CHEMICAL COMPOSITION OF WET PRECIPITATION IN IBADAN, NIGERIA

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ABSTRACT. Rainwater samples were collected for four two-weekly periods at nine sampling points in the city of Ibadan, Nigeria, during May-July, 1999, and analysed for pH, sulphate, nitrate, chloride, phosphate, sodium, potassium, calcium, and magnesium. The rainwater was predominantly neutral with pH values ranging between 5.8 and 7.0, and averaging 6.6±0.3. Average concentrations (µeq/L) for all the sampling points and sampling periods were: SO_4^{2-} (46±22), NO_3^- (1.6±0.3), Cl^- (11±13), PO_4^{3-} (3.2±1.8), Na (11.7±7.9), K (5.6±4.4), Ca (30±26), and Mg (1.2±8.8). Concentrations of the various ions in the rainwater decreased slightly with the progress of the sampling period. The deposition flux (kg km^{-2} $month^{-1}$) was estimated as: SO_4^{2-} (390), NO_3^- (16.8), Cl^- (67.6), PO_4^{3-} (17.5), Na (46.6), K (37.9), Ca (104), and Mg (21.5).

INTRODUCTION

Various gaseous and particulate pollutants are released into the earth's atmosphere as a consequence of man's activities. Rainfall serves as a scavenger which washes down much of these pollutants to the earth's surface, and the chemical composition of rainwater is usually a good indicator of the quality of the atmosphere. Acid rain, derived from the interaction of oxides of sulphur and nitrogen with rainwater, is still a major environmental problem in some countries of the industrialised world. Acid rain has been reported to be the cause of severe damage to vegetation, farm crops, aquatic resources, building materials and soil ecology in some of these countries [1-4]. The monitoring of the composition of wet-precipitation is thus an important part of environmental studies in many countries, being a means of detecting short-term and long-term changes in temporal and spatial patterns of atmospheric pollution [5-10]. Whereas abundant data is available on the composition of rainwater in Europe and North America, there is still a dearth of such information for most of the under-developed countries, especially in Africa. Although pollutant emission loads are relatively much lower in less developed countries, it is known that long distance cross-boundary transport of pollutants may contribute to pollution in areas far removed from the immediate vicinity of emission sources. Kuylenstierna *et al.* [11] carried out an acid–rain sensitivity mapping of the ecosystems of several developing countries and found that many of these rank as highly sensitive to acidic deposition. Thus, incidence of acidity in rainfall in these regions is liable to cause severe damage to the fragile natural resources of these countries.

Nigeria is one of such countries with a high ranking of acid-rain ecological sensitivity. Rapid industrialisation has taken place in this sub-Saharan African country within the last few decades, leading to increased loads of pollutant emissions. Industrial waste management, though legislated, is not effectively enforced, such that much of what is generated as waste is discharged untreated into the environment. The level of pollution may therefore sometime be more than is proportionately expected in comparison with the developed countries. The study reported in this

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paper was conducted in the city of Ibadan. With a population estimate of about four million, it is the second largest in Nigeria. It is not heavily industrialised, being mainly a commercial and residential centre which hosts a few major industries and many small and medium scale ones. Air pollution in Ibadan is mainly derived from fuel combustion in automobiles and small power generating machines. Electricity power generating machines are widely used in industries and homes due to the chronic shortage of electricity supplies. Industrial process emissions and the burning of solid wastes are additional sources. Oluwande [12] and Onianwa *et al.* [13] have reported that automobile-related pollution levels may be significant in some parts of the city. Though there have been several studies of pollution levels in various environmental media within this city, not much information is available on the composition of rainwater. The aim of the study was therefore to determine the average composition of rainwater in the city.

EXPERIMENTAL

Sampling of rainwater was carried out during May 7 to July 5, 1999. Sampling stations were set up at open spaces in nine locations randomly selected to cover the built-up areas of the city. The sampling equipment was placed on a 2 m high platform, and this consisted of a 5-litre polyethylene bottle fitted with a 20-cm wide polyethylene funnel. The sampling bottle was placed on the platform at the beginning of a rain event. After the rainfall, the bottle was removed, covered with a lid and stored in a refrigerator nearby. This was designed to eliminate significant contribution from dry deposition. The samples collected during each two-weekly sampling period were combined and analysed as a single sample. There were four two-weekly sampling periods covered: period 1 (7 May - 21 May); period 2 (22 May - 5 June); period 3 (6 June - 20 June); and period 4 (21 June - 5 July).

