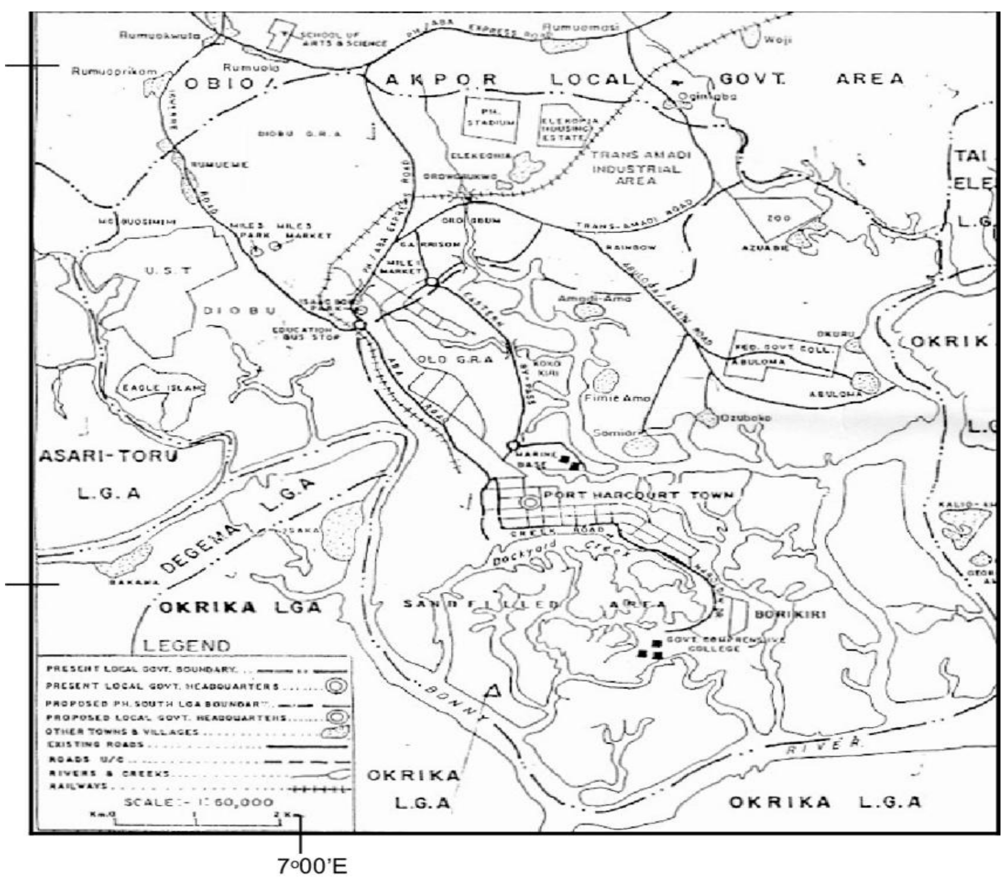

Figure 1: Map showing experimental sample collection site at Borokiri

Global networks comprising the BAPMON (Background Air Pollution Monitoring Network) and GPCP (Global Precipitation Chemistry Project) sites collect precipitation at remote areas and provide worldwide information on the background concentration of air pollutants and long range transport of trace substances in the atmosphere. A large number of local networks are operated in several countries, which address specific scientific questions, abatement strategies and pollution issues. In various countries like Europe, North America regional networks are functioning and documenting spatial and long term trends in deposition of acidic materials [14].

Study Site

RiversState is a predominantly low-lying pluvial state in Southern Nigeria, located in the Eastern part of the Niger Delta on the ocean ward extension of the Benue Trough. RiversState has a total area of 11,077 km² (4,277 mi²), making it the 26th largest state in Nigeria.

Borokiri (the experimental site) is a neighborhood of the city of Port Harcourt situated just south of Old GRA in Rivers State, Nigeria. It lies at latitude 4.749° N and longitude 7.035° E. The neighborhood is bounded by Ahoada Street to the north, Okrika Island to the east, Orubiri oilfield to the south and Ship Builders Road to the west (Google Map).

Igbo Etche (the Control site) is situated in Etche, Rivers, Nigeria, its geographical coordinates are 4° 56' 58" North, 7° 5' 2" East and its original name (with diacritics) is Igbo-Etche.

