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Progressive Changes in Physico-chemical Constituent of Rainwater; a Case of Oyoko, Sekyere-East District of Ashanti Region, Ghana

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Abstract:
This study involves an experimental design where rainwater samples were collected progressively from a single point-source and analyzed with various scientific methods in accordance with standard procedures for analyzing physicochemical properties of water for drinking and for domestic use. The chemical and physical characteristics of rainwater harvested from a typical rooftop were progressively studied. The samples of rainwater collected were analyzed for pH, major ion concentrations, total dissolve solids (TDS), turbidity, and conductivity. As rainfall progresses, all these physico-chemical constituents fell within the world health organization (WHO 1998) guideline limits for drinking water at some point. Almost all the components of rainwater quality measured showed higher concentrations during the early stages of rainfall and reduce as time progresses. There was a downward trend in terms of pH as rain progressed, with 18% of the samples recording pH below the WHO lower limit of 6.5 from the 30 minutes sampling time. It was observed that iron concentration was above the WHO threshold value of 0.3 mg/l on occasions of heavy rains. However the mean monthly and progressive values were all below the WHO standards for drinking water. The results revealed that most of physicochemical characteristics of rainwater samples were generally below the WHO threshold, as such, the rainwater characteristics showed satisfactory conditions in terms of physicochemical constituents.

Keywords: *Conductivity, pH, Physico-chemical, Rainwater quality, and TDS.*

1. Introduction

Rainwater may be considered droplets of fresh water that have condensed from atmospheric water vapour and fall as precipitation from clouds. Water drops larger than 0.5 mm diameter is classified as raindrop, whereas smaller drops below 0.5 mm diameter may be considered as drizzle (Met, 2011). Rainwater acquires its salinity and bacteriological composition partly as it passes through the atmosphere by dissolving air-borne particulates and water soluble gases and also incorporating airborne microbes (Olobaniyi and Efi, 2007). According to Mohammad (2003), the chemical analysis of rainwater shows that the particulate materials from land sources, especially agricultural chemicals considerably impact the general composition of atmospheric moisture. With the increasing world population and its associated demand for water; rainwater has become an alternative source of water supply. The collection of rainwater is appropriate where there is enough rain and traditional water resources either do not exist or are at the risk of being over-used to supply large population. Rainwater serves as a major source of drinking water in rural areas and some urban areas in Ghana (MWR W&H, 2011; and Siabi *et al*., 2008). The opportunities and problems pertaining to harvesting and using rainwater is therefore an important issue to communities and water supply companies.

Mostly, studies on the quality of water resources in tropical African environment have largely been restricted to surface and groundwater to the negligence of rainwater (Ogunkoya and Efi, 2003; Olobaniyi and Owoyemi, 2004). This is due to the assumption that rainwater is usually pure and therefore needs very little investigation. However, likelihood pollutant additions to roof runoff such as inert solids, trace metals, and faecal deposits from birds, insects and climbing animals cannot be overlooked. According to Forster (1996) and Rasid and Rahman (2009), atmospheric deposition, surrounding environmental conditions with regards to proximity to industrial areas, as well as, type of roof material highly influence the quality of rainwater. There is therefore the possibility that rainwater becomes polluted and hence the need to place rainwater quality under scrutiny.

Potential health risks from ingestion of rainwater may results from microbiological or chemical contamination. The nature of microbiological risks is likely to be similar in urban and rural settings, however, for chemical contaminants there may be significant differences between urban and rural areas. In urban areas greater influence of traffic emissions and industrial pollution would be expected relative to the rural areas, while in the rural areas there may be potential for pollution by agricultural chemicals such as pesticides, herbicides and fertilizers. The vulnerability of rainwater to quality degradation from human activities makes its periodic assessment necessary. It is known that from the onset of rain, rainwater is visibly dirty making it less attractive for domestic use such as drinking and cooking. Despite the various levels of contaminants in rainwater people are forced to use it probably because in certain communities, there are no alternatives. During the first stages of rain these contaminants are washed off from rooftops and depending on the intensity of rain the clarity of the water improves with time by visual inspection. It is however not clear whether parameters such as conductivity, total dissolve solids (TDS), suspended solids, acidity, ionic concentrations (Nitrate, nitrites, sulphate, and iron) and bacteriological composition also improve as rain progresses within any particular rain event. The primary focus of this paper is to examine progressive changes that occur in physico-chemical constituent of rainfall as rain progresses within a given rain-event in a typical (rural) environment.

