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Rainwater Chemistry Within the Vicinity of Qua Iboe Estuary, Nigeria

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The Qua Iboe River estuary is one of the most studied ecosystems in the Niger Delta of Nigeria given its proximity to intense industrial activities. There have been concerns regarding possible environmental contamination, which has led to several monitoring studies. In this study, some trace metals (Zn, Mn, Cu, Fe, Cr, Pb, Ni, Cd) in rainwater samples collected around the estuary were investigated using standard analytical methods. Rainwater samples were also analysed for physicochemical characteristics. The results obtained revealed varied levels of trace metals and physicochemical parameters across dry and wet seasons. The average abundance of trace metals in rainwater samples from the study locations is in the order: Fe > Zn > Mn > Cr > Cu > Ni > Cd > Pb. In addition, predominant anions in rainwater samples are in the order $CO_3^{2-} > Cl^- > NO_3^- > SO_4^{2-} > S^{2-} > CN^-$. Results from statistical analyses reveal the relationships across parameters as well as the discrimination of monitored sites based on the intensity of industrial activities. Principal component analysis reveals that soil dust, sea salt, and fossil fuel combustion are major factors affecting the rainwater chemistry of the study area. The significant amounts of trace metals and the physicochemical parameters quantified in the rainwater samples indicate some level of contamination. However, these levels do not indicate serious pollution problems at present.

1. Introduction

Maintaining appropriate air and rainwater quality status is essential for achieving good human and environmental health. Previous studies have found correlations between long-term exposure to polluted air and increased mortality from respiratory as well as cardiovascular diseases.[1] The generated concerns have led to several monitoring campaigns and recommendations for regulation of environmental emissions that may result in air and rainwater pollution.[2–12] However, most of these studies were carried out in developed countries and there have been very few studies on developing countries like Nigeria.[13,14] This is a cause for concern as atmospheric pollution implications span beyond the local environments to regional or even global scales due to its transboundary characteristics.[15,16] For instance, airborne particles may remain suspended for minutes to weeks in the atmosphere and are removed by dry or wet deposition at various distances from the sources.[17,18] More so, the specific findings from one region may not be easily extrapolated for others without monitoring data because of possible differences in pollution mixtures and prevailing environmental dynamics like climate and weather conditions.

Previous studies in Nigeria have established large scale anthropogenic emissions from gas flaring, street dusts, particulates from construction sites, industrial plumes, exhaust fumes from power-generating plants, and vehicles, especially in urban areas.[19] It is important to note that the composition of rainwater tends to reflect the composition of the atmosphere through which it falls.[7,20] On the other hand, the significant deposition and atmospheric fluxes which consequently affect surface runoffs, play an important role in the global biogeochemical cycling of contaminants.[21,22] Furthermore, most rural dwellers in Nigeria utilize rainwater for drinking and domestic purposes and as such poor quality rainwater may result in exposure to hazardous contaminants.

The Qua Iboe estuary (**Figure 1**) is located within 4°30′N and 4°45′N and longitude 7°30′E and 8°45′E as a dominant hydrographical feature in the Niger Delta region of Nigeria.[23] In the estuary, cases of environmental perturbations have been recognised as a result of pollution from nearby oil exploration activities and gas flaring.[24] Its surface water quality assessment has become a major concern for protection of public health and a balanced ecosystem. However, the rainwater quality in the area is yet to be assessed. The objective of the present study was to investigate the levels of rainwater physicochemical contaminants within the vicinity of the Qua Iboe estuary.

