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Environmental Situation of an Agricultural Area in Akure, Nigeria, Based on Physico-Chemical Properties of Rainwater

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ABSTRACT: Acid rain still poses a global problem today, exerting many adverse effects on man, animal, and materials. As its research question, the present study tries to find out whether or not acid rains exist in Akure, Nigeria. For so doing, it determines physico-chemical properties of rain water samples, namely pH, temp, Electrical Conductivity (EC), TDS, acidity, SO_4^-, NO_2^-, Cl^-, and Free CO_2. According to the results, the pH ranged between 6.0 and 7.8, never falling below 5.6 which is an indication of acid rain. Also, the minimum EC was 3µS/cm and the maximum, 201µS/cm. Moreover, TDS was between 1 and 100mg/L, while Free CO_2 had a mean of 23.00 and Standard Deviation of 6.16. The dominant ion was SO_4^- (10-11%), followed by NO_3^-, and Cl^-. Results from the first six months (July-December 2015) reveal slight correlations in the following: TDS with pH (0.532), EC and pH (0.501), Temp and Free CO_2 (0.59), whereas strong correlations have been recorded in the following parameters: Acidity with pH (0.71) and Temperature (0.69), NO_2^- with pH (0.96) and acidity (0.96), SO_4^- with temp (0.68) and NO_2^- (0.83), and finally Cl- with Free CO_2 (0.61), NO_2^- (0.73), and Cl- (0.65). It can be concluded that in the environment under this study there have been no acid rain within the period.

Keywords: global problem, NO_3^- and Cl^-, acid rain, environment, contaminants, WHO, Akure

INTRODUCTION

Rain drops, falling from clouds, have long been known to be pure water without any harmful effect on the environment. Contaminants are absent in clean rainwater, being removed by the natural water cycle (Shafi et al., 2013). Rainwater has many uses, especially in the agriculture.

The contaminants of rainwater are largely due to the aerosols, released by man-made or natural sources locally, or transported from other sources. The ionic, acidity, and alkalinity concentrations of rainwater depend on the quantity of constituent sources, chemical and physical transformation, and their incorporation into the rain during cloud formation process (Herrera et al., 2009; Rao et al., 2016). Rainwater is polluted all over the world due to emissions of different pollutants, which may affect rain characteristics during the washout process, thanks to its solubility (Waziri et al., 2012). Rainwater physicochemical properties have been environmental issues in different parts of the globe, since their environmental impacts are due to acid rain, metal deposition, aquatic eutrophication,

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disturbances of biogeochemical cycling, and global climate change (WMO, update 2017; Huang et al., 2010). Meteorological parameters affect the pollutants, hence acid rain is not limited to the area where the sources are located. Regardless of countries or continent, prevailing winds can carry contaminants in the atmosphere from long distances before letting them deposit, (Beysens et al., 2010).

The study area for this paper is an agricultural area in Akure (Federal College of Agriculture), Nigeria, which apart from the agricultural activities it has witnessed for many years, there has been an increase in the area's population and vehicular activities, as of late. There have been studies (Abulude et al., 2006; Akinnusotu et al., 2015; Abulude et al., 2017) on chemical composition of this location that need determining chemical composition of rainwater in order to quantify the changes and other characteristics of atmospheric pollution.

Acid rain is a present phenomenon, today. The question, however, is whether it exists in Akure, Nigeria, too, or not. As such, the current study has been designed and carried out to answer this pertinent question, for which it has determined physico-chemical properties of rain water samples.

MATERIALS AND METHODS

Rainwater samples were collected from the Rural Education Center (REC) campus of Federal College of Agriculture, Akure, Ondo State, Nigeria (N07^{o} 15’ 46.2’ E005^{o} 14’ 29.1 ± 9ft), which comprised a sum of 12 samples, collected for a period of twelve (12) months (July, 2015 to June, 2016). Figure 1 depicts the study area's map.

