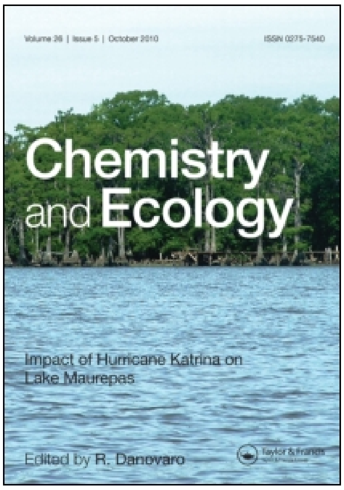

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Trace metals in bulk freefall and roof intercepted rainwater at Ile-Ife, Southwest Nigeria

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Samples of bulk freefall and roof-intercepted rainwater collected over five roof types (*viz*: Iron–Zinc sheets, Aluminum sheets, Asbestos sheets, Slate tiles, and Thatch) at Ile-Ife (SW Nigeria) were analysed for nine trace metals (aluminum, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc) using atomic absorption spectrophotometry (AAS). The mass concentrations and percent detection of the trace metals were generally higher in roof-intercepted samples than in the freefall samples. The ranking order of the mean concentrations of the metals in freefall samples (Al > Cr > Fe > Zn > Pb > Mn > Ni > Cu > Cd) is indicative of an atmospheric environment greatly influenced by heavy vehicular emissions and remobilized suspended particulate matter of soil origin. Mean metal enrichment of samples over the different roofs was in the order of Iron–Zinc > Aluminum > Thatch > Asbestos > Slate roof. Each roof sample type (except Slate samples) was characterized by relatively high enrichment of one or two metals. These include the high enrichment of zinc and iron in Iron–Zinc roof samples, cadmium and manganese in Aluminum roof samples, copper and manganese in Thatch roof samples and cadmium in Asbestos roof samples. The metal concentrations of roof-intercepted rainwater were lower than those of neighboring surface water, packaged table water, and vegetation-intercepted rainwater in the same environment. The metal levels in all the rainwater sources occurred within the allowable guide levels for most public and domestic applications.

Keywords: Atmospheric precipitation; Roof collected rainwater; Public water supply; Water quality; Metal enrichment; Dust remobilization; Vehicular traffic

1. Introduction

Atmospheric precipitation (mainly in the form of rain, hail, and snow) is an integral component of the hydrological cycle. It is an important source of ground water natural recharge and, as runoff, contributes to stream flow, lakes/reservoirs, and other surface water bodies. It is therefore considered the primary source of all water supplies [1, 2]. Rainwater collection harvested over house roofs is one of the practicable sources to derive water for public and domestic purposes. In Nigeria, roof-harvested rainwater is a major part of the public water supply system in parts of the country where there is no pipe-borne water supply and/or where

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ground water sources are not easily accessible through hand-dug wells. The major use of roof harvested rainwater in the country is for drinking and other domestic purposes. To a limited extent, it is also used for homestead fish pond culture and self-supplied industrial establishments, especially for isolated dwellings in the semi-urban and rural areas of the country.

Rainwater in equilibrium with atmospheric carbon dioxide is slightly acidic (pH $\approx$ 5.6). Hence rainwater has greater potential to corrode metals and metallic structures than other surface water sources from which public water supplies are commonly provided. Thus a particular concern about roof collected rainfall relates to the pick-up of metals from leaching of roof materials, especially trace/heavy metals many of which have direct consequences on man and aquatic ecosystems. The hazards of heavy metals pollution evidenced by such episodes as the minamata and Nigata Bay incidents and by the occurrence of itai-itai ('ouch-ouch') disease, caused respectively by mercury and cadmium poisoning are now well known [3].

In the present study area, information has been provided on trace/heavy metals concentrations in airborne suspended particulate matter [4], vegetation-intercepted rain [5], packaged table water or 'pure water' [6], roadside soil and vegetation [7] as well sewage and effluents from oxidation ponds [8]. In the present study, the concentrations of nine trace/heavy metals (namely: Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) and their enrichment in rainwater collected over five different roof types were investigated with regard to differences in the age of the roofing materials as well as the periods of the rainy season. The variations were also related to the general classification of the metals with regard to density, toxicity, and industrial applications [9, 10, 11].

2. Materials and methods

2.1 *Area of study*

This study was carried out at Ile-Ife (or commonly Ife), Osun State, in Southwest Nigeria. The Ile-Ife conurbation covers the land area approximately between latitudes 07° 26–07° 33 N and longitudes 004° 30–004° 35 E. It is about 200 km northeast of Lagos (the former Federal Capital of Nigeria and the principal industrial center of the country), about 120 km north of the Atlantic coast, and about 600 km southwest of Abuja, the present Federal Capital of Nigeria. With a population of about 403,000 [12], Ile-Ife was (1991 estimate) the only town in Osun State that belonged to the group of towns in Nigeria (then comprising only 18 towns) with human population >400,000 people. During the colonial era, houses in the study area and most parts of southwest Nigeria were roofed with grass thatch, iron–zinc (galvanized iron) sheets, and concrete/slate tiles (this was mostly used for government/public buildings). Today thatch roofs have, more or less, disappeared completely while other roofing materials such as asbestos sheets (locally called by the trade name Adex) and aluminum sheets have gained prominence. In decreasing order of occurrence, the ranking of the different roofing materials in Ife area today is: iron–zinc > asbestos > aluminum > concrete/slate tiles > thatch. Although there are no major manufacturing industries in Ife-Ife, its commercial status has grown considerably since the establishment of the Obafemi Awolowo University, OAU (formerly the University of Ife) about four decades ago.