2. Material and Methods

2.1. Study Area

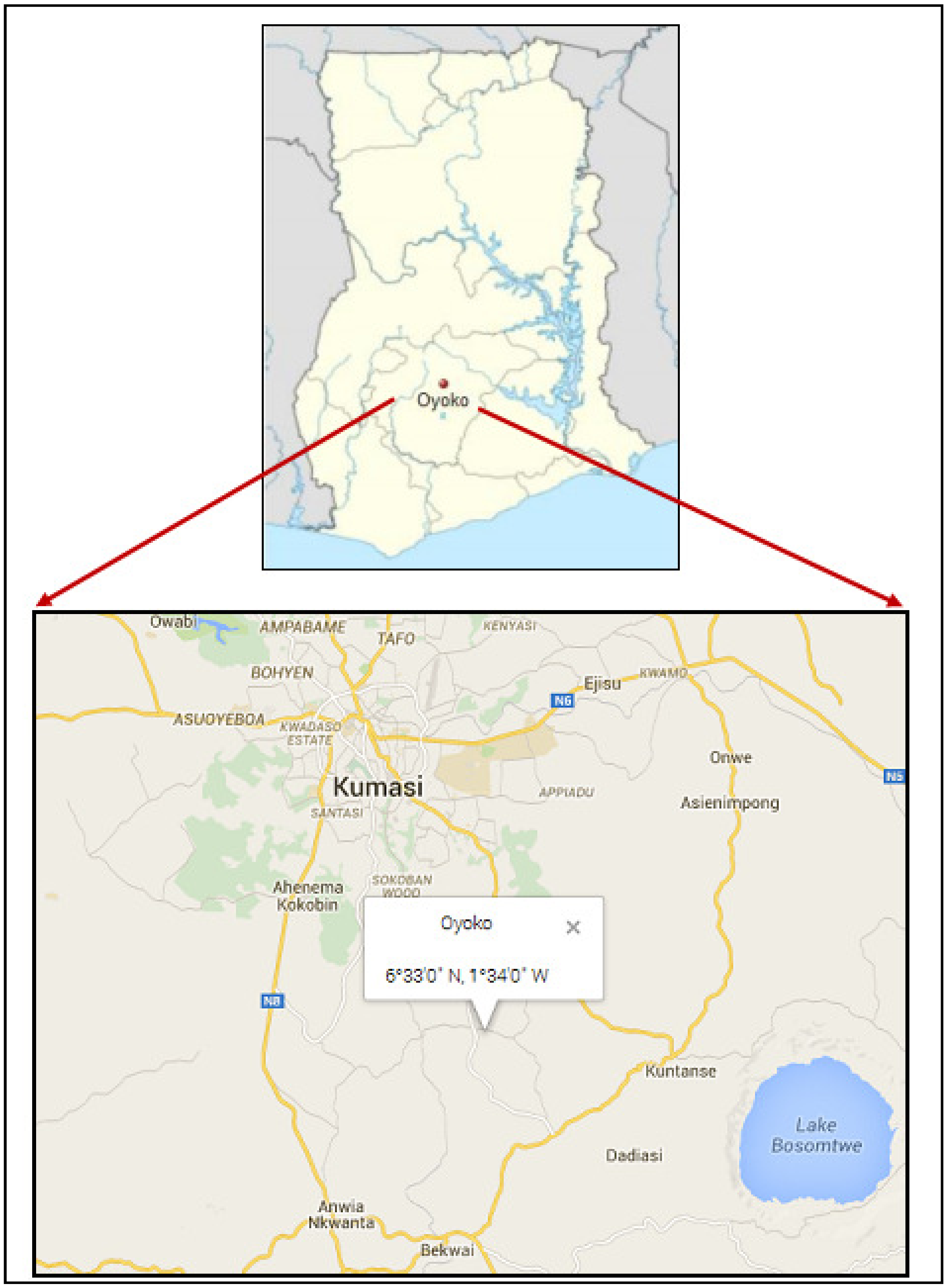

Figure 1: Oyoko rural community in the Sekyere-East District of Ashanti Region of Ghana

