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Levels of Inorganic Contaminants in Rainwater Samples Harvested from Different Rooftops in Uyo Metropolis, Akwa Ibom State, Nigeria.

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ABSTRACT
Rainwater samples were harvested from different rooftops within Uyo metropolis in the months of March and April being onset of the rainy season in the study area. Rainwater samples were also obtained directly from the atmosphere in the vicinity of each roof type and used as Control. These samples and Control were analyzed using atomic absorption spectrophotometer for their iron (Fe); zinc (Zn); cadmium (Cd); aluminium (Al); copper (Cu) and lead (Pb) contents. Results obtained indicated the following: Rainwater samples harvested from aluminium coated roof recorded levels of Zn and Al higher than their recommended limits for drinking water in Nigeria while the concentrations of other metals were within the acceptable limits. Samples obtained from asbestos roof recorded concentrations of Cd and Pb above the Nigerian standards for drinking water whereas the levels of Fe, Zn, Al and Cu recorded were within the acceptable limits. Concentrations of zinc recorded in rainwater samples harvested from zinc galvanized iron roof and zinc roofs were two and three times respectively higher than the Nigerian standard for Zn in drinking water.However, concentrations of other elements analyzed for in samples from both roofs were within their limits for drinking water. Copper roof samples recorded concentrations of Al and Cu above their recommended limits for drinking water while other metals under investigation recorded concentrations within the acceptable standards. Rainwater harvested from ceramic tiles roof recorded concentrations of these metals within the acceptable limits in drinking water by Nigerian standards. Results obtained in this study indicated that roofing materials may contribute substantial amounts of toxic metals to rainwater harvested from them and their concentrations could be influenced by where they are located. These results also indicated that drinking of rainwater harvested from metallic roofs might pose serious health risks to human.
Keywords: Rainwater, Rooftops, Inorganic contaminants, Uyo metropolis, Nigeria.

INTRODUCTION

Rainwater is one of the major sources of water available for man's household utilization nevertheless; its quality is rarely assessed and ascertained especially in the developing countries of the world. Rainwater is relatively free of contaminants except those picked up by rain from the atmosphere; however the quality of rainwater maybe affected during harvesting, storage and household use.

It has also been reported that, due to geographical difference and anthropogenic activities, rainfalls in various regions have their special characters. Even in the same region, synoptic situations and air-borne pollution scattering vary seasonally, resulting in large chemical in rainfalls [13, 38].

Atmospheric wet deposition has been reported as one of the most important pass ways transporting terrestrial natural and anthropogenic contaminants to land and aquatic environments [12]. Atmospheric deposition is also considered to be a major source of toxic metals such as Hg, Cd, Pb and several other trace metals to our ecosystem [8]. Reports by [17] have shown that the rainfall deposition of particles is about twice as great as the dry deposition whereas [33] suggested that at least for some trace metals, the particulate phase may dominate the bulk atmospheric deposition.

Studies by [42, 46] confirmed that roofing material is the major influencing factor on trace metal concentrations in rainwater. Also, contaminants in roof runoff come from three primary sources namely: dry deposition, wet deposition (rainfall) and weathering of the roofing materials. These contaminants have been reported to be higher in urban areas and in close vicinity to point sources such as busy roads, industrial establishments etc than in rural areas. Investigations have also shown that rainwater may contain some toxic metals, disease causing micro-organism, PAHs, pesticides and other toxic substances [11, 14, 16, 22, 23, 35, 43 and 45]. It has been estimated that 80% of ill-health in developing countries comes from lack of safe water and inadequate sanitation [51]. Rainwater cannot be said to be free from contamination, even when taken directly it is polluted by atmospheric pollutants and if taken from the roof it is contaminated as well, so rainwater is said to be unsafe to consume without treatment [54]. In oil

producing areas such as the one under study, there is high rate of rainwater contamination due to trace metals generated from oil exploration, gas flaring and gases from automobile emissions [27].