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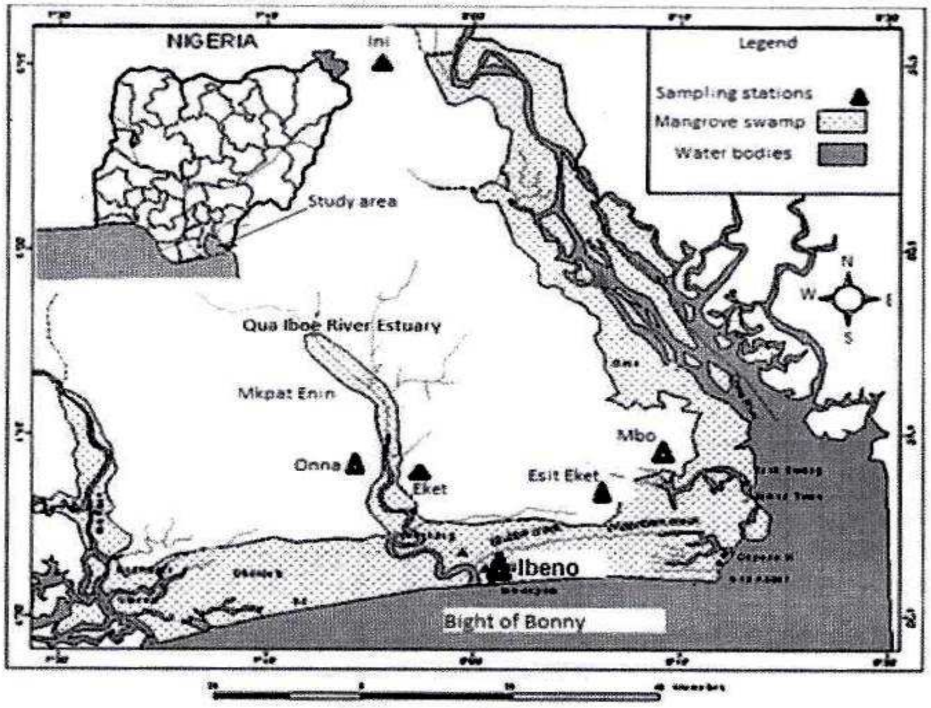

Figure 1. The Qua Iboe Estuary with location of sampling stations and main surrounding industrial activities.

2. Experimental Section

2.1. Description of Study Area and Sample Locations

The Qua Iboe estuary (Figure 1) is located in a typical climatic zone characterized by distinct dry and wet seasons. The wet season, which predominantly begins in March or April and ends in October or November, is always characterized by heavy storms of short duration. This season (about 7 months) is often influenced by the North-Eastern wind arising from the Sahara desert. Generally, the relative humidity is high in the study area. Humidity is highest during the dry season along the Qua Iboe River, but tends to increase in land during the wet season.[25] The Qua Iboe estuary and its tributaries flow through many towns and villages in Akwa lbom State which form the pivot of this study. The sampling sites include the following villages and towns: Ukpenekang and Mkpanak (Ibeno, IBN); Uquo Isi-Edoho and Uquo (Esit Eket, EET); Ukpana and lkot Ebiere (Onna, ONN); Afaha Eket and Ikot Uso Ekong (Eket, KET); Ibaka and James Town (Mbo, MBN) and Ikpe Ikot Nkon/Odoro Ikpe (Ini, INN). In this study, the INN station was considered as the control site. The GPS coordinates of these locations are listed in Table 1.

2.2. Sample Collection

Samples were collected between November 2007 and January 2008 (for dry season) and April to June 2008 (for wet season). Three samples were collected from six sampling stations for the two seasons; making a total of 36 samples. Samples were collected using 5 L polyethene basin containers kept in open spaces avoiding trees and roof tops. The containers were placed few minutes before each rainfall event and were replaced during every weekly sampling session. Samples were transferred into 2 L bottles immediately after rainfall. The bottles were sealed, labelled and conveyed in coolers (at 4 °C) to the laboratory for further analysis. Based on expected changes, in situ measurements of temperature and pH of the rainwater were performed using Jenway pH/temperature probe (model 3017). Analysis of physicochemical parameters and trace metals took place within 48 h after sample collection.

2.3. Sample Analysis

Rainwater samples were filtered through polycarbonate membrane filters. An aliquot (60 mL) of the filtrate was transferred into a high-density polyethylene (HDPE) bottle and acidified with 0.016 M HNO_3 and kept at 4 °C until analysis using atomic absorption spectrophotometry (AAS).[26] AAS (UNICAM model 939) was used to quantify the trace metal content in the sample digest. A calibration curve was prepared for each metal and the concentration of the metal in solution was determined from the calibration curve. All reagents used were of analytical grade purchased from Merck.

Physicochemical parameters in rainwater were determined by standard analytical protocols described in detail elsewhere.[27–29] Briefly, a calorimetric method was employed to

Table 1. Coordinates of sampling stations.

