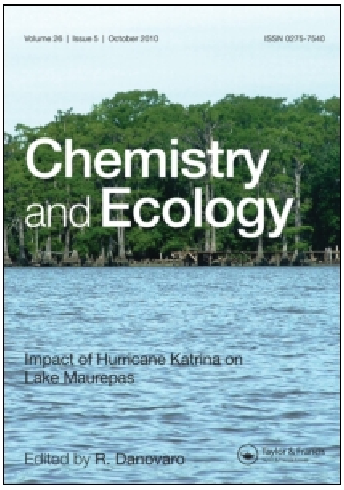

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The physico-chemical and bacteriological quality of rainwater collected over different roofing materials in Ile-Ife, southwestern Nigeria

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Samples of bulk free-fall and roof-intercepted rainwater over five different roof types (iron–zinc corrugated sheets, concrete slate tiles, Adex/asbestos cement sheets, aluminium sheets, and thatch) were collected and analysed using standard methods with adequate quality-control and quality-assurance measures. The mean values of some of the investigated parameters for the roof-intercepted samples occurred within four continuous sets of ranges, viz: $<0.11\,\mathrm{mg\,l^{-1}}$ (NH_4^+), 0.11–$1.00\,\mathrm{mg\,l^{-1}}$ ($Na^+ > Mg^{2+} > K^+$), 1.01–$10.00\,\mathrm{mg\,l^{-1}}$ ($Ca^{2+} > NO_3^- > Cl^- >$ organic matter $> SO_4^{2-}$) and $>10.01\,\mathrm{mg\,l^{-1}}$ (TS $>$ TSS $>$ TDS $> HCO_3^- > SiO_2 >$ alkalinity $>$ acidity $>$ hardness). The other parameters were: pH (6.68–7.45), conductivity (19.4–$122.6\,\mu\mathrm{S\,cm^{-1}}$), colour (25.9–257.6 Pt–Co), and turbidity (6.4–24.7 NTU). The corresponding mean values for the free-fall samples were either within the low end of the same range or about one order of magnitude less than that of the roof-intercepted samples. The enrichment factors of the roof-intercepted samples were within the range of 1.03–4.92 with an overall mean of 2.9 ± 0.3 standard error. Most of the water-quality parameters, including bacterial counts and the number of isolated species were higher both at the beginning and end of the rainy season (when both dry and wet depositions were high) than during the mid-season period (when only wet deposition was high). They also showed an increase with the age of roof materials, especially the samples over Adex and concrete slate roofs. The rainwater sources were not potable without necessary treatment but suitable for a wide range of other applications.

Keywords: Bulk free-fall rainwater; Roof-intercepted rainwater; Water quality; Atmospheric scavenging; Enrichment factor; Potability

1. Introduction

Rainwater is usually considered a safe and suitable source of potable water, and it is commonly used as such, especially in rural areas in developing countries of the world. In most communities in Nigeria, treated pipe-borne water is lacking, so roof-intercepted rainwater and free-fall rain collections are the major sources of potable water supplies during the rainy season. In such communities, as well as other parts of the country where surface freshwater

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sources are scarce and/or where suitable ground water is not easily available (e.g. through hand-dug wells), rainwater is often collected and stored for use over many months of the annual cycle. It is not uncommon for schools in rural areas to use such rainwater sources in place of distilled or deionized water, while food and water vendors use it to produce packaged water (commonly called ‘pure water’ in Nigeria) for sale to the public. The desire to investigate the quality of such water sources in a typical urban but non-industrialized town such as Ile-Ife in southwestern Nigeria has motivated the present study.

Southwestern Nigeria is the most urbanized region of Nigeria [1]. Today, a wide range of roofing materials are used there, while the traditional thatch roofs have virtually disappeared except in the most remote hamlets and farmsteads. In the general order of decreasing frequency of occurrence, the major roofing materials used in Nigeria towns and cities today (this also applies to the study area) are: corrugated iron–zinc sheets, Adex/asbestos cement tiles, long-span aluminium sheets, and concrete slate tiles. Although these materials are generally long lasting, they are affected by age in many ways (changes in appearance, colour, strength, etc.), hence the need to investigate such effects.