The Ile-Ife area falls within the Moist Monsoon world climate type [13] and the moist type of the seasonally Humid Tropical Climates of West Africa [14]. The typical annual cycles of the major meteorological parameters at Ile-Ife are shown in figure 1. Relative humidity

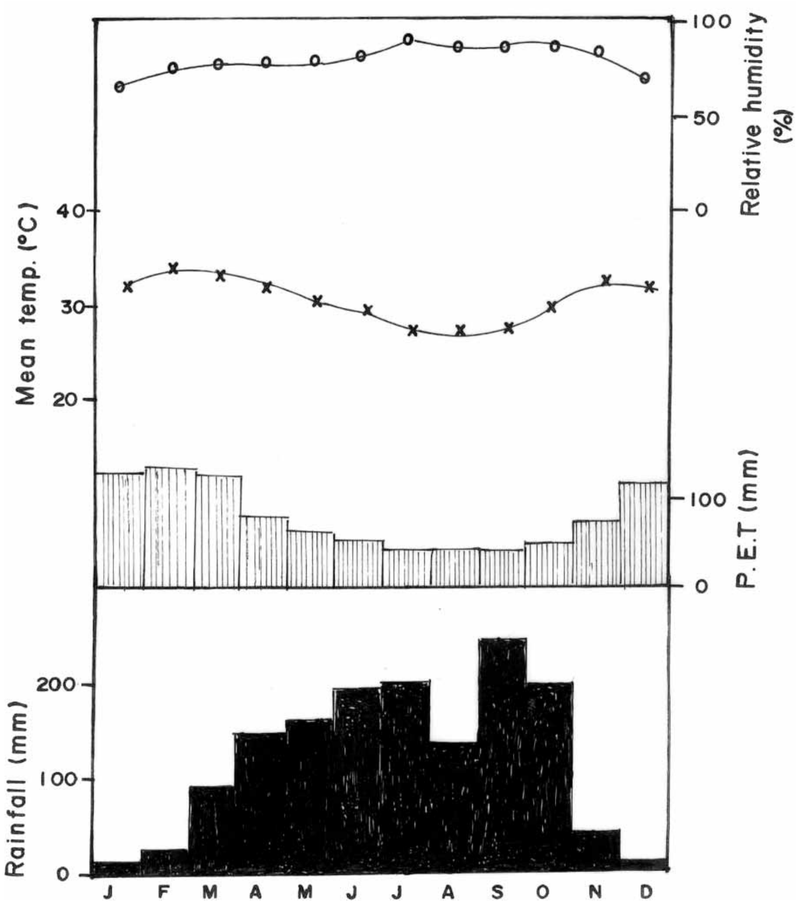

Figure 1. The climate diagram of Ile-Ife.

and temperatures are generally high and characterized by more pronounced diurnal variations than annual variations. The rainfall regime is marked by dual maxima (July and September) as well as dual minima (August break and January). About 90% of the total annual rainfall amount (long term mean, 1955–1998 $= 1433 \pm 256$ mm standard deviation) occurs during the humid period of April–October. The beginning and end of the rainy season are characterized by large-scale traveling disturbance lines associated with thunderstorms [15]. The area is underlain by the Pre-Cambrian Basement Complex rocks of which the major types are gneiss, pegmatite, pegmatite schist, and undifferentiated schists [16] while the soils are Lixosols [17] and Ultisols [18].

2.2 *Sampling sites and sample collection*

The choice of sites for sample collection was made mainly with regard to availability of the desired roofing materials, accessibility to the locations and adequate security of experimental set up and collecting materials to be deployed. Eleven such sites were selected all over the study area for sample collection. Roofs in the age range of less than two years were classified as new while those in the range of 2–10 years were classified as middle age and those >10

Table 1. Site description and the grid co-ordinates of the investigated rain sampling stations at Ile-Ife, Nigeria.