Sampling station	Location	
	Longitude	Latitude
ONN		
Ikot Ebiere	7°49′30.6″E	4°33′00.1″N
Ukpana	7°49′42.6″E	4°35′14.1″N
KET		
Afaha Eket	7°56′16.4″E	4°37′59.4″N
Ikot Uso Ekong	7°56′22.7″E	4°39′37.1″N
MBN		
James Town	8°18′40.1″E	4°39′08.7″N
Ibaka	8°19′15.8″E	4°40′09.9″N
IBN		
Mkpanak	7°59′35.4″E	4°33′06.4″N
Ukpenekang	7°58′41.4″E	4°34′13.2″N
EET		
Uquo Isi Edoho	8°05′00.1″E	4°39′25.9″N
Uquo	8°03′06.1″E	4°39′30.1″N
INN		
Ikpe Ikot Nkon	7°41′18.9″E	5°23′40.2″N
Odoro Ikpe	7°45′04.8″E	5°21′33.9″N

determine sulphide (S^{2-}), nitrate (NO_3^-), cyanide (CN^-) and carbonate (CO_3^{2-}) concentrations of the samples. Sulphate (SO_4^{2-}) anions were determined spectrophotometrically ($\lambda = 420$ nm) while chloride (Cl^-) anions were determined by Mohr's method using silver nitrate as titrant and potassium chromate as end point indicator. The concentration of the chloride ions was calculated from Eq. (1), when 50 mL of sample was used:

$$\text{Conc.Cl}^- = \frac{\text{vol.AgNO}_3 \times 1000}{\text{vol.ofsample}} \tag{1}$$

2.3. Statistical Analysis

The descriptive statistics were performed using Microsoft Excel 2007 while multivariate; principal component analysis (PCA) and hierarchical cluster analysis (HCA) were done using the SPSS statistical software package Version 20.0. Statistical significance was set at $p \leq 0.05$.

3. Results and Discussion

3.1. Physicochemical Parameters and Trace Metals Levels in Rainwater

The results of trace metals levels and physicochemical characteristics of the rainwater for wet and dry seasons are presented in Tables 2 and 3. Generally, trace metals levels were higher during the dry season than in wet season. This could be due to the generation of more suspended particulates and dust during the dry season which increases the chances of cross-matrix contamination. The levels of Zn and Fe were predominant in both seasons followed by Cr. Highest levels were recorded for IBN and EET sampling stations. Lower concentrations of trace metals were obtained at the control site in INN (Table 2). This observation implies that the intensity of the concentrations is related to the prevailing industrial activities. The relative abundance of trace metals in rainwater followed the order: $Fe > Zn > Mn > Cr > Cu > Ni > Cd > Pb$.

The physicochemical characteristics reveal that rainwater samples were almost neutral (pH 6.7) (Table 3), although significant amounts of anions as sulphate (SO_4^{2-}), carbonate (CO_3^{2-}), chloride (Cl^-), sulphide (S^{2-}), nitrate (NO_3^-), and cyanide (CN^-) were measured. The pH of 6.7 implies possible neutralization effects from dissolved metals.[8,30] Generally, the concentrations of anions were higher in the dry season than in the wet season. Predominant anions in rainwater samples followed the order: $CO_3^{2-} > Cl^- > NO_3^- > SO_4^{2-} > S^{2-} > CN^-$. The high concentration of carbonate ions in the rainwater samples is expected due to additional inputs from dissolved ambient atmospheric CO_2. High levels of Cl^- may be linked to inputs from sea salt of the Atlantic Ocean brought about by wind action. The elevated amounts of nitrate and sulphate ions are indication of possible inputs from industrial activities that likely result from elevated amounts of nitrogen and sulphur oxides in the air and consequent dissolution in rainwater. Cyanide ions were recorded in least amounts, and were not detected at the control sites. Overall, the levels of the anions were comparable with those found for other locations in the literature.[20] The physicochemical characteristics of the rainwater samples reveal slight level of contamination.

Comparing the levels of the contaminants with national and international standards, it is observed that most of them were within the recommended limits. However, the level of Mn at the control site (Ini) during the dry season exceeded the Nigerian Standard for Drinking Water Quality (NSDWQ) (published by the Standard Organisation of Nigeria (SON)) and World Health Organisation (WHO) recommended limits.[31,32] On the other hand, chromium levels exceeded the NSDWQ recommended limit at all stations (except the control site) for both seasons but were below the WHO value. Therefore, these levels do not indicate serious pollution problems at present.