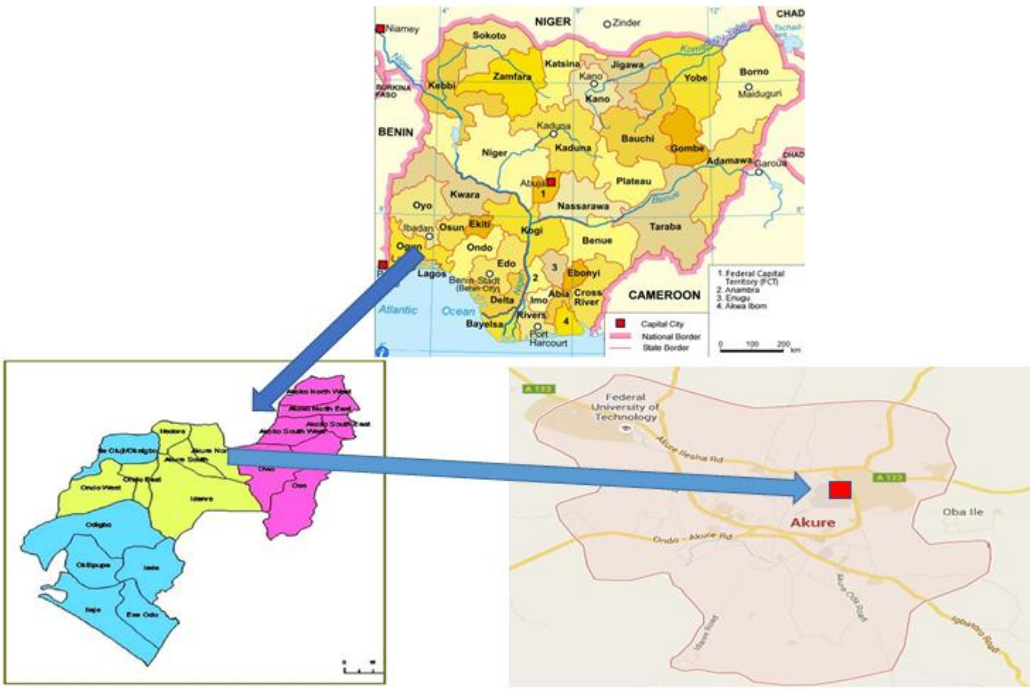

Fig. 1. Map of the study area (N07^{o} 15’ 46.2’ E005^{o} 14’ 29.1 ± 9ft)

Rainwater samples were collected once a month, using the sampler, illustrated in Fig 2: i.e., a simple system, made of a high-density polyethylene (HDPE) bottle (5L), connected to a HDPE funnel, fashioned after the Australian model gauge (Onwudiegwu et al., 2016). The container was placed on the sampling stand 1.5 m above the ground in order to prevent lichen-formation during the sampling period. After a month the rainwater sample collected was filtered, using Whatman ashless filter paper (11.0cm, Cat. No. 14442 110).

The physicochemical parameters (pH, TDS, EC, free CO_2, acidity, temperature, nitrate, sulphate, and chloride) of rainwater samples were subjected to appropriate determinations, using standard methods of analyses (Limgis, 2001).

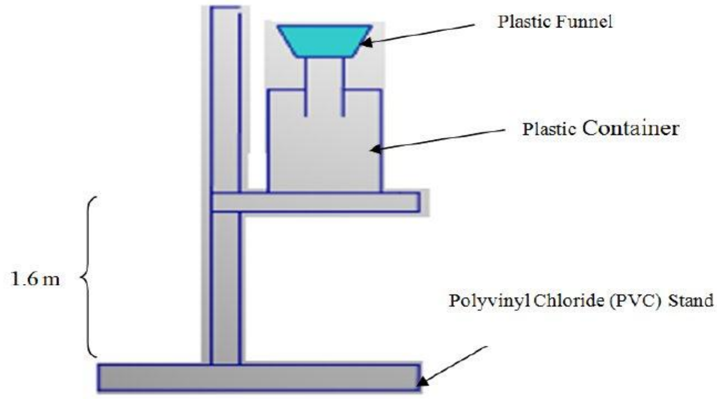

Fig. 2. Illustration of locally assembled TAD gauge

Data obtained (basic descriptions, correlation coefficient, and factor analysis) were generated in triplicates and analyzed, using Minitab 16 Statistical Software.