The study area (Fig. 1) Oyoko, is a rural community in the Sekyere-East District of Ashanti Region of Ghana. It is located at an elevation of 228 meters above sea level, approximately at coordinates 6°33'0" N and 1°34'0" W. The area is within a region which has an average annual rainfall of 1270 mm with two rainy seasons. The major rainy season starts in March, which intensifies in May. It slightly dip in July and a pick in August, tapering off in November. December to February is considered dry, hot, and dusty. The area has intensive agricultural land use where commercial fertilizers and manure are routinely applied to the field. The expected chemical pollutants in the environment are mainly that from fertilizers, pesticides, herbicides etc.
A typical rural area like Oyoko has no reliable water supply network and as a result, some residents at times are forced to compete with animals regarding surface water for domestic use. Due to this and more importantly, in the rainy season, rainwater is traditionally used by the rural folks for drinking and for domestic purposes. With population estimate of 5000, only four boreholes exist in the area (by the time of the research) so rainwater harvesting is the main practice being followed to cover the growing water needs. What is evident in the community is the long queues always seen (Fig. 2a) at all borehole sites days without rainfall or when their harvested rainwater in their respective homes has been exhausted. It is however obvious to observe almost empty scenes (Fig. 2b) at this same borehole sites immediately or a day after rainfall during water-fetching hours. Most often, water fetching is done in two periods; in the morning hours of 4:00-8:00 am and in the evening hours of 4:00-7:00 pm. These long weary hours used in fetching water for domestic use affect the women and children in the Oyoko community since the activity is mostly carried by them.

2.2. Project Design and Sampling
The study involves an experimental design where rainwater samples were collected progressively from a single point source as shown in fig 3 and analyzed with various scientific methods in accordance with standard procedure for examination of physicochemical properties of water and wastewater.

