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Trace Metals Solubility in Rainwater Collected From Different Parts of Benin City

[1]* Imhontu, M.U. [2] Ukpebor, E.E. and [3] Biose, O.

[1,3]National Centre for Energy and Environment, Energy Commission of Nigeria, University of Benin, Benin City, Nigeria
[2]Department of Chemistry, University of Benin, Benin City, Nigeria
Corresponding author's: reemzy2001@yahoo.co.uk, bosadebe@yahoo.com
+234-8061517804, +2348062151153

ABSTRACT

The study comprised the determination of trace metal concentrations in rainwater and the concentrations of 12 metals in wet deposition were reported. V, Cr, Mn, Fe, Co, Cu, Zn, Se, Mo, Sn, Sb and Pb were subject to chemical analysis using the PerkinElmer Elan DRCII Axial Field Technology inductively coupled plasma-mass spectrometer (ICP-MS) The conductivity range was 5.65-83.15 μScm^{-1} while mean pH range of 5.47-6.76 obtained for the rainwater samples indicated that some of the samples could be termed acid rain. Based on the mean concentrations of the trace elements measured: Fe and Zn were found to be greater than 100µg/L; Pb, Cr, Mn, and Cu were with concentrations between 1-100µg/L and Co, V and Sb were with lower concentrations than 1µg/L while Se, Mo and Sn were below the detection limit. The study revealed that low pH values characterized most of the rainwater samples, while other quality parameters such as Fe and Pb showed varying concentrations above the guidelines for drinking water.
Keywords: trace and toxic metals, rainwater and Benin City

INTRODUCTION

Rainwater dissolves the gases of the atmosphere, soluble aerosol, and contains particulate of dust and smoke. Additionally, rain can deposit toxic metals from the air, present as vapours or attached to dust particles, into waterways [1]. Atmospheric deposition of trace elements derived from natural, geochemical and anthropogenic sources, is the main way for up taking of elements into aquatic systems. Pollutants released to the atmosphere as gases and aerosols from human activities are transported and deposited several kilometres away from their source; being removed by dry or wet deposition, with its consequences over living organisms in the ecosystems [2]. Many household in tropics are exposed to abundant but seasonal rainfall and do not have access to an adequate supply of potable drinking water. Rainwater, despite being an age-old practice in many parts of the world, is being used at household level on a large scale. Rainwater is therefore considered as a safe and suitable source of potable water, and is commonly used in the rural areas in developing countries of the world [3]. Although water covers more than 70% of the Earth, only 1% of the Earth's water is available as a source of drinking. [4]. However, some observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability [5].

Rainwater serves as a purifier of the atmosphere whereby particulate matter in the air from automobiles exhaust and industrial processes are transferred into lakes and rivers, consequently, posing threats to the quality of both human and aquatic [1]. Unfortunately, the vast activities of man have resulted in a range of pollutants (wastes) being released into the environment: Most of which are eventually brought down as rainwater.

It is well-documented that natural and anthropogenic sources can significantly increase trace metal concentrations in the atmosphere. This is compounded by acidic precipitation which potentially can make some trace metals more bio available than others. A majority of the anthropogenic and natural material that is loaded to the atmosphere is washed out by rainwater [6] and [7]. Many of the trace elements found in the atmosphere are the result of combustion of fossil fuels, including such additives as the lead in gasoline, processing of earth materials for manufacturing cements, and burning of waste materials [8]. Clean" or unpolluted rain has a slightly acidic pH of over 5.7, because carbon dioxide and water in the air react together to form carbonic acid, but unpolluted rain also contains other chemicals. Therefore, with pH lower than 5.6, it is referred to as acid-rain [9]. Recent interest has been fuelled by the potential environmental effect of trace metals on aquatic and terrestrial ecosystems and potential human health through the consumption of drinking water [10].

MATERIALS AND METHOD

Study Area/Sample Collection

Samples of rainwater were collected from five different places (i.e Uniben, Ringroad, New Benin and Oluku) in Benin City. Care was taken to ensure that the samples were representative of fresh rainwater to be examined and that no accidental contaminations occurred during sampling. The rainwater samples were collected in clean 1(one) litre plastic containers by placing a clean bowl on a raised platform in an open environment in other to ensure that the water had no contact with any object. The bowl used to collect the rainwater samples was only placed just before the rain started and removed immediately after downpour into the plastic containers. This was to avoid other dry atmospheric deposition. Prior to the sample collection, all the 1 (one) litre containers used for the analysis, were initially washed with detergent and rinsed with tap water followed by distilled water. Sampling was done for two months; September and October.