Laboratory analysis was commenced immediately after each sampling period. pH was determined electrometrically, sulphate turbidimetrically, nitrate by the cadmium-reduction colorimetric procedure, phosphate by molybdenum blue colorimetric method, and chloride by mercuric thiocyanate colorimetric method. Sodium and potassium were determined by flame emission photometry, and calcium and magnesium by atomic absorption spectrophotometry. Detailed procedures were followed as described in standard water analysis texts [14]. Reagent blanks for each determination were made by passing the reagents alone through the entire analytical preparations and determination stages for each parameter. Blank corrections were then made to the results as necessary. Appropriate quality control measures for water analysis were observed to specifications [15]. Average rainfall data for the sampling periods were obtained from the meteorological reports of the International Institute for Tropical Agriculture (IITA), Ibadan.

RESULTS AND DISCUSSION

Average results obtained at each of the sampling stations are given in Table 1. Comparison of the results for all stations using the Kruskal-Wallis analysis of variance on ranks indicates that there was no statistically significant difference among the various stations (P = 0.881). The overall average results for Ibadan rainwater (all nine sites and four periods) are presented in Table 2. The rainfall readings for the periods were: period 1 - 64.4 mm; period 2 - 131 mm; period 3 - 90.3 mm; and period 4 - 61.3 mm. pH values at all sampling points were not acidic, typically ranging from 5.8 to 7.0. Average pH was 6.6±0.3. Only pH values lower than 5.6 are regarded as acidic in rainwater, the value 5.6 being that of rainwater in equilibrium with the natural concentration of atmospheric carbon dioxide. Rainwater in Ibadan is thus predominantly neutral. The neutral non-acidic nature of the samples is as a result of neutralisation of the acidity by cations. The acidity would have been derived from the dissolution of sulphur and nitrogen

oxides in the rainwater. Calcium ion occurred in relatively higher concentrations and is perhaps primarily responsible for the neutralisation. Ca is present in the atmosphere as calcium carbonate from dust displaced by the impact of traffic and wind erosion on unpaved roads.

Table 1. Average rainwater composition measured at the various sampling stations.

Parameter	ST*-1	ST-2	ST-3	ST-4	ST-5	ST-6	ST-7	ST-8	ST-9
pH	6.5±0.2	6.4±0.4	6.5±0.3	6.6±0.3	6.6±0.1	6.7±0.4	6.6±0.2	6.6±0.2	6.5±0.4
SO_4^{2-} (µeq/L)	22±14	48±34	40±16	54±10	33±14	54±8	60±22	22±24	58±26
NO_3^- (µeq/L)	3.1±4.5	0.7±0.7	2.3±1.7	2.0±0.8	0.6±0.7	1.2±1.0	1.7±1.5	1.6±1.3	1.7±1.1
Cl^- (µeq/L)	7.8±4.8	26±32	10.3±8.6	11±10	5.6±2.3	13.4±7.0	14.1±9.8	8.5±6.5	8.9±6.2
PO_4^{3-} (µeq/L)	2.6±1.1	2.7±0.2	4.2±2.8	4.0±1.6	2.5±2.7	2.1±1.1	4.2±2.6	4.7±1.8	2.1±0.8
Na (µeq/L)	8.4±5.8	12.8±6.7	8.9±7.1	7.7±8.0	7.6±8.3	21.4±5.0	14.2±5.0	7.9±6.9	16±11
K (µeq/L)	3.9±1.2	7.6±5.3	4.9±3.1	7.1±7.3	4.3±2.6	5.5±1.4	3.8±2.2	3.6±1.7	9.7±8.2
Ca (µeq/L)	12.6±9.9	44±56	29.0±6.6	48±42	18±26	27±14	36±26	34±18	26.0±7.0
Mg (µeq/L)	6.8±4.0	20±14	14±22	7.0±6.2	6.2±4.8	6.0±1.2	15.8±2.4	9.0±5.4	8.4±4.8

*ST = sampling station.

