Progressive Changes in Physicochemical Constituent of Rainwater: A Case Study at Oyoko, a Rural Community in Ghana

J. O. Yeboah, K Aboraa, K. Kodom

***Abstract*—**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, TDS, turbidity, conductivity. All the Physicochemical constituents fell within the WHO guideline limits at some points as rainfall progresses except the pH. All the components of rainwater quality measured during the study 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 limit of 6.5-8.0. It was observed that iron concentration was above the WHO threshold value of 0.3 mg/l on occasions of heavy rains. 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, physicochemistry, rainwater quality, TDS.

I. INTRODUCTION

RAINWATER may be defined as drops of fresh water that fall as precipitation from clouds. Water drops larger than 0.5 mm diameter are classified as rain, whereas smaller drops below 0.5 mm diameter may be considered as drizzle.

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 [1]. According to [2], 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 related demand for water; rainwater has become another source of water supply. The collection of rainwater is suitable wherever there are enough rain and traditional water resources either do not exist or are at the risk of being over-used to supply the large population. Rainwater serves as a main source of drinking water in rural areas and some urban areas in Ghana. The opportunities and problems about harvesting and using rainwater are, therefore, an important issue to communities and the water supply companies.

Previous studies on the quality of water resources in tropical African environment have largely been restricted to surface and groundwater to the negligence of rainwater [3]. This is probably due to the supposition that rainwater is generally pure and, therefore, needs very little research.

The likelihood of birds and climbing animals defecating upon them cannot be overlooked. Roof materials, antecedent dry period and surrounding conditions influence the quality of rainwater [3]. There is, therefore, the possibility that rainwater becomes polluted and hence the need to place rainwater quality is under scrutiny.

Possible health risks from drinking of rainwater may result from microbiological or chemical contaminants in the water. The microbiological risks for intake of rainwater are likely to be similar in urban and rural environment, however for chemical contaminants there may be considerable differences between urban and rural areas. Within urban areas greater influence of traffic emissions and industrialized pollution would be expected compare to the rural areas, whereas in the rural areas there may be potential for pollution from agricultural chemicals such as pesticides, herbicides and fertilizers. The inclination of rainwater to quality degradation from anthropogenic sources 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 in Ghana, 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 dissolved solids, suspended solids, acidity, ionic concentrations, (Nitrate, nitrites, sulphate, iron, etc) and bacteriological composition also improve as rain progresses within any particular rain event.

The primary focus of this project was to examine progressive changes that occur in the physicochemical constituent of rainwater as rain progresses within a given rain event in a typical (rural) environment.

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II. Project Design and Methodology

A. Project Design

This study involves an experimental design where rainwater samples were collected progressively from a single point source shown as Fig. 1 and analyzed with various scientific methods by the standard methods for the examination of water and wastewater.

Fig. 1 Rainwater sample collection point

B. Study Area

The study area, Oyoko is a village in the Sekyere East District of Ashanti Region of Ghana. The area has an intensive agricultural land use where commercial fertilizers and manure are routinely applied to the field. The expected chemical pollutants will mainly be that from fertilizers, pesticides, herbicides, etc.

In a typical rural area like Oyoko, no reliable water supply network exists. People use surface water that is also used by animals. Rainwater is traditionally used in Oyoko for drinking and other domestic purposes. With population estimate of 5000, only four boreholes exist in the area, so rainwater harvesting is the main practice being followed to cover the growing water needs. It was evident that there were always long queues on all the borehole sites whenever rain did not fall for a day or two and absolutely no person at a borehole site for more than a day after rain has fallen. Most often, water fetching is done in two periods – early in the morning (4:00-8:00 am) and the evening (4:00- 7:00 pm). The fetching of water at Oyoko occupies long weary hours, most often for the women and children.

Fig. 2 People queuing to fetch water at a borehole site

C. Sampling

Sampling of rainwater was performed at least once every month from December, 2007 to August, 2008. Fig. 3 is a picture of rainwater falling from the roof gutter.

Fig. 3 Water falling from the roof gutter

The sampling and storage materials included; plastic bottles (300 ml and 1500 ml) a 2-litre plastic container and a funnel of the same material. Before every sampling, all the materials were thoroughly washed with soap and thoroughly rinsed. The materials were then sterilized with iso-butanol after which they were rinsed three times with distilled water. There were two persons involved in the collection and storage of the water samples. One was responsible for collecting the rainwater from the roof gutter with the help of the basin (shown in Fig. 4); and the pouring of the water into the plastic bottles with the help of the funnel whilst one took charge of the stopwatch used in timing the process. The first sample was taken six minutes from the onset of the rain. After every six minutes sampling was done for seven repeated times after which the temperatures were measured, recorded and the water poured into the sterilized bottles.