The composition of rainwater is greatly influenced by factors such as aerial emissions from industrial establishments, roofing materials, rainwater $P^{H,}$, length of dry season and shape of a roof [31, 41]. Studies have shown that, rainwater quality could also be affected by the frequency of rainfall, amount of water collected, quality of rainfall, human and animal activities in the surroundings [30]. According to [26] galvanized iron roofs tend to have high concentrations of zinc and cadmium in the runoff, whereas copper roofs and roofs with copper guttering have an elevated concentration of copper in the runoff. Roofing materials, paints and coatings are also suspected of being important sources of Cu and Pb as well. Roofs with Cu flashing were found to have copper and lead concentrations up to 6-8 times greater than galvanized roofs. Galvanized metal roofs have also been known to contribute more Zn and Cd to roof runoff compared to other roofs [35]. These metals in rainwater are known to come mostly from the rapid corrosion of galvanized metal roofs, gutters, flashings and the leaching of zinc.

In most urban areas, population is increasing rapidly so the supply of adequate water to meet societal needs and to ensure equity in access to water is one of the most urgent and significant challenges faced by the government of the day. Water security, like food security is becoming a major national and regional priority in many areas of the world, thus most people resort to the harvesting and utilization of roof runoff as their source of potable water. Considering the nature of our atmospheric environment where flue gases, pesticides and agrochemicals are being discharged into carelessly, it is expected that levels of toxic contaminants washed down by rainfall will be higher thereby reducing the quality of roof runoff harvested. It is obvious too that, most of the roofing materials used within the study area are metallic in nature and are completely corroded thereby exposing the rainwater harvested from them to high level of contamination. Wet deposition of trace metals remains poorly documented and there have been only limited studies on rainwater quality in Akwa Ibom region. This study is therefore aimed at assessing the levels of some toxic metals in rainwater harvested from different rooftops commonly used in Uyo metropolis (Akwa Ibom State capital). Results obtained from this study could be used to assess the impact of roofing materials on the quality of rainwater harvested from it and possibly educate the people of the state on the way forward.

Uyo (Fig.-1) covers over 2007 hectares of land and is located between latitude 5º 17' N - 5º 25' N and longitude 07º 3' E - 07º 58' E. Uyo, the capital of Akwa Ibom State, Nigeria has experienced an influx of people, high traffic, extensive human, commercial and industrial activities since the State creation on the 23rd September, 1987. This has caused serious anthropogenic contamination to the air, land and aquatic environments within Uyo and its environs. Also as a city within the Niger Delta region of Nigeria where high level of oil exploration and exploitation activities are being carried out, a periodic asessment of the environment should be promoted.