Previous studies on rainwater composition in the present study area have concentrated mainly on through-fall and stemflow over different plant covers at the Obafemi Awolowo University campus, elucidating the inputs and cycling of plant mineral nutrients [2–5]. Isichei *et al.* [6] evaluated the mineral nutrient composition (nitrogen, potassium and phosphorus) of drainage over the inselbergs at the Obafemi Awolowo University campus, while Adeniyi [7] investigated the prevalence of thunder and its effect on rainwater quality in the area. The outdoor atmospheric dust deposition rates in the area occur in the range of 0.7–58.9 tonnes km^{-2} month^{-1} with an annual mean value of 14.7 tonnes km^{-2} month^{-1} and seasonal mean (±s.d) value of 16.5 ± 8.5 tonnes km^{-2} month^{-1} for the dry season and 10.6 ± 7.7 tonnes km^{-2} month^{-1} for the rainy season, respectively [8].

In the present study, the physico-chemical and bacteriological quality of bulk free-fall and roof-intercepted rainwater samples collected during the 2001 rainy season were investigated. Consideration was given to variation in the age of roofing materials as well as the periods of the rainy season as commonly designated in the area (i.e. early rainy season, mid-rainy season, and late rainy season). The investigated water-quality parameters include major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}), some plant nutrients (NO_3^{-}, NH_4^{+}, SiO_2 and organic matter), total bacterial counts and species isolates. The other parameters were pH, electrical conductivity, total acidity, total alkalinity, total hardness, total dissolved solids (TDS), total suspended solids (TSS), turbidity and apparent colour. Some of these parameters have international set standards of allowable and/or maximum permissible concentrations for potable water uses [9, 10].

2. Materials and methods

2.1 *Study area*

This study was carried out at Ile-Ife, Osun State, in southwest Nigeria. Ile-Ife (or commonly Ife) and its immediate satellite villages lie at approximately latitudes 07° 26′ N–07° 33′ N of the Equator and longitudes 004° 30′ E–004° 35′ E of the Prime Meridian at mean altitude of roughly 300 ± 50 m above mean sea level. It is an ancient town comprising the Obafemi Awolowo University campus, the Ife Central Local Government Area and parts of the Ife East Local Government Area of Osun State, Nigeria. Ile-Ife is about 40 km south of Osogbo, the Osun State Capital, about 120 km north of the Atlantic coast, and about 600 km southwest of Abuja, the new capital of the Federal Republic of Nigeria. The Ife area occurs, more or less, within the centre of the cocoa belt of Yoruba land, one of the 20 geographical regions into which Nigeria is divided [11]. With a population of about 400,000 and a projected annual growth of 2.8% [12], Ife is one of the largest towns not only in Osun State but in the entire country.

The climate of the area is of the Moist Monsoon Equatorial type [13, 14]. The humid season forms a continuous series from March to October. The average annual rainfall is 1433 ± 256 mm (1955–1998) with a rainfall surplus of less than 1000 mm. The annual regime is characterized by two peaks (mostly in July and September) separated by a relatively dry spell in August commonly referred to as the 'August break'. Investigations carried out at three different sites in the area have revealed a low rainfall variability [5]. Ambient air temperatures are moderately high throughout the year. Maximum temperatures (32.2–34.4 °C) usually occur in February–March, while minimum temperatures (27.1–27.9 °C) usually occur in July–September. The vegetation of the area is that of the Guinean Congolean forest [15]. Trees shed most of their leaves in the dry season (November–March), produce new leaves with the onset of the rains in April, and attain full canopy leafiness from July to August [5].

2.2 *Sampling sites and sample collection*

The choice of sites for sample collection was made mainly with regard to the availability of the desired roofing materials, accessibility to their locations and adequate security of experimental set-up and collecting materials to be deployed. A total of 11 sites were selected all over the town for sample collection. The description and grid co-ordinates of these sites (determined using portable global positioning system equipment, GPS) are given in table 1.