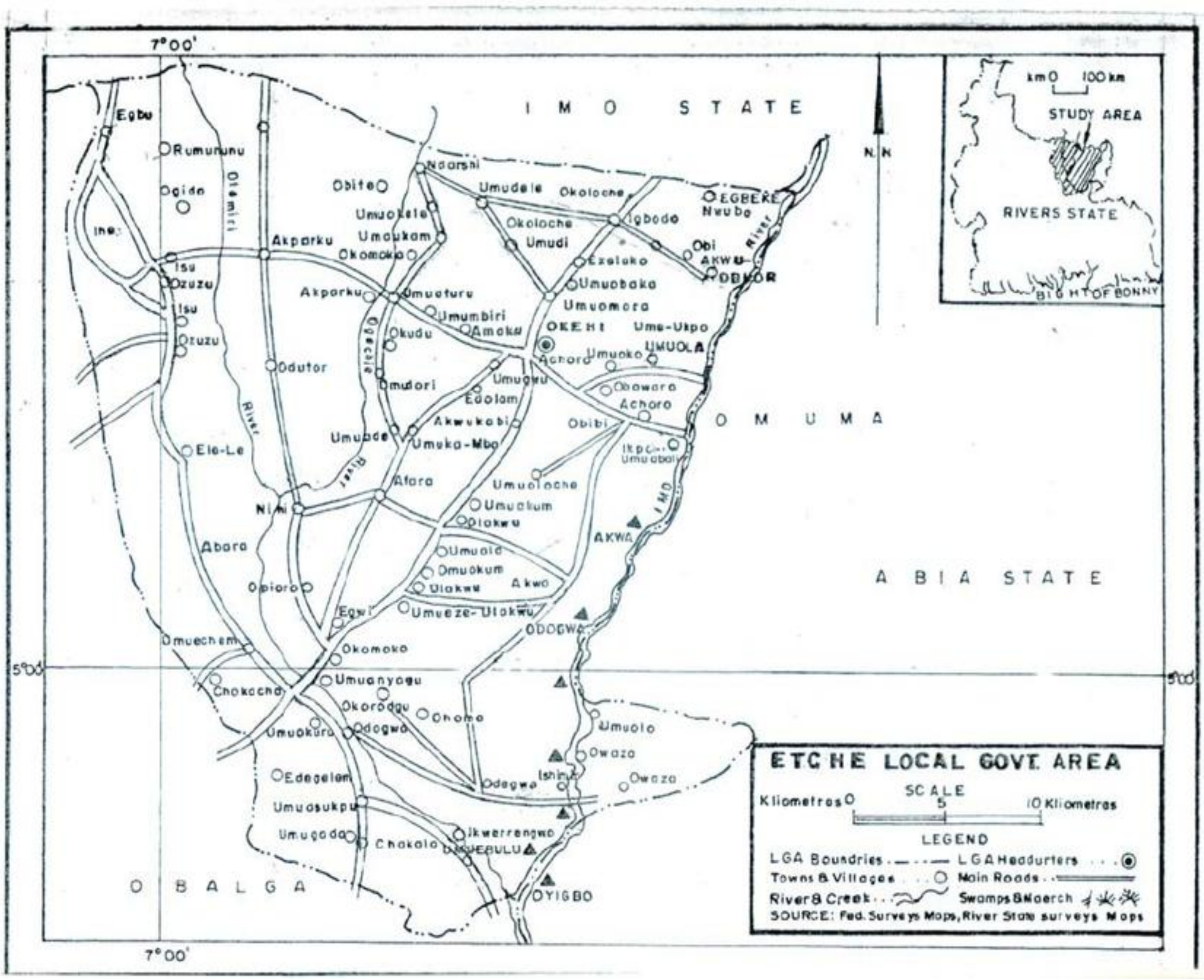

Figure 2: Map showing control sample collection site at Igbo Etche

Collection of Rain Water Samples

Samples of rainwater were collected from three (3) different places (Amadi Creek Zone, Andoni Street, and Ndoki Street) in Borokiri area of Port-Harcourt. The rainwater sample was collected bimonthly from July, 2019 to January, 2020. Care was taken to ensure that samples were representative of rainwater devoid of contamination and the collected samples were taken immediately to the laboratory for analysis. Rainwater samples were collected in clean plastic containers by placing the container on a raised platform in an open environment in other to ensure that the water have no contact with any object before getting into the container. The samples were analysed on the same day of collection to preclude possible chemical reactions that may occur in the samples. Each sample was filtered and divided into two portions. One part was stored at 4˚C for anion analysis and the other portion was acidified with HNO_3 (BDH) for cation analysis. The major cations were determined using Perkin-Elmer Atomic Absorption Spectrophotometer (AAnalyst 700). Anions were analyzed by ion chromatography (Metrohm 761 Compact IC with suppressed module, equipped with an anion-separator column (Dual 2).