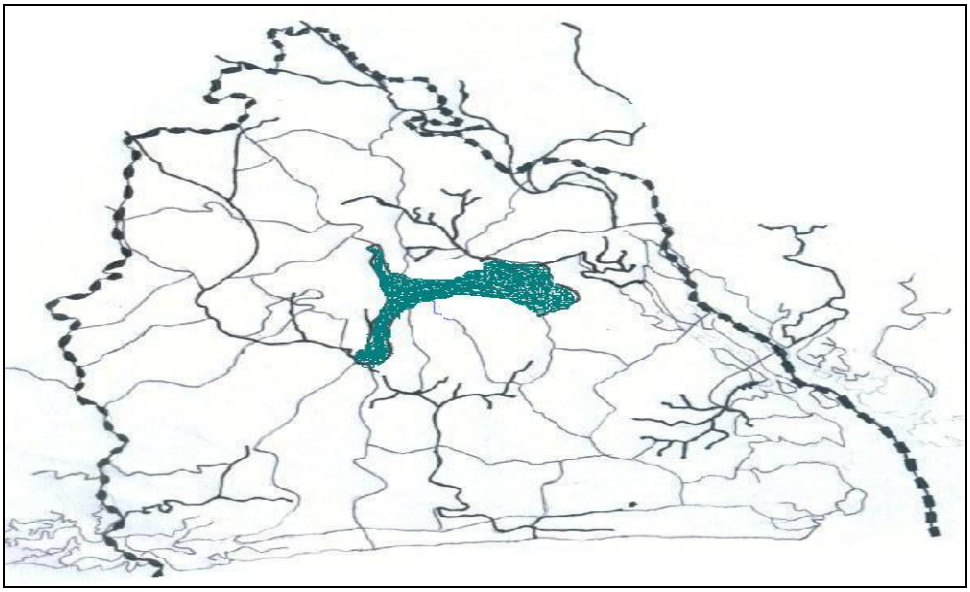

Fig.-1: Map of Akwa Ibom State showing Uyo, the study site

MATERIALS AND METHODS

Rainwater samples used in this study were harvested from different rooftops namely (aluminium coated, asbestos, zinc galvanized iron, Zinc, copper and Ceramic tiles) within Uyo metropolis in the months of March and April being

the onset of rainy season in the study area. Within the vicinity of each rooftop, rainwater samples were also collected directly from the atmosphere without any obstruction and used as Control for each rooftop type. All containers used for the collection of samples were pre-cleaned with 50% HNO_3 and deionized water. The rainwater samples were collected using standard procedures by [6, 50]. The rainwater sampler for samples from both rooftops and Control stations were equipped with a plastic funnel and a polyethylene plastic bucket attached to a narrow end. The samplers were fixed at a height of 1.5m above the ground [26]. Samples collected were filtered and to each 1liter of the sample, 1ml of concentrated HNO_3 was added and stored in a refrigerator at 4ºC prior to metal analysis [4, 12]. Samples were collected in triplicates from each location and a total of thirty six (36) samples were obtained from all the locations. Using atomic absorption spectrophotometer (AAS) Unicam 919 model the levels Fe, Zn, Cd, Al, Cu, and Pb were determined in both the rooftop samples and Control. This was done by the direct aspiration of the samples into an air acetylene flame of the machine [2, 4].

RESULTS AND DISCUSSION

Table-1 shows results for the concentrations (mg/l) of Fe; Zn; Cd; Al; Cu and Pb in rainwater samples harvested from different rooftops within Uyo metropolis, Akwa Ibom State, Nigeria. Table 2 indicates results for the concentrations (mg/l) of Fe; Zn; Cd; Al; Cu and Pb in rainwater samples from the Control sites.

The results in Table 1 has shown that, aluminium recorded the highest metal concentration (3.363mg/l) while cadmium had the lowest concentration of 0.004mg/l in rainwater sample harvested from aluminium coated roof. The high level of Al recorded here is in agreement with the report by [44] on the level of Al in rainwater sample harvested from the same roof.

Table-1: Mean Concentrations of Trace Metal (mg/l) in Rainwater Samples from Roof Tops.

Aluminium coated roof					
Fe	Zn	Cd	Al	Cu	Pb
0.112 ± 0.011	3.183 ± 0.010	0.002 ± 0.001	3.363±0.053	0.019±0.004	0.007±0.002
Asbestos roof					
0.089±0.011	0.063±0.005	0.005±0.001	0.013±0.004	0.008±0.001	0.015±0.003
Zinc galvanized iron roof					
0.062±0.006	7.348±0.003	0.008±0.002	0.214±0.013	0.011±0.002	0.004±0.001
Zinc roof					
0.045±0.012	10.210±1.010	0.004±0.001	0.003±0.001	0.019±0.006	0.003±0.001
Copper roof					
0.076±0.013	0.410±0.060	0.002±0.001	0.3 10±0.005	1.243±0.047	0.005±0.001
Ceramic tiled roof					
0.022±0.001	0.037±0.001	BDL	BDL	0.006±0.003	0.004±0.001

Table-2: Mean Concentrations of Trace Metal (mg/l) in Rainwater Samples from Control Sites.