No.	Sampling station site description at Ile-Ife	GPS grid coordinates Latitude (N)	Longitude (E)	Type of roof cover
1.	Aba Gbooro/Oni Ilare Road	07° 32.702	004° 30.722	Thatch
2.	Road 20A SSQ, OAU campus	07° 31.515	004° 32.635	Adex/Asbestos (old), freefall
3.	Arch. Building, OAU campus	07° 31.253	004° 31.124	Aluminum (new)
4.	Old Power House, OAU campus	07° 30.965	004° 31.428	Aluminum (medium)
5.	Medical Students' Hostel, OAUTHC	07° 30.626	004° 33.485	Adex/Asbestos (medium)
6.	Maintenance Building, OAUTHC	07° 30.304	004° 33.414	Aluminum (old)
7.	Behind Slaughter Slabs, Ede Road	07° 29.731	004° 34.140	Adex/Asbestos (new)
8.	Apostolic Church, Ibadan Road	07° 29.733	004° 30.853	Iron–Zinc (medium)
9.	PPS Assembly, Ibadan Road	07° 29.751	004° 30.804	Iron–Zinc (new), freefall
10.	Residential house, Ibadan Road	07° 29.76	004° 30.793	Iron–Zinc (old)
11.	School of Science, Ondo Road	07° 26.939	004° 32.635	Concrete/Slate (medium)

Arch = Architecture Department; SSQ = Senior Staff Quarters; OAU = Obafemi Awolowo University; OAUTHC = Obafemi Awolowo University Teaching Hospital Complex; GPS = Global Positioning System; PPS = prosperity pace setters.

years as old roofs. The description and grid co-ordinates of these sites as determined using a portable Global Positioning System equipment (GPS) are given in table 1.

At each sampling site, bulk samples [19] of freefall and roof intercepted rainwater were collected using plastic buckets with punched holes on the cover (so that only a portion of each rain event and dry deposition was actually collected into the bucket). Each bucket was placed on a raised platform about 0.5–1.0 m above the ground level (to prevent contamination with soil intercepted rain) and adequately supported so that it could not be blown over by strong wind. Sampling started in May 2001 and lasted throughout the rainy season of the year. The bulk samples for the early rains (May and June) were harvested at the end of June, while those of mid-season rains (July and August) were harvested at the end of August and late rains (September and October) collected at end of October 2001. Subsamples for trace/heavy metals analysis were collected into clean 500 milliliter glass bottles, and acidified to pH $\approx$ 2 [20] prior to analysis.

2.3 *Chemical analysis of samples*

The trace metal analysis of the bulk freefall and roof-intercepted rainwater samples collected in this study was carried out at the Centre for Energy Research and Development (CERD) at the Obafemi Awolowo University (OAU) using Flame Atomic Absorption Spectrophotometry (FAAS). Measurements of the respective metals were carried out at the following wavelengths: 213.9 nm (zinc), 217 nm (lead), 228.8 nm (cadmium), 248.8 nm (iron), 279.6 nm (manganese), 309.3 nm (aluminum), 323.0 nm (nickel), 324.7 nm (copper), and 357.0 nm (chromium) in accordance with the instrument manufacturer's handbook. The commercial standard of each metal was used for the calibration of the instrument. The detection limits of the instrument were in the range of 1–10 $\mu g\,l^{-1}$ for Cd, Cr, Cu, Fe, Mn, Ni, and Zn and 10–100 $\mu g\,l^{-1}$ for Al and Pb. The precision levels of determination were routinely established under condition of triplicate measurements. The methods of analysis for the general physico-chemical variables of the rain samples have been documented fully elsewhere [21]. The data obtained were subjected to appropriate statistical tests, including descriptive statistics (to summarize the data), Duncan Multiple Mean Range Test (to test the degree of difference between mean values), regression and correlation analyses, and cluster analysis by the farthest-neighbor or total linkage method (to show relationship between rainfall sources).

3. Results

3.1 *Mass concentrations and enrichment of trace-metals in rainwater samples*

The mean, median and the percent detection values of the investigated trace metals were generally higher in the roof-intercepted samples than in the freefall samples (table 2) suggesting enrichment of the roof-intercepted samples relative to the freefall samples. The mean mass concentrations of the trace metals in the roof-intercepted samples were all within the following three continuous ranges:

$$<0.01\,\mathrm{mg\,l^{-1}} = \mathrm{Ni} > \mathrm{Cu} > \mathrm{Cd}$$

$$0.01{-}0.10\,\mathrm{mg\,l^{-1}} = \mathrm{Cr} > \mathrm{Fe} > \mathrm{Pb} > \mathrm{Mn}$$

$$>0.10\,\mathrm{mg\,l^{-1}} = \mathrm{A1} > \mathrm{Zn}$$

The mean concentrations of freefall samples occurred in the lower quartile values of roof-intercepted samples for Zn, Cd, and Mn but in the upper quartile values of the roof-intercepted samples for Al, Cu, and Ni. On the other hand, Fe, Cr, and Pb contents of the freefall samples occurred within the second and third quartiles (50–75%) of the roof-intercepted samples. Based on the matrix of correlation coefficients of all recorded values, the nine investigated trace elements could be grouped broadly into two negatively correlated clusters comprising Al, Zn, Cr, and Cd (as one cluster) against Fe, Pb, Mn, Ni, and Cu as the other cluster. The members of the aluminum cluster are mostly non-ferrous metals and are generally lighter (densities = 2.70–8.65 g cm^{-3}) than members of the second cluster, which are mostly ferrous [10] and heavier metals (densities = 7.4–11.3 g cm^{-3}).

Table 2. Descriptive statistics of concentrations of trace metals in bulk freefall and roof-intercepted rainwater at Ile-Ife.