Fig. 4 Collection of water samples falling from the roof gutter

The process was repeated seven times for each precipitation event. The samples were then stored in an ice bag container between $\mathbf{2-8}$ °C and transported to the laboratory in accordance with [4]. The samples were stored in a refrigerator where appropriate (i.e if testing was not done same day). No special preservative was used. 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. 1.

During the design of the project, it was noted that a higher percentage (about 90%) of the conveyance systems used in the village were open gutters. It was also realized that a higher percentage (85%) of roofing material in the village were iron sheets. The use of open gutter and iron sheet for the project would, therefore, provide general information on the quality of collected rainwater in the village.

D.Measurement of Physicochemical Constituents

Using various methods such as argentometric method, simple titration and direct use of equipment such as the spectrophotometer, and pH meter, 168 replicate samples were analyzed for six ions and physical parameters. The ions analyzed included: nitrate, nitrite, sulphate, phosphate, chloride and iron. Other parameters determined are the pH, conductivity and turbidity.

Chemical Analysis: Except for chloride, the methods used for the determination of ions were similar in terms of procedure. The testing equipment is the data logging DR /2010 spectrophotometer.

*pH***:** The pH of samples was determined using WTWPH323 pH meter. The pH meter was calibrated in buffer solutions of pH 7 and 10 respectively. The cap of the meter was removed, and the meter turned on after which the electrode was rinsed with distilled water. A 50 ml of water sample was poured into a clean, dry beaker. The pH meter was directly dipped into the measured sample and stirred until the reading was stabilized. Once the reading stabilized, the pH value was recorded

Determination of Turbidity: This parameter was determined by the use of the digital instrument called NEPHLA-EA turbidimeter. It measured values from 0.001 to 500 NTU. Electrical Conductivity and TDS: Electrical Conductivity and TDS were measured using conductivity meter. This is a digital instrument that makes use of dry cells.

Determination of Chloride: Argentometric titration determined chloride content.

Fig. 5 Yellowish Colour of Kr_2CO_4.in solution

Fig. 6 Pinkish end point colour after titration

The cell and it content was placed into the cell holder, and the light shield closed**.** The read button was pressed, and the reading taken from the display and recorded The Turbid meter was calibrated with the 500 NTU, 100 NTU, 10 NTU, and 0.001 NTU standards.

It measures both conductivity and TDS. The instrument measures values between 0.001 and 1000 μS/cm. The cap of the meter was then removed, and the electrode rinsed in distilled water. The electrode was dipped into a beaker containing 50 ml of the sample whose conductivity was to be determined. The sample was then stirred gently for some few seconds. The display was allowed to stabilize, and the full reading recorded.

III. Results and Discussions

A. Inter -Intra Time Variation in Rainwater Quality

Rainwater was progressively sampled within several rain events at six minutes time interval, and the samples analyzed according to the standard methods for analysis of water for physicochemical parameters. The results for each parameter were recorded. Average values of parameters measured progressively for different rain events at 6minutes time interval were computed and recorded.

1. Physical Variations

a. Time Variations of Turbidity

Turbidity of rainwater collected from 12 precipitation events at six-minute time intervals was determined, and the average values presented in Table I. Graphical representation of the turbidity values versus time is presented as in Fig. 7. The turbidity values decreased sharply within the first 12 minutes from the onset of rain and then gradually decreased 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. Generally, turbidity improves only after 30 minutes from the onset of rain. The higher levels of rainwater turbidity as time progressed, during the rain event may be assigned to the washing away of the dirt particles on the rooftop and collection surface as rain progresses. Turbidity in rainwater is directly related to materials deposited on the roof. ANOVA test revealed that this decrease is significant at all levels of the rain event ($p<0.005$).

2. Conductivity and Total Dissolved Solids (TDS) Variations

The average values of total dissolved solids and conductivity measured during the entire study period are presented in Table I. A Graph of average values of these values was plotted against time and shown in Fig. 7. It was observed that both TDS and conductivity decreased with increasing time of precipitation, and both values fell within WHO acceptable limit. The much-improved TDS and conductivity values recorded progressively with time reflects the significant rate at which falling rain wash particulate matter that come into contact with the water. As water moves through the atmosphere, and then down the collection surface it picks up a variety of dissolved and particulate materials. It was statistically found that both TDS and conductivity values obtained during the study period were significantly different at different times during precipitation ($p<0.001$).