3.2. Statistical Analysis

Data from the physicochemical characteristics were subjected to Pearson correlation analysis and the results are presented in Table 4. Generally, a significant positive correlation was observed between most of the metals and anions measured. This again attests to the neutral state of the rainwater. According to Hu et al.[7] this is supported by observed correlation of acidic components of precipitation (i.e., carbonate, sulfate, and nitrate). There was no significant correlation between chloride and the pH suggesting that the acidity of the rainwater was not due to chloride content. In addition, the significant positive correlation between nitrate and sulphate ions was expected since their precursors (NO_2 and SO_2) are usually co-emitted.[7]

Table 2. Levels of trace metals (mean ± SD) in rainwater samples (mg L^{-1}) during the dry and wet season.

Site/Standard	Zn	Mn	Cu	Fe	Cr	Pb	Ni	Cd
Dry season								
ONN	0.180 ± 0.059	0.003 ± 0.001	0.005 ± 0.002	0.060 ± 0.007	0.011 ± 0.003	0.001 ± 0.000	0.003 ± 0.000	0.001 ± 0.000
EET	0.382 ± 0.100	0.004 ± 0.001	0.006 ± 0.003	0.077 ± 0.002	0.015 ± 0.003	0.001 ± 0.000	0.004 ± 0.001	0.001 ± 0.000
IBN	0.252 ± 0.046	0.004 ± 0.001	0.006 ± 0.001	0.107 ± 0.034	0.016 ± 0.002	0.001 ± 0.000	0.003 ± 0.001	0.001 ± 0.000
KET	0.089 ± 0.005	0.003 ± 0.001	0.003 ± 0.001	0.081 ± 0.020	0.007 ± 0.001	0.001 ± 0.000	0.004 ± 0.001	0.001 ± 0.000
MBN	0.084 ± 0.018	0.002 ± 0.000	0.002 ± 0.00	0.039 ± 0.002	0.005 ± 0.001	0.001 ± 0.000	0.002 ± 0.000	0.001 ± 0.000
Overall mean	0.197	0.003	0.004	0.073	0.011	0.001	0.003	0.001
INN (control site)	0.041 ± 0.024	0.241 ± 0.001	0.001 ± 0.000	0.012 ± 0.010	0.001 ± 0.000	BDL	0.001 ± 0.000	BDL
Wet season								
ONN	0.003 ± 0.001	0.001 ± 0.000	0.002 ± 0.000	0.039 ± 0.005	0.021 ± 0.008	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
EET	0.004 ± 0.000	0.003 ± 0.001	0.004 ± 0.001	0.640 ± 0.0-6	0.014 ± 0.007	0.001 ± 0.000	0.002 ± 0.000	0.001 ± 0.000
IBN	0.065 ± 0.017	0.004 ± 0.000	0.003 ± 0.001	0.145 ± 0.027	0.012 ± 0.004	0.001 ± 0.000	0.002 ± 0.000	0.001 ± 0.000
KET	0.006 ± 0.001	0.003 ± 0.000	0.001 ± 0.000	0.166 ± 0.044	0.013 ± 0.003	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
MBN	0.010 ± 0.001	0.004 ± 0.000	0.001 ± 0.000	0.034 ± 0.003	0.005 ± 0.001	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000
Overall mean	0.018	0.003	0.004	0.070	0.025	0.013	0.001	0.001
INN (Control site)	0.001 ± 0.000	0.240 ± 0.001	0.001 ± 0.000	0.013 ± 0.000	0.002 ± 0.000	BDL	0.002 ± 0.000	BDL
SON[31]	3.00	0.20	1.00	0.30	0.005	0.01	0.02	0.003
WHO[32]	3.00	0.10	2.00	0.30	0.03	0.01	0.07	0.003

BDL, below detection limit; SD, standard deviation.

Table 3. Physicochemical characteristics of rainwater during dry season (mg L^{-1}).