		Descriptive statistics of metal concentrations (mg l^{-1}) in bulk rainwater					
Trace metal	Rain type	% Detection	Maximum	Median	Mean	SE	% CV
Aluminum (Al)	Freefall	40	4.90	0.00	0.91	0.97	151
	Roof-intercepted	36	6.41	0.00	1.44	0.31	192
Zinc (Zn)	Freefall	80	0.040	0.020	0.020	0.004	50
	Roof-intercepted	78	2.431	0.033	0.290	0.100	190
Lead (Pb)	Freefall	20	0.10	0.00	0.02	0.03	200
	Roof-intercepted	34	0.15	0.00	0.03	0.01	150
Copper (Cu)	Freefall	40	0.012	0.000	0.003	0.002	127
	Roof-intercepted	56	0.015	0.001	0.004	0.001	150
Cadmium (Cd)	Freefall	20	0.003	0.000	0.0006	0.0004	200
	Roof-intercepted	20	0.030	0.000	0.002	0.001	300
Iron (Fe)	Freefall	80	0.05	0.02	0.022	0.009	69
	Roof-intercepted	84	0.14	0.02	0.035	0.005	125
Manganese (Mn)	Freefall	40	0.01	0.00	0.004	0.002	123
	Roof-intercepted	63	0.06	0.01	0.011	0.002	100
Chromium (Cr)	Freefall	100	0.06	0.06	0.060	0.004	17
	Roof-intercepted	100	0.13	0.07	0.072	0.004	31
Nickel (Ni)	Freefall	40	0.027	0.000	0.006	0004	140
	Roof-intercepted	50	0.029	0.002	0.008	0.001	125

CV = Coefficient of Variation; SE = Standard Error of Mean.
Ranking Order: Freefall rainwater: Al > Cr > Fe > Zn > Pb > Mn > Ni > Cu > Cd; Roof-intercepted rainwater: Al > Zn > Cr > Fe > Pb > Mn > Ni > Cu > Cd.

Table 3. The mean concentrations (and enrichment factors) of trace metals in rainwater over different roof types at Ile-Ife.

Trace metal ($mg\,l^{-1}$)	Mean concentrations and (enrichment factor) of rainwater over roofs					
	Freefall	Aluminum	Slate	Asbestos	Iron – Zinc	Thatch
Aluminum (Al)	0.909^{a}	1.61^{a} (1.77)	1.23^{a} (1.36)	0.32^{a} (0.35)	0.89^{a} (0.98)	0.001^{a} (0.00)
Zinc (Zn)	0.020^{b}	0.054^{b} (2.5)	0.014^{b} (0.70)	0.027^{b} (1.35)	0.934^{a} (46.7)	0.046^{b} (2.30)
Lead (Pb)	0.02^{a}	0.01^{a} (0.50)	0.02^{a} (1.15)	0.01^{a} (0.65)	0.03^{a} (1.30)	0.05^{a} (2.50)
Copper (Cu)	0.003^{b}	0.006^{b} (2.00)	0.002^{b} (0.67)	0.004^{b} (1.33)	0.001^{b} (0.33)	0.04^{a} (13.30)
Cadmium (Cd)	0.0006^{a}	0.004^{a} (6.67)	0.0001^{a} (0.17)	0.002^{a} (3.33)	0.001^{a} (1.67)	0.0001^{a} (0.17)
Iron (Fe)	0.022^{b}	0.024^{b} (1.09)	0.013^{b} (0.59)	0.022^{b} (1.00)	0.078^{a} (3.53)	0.050^{b} (2.27)
Manganese (Mn)	0.004^{a}	0.021^{a} (5.25)	0.007^{a} (1.75)	0.004^{a} (1.00)	0.007^{a} (1.75)	0.020^{a} (5.00)
Chromium (Cr)	0.060^{a}	0.083^{a} (1.38)	0.077^{a} (1.28)	0.064^{a} (1.07)	0.071^{a} (1.18)	0.070^{a} (1.12)
Nickel (Ni)	0.006^{a}	0.010^{a} (1.17)	0.077^{a} (1.16)	0.002^{a} (0.33)	0.006^{a} (1.00)	0.0001^{a} (0.02)

Values in the row and having similar superscripts letters are not significantly different ($P > 0.05$) while those with different superscript letters are significantly different ($P \leq 0.05$).
Values in bracket indicate enrichment factors.