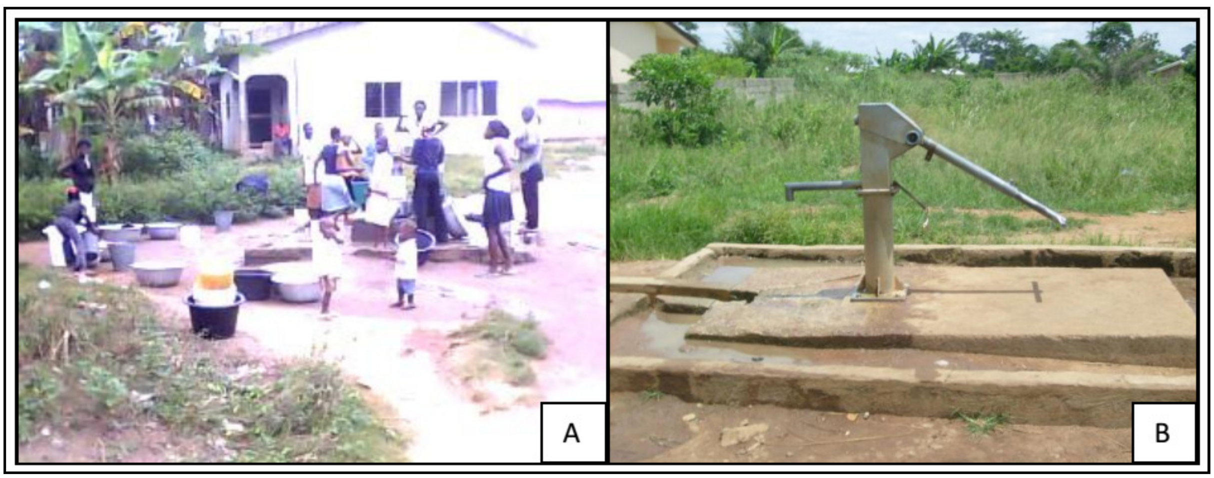

Figure 2: Scene at a borehole sites in the Oyoko community

2.3. Rain Water Sampling and Analysis
A total of 168 replicate samples of rainwater were collected at least once every month from December to August for a period of nine months. The sampling and storage material includes; plastic bottles (300 ml and 1500 ml), a 2 litre plastic container and a funnel. Before each sampling, all the materials were washed with soap and thoroughly rinsed to prevent cross-contamination. Subsequently, they were sterilized with iso-butanol after which distilled-deionized water was then used to rinse them for three consecutive times. These steps were to ensure that collected water samples were true representative of what to be examined and that no accidental contaminations occur during sampling.
Two field workers were involved in the collection and storage of the water samples, of which one was responsible for collecting the rainwater from the roof gutter using a hand basin (Fig.3), and subsequently pouring it into labeled plastic bottles with the help of the funnel. Whiles with close monitoring and observation, the second field worker uses the stopwatch to record the timing process. The first sample was taken six minutes from the onset of the rain and after every six minutes sampling was done for seven repeated times after which the temperatures were recorded and before the water poured into the cleaned labeled bottles.
The process was repeated 7 times for each precipitation event. The samples were then stored in an ice bag container between 2-8 ^{o}C and transported to the laboratory in accordance with ISO/IEC, 2005. Without any special preservatives, samples were stored in a refrigerator in situations where laboratory analyses were not done same day of sample collection. In all 168 replicate samples were collected in twelve precipitation events. The collection surface was an already existing rooftop made of galvanized iron sheet but the conveyance medium was an opened gutter constructed just at the beginning of the project using galvanized iron sheet as shown in fig.3. During the design of the project it was noted that a higher percentage (about 90%) of the conveyance systems used in the community were open gutters. It was also realized that a higher percentage (85%) of roofing material in the community were iron sheets.

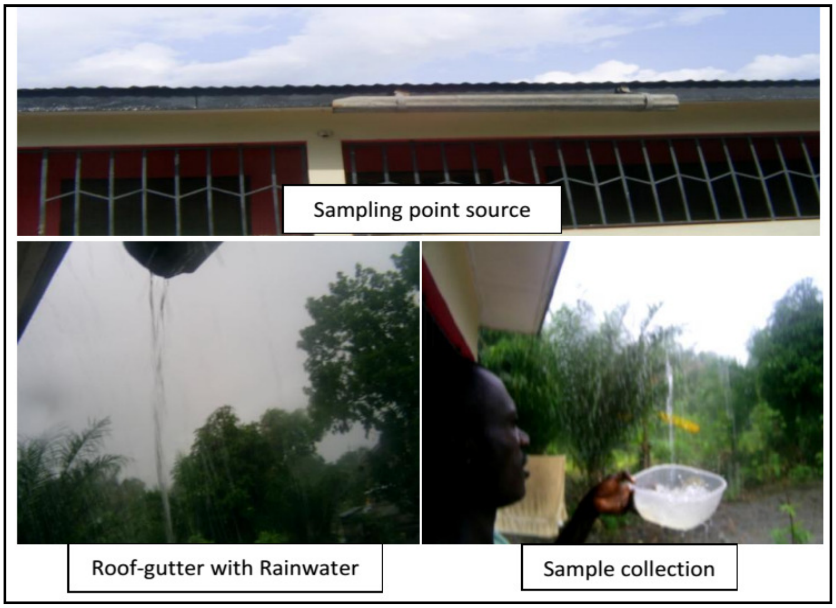

Figure 3: showing sampling point source and rainwater collection through roof gutter

2.4. Physico-chemical constituent analyses

The 168 replicate samples were analyzed for six ions (nitrate, nitrite, sulphate, phosphate, chloride and iron) and physical parameters including *p*H, electrical conductivity, turbidity and total dissolved solids (TDS) using standard procedures of AWWA (1990) and APHA (1992).