RESULTS AND DISCUSSION

Table 1 presents mean pH and conductivity of the rainwater samples, both showing the ionic characteristics of the rainwater samples. With reference to the EPA standard, the pH of the rainwater samples in the area were normal to slightly acidic, but none was below a pH of 4.2 which is indicative of acid rain (EPA, 2017). Back in 2015, in one case did the pH come close to 5.8 and this was in the month of July. The pH of all other recorded values stood above 6. These results were compared with those of the studies, shown in Table 2, with the exception of the results, obtained by Akoto et al. (2011) who reported that the pH was between 4.0 and 5.6 in Ghana. Differences in pH levels during different periods of 2015 and 2016 could be attributed to many factors such as removal of CO by photosynthesis through bicarbonate degradation, dilution of rainwater, and temperature drops (Rajasegar, 2003).

The EC of both years showed average values of 31.0 and 76.7µS/cm, implying that the rainwater samples were relatively clean, free from any dissolved ions. But it should be noted that the extent of the contamination of the rainwater with dissolved ions is somehow variable. The coefficient of variations for EC and TDS were high (between 91 and 109), showing a wide variability in the results. As for EC, The minimum was 3 and the maximum 201µS/cm, while TDS ranged between 1 and 100mg/L. According to Kane et al. (2015), presence of inorganic dissolved solids affects the conductivity in water. Results for both EC and TDS were within the standards, provided by Subramani et al. (2005), which include:

Water Class	EC (µS/cm)	TDS (mg/L)
Excellent	<250	250
Good	250-750	250-500
Permissible	750-2000	500-1500
Doubtful	>2000	1500-3000

Source: Subramani et al., 2005

In 2015, Free CO_2 had a mean of 23.00, with a Standard Deviation (Std Dev) of 6.16, and Coefficient of Variation (Coeff Variation) of 26.80, while the Minimum and Maximum values were equal to 16.00 and 32.00, respectively. As for 2016, the mean value was 20.33; Std Dev, 2.94; and Coeff. Variation, 4.48, while the Minimum and Maximum turned out to be 16.00 and 24.00, respectively. The parameters under consideration depicted low and high variations, meaning that they were under low and high influences of different (anthropogenic) factors.

The pie charts in Figures 3-5 illustrate seasonal variation of the parameter concentrations in percentage, showing that 20% of the analyzed samples in October 2015 had acidic characteristics (pH), while 22% had the highest rates in April 2016. This trend is acceptable, if compared to the reference value of 5.6 for acid rain (Subramani et al., 2005). The sampling months showed no significant variations in pH values. The highest ratio of 45% was recorded for TDS in December, followed by 20% in November 2015. Lower percentages were obtained for 2016, which might be due to dissolution of the ions in the sample as a consequence of high rainfall in these periods. The same results were observed in EC. The data showed that samples' acidity and conductivity were slightly higher in less rainy periods of 2016, which could be due to the fact that in dry periods, the atmosphere is more polluted, so the wet scavenging process carries a higher load of compounds, increasing the measured parameters (Cerqueira et al., 2014).

In 2015, SO_4^{2-} and NO_2^- showed the highest anion concentrations (22%), which might be originated from a significant wood burning contribution. Also in 2016, $SO4^{2-}$ and Cl^- had the highest anion concentrations (24% and 26%, respectively), perhaps due to planting periods in the area. During these times, lots of chemicals (herbicides, insecticides, and pesticides) and fertilizers were used. Winds may also have blown SO_2 and NO_X over long distances and across borders to this agricultural area. The pH of natural rain was found to range from 5 to 7. The term acid rain is customarily applied to rainwater with a pH below 5.0. Low pH values are obtained only in the presence of large amounts of man-made pollution. The seasonal variations of 2015 and 2016 were low with regard to SO_4^{2-}/ NO_2^- (1.84 and 3.14, respectively), indicating that the agricultural area was not polluted. The SO_4^{2-}/ NO_2^- ratio is generally used to quantify the sources of emissions, which affect the atmospheric rainfall (Rai, 2014).