Table 3 presents data on the metal mean concentrations (based on Duncan multiple mean range test) and enrichment factor in roof-intercepted rainwater (*i.e.* roof-intercepted value/freefall value) over the different roofing materials. The mean levels of Zn, Cu, and Fe were significantly different ($P < 0.05$) among the different roof-intercepted and freefall rain samples. Zn and Fe were significantly higher in samples collected over Iron–Zinc roofs than in the other sample types. On the other hand, the mean concentration of Cu was significantly higher in Thatch roof samples than in the other rain samples. On the basis of their mean metal contents, the sample sources could be grouped into two distinct clusters ($P < 0.05$) comprising Thatch roof samples against the other sample over other types (figure 2). Thatch roof samples were characterized by low contents of Al but with relatively high values of Pb and Cu compared to the other sample types. On the whole, samples over Slate and Asbestos roofs were characterized by relatively low enrichment of trace metals while Aluminum and Iron–Zinc roofs were characterized by relatively high values. Aluminum roof samples had relatively high

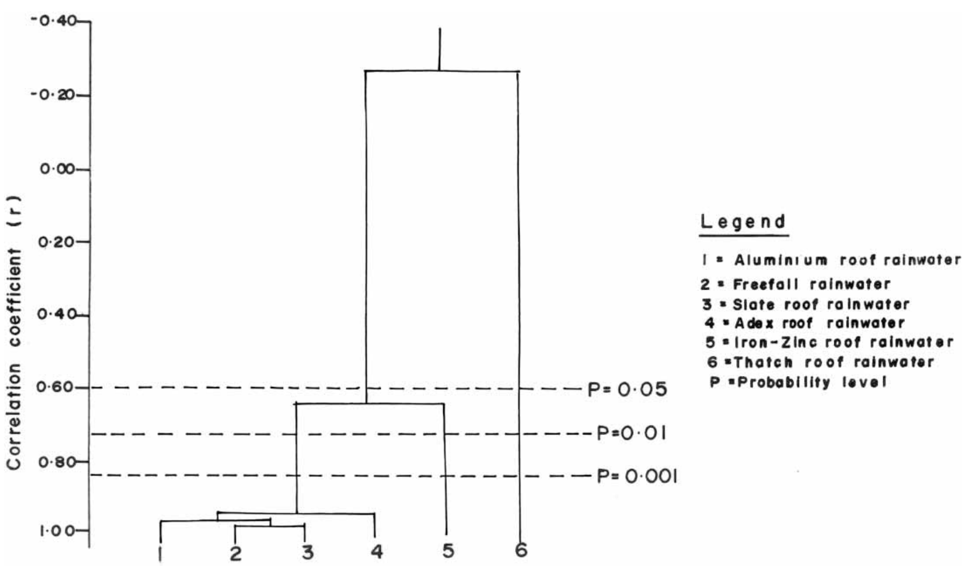

Figure 2. Cluster analysis showing the relationship between the different roof-intercepted rainfall sources.

cadmium and manganese enrichment, iron–zinc roof samples were characterized by zinc and iron metal enrichment while Thatch roof samples were characterized by high copper and manganese enrichment. The enrichment factors for the roof samples occurred mostly in the range of 1–2 while values >3 were recorded for only less than 20% of the total roof-intercepted samples. Excluding the highest outlying value of 46.7 (recorded for Iron–Zinc roof sample) the overall mean enrichment value was 1.8 ± 0.3 standard error.

3.2 *Relationship between trace metal contents and general water quality parameters*

Organic matter, nitrate and acidity of the rainwater samples showed positive correlation with most of the trace metals while TDS, NH_4^+, Cl^-, alkalinity, and SiO_2 mostly showed negative correlations with the metals (table 4). Sample pH as well as Ca^{2+} and Mg^{2+} contents showed positive correlations with the non-ferrous trace metals but negative correlations with the ferrous trace metals. On the other hand, sample apparent colour, turbidity, Na^+, K^+, SO_4^{2-}, and NO_3^- contents showed negative correlation with the non-ferrous trace metals but positive correlation with the ferrous metals.

3.3 *Variation in trace metals contents with roof age and period of the rainy season*

The concentrations of trace metals (especially for Al, Cr, Mn, and Cu) were generally higher ($P > 0.05$) in samples collected over new aluminum roofs than those collected over the old roofs of the same material. On the contrary, the concentrations of Al, Zn, Cd, and Ni were generally higher in samples collected over old Iron–Zinc roofs than in samples collected over new Iron–Zinc roofs. Again, most of the trace metals (notably Zn, Cu, Cd, Fe, and Ni) were slightly higher in samples over old Asbestos roofs than over the new roofs of the same material. The temporal variation in the concentrations and enrichment of trace metals in rainwater samples did not show a definite pattern. However, for most of the trace metals, concentrations were slightly higher both in early and late rain samples than in the mid-season samples. This generalization was particularly applicable to the concentrations of Al, Pb, Cu, and Fe.

4. Discussion

4.1 *Suitability of water for drinking and other applications*

Of the nine metals investigated in the present study, five of them (namely: cadmium, chromium, copper, lead, and nickel) fell within the group widely regarded with serious concern while the other four metals (aluminum, iron, manganese, and zinc) are not known to be harmful to humans in concentrations commonly found in natural water sources. Cadmium, chromium, copper, and lead are among the Type A Group of inorganic chemicals of public health concern, and are regulated in drinking water (for toxicity and/or carcinogenicity) by the European Community (EC) and the World Health Organization (WHO) [22]. Aluminum, nickel, and zinc (Type B inorganic chemicals) are of limited concern while manganese and iron (Type C inorganic chemicals) are considered safe although they do have some aesthetic and organoleptic effects [2].