2.4.1. Physical Analysis

With the Physico-chemical analysis, distilled-deionized water was used in all preparations and analyses. All the reagents and chemicals used (reagent powder pillows, $KCrO_4$ indicator, Silver Nitrate, EDTA NH_4-NH_4OH buffer, Eriochrome Black T indicator) were of analytical grade.

The electrical conductivity and total dissolved solids (TDS) were measured using a digital WTWcond303i- conductivity meter, which is a bench combined conductivity/TDS meter which measures values between 0.001 and 1000 µS/cm. Turbidity (NTU) of the water samples were measured using a potable turbidity meter (NEPHLA-EA turbidimeter), capable of measuring values from 0.001 to 500 NTU whereas, a digital *p*H meter (WTWPH323 pH meter) was used to measure the *p*H of the sampled water which was calibrated in buffer solutions of *p*H 7 and 10.

2.4.2. Chemical Analysis

For the chemical analysis, except for chloride (which was determined by argentometric titration), the methods used for the determination of all the ions (nitrite, nitrate, sulphate, phosphate, total iron) were similar in terms of procedure and standards, using a testing equipment of the data logging Hach DR/2010 spectrophotometer. The 10 ml of each sample was mixed with the reagent (powder pillow) and then placed in cell holders, after which the "Read" button on the equipment is pressed subsequent to the screen-displays allowed to stabilize to record the concentration values in mg/l and procedure repeated for remaining ions.

2.4.2.1. Chloride test

Using titrimetric methods, 100ml of water sample was measured into a conical flask and 1 ml of potassium chromate ($KrCO_4$) solution added as an indicator. However, for highly coloured and turbid water samples, 3 ml Al $(OH)_3$ is added, allowed to settle and then filtered prior to the addition of the indicator. The mixture (in conical flask) was then titrated directly against silver nitrate ($AgNO_3$). The end point was indicated by the solution changing from yellowish to pinkish-red. The same procedure was carried out for distilled water as blank. The whole process was repeated for the other samples and results calculated and tabulated.

2.5 Statistical Analysis

Descriptive and inferential statistical analyses were employed for the obtained data. The mean, range, standard deviation and ANOVA were determined. The parameters (Physico-chemical) were tested for any significant difference at all levels of the rain event.

3. Results and Discussions

Mean values of Physicochemical parameters measured for the rainwater samples collected for each month for the entire study period of the study were computed from the results obtained and presented as shown in table 1. These mean values of the parameters were measured progressively for different rain events at six (6) minutes time- interval.

3.1. Physical Variations

Turbidity (NTU) of the rainwater samples collected for 12 precipitation events at six (6) minutes time-interval was determined and the average values presented in table 2. Graphical representation of the effect of turbidity, TDS and electrical conductivity (EC) with time is presented as fig.7. However, all the parameters showed similar characteristics, where values decreased sharply within the first 12 minutes of rainfall and gradually decreases afterwards with the length of duration for all precipitation events monitored. It was also observed that all turbidity values obtained fell outside the WHO acceptable limit of 5 NTU.

Physico-chemical Parameter	Months									Limits (**WHO)
	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	
*p*H value	5.55	5.91	6.32	6.3	6.93	6.04	6.43	5.43	5.38	6.5-8.5
Conductivity(μS/cm)	26.2	50.8	34.3	20.1	14.7	8.3	4.6	5.4	5.5	500
Turbidity (*NTU)	10.65	33.92	32.07	15.12	3.33	4.17	5.62	3.87	2	5
TDS (mg/l)	20.9	31.7	28.9	16.8	11.9	4.9	3.9	4.7	5.2	1000
Chloride (mg/l)	6.9	3.54	6.45	5.19	2.33	4.15	3.02	4.27	4.5	250
Nitrate (mg/l)	0.92	1.54	1.08	0.57	0.44	0.31	0.59	0.42	0.6	10
Nitrite (mg/l)	0.0042	0.0033	0.023	0.0105	0.0074	0.0109	0.0041	0.0052	0.002	0.1
Sulphate (mg/l)	0.4	4.0	3.9	1.4	1.0	13.7	9.5	1.7	1.0	250
Phosphate (mg/l)	0.20	1.53	0.99	0.50	0.18	0.25	0.24	0.32	0.35	2.5
Iron (mg/l)	0.043	0.063	0.045	0.039	0.047	0.171	0.171	0.171	0.054	0.3