Immediately after each sample collection, the temperature and pH were measured insitu with a thermometer and digital pH meter. After which they were taken to the analytical laboratory. All samples were analyzed as soon as possible after collection or stored at a temperature of 4^0C - 5^0C, according to recommendations given by the standard methods. The pH of the rainwater sample was determined insitu with a pH meter, Model: EXTECH ExStick EC500. A Conductivity meter of model: HACH C0150 was used to measure the conductivity of the rainwater sample in µScm-^{1}.

Table 1: Rainwater sampling sites and description.

S/N	Site Code	Site Description
1	RR	3 metres from ring road with high traffic volume and commercial activities
2	NB	New Benin road junction, where commercial activities (markets) take place and high traffic emissions (presence of different motor parks)
3	OL	Oluku, an Industrial area; By 7up Bottling Company
4	EC	National Centre for Energy and Environment (NCEE), University of Benin; a research institute in an academic community
5	CA	Capitol; This is a pristine environment and a residential area where little or no human activity occurs(Control site)

RR: Ring Road
OL: Oluku by 7up bottling Company
NB: New Benin
CA: Capitol Uniben
EC: National Centre for Energy and Environment (Energy Centre, Uniben)

DETERMINATION OF TRACE METALS

The analytical technique used in the determination of trace and toxic metals was the PerkinElmer Elan DRCII Axial Field Technology Inductively Coupled Plasma – Mass Spectrophotometer (ICP-MS) with ASX-510 Auto Sampler. This is because it measures most of the elements in the periodic table with particular reference to the d-block transition metals and the rare – earth metals (i.e. the f- block transition metals) which are the metals of interest for this study. After the preparation of the calibration standards and samples, each were then turned into small plastic sample containers including the blank solution which is 2% of the nitric acid(solvent) minus the analyte of interest which is the rainwater samples was also made. 10ppb of Ga, In and Bi was prepared and used as internal standards in 2% nitric acid. To 10ml of the rainwater samples, 2-3drops of 2% HNO_3 was added and set up for running. All of these were placed accordingly in the auto sampler tray which is numbered. The blank was initially run on the ICP-MS followed by the certified reference material (CRM) and standards, then blank again and then the rainwater samples. After which the ICP-MS was then automated using the software on a computer system. The results were then extrapolated in Microsoft excel and then the best isotope having no interference for each element was selected and printed out. MS The next step in the development of the analysis methodology was to program the instrument, using the computer software provided with the instrument, to perform the data collection, handling and processing steps, this was left to run simultaneously. The results were measured in ppb and printed out.

RESULTS AND DISCUSSION

The mean concentrations of the physicochemical analysis of the rainwater samples collected in September and October are presented in Table 2-4 below.

Table 2: Mean Values of Temperature, pH, and Conductivity

Sample Sites	RR	NB	EC	OL	CA	WHO Guidelines for drinking water quality
Temperature	26.1	27.30	27.05	26.40	25.6	20-32
pH	5.56	5.51	6.18	5.47	6.76	6.50-8.50
Conductivity (µS/cm)	10.05	83.15	7.65	5.65	8.10	1400.00

Table 3: ICP-MS Mean Values of Trace/ Toxic Metals of Rainwater Samples

Trace Metal	Isotope	Limit of Detection	RR	NB	EC	OL	CA	WHO Guidelines for drinking water quality	NESREA Standards for Drinking water
Vanadium (µg/L)	51	0.323	0.221	1.051	BDL	BDL	BDL	-	-
Chromium (µg/L)	52	0.934	9.839	10.065	2.656	BDL	2.106	50	50
Manganese (µg/L)	55	0.484	44.983	97.360	18.053	23.515	11.630	500	200
Iron (µg/L)	57	47.730	404.621	759.156	75.448	63.470	61.205	300	1500
Cobalt (µg/L)	63	0.184	0.615	0.732	0.322	0.190	BDL	-	-
Copper (µg/L)	66	0.455	13.043	37.655	13.683	5.736	9.218	1000	1500
Zinc (µg/L)	66	1.148	642.113	141.207	70.322	583.77	37.240	3000	3000
Selenium (µg/L)	82	3.910	BDL	BDL	BDL	BDL	BDL	40	10
Molybdenum(µg/L)	98	0.449	BDL	BDL	BDL	BDL	BDL	-	-
Tin (µg/L)	120	0.352	BDL	BDL	BDL	BDL	BDL	-	-
Antimony (µg/L)	121	0.503	2.284	1.810	0.792	0.780	0.709	20	-
Lead (µg/L)	208	0.184	11.490	47.168	10.949	1.615	2.560	10	10