In the present study, all but one of the nine investigated metals (chromium) had 100% compliance with guide levels [21, 23] for drinking (table 5). However chromium values occurred over a narrow range (0.03–$0.13\ \mathrm{mg\,l^{-1}}$) with mean/median values not significantly different

Table 4. Matrix of correlation coefficients between general water quality parameters (x) and trace metal concentration (y) in bulk rainwater at Ile-Ife.

	Trace metal concentrations ($mg\,l^{-1}$)								
	Non-ferrous metals					Ferrous metals			
Parameter	Al	Zn	Pb	Cu	Cd	Fe	Mn	Cr	Ni
Apparent colour (Pt-Co)	−0.0465	−0.0553	0.0461	0.2842	−0.0504	0.3968*	0.2488	−0.1826	0.2109
Turbidity (NTU)	−0.0248	−0.0421	−0.0825	0.2443	−0.0151	0.1359	0.2103	−0.2429	0.3681*
TSS ($mg\,l^{-1}$)	−0.3291*	0.1524	−0.0378	0.0307	−0.0630	−0.1796	0.2386	−0.0373	0.1964
TDS ($mg\,l^{-1}$)	−0.1630	−0.3168	0.0258	−0.1871	−0.0411	−0.0964	−0.2009	−0.1368	−0.0274
Conductivity ($uS\,cm^{-1}$)	−0.1732	−0.2336	0.1283	0.2978	0.0079	0.4003*	0.1249	−0.0446	−0.0559
pH (pH unit)	0.1024	−0.3354*	0.0266	0.2457	0.1108	−0.0464	−0.1097	0.0304	−0.2189
Ca^{2+} ($mg\,l^{-1}$)	0.0395	−0.2219	0.0261	0.0826	0.0203	0.1606	−0.1438	−0.1456	−0.0293
Mg^{2+} ($mg\,l^{-1}$)	0.3435*	0.0823	0.0159	−0.0773	0.1998	0.2306	−0.0402	−0.2207	−0.0131
Na^{+} ($mg\,l^{-1}$)	−0.0511	−0.0931	0.1138	−0.0240	−0.0666	−0.0456	0.1005	−0.0515	0.0071
NH_4^{+} ($mg\,l^{-1}$)	0.0469	−0.0479	−0.3898*	0.0265	0.1770	−0.0896	−0.2820	−0.0375	0.1482
SO_4^{2-} ($mg\,l^{-1}$)	−0.2024	−0.0381	0.0065	−0.0013	−0.1353	0.3971*	−0.1015	0.0974	0.2659
Cl^{-} ($mg\,l^{-1}$)	−0.1031	0.0223	0.1536	−0.2064	−0.0752	−0.1370	0.0001	−0.0209	−0.0319
NO_3^{-} ($mg\,l^{-1}$)	−0.0993	−0.0836	−0.0898	0.1586	0.0190	0.0467	0.1004	0.0898	0.0211
Acidity $CaCO_3$ ($mg\,l^{-1}$)	0.0346	0.4906*	−0.0344	0.0925	0.02051	0.1558	0.3106	0.2772	0.1718
Alkalinity $CaCO_3$ ($mg\,l^{-1}$)	−0.1461	−0.2548	−0.0861	−0.0205	−0.1047	−0.1372	−0.2440	−0.1548	−0.1721
Hardness $CaCO_3$ ($mg\,l^{-1}$)	0.1472	−0.1484	0.0260	0.0393	0.0837	0.2053	−0.1275	−0.1900	−0.0276
Organic matter ($mg\,l^{-1}$)	−0.1910	−0.0522	0.1511	0.1688	0.0777	0.4741**	0.0756	0.0918	0.1575
SiO_2 ($mg\,l^{-1}$)	−0.0937	−0.2279	0.0992	−0.2278	−0.0788	−0.1788	−0.0928	−0.0653	0.1412

*$P \leq 0.05$; **$P \leq 0.01$.

Table 5. Guide level compliance and likely contribution of rainwater to mineral nutrition of humans at Ile-Ife.

	Guidelevel (GL) for drinking ($mg\,l^{-1}$)					% Contribution to PCIPD from water			
Trace metal	WHO [23]	CEC [24]	USEPA [25]	Compliance with GL*	PCIPD** (mg/day/man)	Typical**	Max**	Freefall rain***	Roof intercepted***
Aluminum (Al)	ND	ND	ND	100%	20	ND	ND	9.10	14.40
Zinc (Zn)	5	5	ND	100%	12.4	ND	ND	0.32	4.68
Lead (Pb)	0.05	0.05	ND	100%	0.038	ND	ND	0.02	0.03
Copper (Cu)	1.0	0.1	ND	100%	4	12	38	0.15	0.20
Cadmium (Cd)	0.005	0.005	ND	100%	0.058	ND	ND	2.1	6.90
Iron (Fe)	0.3	0.5	ND	100%	19	2.5	23	0.21	0.36
Manganese (Mn)	0.05	0.05	0.05	100%	3.6	1–5	29–72	0.22	0.68
Chromium (Cr)	0.05	0.05	ND	16%	0.2	ND	ND	60	72
Nickel (Ni)	ND	ND	0.15	100%	0.46	2.6	23–50	2.6	3.48