Table 1: Mean monthly values of Physico-chemical constituents of rainwater Quality
**Nephelometric Turbidity Units*
***World Health Organization (WHO) International Standard for Drinking Water (1998)*

Generally, turbidity improves only after 30 minutes from the onset of rain. This higher level of rainwater turbidity during the rain event, as time progressed, may be due to the washing away of dirt and other particulate matter on rooftop and roof catchment including the roof gutter as rain progresses. Turbidity in rainwater is directly related to materials deposited on the roof. Nevertheless, the ANOVA test revealed that this decrease is significant at all levels of the rain event ($p<0.005$).

Physico-chemical Parameter	Sampling Time (min)						
	6	12	18	24	30	36	42
pH	6.25	6.15	6.16	6.1	5.97	5.97	5.98
Conductivity(μS/cm)	26.6	16.4	14.6	12.6	18.7	17.5	17.8
Turbidity (*NTU)	21.66	12.98	10.16	7.36	8.34	11.67	5.61
TDS (mg/l)	19.4	13.7	11.6	10.6	11.5	13.3	12.2
Chloride (mg/l)	5.7	4.4	3.4	1.8	2.8	4.6	6.9
Nitrate (mg/l)	1.65	0.68	0.36	0.48	0.45	0.5	0.42
Nitrite (mg/l)	0.018	0.012	0.011	0.015	0.007	0.006	0.007
Sulphate (mg/l)	4.2	1.5	3.7	5.8	6.7	3.7	5.3
Phosphate (mg/l)	0.65	0.33	0.49	0.45	0.39	0.46	0.42
Iron (mg/l)	0.054	0.011	0.1	0.077	0.05	0.061	0.053

Table 2: Progressive changes in Physico-chemical constituent
**Nephelometric Turbidity Units*

Both the TDS and EC decreased with increasing time of precipitation (Fig. 4) and both values fell within WHO acceptable limit of 1000 mg/L and 500 µS/cm respectively. The much improved TDS and conductivity values recorded progressively with time reflect the significant rate at which rainfall wash particulate matter from the roof catchment and the atmosphere. It was statistically found that both TDS and conductivity values obtained during the study period were significantly different at different times during precipitation ($p<0.001$).