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The mean pH values for all the rainwater samples at the different locations were acidic with a range of 5.47- 6.76 as shown in table 2. In previous work, rainwater samples collected from some industrial areas of Lagos state had a slight acidic mean pH range of 6.57- 6.9 [11], which is not as acidic as that collected in Benin city. The acidic level was highest at OL, with a mean pH value of 5.47, followed by NB (5.51), RR (5.56) and EC (6.18) which were however lower than the WHO Guidelines for drinking water. This showed that these locations are highly polluted due to the anthropogenic activities carried out in these areas such as OL which is an industrial area and NB, a commercial area. Rainwater samples collected at CA, recorded the least acidic mean pH value of 6.76. This is the only sample that fell within the WHO recommended levels. This indicates that there is little or no human activity (sparsely populated) taking place at CA, which is the control site. The conductivity mean values varied from 5.65-83.15 µS/cm which fell within the WHO guidelines.

The mean concentration of Vanadium varied from 0.221 – 1.051µg/L as shown in Table 3. Vanadium was not detected at EC, OL and CA. The mean concentrations of Cr were of the range: (2.106-10.065µg/L).All the mean concentrations fell below the WHO and NESREA standards for drinking water. Mn and Mo are not of health concern at levels causing acceptability problems in Drinking water. Mean concentrations of Mn fell below the WHO (500µg/L) and NESREA (200µg/L) guidelines for drinking water. Mo was not detected in any of the rainwater samples. It was observed that for Fe, New Benin had mean concentrations of 759.156µg/L and RR had mean concentrations of 404.621µg/L which did not conform to the WHO guidelines while EC, OL and CA had mean concentrations of about 60µg/L which fell below the NESREA and WHO guidelines. In previous works, lower concentrations of Fe were recorded to be between 30- 80µg/L in Benue state [12]. The high concentration of Iron observed at NB and RR (commercial areas) may be as a result of the fact that iron is applied worldwide for commercial purposes, and is produced in amounts of 500 million tons annually. Some 300 million tons are recycled [13]. The main reason is that iron is applicable in more areas than possibly any other metal. Alloys decrease corrosivity of the metal. Steel producers add various amounts of carbon. However, Iron alloys are eventually processed to containers, cars, laundry machines, bridges, buildings, and even small springs. Burning of these containers, machines and car parts made of iron may result in iron particulates getting into the atmosphere which is then washed down as rain. Iron compounds are also applied as pigments in glass and email production, or are processed to pharmaceutics, chemicals, iron fertilizers, or pesticides. These are also applied in wood impregnation and photography.

Cobalt varied from 0.19-0.376 µg/L. The highest concentration was recorded at NB (0.376µg/L) and lowest concentration was observed at OL (0.184 µg/L). A concentration below the detection limit was found at CA, thus indicating that Co was not detected. Cu had a range of 5.736-37.655µg/L. NB had the highest mean concentration of Cu and the lowest was at OL (5.736µg/L). RR, EC and CA had mean concentrations lower than 20 µg/L. The mean values of Cu and Co were below the WHO and NESREA guidelines for drinking water. The mean concentration of Zn varied from 37.240 - 642.113µg/L while [12] observed a range of 10-360 µg/L in the rainwater samples collected in Benue state. Rainwater is heavily contaminated with zinc in areas where zinc has to be mined or refined, or where sewage sludge from industrial areas has been used as fertilizer [13]. Moreover, high concentrations noticed in the rainwater samples collected at RR, a commercial area may be due to the fact that Zinc being the fourth most common metal in use, trailing only iron, aluminum and copper with an annual production of about 12 million tons [14], may get into atmosphere through different anthropogenic activities such as burning.

All the rainwater samples were at concentrations below the detection limit for Se and Sn. This means that they could not be detected by the ICP-MS. Mean concentrations of Sb varied from 0.709µg/L-2.284µg/L with the highest mean concentration at RR. This was followed by NB (1.810µg/L) and EC (0.792µg/L). All Sb concentrations fell below the WHO guidelines for drinking water.