Site/Standard	NO_3^-	S^{2-}	SO_4^{2-}	CN^-	CO_3^{2-}	Cl^-	pH
Dry season							
ONN	0.845 ± 0.065	0.045 ± 0.012	0.080 ± 0.006	0.001 ± 0.000	27.666 ± 0.577	15.374 ± 1.300	6.546 ± 0.030
EET	1.633 ± 0.3281	0.062 ± 0.014	0.077 ± 0.019	0.001 ± 0.000	29.511 ± 1.696	22.131 ± 2.134	6.689 ± 0.031
IBN	0.811 ± 0.099	0.057 ± 0.015	0.093 ± 0.017	0.001 ± 0.000	40.109 ± 1.420	22.075 ± 1.876	6.978 ± 0.018
KET	1.070 ± 0.340	0.072 ± 0.018	0.113 ± 0.008	0.001 ± 0.000	28.532 ± 2.326	18.225 ± 0.142	6.807 ± 0.041
MBN	0.668 ± 0.099	0.046 ± 0.003	0.066 ± 0.011	0.001 ± 0.000	25.951 ± 1.185	21.403 ± 0.688	6.631 ± 0.028
Overall mean	1.005	0.056	0.086	0.001	19.842	25.754	6.730
INN (Control site)	0.129 ± 0.008	0.012 ± 0.001	0.033 ± 0.016	*BDL*	16.652 ± 3.400	16.652 ± 3.400	6.688 ± 0.33
Wet season							
ONN	0.391 ± 0.085	0.049 ± 0.013	0.049 ± 0.010	0.001 ± 0.000	13.842 ± 1.817	23.637 ± 0.408	6.696 ± 0.021
EET	0.625 ± 0.046	0.061 ± 0.019	0.073 ± 0.021	0.001 ± 0.000	18.763 ± 0.710	28.634 ± 2.320	6.658 ± 0.038
IBN	0.707 ± 0.054	0.069 ± 0.004	0.088 ± 0.038	0.001 ± 0.000	19.251 ± 0.203	39.679 ± 1.961	6.913 ± 0002
KET	0.601 ± 0.089	0.041 ± 0.12	0.092 ± 0.029	0.001 ± 0.000	13.45 ± 0.933	28.126 ± 0.000	6.712 ± 0.043
MBN	0.476 ± 0.086	0.027 ± 0.006	0.049 ± 0.004	0.001 ± 0.000	19.363 ± 1.833	34.544 ± 0.579	6.687 ± 0.029
Overall mean	0.560	0.049	0.070	0.001	30.924	16.933	6.734
INN (Control site)	0.025 ± 0.001	0.012 ± 0.001	0.009 ± 0.000	BDL	14.431 ± 1.175	9.126 ± 0.623	6.943 ± 0.018
SON[31]	50.00	0.05	100.00	0.01	150.00	250.00	6.5–8.5
WHO[32]	50.00	–	250.00	0.17	200.00	300.00	6.5–8.5

BDL, below detection limit.

Table 4. Pearson correlation matrix of trace metals and physicochemical parameters in rainwater samples in both seasons.

	Zn	Mn	Cu	Fe	Cr	Pb	Ni	Cd	NO_3^-	S^{2-}	SO_4^{2-}	CN^-	CO_3^{2-}	Cl^-	pH
Zn	1	−0.276	**0.846****	−0.111	0.307	0.280	**0.765****	0.280	**0.808****	0.405	0.387	0.280	**0.794****	−0.166	0.024
Mn		1	−0.461	−0.245	−0.660*	−1.000**	−0.277	−1.000**	−0.646*	−0.785**	−0.760**	−1.000**	−0.385	−0.572	0.245
Cu			1	**0.330**	**0.546**	**0.464**	**0.768****	**0.464**	**0.756****	**0.640***	0.536	0.464	**0.800****	−0.037	0.038
Fe				1	0.284	0.245	0.089	0.245	0.102	0.410	0.190	0.245	0.009	0.293	−0.097
Cr					1	**0.659***	0.142	**0.659***	0.429	**0.631***	0.451	**0.659***	0.182	0.337	−0.014
Pb						1	0.279	**1.000****	**0.649***	**0.786****	**0.763****	**1.000****	0.389	0.575	−0.243
Ni							1	0.279	**0.797****	**0.599***	0.541	0.279	**0.764****	−0.303	0.147
Cd								1	**0.649***	**0.786****	**0.763****	**1.000****	0.389	0.575	−0.243
NO_3^-									1	**0.752****	**0.718****	**0.649***	**0.651***	0.147	−0.144
S^{2-}										1	**0.847****	**0.786****	0.486	0.409	0.079
SO_4^{2-}											1	**0.763****	0.553	0.354	0.010
CN^-												1	0.389	0.575	−0.243
CO_3^{2-}													1	−0.145	0.174
Cl^-														1	0.023
pH															1

Positive correlations are presented in bold.
*Correlation is significant at the 0.05 level (2-tailed);
**Correlation is significant at the 0.01 level (2-tailed).