Aluminium coated roof					
Fe	Zn	Cd	Al	Cu	Pb
0.013±0.003	0.030±0.007	BDL	BDL	0.010±0.002	0.005±0.001
Asbestos roof					
0.015±0.001	0.034±0.004	BDL	BDL	0.006±0.001	0.005±0.002
Zinc galvanized iron roof					
0.014±0.001	0.021±0.003	BDL	BDL	0.006±0.001	0.004±0.002
Zinc roof					

0.011±0.003	0.013±0.002	BDL	BDL	0.005±0.001	0.004±0.001
Copper roof					
0.010±0.002	0.031±0.004	BDL	BDL	0.007±0.002	0.004±0.001
Ceramic tiled roof					
0.018±0.001	0.028±0.003	BDL	BDL	0.006±0.003	0.002±0.001

Table-3: Federal Environmental Protection Agency (FEPA) Standards for Drinking Water Guidelines in Nigeria [20].

Metals	Concentration (mg/l)
Aluminium(Al)	0.2
Cadmium (Cd)	0.003
Copper (Cu)	1.0
Lead (Pb)	0.01
Zinc(Zn)	3.0
Iron(Fe)	0.3

This result revealed that, levels of Fe, Cd, Cu and Pb recorded in this study were within the acceptable standards for drinking water in Nigeria while Zn and Al concentrations were above the Nigerian standards for drinking water (Table 3). This therefore rendered the water harvested from Al-coated roof unsafe for human consumption as this can lead to Zn and Al toxicities and their attendants' effects as reported by [18, 32, 48, 46 and 52]. The high levels of Al and Zn maybe attributed to the roofing material from where sample was harvested and the Zinc galvanized gutters respectively as indicated by [29]. Nevertheless, the Zn level reported in this study is not as high as 101µg/l obtained by [7] in rainwater harvested from anodized aluminium roof. This result also indicated that, Al-coated roof can contribute a substantial amount of Al to rainwater collected from such roof since the level of Al in the Control sample was below detectable limit (BDL). The level of Pb recorded in this study even though within the acceptable limit for drinking water in Nigeria was high. This high Pb level maybe attributed to aerial deposition of the metal on the roofs from vehicle emissions as these roofs are located by the roadside [19, 40, 56]. Results in Table 2 have shown that, concentrations recorded for all the metals at the Control sites are within the acceptable limits for drinking water in Nigeria except for Cd and Al with concentrations below detectable limits. This showed that the roofing materials may have an influence on the quality of rainwater harvested from them.

Levels of Fe, Zn, Al and Cu recorded in samples harvested from asbestos roof were within the acceptable limits for drinking water in Nigeria but concentrations of Cd and Pb were above their recommended limits (Table 3). This result indicated that, harvesting of drinking water from asbestos roofs should be discouraged since this can lead to some health implications associated with Cd and Pb toxicities reported as by [9, 10, 19, 28, 37, 47 and 53]. The high level of Cd and Pb recorded in this study is in agreement with the results reported by [25] in rainwater harvested from asbestos roof. These high concentrations of Cd and Pb maybe attributed to roofing and painting materials, aerial deposition from automobiles and insecticides used within the area [3]. Results in Table 2 indicate that, asbestos roof may have contributed substantial amounts of these trace metals to the rainwater harvested from it since concentrations of these metals in the roof sample are relatively higher than their corresponding levels in the Control sample.