The mean concentration of Pb was highest at NB (47.168µg/L) and lowest at CA. The range of Pb in the rainwater samples were: 2.560-47.168µg/L. [10] recorded a concentration of 2.10µg/L. The concentrations at NB and RR (11.490µg/L) were higher than the WHO recommended value (10µg/L) while EC, OL and CA had mean Pb values below the WHO guidelines for drinking water. The high concentrations of lead at NB and RR could be probably due to the influx of high traffic of automobiles which use leaded fuels and also emissions from generators being used by market sellers.

The mean concentrations of trace metals with toxicity observed in Benin City rainwater followed the order: Fe> Zn >> Mn> Pb > Cu> Cr >> Sb> V> Co. The solubility of toxic metals was found in the order of Cd> Cu> V> Zn> Ni> Pb> Cr in the rainwater samples collected at a water-shed in Istanbul, India investigated by [6]. From the results gotten from trace metals in rainwater samples collected in Hyderabad India, Istanbul Turkey and Singapore, it can be said that the Benin City rainwater recorded highest concentrations for most of the trace metals analyzed resulting in more pollution of the rainwater.

STATISTICAL ANALYSIS

Table 5: Correlation Coefficient Matrix of the Trace Metals Analysed Using the ICP-MS in September

	Cr	*Mn*	*Fe*	*Co*	*Cu*	*Zn*	*Sb*	*Pb*
Cr	1							
Mn	0.241	1						
Fe	0.358	0.036	1					
Co	-0.03	0.598	0.551	1				
Cu	0.526	0.417	0.91	0.717	1			
Zn	-0.55	0.397	-0.39	0.52	-0.209	1		
Sb	-0.29	-0.3	-0.47	-0.78	-0.623	-0.401	1	
Pb	0.969	0.451	0.25	0.031	0.4997	-0.43	-0.25	1

Table 6: Correlation Coefficient Matrix of the Trace Metals Analysed Using the ICP-MS in October

	V	*Cr*	*Mn*	*Fe*	*Co*	*Cu*	*Zn*	*Sb*	*Pb*
V	1								
Cr	0.489	1							
Mn	0.93	0.768	1						
Fe	0.877	0.845	0.991	1					
Co	0.71	0.95	0.897	0.946	1				
Cu	0.964	0.698	0.985	0.967	0.871	1			
Zn	-0.1	0.818	0.266	0.389	0.613	0.162	1		
Sb	0.797	0.849	0.955	0.966	0.891	0.892	0.451	1	
Pb	0.963	0.701	0.992	0.973	0.865	0.998	0.169	0.914	1

A correlation matrix of the trace metals is depicted in Table 5 and Table 6. Correlation between the trace metals were high and all the metals correlated to each other in table 5 apart from Zn and V. A similar situation was also reported by [15]. Some of the studied trace metals are known to have anthropogenic sources. In addition to that, they may be emitted from the same industrial facilities and reach the sampling area. Elements that are emitted from different sources may show correlations due to similar physical properties of the particles that carry them [16]. Cu and Pb were significantly correlated especially in Table 6. It is well known that the major source of Pb in the atmosphere is motor vehicles. It was previously suggested that correlation between Pb and Cu may be ascribed for by the road traffic [17]; [18]. Probably some part of the Cu observed in Benin City was caused by road traffic. Strong correlations were also observed between Mn, Fe, Co, Cu, Sb, Pb and V in Table 6. This maybe because they show similar behavior under certain physical conditions such as wind speed, air temperature, and rainfall amount.

CONCLUSION

This study revealed that the concentrations of trace metals with toxicity obtained in this research work showed that Pb and Fe levels recorded at New Benin (NB) and Ring road (RR) were higher than the WHO and NESREA recommended standards for drinking water while the trace metals recorded at other locations (OL, EC and CA) conformed. Also, the rainwater samples collected at NB and RR recorded the highest concentrations of trace metal contaminations compared to the other sampling sites. Moreover, the trace metals which are not of health concern at levels found in drinking water, all conformed to the WHO and NESREA guidelines for drinking water. It was discovered that the acidic level of rainwater from some locations in Benin City could be termed acid rain as could be seen from the pH values in the industrial area and places of high traffic density.

Therefore, this showed that rainwater collected from high traffic density areas and industrial areas is contaminated by the emissions from the industries and emissions from automobiles. Thus, rainwater is not considered as a safe and suitable source of potable drinking water.

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