Table 5. Principal component loadings of parameters in rainwater.

Parameter	PC1	PC2	PC3
CN^-	**0.953**	0.219	0.056
Cd	**0.953**	0.219	0.056
Pb	**0.953**	0.219	0.056
Mn	−0.953	−0.216	−0.056
Cl^-	**0.744**	−0.376	0.135
S^{2-}	**0.743**	0.465	0.304
SO_4^{2-}	**0.738**	0.456	0.024
Cr	0.641	0.195	0.320
Ni	0.083	**0.930**	0.065
Zn	0.102	**0.917**	−0.099
CO_3^{2-}	0.204	**0.863**	−0.073
Cu	0.270	**0.857**	0.334
NO_3	0.510	**0.774**	0.001
Fe	0.188	−0.009	**0.954**
pH	−0.132	0.086	−0.030
Eigen value	7.987	2.994	1.172
% Total variance	53	20	8
% Cumulative variance	53	73	81
Possible sources	Fossil/leaded fuel burning, sea salt	Biomass burning	Soil dust

Significant r-values are presented in bold ($p < 0.01$).

PCA was conducted to attempt source apportionment by receptor modelling.[12] Each of the principal components (PC) indicates correlation of each variable as loadings (loadings >0.70 were considered significant in this study). The results are presented in **Table 5**. The data revealed three main components accounting for 81% of the total variance (PC1, 53%; PC2, 20%; and PC3, 8%). The first PC was correlated with Cd, Cl^-, CN^-, S^{2-}, SO_4^{2-}, and Pb. High loadings of Cl^- may imply inputs from sea salt whereas that of Pb may be as a result of gas flaring and combustion of leaded fuels in the area. Previous studies have

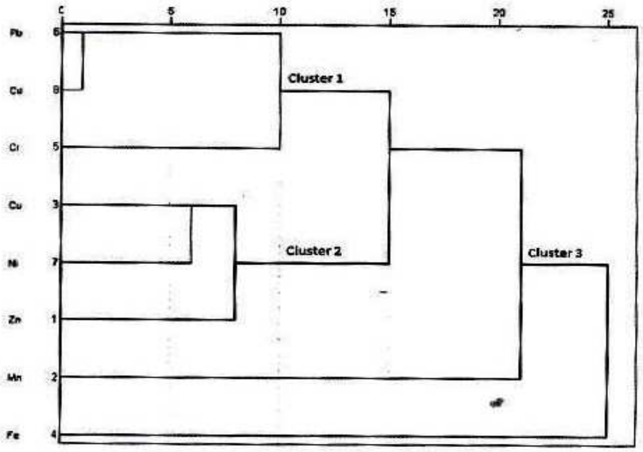

Figure 2. Relationship of trace metals discriminated based on possible source.

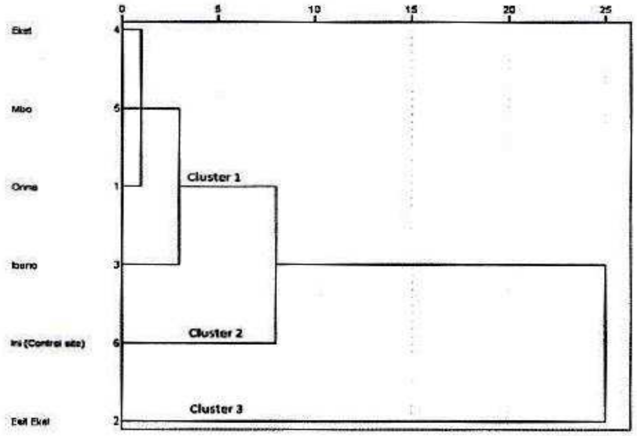

Figure 3. Discrimination of sample stations based on contamination levels.

proven that trace metals (Fe, Zn, Mn, Cr, Cu, Ni, Cd, Pb) could get into the atmosphere through combustion of crude oil and allied products, like flared gases and vehicle exhaust fumes.[33–35] Furthermore, the data reveal lower concentrations of Pb than Cr and Ni, which are also constituents of flared gases and exhaust fumes. This trend may be a result of prohibition of leaded petrol in Nigeria since 2004 and subsequent reduction in environmental matrices.[36–38] Although it is prohibited since 2004, commercial petrol in Nigeria still contains significant amount of lead[35] that can result in environmental contamination.[39–42] The second PC was correlated with Ni, Cu, Zn, CO_3^{2-}, and NO_3^-. These factor loadings, especially carbonate and nitrate, are indicative of combustion of biomass containing carbon and nitrogen like in the case of forest fires as a result of farming practices as well as bush burning. The third PC was correlated with Fe only. This indicates inputs of iron from the earth crust in form of soil dust blown into the atmosphere and with eventual fate of wet deposition.