Galvanized iron roof sample recorded concentrations of Fe, Al, Cu and Pb within the acceptable limits for drinking water by Nigerian standards while the levels of Zn and Cd were above their limits. This high levels of Zn and Al recorded in this study is in agreement with the findings by [26, 29] in their studies in rainwater harvested from zinc galvanized iron roofs. Nevertheless, [7] obtained higher levels of Pb (302µg/l) and Zn (12,200µg/l) in rainwater sample harvested from galvanized roof. The high Zn and Al contents recorded in this work could be attributed to the roofing materials and the aluminium gutters on the roof as obtained by [49]. It has also been observed that, the sample harvested from galvanized iron roof recorded higher concentrations for the metals than obtained in the Control sample thus, it could be inferred that, the roof contributed some of these metals to rainwater harvested from it. These high concentrations of Zn and Al has rendered the rainwater harvested from galvanized iron roof unfit for human consumption since there are some health implications associated with high Al and Zn in human body [5, 34, 39 and52].

Results obtained from the sample harvested from zinc roof indicated that, concentrations of Fe and Cu were within the Nigerian acceptable standards while the levels of Zn and Cd were above the standards. These high levels of Zn

and Cd recorded in this study maybe attributed to the leaching action by rainwater of Zn from the Zn roof [35]. The high Cd content recorded maybe attributed to the metal being a major impurity in Zn, the painting materials used on the roof and pesticides used within the area [1, 24, 36 and55]. It has also been observed from the results that, concentrations of the metals analyzed for in samples harvested from the rooftops were relatively higher than their levels in the Control sample. This showed that, the roofing materials may have influenced the levels of these metals in the rainwater harvested from them.

Rainwater sample harvested from copper roof indicated that, concentrations of Fe; Zn; Cd and Pb were within their recommended limits in Nigeria for drinking water. Nevertheless, Al and Cu recorded concentrations higher than Nigerian standards for drinking water as indicated in Table 3. These high levels of Al and Cu could be accredited to the Al gutters and the copper metal on the roof respectively. The high copper level recorded in this study is in agreement with the result obtained by [26] in rainwater harvested from a copper roof.

Results in Tables 1 and 2 have shown that, concentrations of the metals are higher in sample obtained from the copper roof than in the Control sample. Consequently, the roofing materials may have been the source of these metals to rainwater harvested from it [41, 42]. These high levels of Al and Cu rendered rainwater harvested from a copper roof unfit for human consumption as this may lead to Alzheimer's disease, problems in kidney, central nervous system and digestive system [21, 52]. It may also cause acute toxicity which results in hypotension, coma and death in human [18, 52].

Sample collected from ceramic tiled roof recorded concentrations of all the metals analyzed for within the acceptable limits for drinking water by Nigerian standards (Table 3). Comparing results from rooftops with Control sample, it was observed that has, concentrations of metals analyzed for in both the roof and Control samples were almost the same. This confirmed that rainwater harvested from metallic roofs may have picked some amounts of these metals from the roofing materials as reported by [46]. This result revealed too that rainwater harvested from roof made of ceramic tiles could be safer as compared to metallic roofs. However, [52] reported that, rainwater is unsafe to be consumed if not treated thus rainwater irrespective of the source should be treated to eliminate the organic, inorganic and microbial contaminants before its utilization. The high concentrations of metals recorded in this study may also be attributed to the samples being the first flush after the long dry season since according to [15] concentrations of contaminants in roof runoff decrease with increase in the dilution rate. Also, the higher levels of metals in roof runoff than their corresponding levels in the background (Control) samples observed in this work are in agreement with the observations by [42]. The site to site fluctuations in the level of metals recorded in this study maybe attributed to variations in the source of the samples and in human activities done at each station.

CONCLUSION

This study has shown the extent of contamination by metals in rainwater harvested from different rooftops within Uyo metropolis over some period of time. The experimental results recorded in this work have shown that, metallic rooftops can contribute substantial amounts of metals to rainwater harvested from them. It is therefore necessary to develop and use safer materials for the construction of roofs where rainwater could be harvested for domestic and agricultural use. Also, some physical, chemical and biological parameters not analyzed for in this study should be investigated in future research works to ascertain the rainwater quality in Uyo. This study has also shown that, the quality of the air environment has a great influence on the quality of the rainwater harvested from a particular environment thus air quality standards should be reviewed and enforced.

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