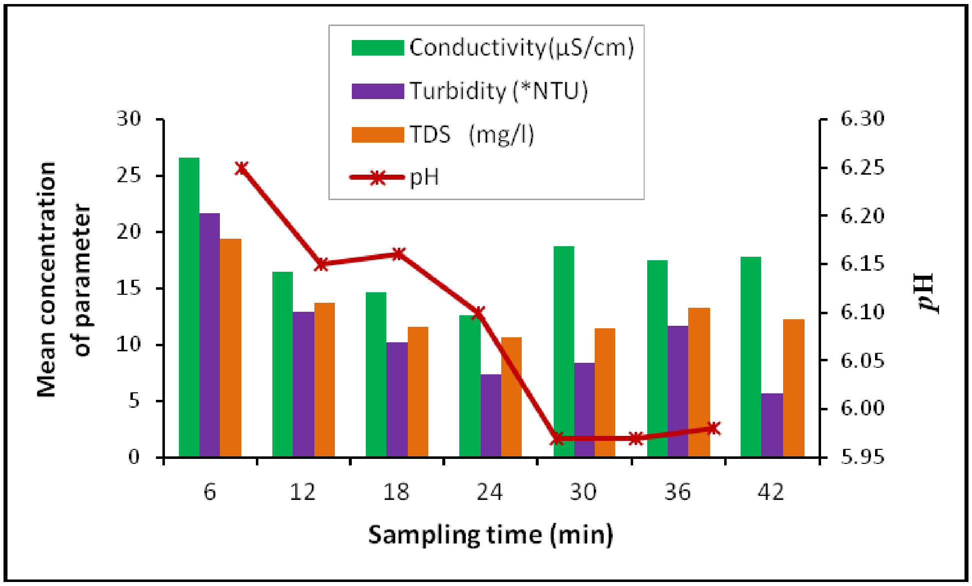

Figure 4: Trends of selected physical parameters during rain event

The *p*H values of rainwater varied throughout the rain events and progressively decreased as shown in fig. 4 above. Out of the 168 samples progressively collected at the 6 minutes interval, only 30 samples (17.8%) fell within WHO limit of 6.5-8 whilst the rest fell below the 6.5 value. The acidity in rain increased with increased in precipitation as the *p*H values decreases (Fig. 4). Most of the samples with low *p*H were those collected 30 minutes from the onset of rainfall with the least value of 5.19 collected on the 42nd minute in the month of August. As rain progresses, the sampled rainwater measured a normal *p*H value (around 5.5-6.5). The trend in acidity may also be accounted for largely by the presence of sulphric acid (H_2SO_4) in rainwater. This is because there was a direct correlation between SO_4^{2-} and *p*H values. However, the study could not ascertain which specific contaminant accounted for this trend. There was no strong relation between *p*H and intensity of rain. Statistically, there was significant change in the acidity ($p< 0.005$) from the 6th to the 30th minute of rainfall.

3.2. Chemical Variations

For the ionic compositions, results of the ions (nitrate, nitrite, sulphate, iron, phosphate and chloride) analyzed in this study (tables 1 and 2) showed that all the ions analyzed in this study showed higher concentrations at the initial rains collected for each rain event.

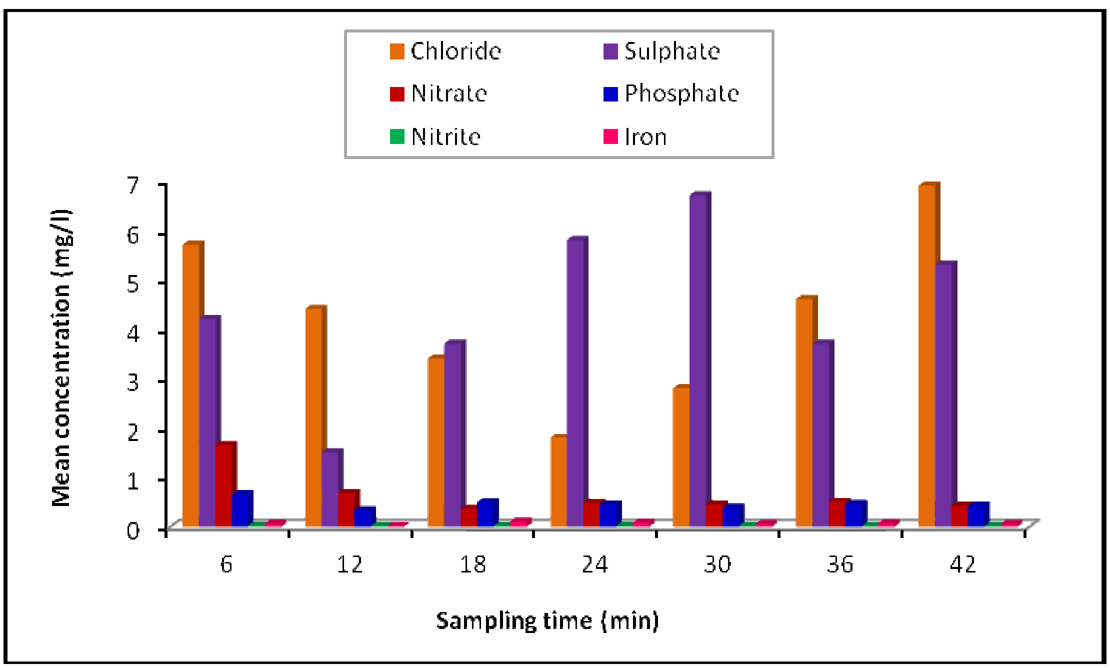

Figure 5: Trends in some selected chemical constituents as rain progresses

The nitrate and nitrite concentration ranged from 0.31 - 1.54 mg/l and 0.002 - 0.023 mg/l respectively, which were below the WHO limits of 10 mg/l and 0.1 mg/l respectively. However, the initial high concentration of nitrate (Fig. 5) may be attributed to forest fires and farm-based fertilizers during dry seasons as stated by Cerón *et al*., 2002. According to Cerón *et al*., 2002, forest fires emit nitrogen oxides that rapidly are converted to HNO_3 and in agricultural areas, nitrogen-based fertilizers are a major source of nitrate contamination for drinking water.