Physical Parameters

The rainwater was tested for the following parameters: temperature, turbidity, odour, taste and colour while pH,and conductivity. The levels of the physical parameters were determined insitu since they could change over time.

Temperature

The temperature was measured with the Checktemp 2C pocket sized Thermometer-HANNA instruments at 8.00 hrs and 16.00hrs. The thermometer was immersed in water sample for 1-2 minutes and the reading was taken. The reading was taken in triplicates and the average level recorded.

Turbidity

A turbidimeter (HACH 2100Q Portable Turbidimeter, HACH) was used to determine the turbidity of the water samples.

Odour and Taste

Samples were collected in odour free glassware. Tests were performed only on samples which are known to be sanitary acceptable for ingestion.

Colour

Colour is pH dependant. The colour of the samples was observed by filling a matched Nessler tube to mark 50ml with the water to be examined and comparing it with the standards (distilled water). The tube was looked vertically downward toward white surface placed at an angle that light is reflected upward through the columns of liquid. The tubes were placed in the comparator and the true colour was read. The results of colour determinations were expressed in whole number and recorded as Hazen units.

Chemical Parameters

Chemical analysis carried out on the rainwater sample includes the following; pH, total acidity, total alkalinity, chloride, residual chlorine, calcium, nitrate and carbon dioxide.

pH

The pH/EC/TDS Water proof family-HANNA instrument pH meter was used to determine the pH at temperature of the water sample. 50 ml of the rainwater was placed in a 100 ml beaker. The instrument was dipped in sample water for 2-3 minutes and a reading was recorded. This was read-off the calibration chart and the pH was determined with reference to temperature of water sample.

Total Alkalinity

100m1 of rain water sample was collected and poured into a conical flask. To this, three drops of methyl orange indicator was added. The solution was then titrated against 0.02N Sulphuric acid solution until an orange coloration was observed which indicated the endpoint.

Chloride Test

100m1 of rain water sample was collected and poured into a conical flask. To this, 1.0 ml of Potassium Chromate Solution indicator was added. The solution was then titrated against Silver Nitrate solution until a colour change from yellow to red was observed. This indicates the end point of the reaction.

Residual Chlorine

The principle applied for the residual chloride was that of matching colours. The comparator cells were washed with rainwater samples and this was later filtered. To this sample, a tablet of DPP (diethyl-p-phenylenediamine) was added to the rainwater samples introducing some degree of colouration. This sample was left standing for about 5 minutes. The cells in the comparator were filled with water samples and the standard Chloride Disc was placed. This comparator was then rotated until the colours marched. The Number indicated when the colours match indicates the residual Chlorine in mg/l.

Calcium Hardness

100m1 of rain water sample was collected and poured into a conical flask. To this, 2.0 ml of Sodium Hydroxide Buffer Solution was added while mixing. To this, 0.4g of ammonium pupate (murexide) indicator was added. The solution was then titrated against Sequestric acid solution until a colour change from pink to purple was observed. This indicates the end point of the reaction.

Magnesium

Magnesium is one of the ions responsible for the hardness of water and the exchangeable ions concentration was determined using the modified Unicam Atomic Absorption Spectrophotometer [15].

Sodium and potassium

The standard method(SM) used for the determination of the concentration of sodium and potassium ions in water was the flame emission method [15].

Nitrate Test

Five (5) drops of rainwater sample was placed in an evaporating dish. To a conical flask, two (2) drops of diphenyl amine was added to Sulphuric acid. The solution in the flask was then added to the evaporating dish and the content of the dish heated up. Blue colouration was observed which is indicative of the presence of Nitrate. The absorbance of this mixture was read at a wavelength of 520nm in a spectrophotometer.

Carbon (IV) Oxide

10ml of rainwater sample was collected and put in a measuring cylinder**.** To this, four (4) drops of phenolphthalein indicator was added. The colourless solution observed was then titrated with 0.045 M of sodium carbonate solution. Iron rod was used to stir gently while adding sodium carbonate in bits. A faint pink colouration that remains for at least 30 seconds indicates the presence of carbon (IV) oxide.

i. The quantity of CO_2 was calculated as;

$$CO_2(mg/l) = \pi \frac{NaCO_3\ x\ N\ x\ 22\ x\ 100}{volume\ of\ sample}$$

Results and Discussion

The results of the different physicochemical parameters obtained from the rainwater in Borokiri and control sites are shown in tables 1. The WHO limits for these parameters are also shown in table 1 below.