*This study based on range of values; **Source = USNAS (1981); ***Mean value for this study; ND = No data; PCIPD = Per capita intake per day.

from the set guide level for drinking ($0.05\,mg\,l^{-1}$) [23, 24]. It is also interesting to note that the recorded mean rainwater chromium levels can make substantial contribution (ca. 60–70%) to human dietary requirement for the element, unlike the other metals which make negligible contributions (table 5). In spite of all these, even the highest value of $0.13\,mg\,l^{-1}$ of chromium obtained is about one order of magnitude less than the $1\,mg\,l^{-1}$ guide level for fish culture, invertebrate aquatic lives, and livestock watering [26] and about two order of magnitude lower than the level considered to be toxic to several species of algae [3, 11]. Thus, the levels of chromium and all the other investigated metals in rainwater sources in the present study are considered safe and suitable for a wide range of applications including drinking.

It is possible, if so desired, to take advantage of the relationship between the investigated trace metals and the other parameters of rainwater quality (table 4) to effect further decrease in the concentrations of the metals in rainwater sources for wider applications of the rainwater sources. Such metal reduction can be achieved by effecting appropriate increase in the total alkalinity/pH or a decrease in the total acidity of harvested rainwater, probably by liming. Such treatment can effect a significant decrease especially in zinc and manganese both of which showed fairly high negative correlation with alkalinity (table 4). As metal enrichment was generally higher in samples over new roofs than over old roofs and also higher during early rains than in later rains the collection of rain relatively low in metal could also be achieved by preferentially collecting rain over old roofs and/or during the later part of the rainy season. It is probably for the latter reason that the need to prevent the use of early flushing of roof-harvested rainwater has been recommended [2]. In this regard, the three heavy metals (Cu, Mn, and Fe) commonly associated with water discolouration were all highly correlated with water colour in the present study (table 4) and also characterized with the highest mean concentrations during the early rains Thus the collection of mid-season through late rains in preference to early rain will imply reduction in the concentration of Cu, Mn, and water colouration.

4.2 *Background concentrations and probable sources of metals*

Table 6 presents data on the general levels of the nine investigated metals in the study area. A significant direct correlation ($P < 0.05$) exists between the concentrations of the metals in outdoor air particulate matter and those of the freefall rainwater as measured in the present study. Although the concentrations in the former were generally about 5–6 order of magnitude higher than those in the latter, the ranking order of the metals in the two media were close to

Table 6. Levels of trace metals in Ile-Ife environment.

Metal (ppm)	Airborne SPM[a] (mean ± CV)	Stream at OAU[b] (mean ± SE)	Vegetal interception (mean ± SE)[c]		Packaged water[d] (mean ± SE)	This study (mean ± SE)	
			Throughfall	Stemfall		Freefall rain	Roof intercepted
Al (Al_2O_3)	235,700 ± 21%	ND	ND	ND	ND	0.909 ± 0.973	1.440 ± 0.310
Fe (Fe_2O_3)	185,000 ± 50%	1.80 ± 0.01	3.23 ± 1.40	2.82 ± 0.56	ND	0.022 ± 0.009	0.035 ± 0.005
Zn (ZnO)	3,400 ± 18%	0.12 ± 0.01	9.80 ± 1.25	7.78 ± 2.01	0.30 ± 0.17	0.020 ± 0.004	0.290 ± 0.100
Pb	ND	<0.008	ND	ND	0.09 ± 0.03	0.020 ± 0.03	0.030 ± 0.005
Cu	287 ± 47%	ND	0.11 ± 0.03	0.12 ± 0.01	ND	0.003 ± 0.002	0.004 ± 0.001
Mn	1,660 ± 19%	0.04 ± 0.01	0.22 ± 0.09	0.30 ± 0.19	0.02 ± 0.01	0.004 ± 0.002	0.011 ± 0.002
Cr	282 ± 22%	<0.001	ND	ND	ND	0.060 ± 0.004	0.072 ± 0.004
Ni	102 ± 30%	ND	ND	ND	ND	0.006 ± 0.004	0.008 ± 0.001
Cd	ND	<0.001	ND	ND	ND	<0.001	0.002 ± 0.001

[a]Akeredolu (1989); [b]Ogunfowokan *et al.* (2005); [c]Muoghalu and Oakhumen (2000); [d]Ogunfowokan *et al.* (2000).
SPM = Suspended Particulate Matter; OAU = Obafemi Awolowo University, Ile-Ife; ND = Not Determined; CV = Coefficient of Variation.

each other and similar to that of the typical soil as evident in the following:

Airborne particulate matter [4]: Al > Fe > Zn > Mn > Cu > Cr > Ni

Freefall rainwater: Al > Fe > Cr > Zn > Pb > Ni > Mn > Cu > Cd

Typical soil [27]: Al > Fe > Mn > Zn > Cr > Ni > Pb > Cu > Cd.