At each sampling site, bulk samples *sensu* [16] of free-fall 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 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 the end of October 2001. This set-up applied to both free-fall and roof-intercepted rainwater collection. Each sample was

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

		GPS grid coordinates		
No.	Sampling sites at Ile-Ife	Latitude (N)	Longitude (E)	Type of roof cover
1.	Aba Gbooro/Oni Ilare Road	07° 32.70′	004° 30.72′	Thatch
2.	Road 20A SSQ, OAU campus	07° 31.52′	004° 32.64′	Adex/asbestos (old), free-fall
3.	Arch. Building, OAU campus	07° 31.25′	004° 31.12′	Aluminium (new)
4.	Old Power House, OAU campus	07° 30.97′	004° 31.43′	Aluminium (medium)
5.	Medical Students' Hostel, OAUTHC	07° 30.63′	004° 33.49′	Adex/asbestos (medium)
6.	Maintenance Building, OAUTHC	07° 30.30′	004° 33.41′	Aluminium (old)
7.	Behind Slaughter Slabs, Ede Road	07° 29.73′	004° 34.14′	Adex/asbestos (new)
8.	Apostolic Church, Ibadan Road	07° 29.73′	004° 30.85′	Iron–zinc (medium)
9.	PPS Assembly, Ibadan Road	07° 29.75′	004° 30.80′	Iron–zinc (new), free-fall
10.	Residential House, Ibadan Road	07° 29.76′	004° 30.79′	Iron–zinc (old)
11.	School of Science, Ondo Road	07° 26.94′	004° 32.64′	Concrete/slate (medium)

Note: Arch: Architecture Department; GPS: global positioning system; OAU: Obafemi Awolowo University; OAUTHC: Obafemi Awolowo University Teaching Hospitals Complex; SSQ: senior staff quarters.

harvested into a clean 2 l plastic bottle and labelled appropriately for subsequent handling. The actual amount of rainfall during each month and hence for each period of the entire rainy season was obtained from the meteorological station at the Obafemi Awolowo University campus.

2.3 *Laboratory analyses of samples*

The analytical determinations of the physico-chemical parameters of rainwater quality considered were carried out on the samples harvested within the holding time of each parameter, following applicable standard methods [17–20]. Sample pH was measured using a pH meter with a glass electrode (by Electronic Instrument Limited, model 7020), while electrical conductivity was measured with a conductivity meter, which gave readings directly in microsiemens per centimetre ($\mu S\,cm^{-1}$) at 25 °C. The conductivity meter (K constant $= 0.1$) was standardized from time to time using a set of potassium chloride (KCl) standard solutions [20].

The total residue or total solids (TS) as well as the non-filterable residue or total dissolved solids (TDS) of samples were determined gravimetrically after the samples were oven dried to constant weight at $105 \pm 2\,°C$ [21]. TSS was calculated as the difference between TS and TDS. Total acidity, total alkalinity, total organic carbon, and chloride ions (Cl^-) contents were determined by titrimetric methods [20], while ammonium (NH_4^+), nitrate (NO_3^-) and sulphate (SO_4^{2-}) ions were determined by spectrophotometric methods [19]. Organic matter (OM) was calculated from organic carbon (OC) as: $OM = OC \times 1.724$ [22]. Sodium (Na^+) and potassium (K^+) were determined by the atomic emission spectrophotometric method using a flame analyser, while silicon, calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined using a flame atomic absorption spectrophotometer (FAAS). Colour was determined colorimetrically using a set of potassium chloroplatinate–cobalt chloride solutions as Pt–Co standards, while turbidity was determined using a turbidimeter with values expressed in nephelometric turbidity units (NTU). Each water chemical parameter was measured in triplicate.

Total heterotrophic bacteria (THB) abundance was determined by the pour plate count technique [23]. One millilitre of each water sample was serially diluted in a set of test tubes each containing 9 ml of sterile distilled water. Then, 1 ml of each dilution was plated out respectively in duplicates employing the use of nutrients agar medium kept in molten form at 45 °C. Having allowed the agar medium to set, the culture plates were incubated aerobically at 35 °C for 48 h. The plates were observed for growth and selected for counts. The culture plates in which the number of colonies was in the range of 30–300 and their respective duplicates were selected. The average count was multiplied by the reciprocal of the dilution and expressed as the number of colony-forming units (cfu) per millilitre of original sample. Where the least diluted culture plate(s) for a water sample showed fewer than 30 colonies or no growth, 1 ml of the water (undiluted) was plated out also in duplicates and incubated as previously stated. When the average count obtained was slightly fewer than 30 colonies, the viable count was then recorded as nil. Samples were also cultured in various media to determine the available bacterial species isolates [23–26]. Such isolates were identified based on cultural and morphological characteristics as well as the results of series of biochemical tests using Bergey's manual [23, 27]. All necessary tests (presumptive, confirmed and completed tests) were carried out to determine the occurrence of *Escherichia coli* (*E. coli*) and *Enterobacter aerogenes* [23].