Table 1

Parameter	Site	July	September	November	January	Mean	WHO Limit
Temperature	1	25.42	28.74	29.62	31.30	28.7700	**20-32**
(^{o}C)	2	24.45	27.32	29.44	30.22	27.8575	
	3	25.88	28.68	30.62	31.26	29.1100	
	Control	31.44	26.56	27.78	29.56	28.8350	
Colour	1	12.5	15.0	18.0	36.5	20.5000	**5-35**
(Hazen Unit)	2	13.3	15.5	19.5	36.0	21.1250	
	3	10.0	12.5	15.0	38.5	19.0000	
	Control	5.0	6.0	6.5	8.0	6.3750	
Conductivity (µS/cm)	1	0.212	0.146	0.136	0.114	0.1520	**<200**
	2	0.112	0.098	0.112	0.100	0.1055	
	3	0.132	0.112	0.108	0.104	0.1140	
	Control	0.060	0.070	0.060	0.060	0.0625	
Turbidity	1	0.202	0.290	0.300	0.402	0.2985	**<0.25**
(NTU)	2	0.180	0.290	0.320	0.412	0.3005	
	3	0.250	0.280	0.354	0.500	0.3460	
	Control	0.102	0.110	0.100	0.120	0.1080	
pH	1	6.52	6.30	6.22	6.10	6.2850	**6.5-9.5**
	2	6.62	6.42	6.24	6.00	6.3200	
	3	6.80	6.72	6.30	6.02	6.4600	
	Control	6.72	6.90	7.22	7.10	6.9850	
Residual Chlorine (mg/L)	1	0.32	0.26	0.24	0.14	0.2400	**0.1-0.5**
	2	0.2	0.18	0.14	0.16	0.1700	
	3	0.14	0.22	0.24	0.12	0.1800	
	Control	0.10	0.10	0.10	0.10	0.1000	
Chloride (mg/L)	1	12.62	15.82	18.72	12.66	14.9550	**250**
	2	14.42	15.52	17.24	13.46	15.1600	
	3	11.22	12.24	15.20	16.28	13.7350	
	Control	20.64	20.44	15.88	18.56	18.8800	
Free CO_2(mg/L)	1	34.20	38.62	49.20	52.10	43.5300	**6-60**
	2	38.42	44.46	48.20	51.22	45.5750	
	3	41.10	44.00	48.28	56.26	47.4100	
	Control	23.22	25.44	26.20	30.62	26.3700	
Total Acidity (mg/L)	1	17.98	19.74	22.48	28.42	22.1550	**47-146**
	2	20.20	18.46	19.42	26.62	21.1750	
	3	16.44	18.84	22.20	27.34	21.2050	
	Control	15.10	15.20	11.22	17.24	14.6900	
Total Alkalinity (mg/L)	1	34.92	30.66	26.32	22.12	28.5050	**30-50**
	2	20.24	25.12	28.56	25.18	24.7750	
	3	27.32	29.46	33.12	38.26	32.0400	
	Control	20.12	38.24	38.56	39.32	34.0600	
Calcium (mg/L)	1	20.22	22.24	19.36	17.62	19.8600	**200**
	2	22.76	21.18	18.42	16.52	19.7200	

	3	24.12	24.22	25.46	20.28	23.5200	
	Control	18.28	16.24	16.22	10.20	15.2350	
Magnesium (mg/L)	1	68.24	69.34	72.24	74.48	71.0750	**100**
	2	45.44	62.12	65.46	70.12	60.7850	
	3	56.26	62.32	66.12	69.10	63.4500	
	Control	25.22	29.20	32.12	44.10	32.6600	
Potassium (mg/L)	1	12.54	15.36	13.12	11.26	13.0700	
	2	13.34	12.28	12.44	10.40	12.1150	
	3	15.56	12.32	11.44	10.34	12.4150	
	Control	10.22	11.42	11.44	12.32	11.3500	
Sodium (mg/L)	1	56.48	43.44	47.36	39.20	46.6200	**200**
	2	34.28	30.12	28.12	25.26	29.4450	
	3	28.12	26.32	22.56	20.64	24.4100	
	Control	34.52	26.42	26.78	22.62	27.5850	
Nitrate (mg/L)	1	25.68	32.48	34.56	38.22	32.7350	**50**
	2	23.34	26.52	28.24	32.24	27.5850	
	3	32.54	37.54	41.24	42.38	38.4250	
	Control	15.22	13.36	16.28	20.12	16.245	