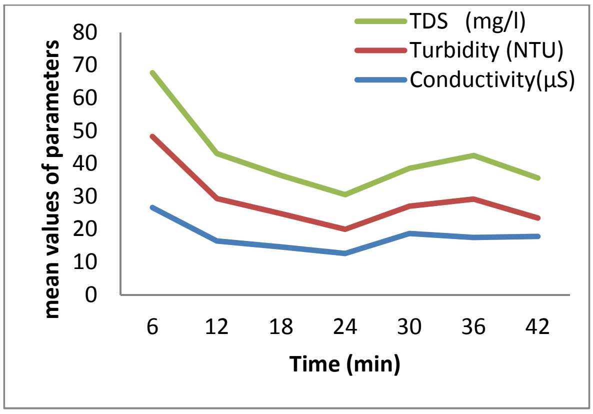

Fig. 7 Trends of selected physical parameters during rain event

3. Variations of chemical constituents

a. Ionic Compositions

Results of the ions (nitrate, nitrite, sulphate, phosphate iron and chloride) analyzed in this study can be found in Table I. Fig. 8 is a graph of average values of the ions plotted against time. All the ions analyzed in this study showed higher concentrations at the initial rains collected for each rain event.

Nitrate /nitrite: The initial high concentration of nitrate may be attributed to forest fire and farm-based fertilizer. Wind data analysis by [5] revealed that nitrate concentration depends on wind direction. From the analysis, concentration peaked when the wind blew, and it was higher when forest fire was spotted. Reference [5] concluded that forest fire must have been the main nitrate source during the dry period. They further explained that forest fire emit nitrogen oxide that rapidly are converted to HNO_3. In agricultural areas, nitrogen-based fertilizers are a major source of nitrate contamination for drinking water.

Chloride: Chloride showed higher concentration at initial stages of rain, low concentration as rain progressed but the higher concentration at the later stages of rain. According to [6], [8] chloride ion originates from human activities and may also result from refuse incineration such as PVC, which produces HCl in the gas phase. Chloride is measured in milligram per litre (mg/l)

Chloride is responsible for the brackish taste in water and is an indicator of sewage pollution. A high level of chloride content may harm metallic pipes, structures as well as growing plants [7]. Some ions decreased to low values in the later part of the rain (Fig. 8).

Sulphate: Sulphate just like Chloride showed higher concentration at initial stages of rain, low concentration as rain progressed but the higher concentration at the later stages of rain. Reference [8] reported that sulphate constitutes the major anion component in rainwater. Reference [9] stated in their report that it is accepted that sulphate is formed in the atmosphere by the chemical conversion of SO_2 which is discharged into the atmosphere from natural and anthropogenic sources.

Iron: It was revealed from the study that for very few occasions of heavy rain (intensity of >7mm/h), iron concentrations were in the range of 0.3-0.58 mg/l and were above the WHO guideline limit of 0.3mg/l. This indicates the ability of rain to erode the surface of rusted iron sheets into storage tanks. It is therefore recommended that rainwater user should not use an old galvanized iron sheet to collect rainwater that is intended for drinking and cooking since the presence of iron in the tissue has health effects on the eye.

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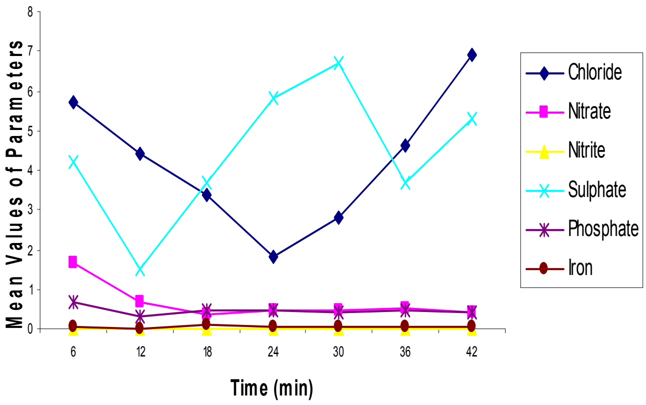

Fig. 8 Trends in some selected chemical constituents as rain progresses

4. Time variations of pH in rainwater

The pH values of rainwater varied throughout the rain events. The graph of pH versus time is shown in Fig. 8. Out of the 168 samples collected progressively at six minutes intervals only 30 samples (17.8%) fell within WHO range 6.5-8 while the rest fell below the 6.5. The acidity in rain increased with increased in precipitation (Fig. 8). Most of the samples with low pH were those collected 30 minutes from the onset of rain with the least pH (pH=5.19) collected in the 42nd minute in the month of August. August and December show low pH values, and this suggests that the acidity of rainwater is likely to be high from August to December though this study failed to cover the months of September, October, and November. The levels of pH during the initial stages of rain and subsequent reduction as the rain progressed may be due to the fact that there are always high levels of contaminant during the first stages of rain that influence the natural acidity of rainwater. As rain progresses, and these materials are washed off, rainwater assumes it normal pH level that is 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 pH values. However, the study could not ascertain which specific contaminant accounts for this trend in pH values. There was no strong relation between pH and intensity of the rain. A statistical analysis conducted showed a significant change in the acidity from the 6th to the 30th minute of rain ($p< 0.005$).