The above orders suggest that the metal contents of freefall rainwater reflect largely that of outdoor air particulate dust matter that is essentially of soil origin [4]. As already revealed in an earlier work [4] the major sources of outdoor air suspended particulate matter (SPM) in the study area are remobilized dust produced by motor vehicle traffic on roads (1445 tonnes/years for unpaved roads and 440 tonnes/year for paved roads), and domestic waste incineration (200 tonnes/year). In the area, dwelling houses are located very close to the kerbs along road corridors and about 80% of the roads are unpaved such that vehicles generate much dust as they travel over them. In the last five years, *i.e.* since the life of the present democratic government in Nigeria, vehicular traffic has more than doubled while the proportion of unpaved to paved roads remain more or less the same.

The predominance of aluminum and iron in the general environment of the study area (soil, suspended particulate matter, and rainwater) seems to reflect the nature of the bed rock geology of the area. The area is underlain by crystalline metamorphic rocks of the lower green-schist upper amphibolite facies that consist mainly of hornblende, gneisses, pegmatite and muscovite-sericite schist [16]. The mineralogical assemblages are quartz, feldspars, micas and other ferromagnesium minerals. Biotite, hornblende, and muscovites, all of which are widespread in the area, are known to have Fe and Al as their major constituents, and Ni, Co, Mn, Zn, and Cu as trace constituents [28].

Another notable observation on the metal ranking orders is the enhanced positions of Cr and Pb in rainwater as compared to the typical soil and/or ambient air particulate matter content. This situation may be due to the increase in vehicular traffic in the study area. This might have been enhanced by the effects of the two-year intracommunial warfare that ended in the study area just before this study was carried out. Prior to the war, about 0.2–3.1 tonnes/year of lead particulate was reported injected into the atmosphere along with remobilized road dust in the study area [4]. This was in addition to the possible emissions from about fifty gas stations in the area. Many workers have established such emissions and those resulting from the combustion of fossil fuels (gasoline) which constitute an important source of a number of heavy metals *e.g.* (Cr, Cd, Ni, and Zn) in addition to lead (Pb), the compounds of which are used as an antiknocks in most combustion engines. In Nigeria the Pb content of gasoline remains one of the highest in the world ($0.74\,g\,l^{-1}$) [29]. Apart from Pb emission, other elements, which are constituents of crude oil such as V, Cd, and AS are released into the atmosphere during combustion of petroleum products. Other toxic elements such as Fe and Sb which are essential components of motor vehicle parts are also emitted as a result of wear and tear [29].

During, the two-year intracommunal warfare in the study area, ammunition and a wide range of explosives were freely used. Chromium, aluminum, and lead are the major metals expected to be released into the atmosphere as a result of warfare [11]. It is probable that the combined effect of the warfare, the heavy vehicular traffic and wide spread gas stations in the study area account for the elevated levels of Al, Cr, and Pb in the freefall rain compared to the nearby stream in the area (table 6, column 3) or the typical soil.

4.3 *Metal enrichment of rain over roofs*

The metal enrichment of bulk rainwater over the test roofs was generally low (mean 1.8) especially when compared with the corresponding values for the physico-chemical parameters of rainwater samples (mean = 2.9). It is however noteworthy that in spite of the generally low metal enrichment values obtained, samples over each roof type (except slate) was characterized by relatively high enrichment of one or two metals (table 3). The metals involved (Zn, Cu, Mn, Fe, and Cd) could be separated into two groups with regard to potential health concern, namely: Cu and Cd (Type A inorganic chemicals) against Zn, Fe, and Mn (Type B inorganic chemicals). In general, the high enrichment of these metals do not potent any health risk in view of their relatively low concentrations and compliance with guide levels for drinking.

The relatively high enrichment of copper and manganese in Thatch roof samples could be due to the fact that the roofing materials (palm fronds) were collected from a cocoa plantation frequently sprayed with pesticides of which copper sulphate ($CuSO_4$) was an important active ingredient. The high enrichment of zinc and iron in the samples over Iron–Zinc roofs was expected. Zinc and zinc-based alloys are of wide industrial application usually in alloys with some other metals. An important use is in coating iron in hot dip galvanizing or electro-galvanising to produce roofing sheets. Cadmium and copper occur as impurities in the zinc although they play little part in the galvanizing process [30]. Zinc–aluminum alloys with their good ability to be cast fill a gap between plastics and the stronger but higher melting point aluminum alloys, the brasses and nickel containing alloys. Zinc coatings are one of the best methods for the protection of steel work against corrosion for at least two reasons. Firstly, zinc itself is resistant to normal atmospheric corrosion, and instances have been recorded where zinc roofing sheets has given service for over 100 years [30]. The second reason arises from the fact that zinc is considerably more electronegative than iron (as well as Cd, Pb, Sn, and Cu) and when the two metals are in contact in an electrolyte, zinc tends to dissolve leaving the iron unattached. The latter probably explains the much higher enrichment of zinc over iron in rainwater samples over iron–zinc roofs in the present study. The enrichment of Al over aluminum roof was generally high even at the high background level of the metal. It is probably for this reason and the fact that new aluminum roofs tend to leach intensely that aluminum roofs in market in Nigeria today are painted to reduce corrosion.

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