Site 1 is Amadi, Site 2 is Andoni and Site 3 is Ndoni and control Igbo Etche

Discussion

Due to the increased industrial activities going on in Borokiri area, the physicochemical characteristics of the rainwater have been quite altered as evidenced in the results from the pre-exposed samples, making the water relatively unsafe for consumption. The rainwater in these regions could be able to pick up contaminants such as pesticides, hydrocarbons and solid particles from the atmosphere [16].

The mean values of the temperature of rainwater from the different sites examined were 28.77 ºC, 27.85 ºC, and 29.11 ºC for site 1, 2 and 3 respectively and a control value of 28.83 ºC. All the observed value of temperature in both control and experimental stations were within the WHO value for drinking water. The observed value of the rainwater temperature is in agreement with the values recorded by Obioma *et al* [17] in selected communities in Niger Delta, Nigeria, but slightly higher than the values observed in different parts of University of Maiduguri Staff Quarters by Waziri *et al*., [18].

The mean values of the colour obtained from rainwater from the sampled sites were 20.50, 21.125 and 19.00 Hazen units for sites 1, 2 and 3 respectively and a control value of 6.37 Hazen units. The observed values of colour in the Borokiri area as observed in this study was higher than those of Dinrifo *et al*., [19] in some industrial areas of Lagos, Nigeria. Coloured water is not palatable for drinking because it is associated with taste and in most cases stinks [20].

The mean values of conductivity observed in the rainwater from the different stations examined in Borokiri were 0.1520, 0.1055 and 0.1140 µS/cm at site 1, 2 and 3 and a control value of 0.0625µS/cm. All the values of conductivity in the rainwater obtained from the different sites investigated within Borokiri axis of Port Harcourt were within the WHO value for drinking water. The values of conductivity observed in the present work were lower than those of Pawan *et al* [21] in rainwater collected from industrial area of Panipat, India and also lower than the values observed in rainwater collected from Western Niger Delta Region, Nigeria [22].

The mean site values of turbidity of rainwater obtained from Borokiri area of Port Harcourt were 0.2985, 0.3005 and 0.3460 NTU for stations 1, 2 and 3 and a control value of 0.1080 NTU. All the observed values were lower than the WHO value of 5 NTU recommended for drinking water. The values of turbidity observed in this work, although were found to be within the required WHO limit, yet were higher than those of Adarsh and Anil [23] in rain water from Calicut and Malappuram districts of Kerala State, India, but lower than those of Olowoyo [24] in rainwater from Warri, Delta State, Niger Delta, Nigeria.

The mean values of pH observed in rainwater from the different sites were 6.28, 6.32 and 6.46 for site 1, 2 and 3 respectively and a control value of 6.98. All the rainwater samples from the different stations except the control were lower than the WHO value recommended for drinking water. The values of pH observed in rainwater samples from different parts of Borokiri did not agree with the observations of Suresh [25] in rainwater collected from industrial areas of Hisar, India, where the values fluctuated between acidic and alkaline values, but slightly higher than the values observed in rainwater from parts of Ondo State, Nigeria [26].

The residual chlorine content of the rainwater collected from Borokiri area of Port Harcourt were 0.24, 0.17 and 0.18 mg/L in sites 1, 2 and 3 respectively and a control value of 0.1000 mg/L. All the examined values were within the range recommended for consumption by WHO. The residual chlorine content of rainwater from the selected sites were in agreement with the observed values in rainwater from manufacturing sites of Hisar, India [25] and selected industrial sites in Lagos metropolitan city, Nigeria.

The concentrations of chlorides in the rainwater samples from the experimental sites in Borokiri, Port Harcourt were 14.9550, 15.1600 and 13.7350 mg/L at sites 1, 2 and 3 respectively. The control value observed was 18.8800 mg/L. All the determined values of chlorides in the stations were lower than the WHO standard value for drinking water. The concentrations of chloride in rainwater from the sites examined were within the range of values observed in industrial areas of Hisar, India [25], industrial areas of Lagos State Nigeria [19] and in rainwater from southeastern site of Brazil [27].