Table 2. Summary of results for all sampling stations and sampling periods.

Parameter	Mean±S.D.	Range
pH	6.6±0.3	5.8-7.0
SO_4^{2-} (µeq/L)	46±22	9.76-83.4
NO_3^- (µeq/L)	1.6±1.8	0.16-9.77
Cl^- (µeq/L)	11±13	1.82-73.9
PO_4^{3-} (µeq/L)	3.2±1.8	0.33-6.33
Na (µeq/L)	11.7±7.9	0.43-27.8
K (µeq/L)	5.6±4.4	1.28-19.7
Ca (µeq/L)	30±26	0.50-125
Mg (µeq/L)	10.2±8.8	0.82-40.4

Sulphate concentrations ranged from 9.76 to 83.4 µeq/L with an average of 46±22 µeq/L while nitrate concentrations ranged from 0.16 to 9.77 µeq/L with an average of 1.6±1.8 µeq/L. Average chloride concentration was 11±13 µeq/L with a range of 1.82 to 73.9 µeq/L. The average for phosphate was 3.2±1.8 µeq/L. Concentrations of the anions were observed to decrease from period 1 to period 4 as the rainfall season progressed (Figure 1). The change in the concentration of phosphate was not very remarkable. Sulphate concentration of 54±18 µeq/L in period 1 decreased to 20±10 µeq/L between period 3 and period 4, the levels being fairly constant during period 1 to period 3. Average nitrate concentration was 2.5±3.0 µeq/L for period 1, but declined to 0.50±0.45 by period 4. The magnitude of decrease was more significant for chloride. From 21±21 µeq/L in period 1, the concentration decreased to about 11 µeq/L during periods 2 and 3, and further to 3.9±2.9 µeq/L by period 4. The decreases are attributable to the 'washing out' of mobilised anion-bearing dust particles from the atmosphere. As the rains progressed and the environment became less dusty, the concentrations detected in the rainwater declined.
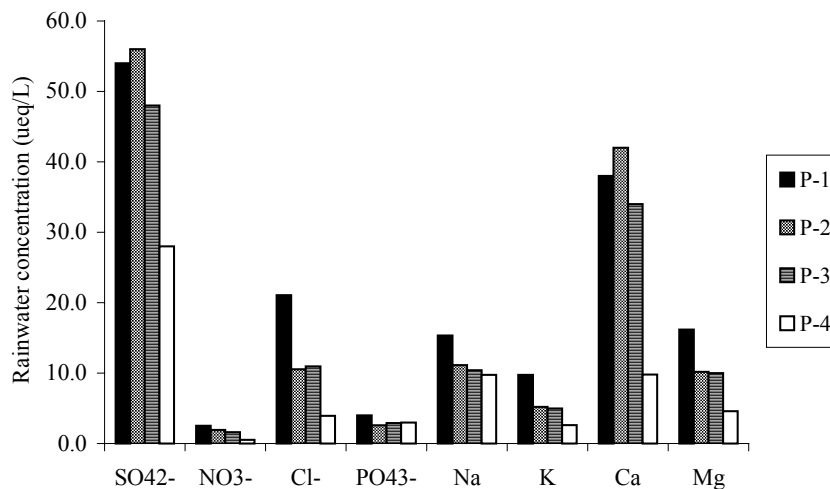
Figure 1. Variation of ion concentrations in rainwater with sampling periods.

Overall average concentrations of the major cations Na, K, Ca and Mg were 11.7±7.9, 5.6±4.4, 30±26, and 10.2±8.8 μeq/L, respectively. Figure 1 also shows that the concentrations of the cations generally declined through periods 1 to 4, the decrease being more significant for Ca and K.