Table 3 shows the correlation matrix *r* of rainwater samples. It shows that there are some correlations between the parameters. The results of the first six months (July-December 2015) revealed slight correlations in TDS with pH (0.532), EC with pH (0.501), and Temp with Free CO_2 (0.59), while strong correlations were recorded in Acidity with pH (0.71) and Temp (0.69), NO_2^- with pH (0.96) and acidity (0.96), SO_4^- with temp (0.68) and NO_2^- (0.83), and finally Cl- with Free CO_2 (0.61), NO_2^- (0.73), and Cl- (0.65). As for the next six months (January - June, 2016) pH proved to have strong correlations with TDS (0.89) and EC (0.89), while the correlation of Free CO_2 with TDS and EC was equal (0.70). The correlation of Acidity with Free CO_2 and temp was 0.94 and 0.89, respectively. Cl- had a weak correlation of 0.52 with SO_4^-. The TDS is associated with the presence of dissolved Cl^-, SO_4^{2-}, HCO_3^-, and CO [15], which could be the reason for high correlation between TDS and the ion parameters. Also, it shows that these parameters may vary positively. The high correlation of SO_4^- with NO_2^- and Cl^- with Free CO_2 and NO_2^- depicted that they were from the same sources. According to Fahimeh and Azadeh (2017), they may ascend together.

Four significant factors were generated, using Factor Analysis. Factor 1 correlated with TDS and EC and indirectly with acidity.

Factor 3 correlated with Free CO_2 and indirectly with NO_2^-. Finally, Factor 4 correlated with SO_4^{2-} and indirectly with Cl^-. The total variance of Factor 1 in the variables was 32-34% for the two seasons while that of Factor 3 was 17%. The low percent of the factors suggested that the variability enrichment values could be due to the influence of anthropogenic (agricultural) activities on the rainwater samples.