Chloride showed higher concentration at initial stages of rain, low concentration as rain progressed but higher concentration at the later stages of rain (Fig. 5). However, some mean concentration values of irons decreased to low values in the later part of the rain (Fig. 5). According to Sigg *et al*., 1987 and Daifullah and Shakour, 2003 chloride ion originates from anthropogenic activities such as refuse incineration which produces and releases *HCl* in gas phase into the atmosphere.

The Sulphate, unlike Chloride, showed relatively lower concentration at initial stages of rain, but subsequently showed higher concentrations as rain progressed and decreased at the last six (6) minutes of rain (Fig. 5). Daifullah and Shakour, 2003 reported that sulphate constitutes the major anion component in rainwater. It is generally accepted that sulphate is formed in the atmosphere by the chemical conversion from SO_2 (Harrison and De Mora, 2002), which is discharged into the atmosphere from natural and anthropogenic sources.

It is important to note that all the values obtained for the ions were within the WHO threshold limit values. The initial high concentrations observed are attributed to dissolution of atmospheric deposits and dry deposits previously collected on the roof catchment. The total ionic contribution to the rainwater samples by this process can be related linearly to the length of the dry period preceding the storm. According to the ANOVA test, all the major ions showed significant variations in the first 6 minutes of rain, insignificant changes thereafter and significant variation also after the next 36 minutes. The irregular trend of sulphate and chloride observed could not be accounted for in this study.

4. Conclusion

The Physico-chemical quality of harvested rainwater in the Oyoko community is considered of good quality as of the time of the research. Results of the progressive monitoring of rainwater revealed that all ions analyzed in this study, except for iron, were within the WHO threshold limit values for drinking water. Of the 168 samples tested for pH, 81.5% failed to meet the WHO standard for drinking water. These results obtained for the pH suggested an acidic sampled rainwater which is considered normal according to the WHO standards since pH of normal rainwater is in the range 5.5-6.5. It was further revealed from the study that, for few occasions of heavy rainfall (intensity of >7mm/h), iron concentration range between 0.3-0.8 mg/l which is above the WHO limit of 0.3mg/l.

The outcome of the study revealed that parameters such as turbidity, conductivity and TDS concentrations drastically reduced during first stages of rainfall but increased as rain progresses. The research further revealed that, there are seasonal variations in all of the physical parameters analyzed for the two major seasons (dry and wet). Also, the results revealed that most Physico-chemical characteristics of rainwater samples were generally within the WHO threshold limit at all times during rain event with few exceptions. Iron concentration at high intensity fell outside the WHO drinking water requirements whereas, pH values decreased as rain progressed (to as low as 5.19). As such, the rainwater from the Oyoko community and its environs can be said to establish substandard concentrations with regards to pH and iron concentrations during rain events. However, with enough treatment (for pH and iron content), the rainwater from the rural community may be harvested and stored for human consumption and house-hold chores.

Due to the high concentration of iron recorded in the study, there is high propensity of rainfalls eroding surfaces of rusted iron roofing sheets into storage tanks. Therefore, it will be recommended not to use old galvanized iron sheet as roof catchment to harvest and store rainwater for drinking and cooking purposes, since the presence of iron in human tissues has adverse health effects. Also, more studies should be conducted on different types of roofing materials (apart from the iron roofing sheets) and locations to investigate the impact of roof catchment on rainwater quality and its effects on human consumption. To preclude possible chemical reactions that may occur within samples, all possible attempts should be made to analyze the sampled rainwater same day of collection without delay or refrigerate the remnant samples.

5. Acknowledgement

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