HCA revealed three sources of trace metals; one being associated with soil dust (cluster 3) and the other two being associated with flared gases, combustion of leaded fuel as well as other geochemical relationships (clusters 1 and 2) (**Figure 2**). Three primary clusters were obtained for site discrimination using HCA (**Figure 3**). Cluster 1 revealed the relationship with the sites that were highly contaminated as a result of intense industrial activities while clusters 2 and 3 grouped sites with low contamination levels including the control site (INN).

4. Concluding Remarks

The present study reveals the prevalence of trace metals in rainwater samples collected within the vicinity of Qua Iboe estuary. Variations in the distribution of trace metals and other physicochemical parameters suggest influence by seasons and different sources such as soil dusts, sea salts, biomass burning, flared gases and vehicle exhaust fumes. Results from statistical analyses also revealed the discrimination of monitored sites based on intensity of industrial activities. The significant amounts of trace metals and the physicochemical parameters in the rainwater samples reveal some level of contamination. However, these levels do not indicate serious pollution problems at present based on the comparison with national and WHO standards for drinking water quality.

Abbreviations

AAS, atomic absorption spectrometry; EET, Esit Eket sampling station/site; HCA, hierarchical cluster analysis; HDPE, high-density polyethylene; IBN, Ibeno sampling station/site; INN, Ini sampling station/site; KET, Eket sampling station/site; MBN, Mbo sampling station/site; NSDWQ, Nigerian Standard for Drinking Water Quality; ONN, Onna sampling station/site; PC, principal component; PCA, principal component analysis; SON, Standards Organisation of Nigeria; WHO, World Health Organisation

Conflict of Interest

The authors have declared no conflict of interest.

Keywords

air pollution, physicochemical characteristics, rainwater chemistry, source apportionment, trace metals

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[1] G. Hoek, B. Brunekreef, S. Goldbohm, P. Fischer, P. A. Van Den Brandt, *Lancet* **2002**, *360*, 1203.
[2] J. C. Chow, *J. Air Waste Manage. Assoc.* **1995**, *45*, 320.
[3] F. Var, Y. Narita, S. Tanaka, *Environ.* **2000**, *34*, 2755.
[4] P. A. Tanner, A. Y. S. Wong, *Water Air Soil Pollut.* **2000**, *122*, 261.
[5] M. Flues, P. Hama, M. J. L. Lemes, E. S. K. Dantas, A. Fornaro, *Atmos. Environ.* **2002**, *36*, 2397.
[6] H. Akimoto, *Science* **2003**, *302*, 1716.
[7] G. P. Hu, R. Balasubramanian, C. D. Wu, *Chemosphere* **2003**, *51*, 747.
[8] P. D. Safai, P. S. P. Rao, G. A. Momin, K. Ali, D. M. Chate, P. S. Praveen, *Atmos. Environ.* **2004**, *38*, 1705.
[9] S. Utsunomiya, K. A. Jensen, G. J. Keeler, R. C. Ewing, *Environ. Sci. Technol.* **2004**, *38*, 2289.
[10] M. K. Ghose, S. R. Majee, *Environ. Monit. Assess.* **2007**, *130*, 17.
[11] J. C. Holecek, M. T. Spencer, K. A. Prather, *J. Geophys. Res.* **2007**, *112*, 1.
[12] S. Tiwari, U. C. Kulshrestha, B. Padmanabhamurty, *Atmos. Environ.* **2007**, *41*, 5595.
[13] E. E. Ukpebor, J. E. Ukpebor, E. Aigbokhan, I. Goji, A. O. Onojeghuo, A. C. Okonkwo, *J. Environ. Sci.* **2010**, *22*, 1073.
[14] E. G. Olumayede, *Int. J. Atmos. Sci.* **2014**, *2014*, 1.
[15] J. M. Pacyna, E. G. Pacyna, *Environ. Rev.* **2001**, *9*, 269.
[16] F. De Santis, A. Fino, S. Menichelli, C. Vazzana, I. Allegrini, *Anal. Bioanal. Chem.* **2004**, *378*, 782.
[17] P. R. Buseck, K. Adachi, *Elements* **2008**, *4*, 389.
[18] J. H. Seinfeld, S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York **1998**.