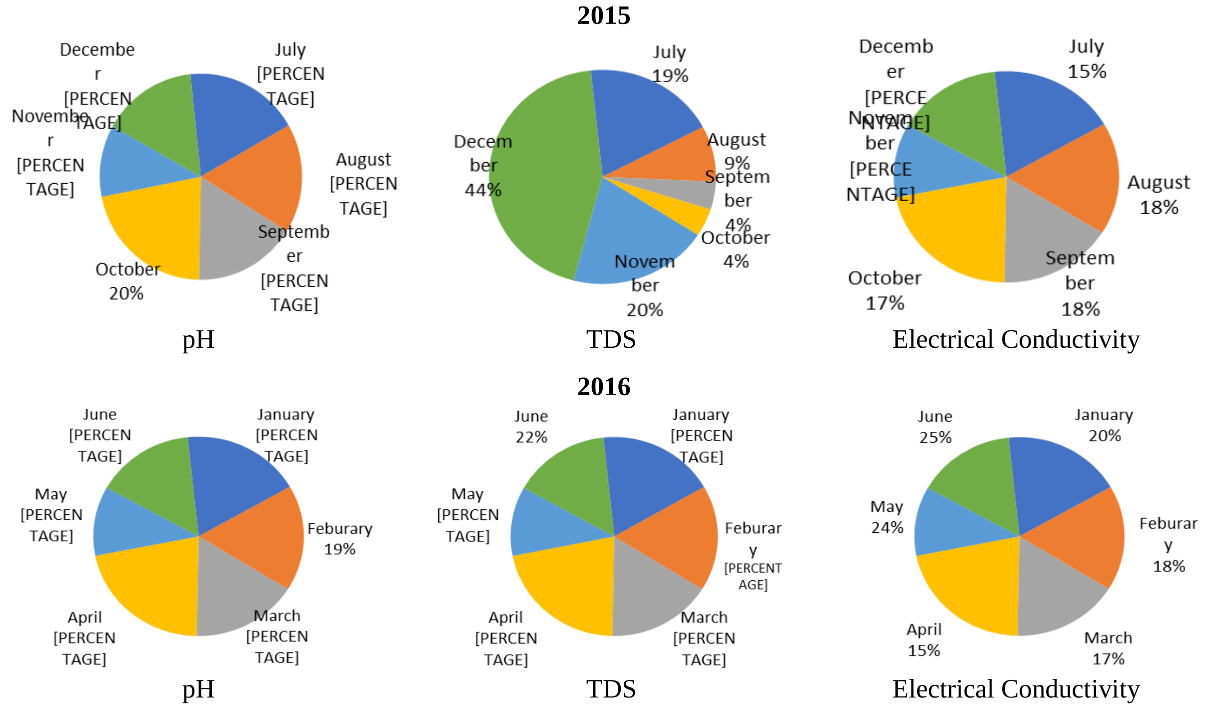

Fig. 3. Physico-chemical properties of pH, TDS, and Electrical Conductivity

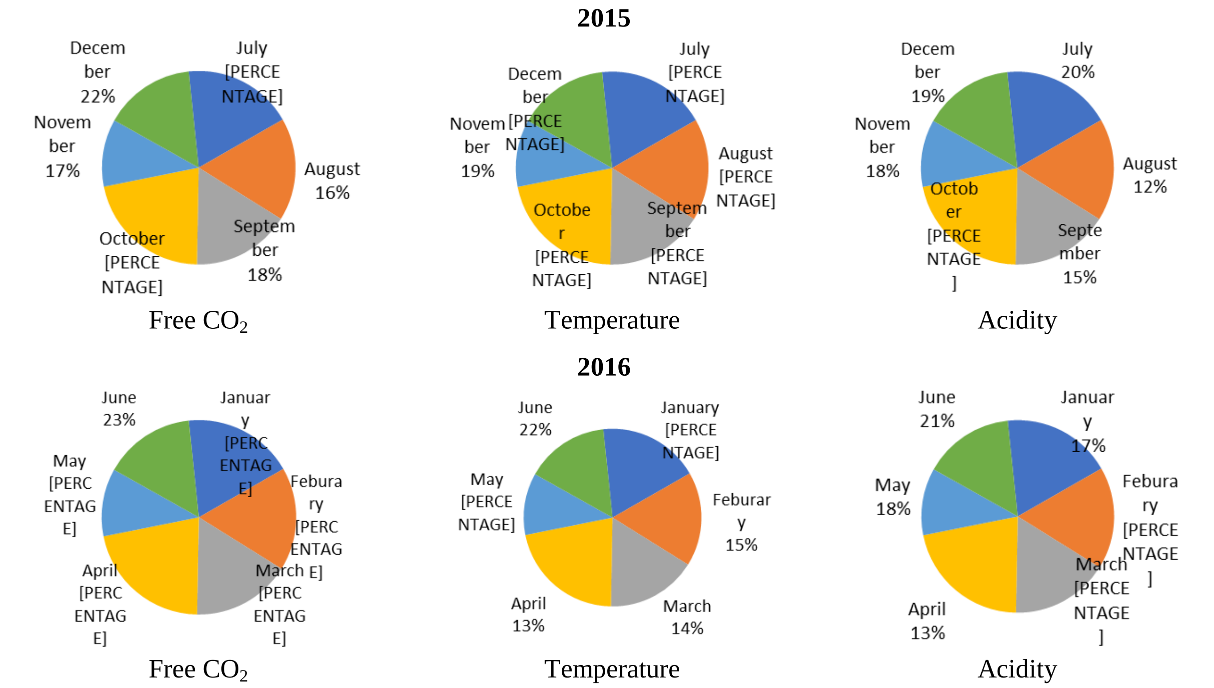

Fig. 4. Physico-chemical Properties of Free CO_2, Temperature, and Acidity

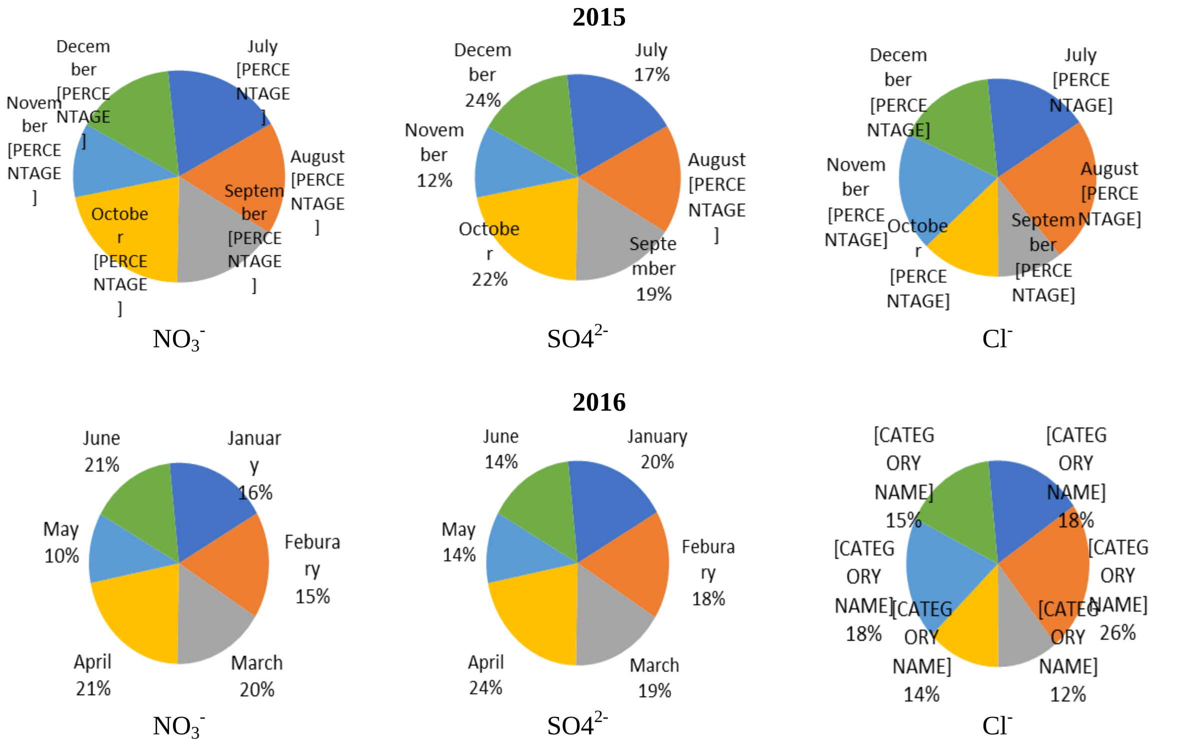

Fig. 5. Physico-chemical Properties of NO_3^-, SO_4^{2-}, and Cl^-

Table 1. Basic Description of the parameters

Parameters	Mean	Std Dev.	Coff Variation	Minimum	Maximum
			2015		
pH	6.58	0.80	12.21	6.00	7.60
TDS	15.83	14.43	91.12	4.00	84.00
EC	31.00	28.80	92.84	8.00	84.00
Free CO_2	23.00	6.16	26.80	16.00	32.00
Temperature	28.50	1.64	5.77	27.00	31.00
Acidity	278.3	25.10	9.03	235.00	304.00
NO_2^-	26.83	6.01	22.41	16.00	32.00
SO4^{2-}	49.50	9.01	18.19	39.00	60.00
Cl^-	17.00	5.48	32.22	10.00	24.00
			2016		
pH	7.10	0.49	6.90	6.50	7.80
TDS	36.20	39.50	109.09	1.00	100.00
EC	76.70	81.90	109.89	3.00	201.00
Free CO_2	20.33	2.94	14.48	16.00	24.00
Temperature	28.50	1.05	3.68	27.00	30.00
Acidity	263.70	33.50	12.72	220.00	301.00
NO_2^-	21.67	5.28	24.36	14.00	28.00
SO4^{2-}	68.00	13.96	20.53	46.00	88.00
Cl^-	15.50	4.28	27.60	10.00	22.00