TABLE I
MEAN VALUES OF PHYSICOCHEMICAL CONSTITUENTS OF RAINWATER AS RAIN PROGRESSES

Parameters	Time (minutes)							Guideline
	6	12	18	24	30	36	42	
pH	6.25	6.15	6.16	6.1	5.97	5.97	5.98	6.5-8.5
Conductivity(µS)	26.6	16.4	14.6	12.6	18.7	17.5	17.8	500
Turbidity (NTU)	21.66	12.98	10.16	7.36	8.34	11.67	5.61	5
TDS (mg/l)	19.4	13.7	11.6	10.6	11.5	13.3	12.2	1000
Chloride (mg/l)	5.7	4.4	3.4	1.8	2.8	4.6	6.9	250
Nitrate (mg/l)	1.65	0.68	0.36	0.48	0.45	0.5	0.42	10
Nitrite (mg/l)	0.018	0.012	0.011	0.015	0.007	0.006	0.007	0.1
Sulphate (mg/l)	4.2	1.5	3.7	5.8	6.7	3.7	5.3	250
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	0.3

IV. CONCLUSION

Results of progressive monitoring of rainwater at Oyoko revealed that all ions analyzed in this study except iron were within the threshold values of the World Health Organization (WHO) for drinking water. Some pH values fell outside the WHO limit at some point during a rain event.

These results obtained for pH seems to suggest that rainwater is acidic, but this is normal since pH of normal rainwater is in the range of 5.5-6.5.

The outcome of the study revealed that physical parameters reduce drastically during first litres of rain with increased duration of rain, but ionic constituents reduce slightly. Iron at high intensity fell outside the WHO drinking water requirements, pH values decreased as rain progressed (to as low as 5.19). The high initial concentrations observed are attributed to the dissolution of atmospheric deposits and dry deposits previously collected on the collecting surface. 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. ANOVA test showed that all the major ions showed significant variation in the first 6 minutes of rain, insignificant changes after that 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. As such, the rainwater showed unsatisfactory concentrations in terms of pH and iron at Oyoko and its environs during rain events. However, rainwater from these rural communities may be harvested, stored for human consumption and for other uses by the inhabitants though some treatments are needed in terms of their pH and iron.

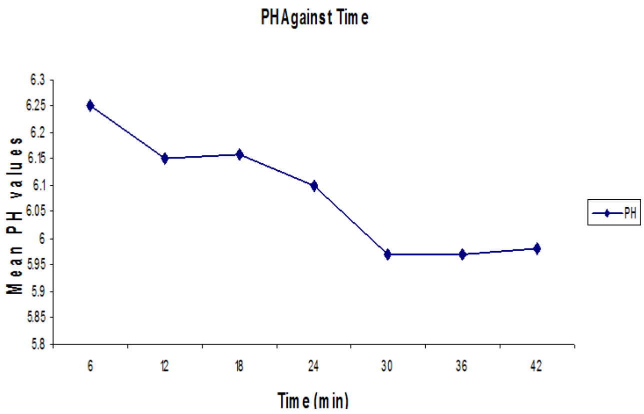

Fig. 9 pH of rainwater as rain progresses

REFERENCES

[1] Olobaniyi S B and Efe S I (2007), Comparative assessment of rainwater and groundwater quality in an oil producing area of Nigeria: environmental and health implications, (6) 2.
[2] Mohammad, Z. I, (2003), Impact of Atmospheric Aerosols on the Composition of Rainwater Leading To Ecosystem Damage in Northeastern Iowa, Department of Earth Science University of Northern Iowa Cedar Falls, Iowa 50614.
[3] Olobaniyi S B and Owoyemi, FB (2004). Quality of Groundwater in the Deltaic Plain Sands aquifer of Warri and environs, Delta State, Nigeria. Water Resources- Journal of the Nigerian Ass. Hydrogeologists, 15, 38-45.
[4] ISO/IEC, 17025 International Standard General requirements for the competence of testing and calibration laboratories, ISO/IEC 2005
[5] Ceron *et al* (1992), Chemical composition at the end of the mid – summer drought in the Caribbean shore of the Yucatan Peninsula. (4)4 pp6-13.
[6] Sigg L. Stumm, W. Zobrist, J. and Zurdren, F. (1987) The chemistry of log factors regulating its compositon. Chimia 41, 159- 165.

[7] Tebbutt, T H Y, (1983), Principles of water quality control, 3rd edition, Pergamon Press.
[8] Daifullah, A.A M, and Shakour, A.A (1998), Chemical composition of rainwater in Egypt. Electronic Version, (Accessed August 2008).

[9] Harrison, R.M and De Mora, S J (2002), Introductory chemistry for the Environmental Sciences 2nd edition. Cambridge University press.pp267-277.