[19] A. E. Ite, I. I. Udousoro, J. U. Ibok, *Am. J. Environ. Prot.* **2014**, *2*, 22.
[20] O. A. Al-Khashman, *Atmos. Res.* **2009**, *91*, 53.
[21] C. Bilos, J. C. Colombo, C. N. Skorupka, M. J. Rodriguez Presa, *Environ. Pollut.* **2001**, *111*, 149.
[22] S. Garnaud, J. M. Mouchel, G. Chebbo, D. R. Thévenot, *Sci. Total Environ.* **1999**, *235*, 235.
[23] S. I. Eduok, G. A. Ebong, E. P. Udoinyang, J. N. Njoku, E. A. Eyen, *Pak. J. Nutr.* **2010**, *9*, 35.
[24] J. P. Essien, G. A. Ebong, J. E. Asuquo, A. A. Olajire, *Chem. Ecol.* **2012**, *28*, 421.
[25] F. O. Amubode, Biology and Socio-economic Survey of Stubbs Creek Forest Reserve, Akwa Ibom State. Uyo, Nigeria, Nigerian Conservation Foundation, Uyo, Nigeria **1992**.
[26] A. Báez, R. Belmont, R. García, H. Padilla, M. C. Torres, *Atmos. Res.* **2007**, *86*, 61.
[27] C. M. A. Ademoroti, *Standard Methods for Water and Effluents Analysis*, Foludex Press, Ibadan, Nigeria **1996**.
[28] M. Radojevic, V. N. Bashkin, *Practical Environmental Analysis*, 2nd edn., Royal Society of Chemistry, Cambridge, UK **2006**.
[29] P. Narayanan, *Environmental Pollution: Principles, Analysis and Control*, CBS Publishers, New Delhi, India **2007**.
[30] I. F. Al-Momani, S. Aygun, *J. Geophys. Res.* **1998**, *103*, 8287.
[31] Standards Organisation of Nigeria (SON), Nigerian Standard for Drinking Water Quality, Standards Organisation of Nigeria (SON), Lagos, Nigeria **2007**.
[32] World Health Organisation (WHO) *Guidelines for Drinking Water Quality*, 4th edn., World Health Organisation (WHO), Geneva, Switzerland **2011**.
[33] F. E. Huggins, G. P. Huffman, W. P. Linak, C. A. Miller, *Environ. Sci. Technol.* **2004**, *38*, 1836.
[34] R. A. A. Munoz, P. R. M. Correia, A. N. Nascimento, C. S. Silva, P. V. Oliveira, L. Angnes, *Energy Fuels* **2007**, *21*, 295.
[35] L. A. Jimoda, S. O. Olatunji, J. A. Adeniran, B. S. Fakinle, J. A. Sonibare, *Pet. Sci. Technol.* **2014**, *32*, 2921.
[36] M. Burke, *Environ. Sci. Technol.* **2004**, *38*, 326A.
[37] E. O. Adebamowo, O. A. Agbede, M. K. C. Sridhar, C. A. Adebamowo, *Sci. Total Environ.* **2006**, *372*, 94.
[38] J. O. Ojo, O. O. Oketayo, C. A. Adesanmi, M. Horvat, D. Mazej, J. Tratnik, *Environ. Sci. Pollut. Res. Int.* **2014**, *21*, 1124.
[39] E. O. Adebamowo, C. S. Clark, S. Roda, O. A. Agbede, M. K. C. Sridhar, C. A. Adebamowo, *Sci. Total Environ.* **2007**, *388*, 116.
[40] A. A. Adeniyi, O. J. Owoade, *Environ. Monit. Assess.* **2010**, *167*, 625.
[41] O. O. Odukoya, P. C. Onianwa, O. I. Sanusi, *Environ. Monit. Assess.* **2010**, *168*, 1.
[42] V. F. Doherty, A. A. Otitoloju, *Environ. Monit. Assess.* **2013**, *185*, 4159.