In some studies, Na and Cl⁻ in wet precipitation have been found to be derived from the sea, usually in areas close to seashores [10, 16]. In such cases the ratio of the concentrations (μeq/L) of the two elements would be very close to 1:1 as occurs in NaCl of the sea. Ibadan city is located about 150 km inland from the sea coast in Nigeria. The predominant wind of the sampling period is the South-West wind which blows inland from the Atlantic Gulf of Benin to bring the rains. Thus, some contribution of the rainwater content of NaCl may be expected from the sea. Results obtained in this study for Na and Cl⁻ at the different sampling stations were in many cases close to 1:1 ratio (Table 1). Correlation coefficients for inter-parameter associations in the rainwater are given in Table 3. Na was significantly correlated with sulphate, chloride and potassium, which suggests that some fraction of these elements may have been derived from marine sources. If sulphate was primarily derived from marine Na_2SO_4 or K_2SO_4, the sulphate μeq/L concentration would be expected to be half those of Na and K. The results show that this was not the case (Tables 1 and 2), because a major proportion of the sulphate is actually derived from land-derived sulphur dioxide. Table 3 shows sulphate to be strongly correlated with all cations. On the other hand, nitrate and phosphate are very poorly correlated with Na and K, indicating the non-marine origin of the nitrate and phosphate ions. The results generally point to two sources of the major ions in the rainwater, *i.e.* some contribution from marine sources in addition to the land-based pollution derived main fraction.

Table 3. Correlation matrix for association of analytical parameters.

	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	Na	K	Ca
NO_3^-	0.0985[a]						
Cl^-	0.518[c]	0.0090[a]					
PO_4^{3-}	0.0940[a]	0.178[a]	0.0542[a]				
Na	0.548[d]	0.0883[a]	0.380[b]	0.163[a]			
K	0.524[c]	0.0524[a]	0.442[c]	0.0221[a]	0.448[c]		
Ca	0.665[d]	0.109[a]	0.741[d]	0.0364[a]	0.0126[a]	0.177[a]	
Mg	0.528[c]	0.117[a]	0.617[d]	-0.0294[a]	0.283[a]	0.447	0.425[b]

[a] $(P > 0.05)$; [b] $(P < 0.05)$; [c] $(P < 0.01)$; [d] $(P < 0.001)$; correlations are significant at $P < 0.05$.

Using the values of rainfall data obtained from the IITA meteorological stations, and the known land area of the city (approximately 400 km^2), the total volume of rainfall for the two months study period was estimated. The average concentration of ions in the samples was then used in conjunction with the rainfall data to calculate the average monthly deposition flux (kg km^{-2} $month^{-1}$). The results are given in Table 4. The flux of the major anions followed the order $SO_4^{2-} >> Cl^- > PO_4^{3-} \approx NO_3^-$, while for the cations the order was $Ca > Na > K > Mg$.

Table 4. Estimates of average monthly deposition flux in the wet precipitation.

Ion	Deposition flux (kg km^{-2} $month^{-1}$)
H^+	4.3×10^{-8}
SO_4^{2-}	390
NO_3^-	16.8
Cl^-	67.6
PO_4^{3-}	17.5
Na	46.6
K	37.9
Ca	104
Mg	21.5

Results obtained in this study are compared with those which have been observed elsewhere in the world (Tables 5 and 6). Average pH of 6.2 in this study is higher than average values obtained from all the other studies, where pH tended to range between 4.2 and 5.5. Sulphate concentration in this study (46±22 μeq/L) is comparable to the values obtained in Wales (42±10 μeq/L), New Hampshire (43.4±6.9 μeq/L), and Japan (44±13 μeq/L). The Ibadan levels are higher than those of France (13.8 μeq/L) and Minnesota (22.8 μeq/L), but lower than values obtained in Israel (187±130 μeq/L), La Esperanza (63.6 μeq/L), Amman (249 μeq/L) and Istanbul (478 μeq/L). Rainwater sulphate levels in the more industrialised countries, USA, France, Germany, Wales (UK) are generally either lower than or just about the values obtained in Ibadan. This is the result of deliberate emission reduction policy measures in these developed countries. Nitrate levels in this study (1.6±1.8 μeq/L) are however lower than those obtained from most other studies, being only close to those of France and Wales. Na and Cl^- ion concentrations are higher for France, Japan, Wales, Israel and Jordan than Ibadan. Ratios of Na:Cl^- were in some of these studies similarly close to 1:1 as in marine-derived sources. The Ibadan Na and Cl^- levels compare well with those of Venezuela.