Units of Parameters: EC (μS/cm), Temp (^oC), TDS – (mg/L), Free $CO_{2\,-}$ (mg/L), Acidity (mg/L), NO_3^- $_{(}$μg/m^3), SO4^{2-} (μg/m^3), Cl^- (μg/m^3).

Table 2. Comparison of Current Study with other Researches and International Standards

S/N	pH	EC (µS/cm)	Temp (^0C)	TDS (mg/L)	Free CO_2 (mg/L)	Acidity (mg/L)	NO_3^- (µg/m^3)	$SO4^{2-}$ (µg/m^3)	Cl^- (µg/m^3)	References
1	6.0-7.8	3-201	27-31	1-100	16-32	220-304	14-32	39-88	10-22	This Study
2	7.3-7.5	310-461	24.3-27.4	-	-	-	7-60	-	-	Abulude et al., (2006)
3	5.6-6.9	4.0-56.0	-	-	-	-	17-38.5	-	-	Del Rosario and Palmes (2011)
4	6.4-7.0	50-187.8	-	-	-	-	0.9-2.6	7.8-19	2.3-3.5	Benrejdal et al., (2017)
5	4.3-6.9	3.4-35.2	-	-	-	-	3.4-72.7	4.3-39.8	5.8-45.9	Cerqueira et al., (2014)
6	5.6-6.4	91.42	-	-	-	-	26-50.6	39-91.6	-	Rao et al., (2016)
7	-	-	-	-	-	-	30.32	145.53	27.92	Alahmr et al., (2012)
8	6.4-6.8	35.2-43.5	28.7-29.2	22.31	-	-	0.2-0.25	0.2-0.3	-	Olowoyo (2011)
9	4.0-5.6	7.15-59.6	-	6.8-24.1	-	-	0.1-0.11	8.9-11.0	3.2-6.2	Akoto et al., (2011)
10	5.4-7.6	140-279	-	79.1-187	21.25	45-66	-	18-47	5.6-17.1	Subramani & Devaanandan (2015)
11	6.5-8.5	1000	Ambient	500	-	-	-	-	250	SON (2007)
12	6.5-8.5	250	25	500	-	-	-	-	250	EU (1988)
13	7.5-8.5	-	-	500-2000	-	-	45	200-400	-	WHO (1984)