The concentrations of free CO_2 in rainwater from the different sampled locations at Borokiri, Port Harcourt were 43.5300, 45.5750 and 47.4100 mg/L for sites 1, 2 and 3, while the control value was 26.3700 mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking by WHO. The concentrations of carbon dioxide (CO_2) in the assessed rainwater samples from Borokiri were slightly higher than the values observed in industrial parts of Lagos, Nigeria (Dinrifo*etal*., 2010). Carbon (IV) oxide is a colourless, odourless, and poisonous gas. High levels of carbon dioxide in rainwater may be due to high level presence in the atmosphere, which were dissolved in the rainwater during precipitation.

The total acidity value of the rainwater samples obtained from the study area were22.1550, 21.1750 and 21.2050mg/L in stations 1, 2 and 3 respectively, while the control value was 14.6900 mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking by WHO.

The total alkalinity value of the rainwater samples obtained from the study area were 28.5050, 24.7750 and 32.0400mg/L in stations 1, 2 and 3 respectively, while the control value was34.0600 mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking waterby WHO. The observed alkalinity values in the present work is within the range of values observed in industrial parts of Lagos, a coastal city in Nigeria [19], but higher than the values observed in some Niger Delta communities in Nigeria [17].

The values of calcium in the rainwater samples obtained from the study area were19.8600, 19.7200, and 23.5200mg/L in stations 1, 2 and 3 respectively, while the control value was15.2350mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking water by WHO. The concentrations of calcium observed in rainwater from the study sites were lower than the values observed in rainwater from industrial area of rural Panipat (Haryana), India [21]. In general, the ingestion of calcium in excess for a short period of time has no adverse effect but when it is consumed in excess may lead to urinary tract calculi, by percalcemia (increased level of calcium in blood), calcification in soft tissues such as arterial walls, kidneys and the suppression of bone remodeling [28].

The values of magnesium in the rainwater samples obtained from the study area were 71.0750, 60.7850 and 63.4500 mg/L in stations 1, 2 and 3 respectively, while the control value was 32.6600 mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking by WHO. The concentrations of magnesium in the rainwater samples from the Borokiri axis of Port Harcourt were higher than the values of Obioma *et al* [17] in some Niger Delta communities in Nigeria. Magnesium presence in water is unarguably important because it is very essential to both plants and animals in its photosynthetic role in plants. Lack of magnesium in animals can lead to convulsion and tetanus and yellowing of leaves in plants [29].

The values of potassium in the rainwater samples obtained from the study area were 13.0700, 12.1150 and 12.4150 mg/L in stations 1, 2 and 3 respectively, while the control value was 11.3500 mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking by WHO. When potassium is consumed, it has the capacity to regulate osmotic pressure in the internal cell of organisms and the acid-basic balance of animals in stressed conditions.

The values of sodium in the rainwater samples obtained from the study area were 46.6200, 29.4450 and 24.4100mg/L in stations 1, 2 and 3 respectively, while the control value was 27.5850mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking by WHO. The concentrations of sodium in the rain water from Borokiri, Port Harcourt was higher than the values obtained by Ghanem *et al*., [30] in rainwater from Ramallah District, Palestine and also those of Marcos *et al* [27] in rainwater from selected industrial sites in southeastern Brazil.

The values of nitrates in the rainwater samples obtained from the study area were 32.7350, 27.5850 and 38.4250mg/L in stations 1, 2 and 3 respectively, while the control value was16.2450mg/L. The values observed in rainwater in all the stations were within the required concentration for drinking by WHO. The observed concentrations of nitrates in rainwater from the experimental sites in Borokiri axis of Port Harcourt were higher than the values observed in southeastern, Brazil [27] and those of Adarsh and Anil [23] in rainwater in Calicut and Malappuram districts of Kerala State, India, but within the range of values observed in rainwater from rainwater samples collected from some communities in Niger Delta Region, Nigeria [17, 22]. The assimilation of nitrates might lead to a diseased condition in children called methemoglobinemia (widely known asblue baby syndrome).

Conclusion

The study on the physicochemical properties of rainwater from Borokiri axis of Port Harcourt revealed that all the parameters were within the WHO standards for potable water.

The higher values of all the parameters in the sampled area over the control was due to dominance of both anthropogenic (industrial and home) activities in the area and secondly the natural factor of being close to the river (which is of brackish origin) whose tidal wave constantly blow through environment carrying particle along.

The result indicated that human influence along with natural factors contributed to the higher values of parameters in the experimental stations than those of the control.

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