Table 5. Results of pH and anions in this study compared with those of studies elsewhere.

Study area	Study period	PH	SO_4^{2-} (µeq/L)	NO_3^- (µeq/L)	Cl^- (µeq/L)	PO_4^3 (µeq/L)	Ref.
Ibadan, Nigeria (this study)	1999	6.6±0.3	46±22	1.6±1.8	11±13	3.2±1.8	This study
Istanbul, Turkey	Jan-Oct, 1996	6.15	478	124	-	-	[17]
Minnesota, USA	1998	5.49 (4.92–6.87)	22.8 (3.12–54.9)	15.1 (6.3– 50.3)	1.49 (0.28–16.1)	-	[18]
Wales	1995	4.88±0.11	42±10	3.71±0.96	127±39	0.13±0.06	[10]
New Hampshire, USA	1979 to 1989	4.3±0.1	43.4±6.9	25.5±4.9	5.8±1.4	-	[19]
Amman, Jordan	1998	-	249	46.9	129	-	[20]
East Germany	1995	-	50.5 – 92.2	36.7 – 45.8	13.1- 41.6	-	[21]
France	1993-94	-	13.8	5.00	56.9	-	[22]
New Delhi, India	1994	4.4 – 5.9	2.6-127	2.1-46.0	0.79-20.3	-	[23]
Japan	1989-93	4.8±0.7	44±13	14.1±4.1	64±80	-	[6]
La Esperanza, Venezuela	1988-89	4.2 (3.4 – 4.23)	63.6 (2.9 – 396)	12.0 (3.5 – 59.0)	12.1 (2.0 – 146)	0.7 (0.1 – 8.6)	[24]
Haifa, Israel	1988-1998	5.3±1.1	187±130	15±14	318±206	-	[25]
Hartwood, Scotland	1989-98	-	39.6	4.21	162	-	[16]

Table 6.   Results of cations (µeq/L) in this study compared with those of studies elsewhere.

Study area	Study period	Na	K	Ca	Mg	Ref.
Ibadan, Nigeria (this study)	1999	11.7±7.9	5.6±4.4	30±26	10.2±8.8	This study
Istambul, Turkey	Jan-Oct, 1996	-	-	180	-	[17]
Minnesota, USA	1998	1.64 (0.52–17.1)	0.83 (0.33–9.41)	11.6 (4.99–57.9)	3.53 (1.4 – 30.8)	[18]
Wales	1995	100±30	3.1±1.0	10.5±4.0	25.5±8.2	[10]
New Hampshire, USA	1979 to 1989	4.1±1.1	1.3±0.5	3.8±1.1	1.9±0.4	[19]
Amman, Jordan	1998	137	19.7	294	78.7	[20]
East Germany	1995	9.0-37.6	2.4-3.4	15.4-36.6	4.0-7.6	[21]
France	1993-94	52.2	4.10	33.5	14.0	[22]
New Delhi, India	1994	0.82-2.03	0.20-37.8	9.36-61.4	0.60-10.7	[23]
Japan	1989-93	49±70	3.1±2.8	16.0±8.4	13±16	[6]
La Esperanza, Venezuela	1988-89	9.6 (0.7 – 116)	1.3 (0.5 – 9.4)	1.3 (0.4 – 32.4)	0.2 (0.01 – 5.0)	[24]
Haifa, Israel	1988-98	300±198	19±31	228±168	119±85	[25]
Hartwood, Scotland	1989-98	147	-	44.4	40.2	[16]

    Overall, the characteristics of the rainwater in Ibadan city reflect an area of relatively moderate atmospheric pollution as indicated by the acidity-free rainfall, and the concentration of the ions in the rainwater.