Table 3. Correlation Matrix of Rainwater Samples

	July-December 2015								January-June 2016							
	pH	TDS	EC	Free CO_2	Temp	Acidity	NO_2^-	SO_4^-	pH	TDS	EC	Free CO_2	Temp	Acidity	NO_2^-	SO_4^-
TDS																
	0.53	1							0.887	1						
EC																
	0.501	0.000	1						0.894	0.000	1					
Free CO_2																
	0.142	0.348	0.352	1					0.054	0.704	0.706	1				
Temp																
	0.018	0.137	0.121	0.592	1				0.496	0.175	0.140	0.712	1			
Acidity																
	0.711	0.105	0.103	0.252	0.693	1			0.441	0.147	0.150	0.937	0.889	1		
NO_2^-																
	0.964	0.344	0.318	0.268	0.763	0.961	1		0.793	0.374	0.373	0.708	0.132	0.792	1	
SO_4^-																
	0.546	0.163	0.142	0.388	0.680	0.162	0.836	1	0.223	0.737	0.713	0.912	0.490	0.119	0.277	1
Cl-																
	0.254	0.238	0.256	0.613	0.075	0.436	0.729	0.647	0.225	0.191	0.205	0.252	0.206	0.495	0.150	0.516

Table 4. Factor Analysis of Samples (July – December 2015)

Variable	Factor1	Factor2	Factor3	Factor4	Communality
pH	0.048	-0.894	-0.192	0.036	0.840
TDS	**0.920**	-0.269	0.127	-0.060	0.938
EC	**0.922**	-0.287	0.136	-0.037	0.952
Free Co2	-0.320	0.279	**0.720**	-0.124	0.714
Temp	0.217	-0.859	-0.015	-0.264	0.856
Acidity	-0.770	-0.368	0.363	0.057	0.864
NO2-	-0.286	-0.004	-0.844	-0.111	0.806
SO4-	0.547	-0.146	-0.252	**0.643**	0.797
Cl-	0.324	-0.335	-0.171	-0.810	0.902
Variance	2.9258	2.0393	1.5265	1.1759	7.6675
% Var	32	22	17	13	0.852

Table 5. Factor Analysis of Samples (January – June 2016)

Variable	Factor1	Factor2	Factor3	Factor4	Communality
pH	0.059	-0.856	-0.112	0.066	0.836
TDS	0.958	-0.265	0.125	-0.045	0.955
EC	0.972	-0.235	0.116	-0.047	0.962
Free Co2	-0.320	0.212	0.766	-0.124	0.737
Temp	0.217	-0.859	-0.015	-0.274	0.828
Acidity	-0.770	-0.268	0.473	0.057	0.879
NO2-	-0.186	-0.004	-0.821	-0.121	0.816
SO4-	0.566	-0.156	-0.233	0.643	0.768
Cl-	0.324	-0.327	-0.128	-0.710	0.912
Variance	2.9156	2.0355	1.5662	1.1557	7.6381
% Var	34	23	17	12	0.872

CONCLUSION

The present study was conducted between July, 2015, and June, 2016, including both rainy and dry seasons. Mean pH values of the samples were 6.58 (2015) and 7.01 (2016). The two mean pH values were not close to acid rain value of < 4.2, indicating that the area under the study did not experience acid rain during this study. The mean values (order of abundance) of the ions were as the following: $SO4^{2-} > NO_2^- > Cl^-$. The ions showed high correlation matrixes *r*, meaning they were from the same sources.

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