All the adopted methods have their precision levels in the range of 0.1–10%, and all the recommended quality-control (QC) and quality-assurance (QA) measures were taken for the respective determinations.

2.4 *Data analysis*

The data generated were subjected to appropriate statistical analyses including descriptive statistics, Duncan's multiple mean range test, correlation analysis, analysis of variance (ANOVA), and cluster analysis (the farthest-neighbour method) using the appropriate SPSS software [28].

3. Results

3.1 *General water quality of bulk rainwater sources*

The values of the water quality parameters of the bulk free-fall and roof-intercepted rainwater samples analysed in this study are summarized in table 2. The mean value of some of the investigated parameters for the roof-intercepted samples occurred within the following sets of ranges:

- $<0.11\,\mathrm{mg\,l^{-1}} = \mathrm{NH_4^+}$
- $0.11–1.0\,\mathrm{mg\,l^{-1}} = \mathrm{Na^+} > \mathrm{Mg^{2+}} > \mathrm{K^+}$
- $1.01–10.0\,\mathrm{mg\,l^{-1}} = \mathrm{Ca^{2+}} > \mathrm{NO_3^-} > \mathrm{Cl^-} >$ organic matter $> \mathrm{SO_4^{2-}}$
- $10.01–100.0\,\mathrm{mg\,l^{-1}} =$ TS > TSS > TDS > $\mathrm{HCO_3^-} > \mathrm{SiO_2} >$ alkalinity > acidity > hardness

The mean values for the other parameters were in the following ranges: pH (6.68–7.45), conductivity (19.4–122.6 $\mu\mathrm{S\,cm^{-1}}$), apparent colour (25.9–257.6 Pt–Co) and turbidity (6.4–27.4 NTU). The corresponding mean values for the free-fall samples were either within the low end of the same range or about one order of magnitude less than that of the roof-intercepted samples. The parameters in the former category include $\mathrm{NH_4^+}$, pH, TDS, TSS, colour, TS and turbidity, while all the other parameters fell into the latter category. In general, values for roof-intercepted samples were higher than those of free-fall samples. The 'enrichment factor' (i.e. roof-intercepted/free-fall values) of roof-intercepted samples for all the parameters occurred within the range of 1.03 (for pH)–4.92 (for $\mathrm{Ca^{2+}}$) with an overall mean of 2.9 ± 0.3 (standard error mean). The three physical parameters (colour, TSS and turbidity) and most of the nutrient compounds (ammonium, silica and organic matter) were characterized by enrichment factors less than the average of 2.9, while most of the major ions as well as conductivity, total alkalinity and total hardness were characterized by enrichment factors above the overall average.

Sample pH values were within the range of 6.11–8.41 with the mean of 6.68 ± 0.12 SEM for the free-fall samples for the entire roof-intercepted samples (6.91 ± 0.09). The lowest pH value recorded (6.11) was for a sample collected over an old aluminium roof during the mid-rainy season, while the highest value (pH = 8.41) was recorded for the sample collected over a middle-aged iron–zinc roof during the late rainy season. The mean levels of conductivity, total alkalinity, total acidity, total hardness, TDS and TS indicate that the rainwater samples were generally low in electrolytes, poorly buffered, and soft, particularly the free-fall samples. They also showed that total hardness comprised solely carbonic hardness (i.e. the non-carbonic hardness equals zero).

The dominant major ions were bicarbonate ($\mathrm{HCO_3^-}$) and calcium ($\mathrm{Ca^{2+}}$) ions, while chloride ($\mathrm{Cl^-}$) and sulphate ($\mathrm{SO_4^{2-}}$) followed in that order. Magnesium, sodium and potassium were generally less than $8\,\mathrm{mg\,l^{-1}}$. The ionic orders of dominance of the milliequivalent values of the major ions were essentially the same for both the free-fall and roof-intercepted samples. The orders were: $\mathrm{Ca^{2+}} > \mathrm{Mg^{2+}} > \mathrm{Na^+} > \mathrm{K^+} > \mathrm{NH_4^+}$ for the cations and $\mathrm{HCO_3^-} > \mathrm{Cl^-} > \mathrm{NO_3^-} > \mathrm{SO_4^{2-}}$ for the anions. Inorganic nitrogen occurred mainly as nitrate

Table 2. Range and mean values of bulk rainwater physico-chemical quality parameters at Ile-Ife.