REFERENCES

1. Pan, J.; Yang, D.M.; Li, J.H.; Ning, X.G.; Ye, H.Q.; Fukunaga, H.; Yao, Z.K.; Bellani, L. M.; Rinallo, C.; Muccifora, S.; Gori, P. *Environ. Pollut.* **1997**, 95, 357.
2. Walna, B.; Drzymala, S.; Siepak, J. *Sci. Total Environ.* **1998**, 220, 115.
3. Etyemezian, V.; Davidson, C.I.; Zufall, M.; Dai, W.; Finger, S.; Striege, L.M. *Atmos. Environ.* **2000**, 34, 2399.
4. Peart, M.R. *Chemosphere* **2000**, 41, 25.
5. Conlan, D.E.; Lindley, S.J.; Longhurst, J.W.S. *Water, Air, Soil Pollut.* **1995**, 85, 2095.
6. Hara, H.; Kitamura, M.; Mori, A.; Noguchi, I.; Ohizumi, T.; Seto, S.; Takeuchi, T.; Deguchi, T. *Water, Air, Soil Pollut.* **1995**, 85, 2307.
7. Naik, M.S.; Momin, G.A.; Pillai, A.G.; Safai, P.D.; Rao, P.S.P.; Khemani, L.T. *Water, Air, Soil Pollut.* **1995**, 85, 2161.
8. Wang, W.; Wang, T. *Water, Air, Soil Pollut.* **1995**, 85, 2295
9. Sequeira, R.; Lai, C.C. *Atmos. Environ.* **1998**, 32, 133.
10. Reynolds, B.; Lowe, J.A.H.; Smith, R.I.; Norris, D.A.; Fowler, D.; Bell, S.A.; Stevens, P.A.; Ormerod, S.J. *Environ. Pollut.* **1999**, 105, 251.
11. Kuylenstierna, J.C.I; Cambridge, H.; Cinderby, S.; Chadwick, M. J. *Water, Air, Soil Pollut.* **1995**, 85, 2319.
12. Oluwande, P. *Intern. J. Environ. Stud.* **1977**, 11, 197.
13. Onianwa, P.C.; Fakayode, S.O.; Agboola, B.O. *Bull. Chem. Soc. Ethiop.* **2001**, 15, 71.
14. American Public Health Association-American Water Works Association-Water Pollution Control Federation (APHA-AWWA-WPCF). *Standard Methods for the Examination of Water and Wastewater*, APHA-AWWA-WPCF: Washington; **1981**.
15. United States Environmental Protection Agency (USEPA) *Handbook for Analytical Quality Control in Water and Wastewater Laboratories*, EPA-600/4-79-019, Environmental Monitoring and Support laboratory, USEPA: Cincinnati; Ohio, **1979**.
16. Miller, J.D.; Kelly, A.; Milne, F.W. *Sci. Total Environ.* **2000**, 262, 137.
17. Gulsoy, G.; Tayanc, M.; Erturk, F. *Environ. Pollut.* **1999**, 105, 273.
18. Krupa, S.; Nosal, M. *Environ. Pollut.* **1999**, 104, 477.
19. Martin, C.W.; Likens, G.E.; Buso, D.C. *Water, Air, Soil Pollut.* **2000**, 120, 359.
20. Jaradat, Q.M., Momani, K.A., Jiries, A.G., El-Alali, A., Batarseh, M.I., Sabri, T.G.; Al-Momani, I.F. *Water, Air, Soil Pollut.* **1999**, 112, 55.
21. Brueggemann, E.; Rolle, W. *Water, Air, Soil Pollut.* **1998**, 107, 1.
22. Ulrich, E.; Lelong, N.; Lanier, M.; Schneider, A. *Water, Air, Soil Pollut.* **1998**, 102, 239.
23. Kulshrestha, U.C.; Sarkar, A.K.; Srivastava, S.S.; Parashar, D.C. *Water, Air, Soil Pollut.* **1995**, 85, 2137.
24. Morales, J.A.; Bifano, C.; Escalona, A. *Water, Air, Soil Pollut.* **1995**, 85, 2325.
25. Mamane, Y.; Gottlieb, J. *Water, Air, Soil Pollut.* **1995**, 82, 549.