Parameters		Units	Free-fall rain (Ffr)		Roof-intercepted rain (Rir)		Mean enrichment*
			Range	Mean ± S.E.	Range	Mean ± S.E.	
Physical variables	Colour	Pt–Co	11.2–68.7	45.3 ± 12.4	0.5–310.5	66.4 + 13.4	1.5
	TSS	$\mathrm{mg\,l^{-1}}$	6.7–25.6	20.1 + 5.5	16.2–112.7	40.1 + 4.1	1.9
	Turbidity	NTU	1.7–9.5	6.3 + 1.4	0.2–38.3	9.1 + 1.6	1.4
Secondary physico-chemical variables	pH	pH unit	6.45–7.15	6.68 + 0.12	6.11–8.41	6.91 + 0.09	1.1
	Conductivity at 25 °C	$\mu\mathrm{S\,cm^{-1}}$	5.7–16.5	10.4 + 1.7	4.5–174.2	47.5 + 6.7	4.6
	T. Acidity ($CaCO_3$)	$\mathrm{mg\,l^{-1}}$	5.0–6.0	5.4 + 0.3	6.0–23.0	11.7 + 0.8	2.2
	T. Alkalinity ($CaCO_3$)	$\mathrm{mg\,l^{-1}}$	0.5–7.0	3.2 + 1.1	0.5–61.0	14.7 + 2.7	4.6
	T. Hardness ($CaCO_3$)	$\mathrm{mg\,l^{-1}}$	1.7–3.9	2.5 + 0.4	0.0–49.5	11.8 + 2.1	4.7
	TDS	$\mathrm{mg\,l^{-1}}$	9.1–39.3	19.3 + 3.7	1.0–79.8	28.7 + 3.4	1.6
	TS	$\mathrm{mg\,l^{-1}}$	28.0–64.9	42.4 + 7.8	26.4–160.1	68.8 + 5.2	1.6
Major ions	Calcium (Ca^{2+})	$\mathrm{mg\,l^{-1}}$	0.53–1.10	0.77 + 0.10	0.5–16.74	3.80 + 0.68	4.9
	Magnesium (Mg^{2+})	$\mathrm{mg\,l^{-1}}$	0.05–0.26	0.14 + 0.04	0.1–5.74	0.54 + 0.82	3.9
	Sodium (Na^{+})	$\mathrm{mg\,l^{-1}}$	0.10–0.34	0.21 + 0.05	0.08–7.01	0.57 + 0.22	2.7
	Potassium (K^{+})	$\mathrm{mg\,l^{-1}}$	0.00–0.11	0.06 + 0.02	0.0–2.0	0.23 + 0.07	3.8
	Bicarbonate (HCO_3^{-})	$\mathrm{mg\,l^{-1}}$	0.6–8.5	5.5 + 1.3	0.6–74.1	17.8 + 3.2	3.2
	Chloride (Cl^{-})	$\mathrm{mg\,l^{-1}}$	0.7–3.0	1.70 + 0.4	0.0–21.2	2.25 + 0.6	1.3
	Sulphate (SO_4^{2-})	$\mathrm{mg\,l^{-1}}$	0.0–1.27	0.5 + 0.2	0.0–10.5	1.2 + 0.4	2.4
Nutrient compounds	Ammonium (NH_4^{+})	$\mathrm{mg\,l^{-1}}$	0.03–0.06	0.05 + 0.01	0.0–0.07	0.10 + 0.01	2.1
	Nitrate (NO_3^{-})	$\mathrm{mg\,l^{-1}}$	0.00–2.77	0.86 + 0.56	0.0–22.64	3.40 + 0.85	4.0
	Silica (SiO_2)	$\mathrm{mg\,l^{-1}}$	0.0–22.4	8.5 + 3.9	0.0–32.1	16.3 + 1.5	1.9
	Organic matter (OM)	$\mathrm{mg\,l^{-1}}$	0.24–1.66	0.92 + 0.24	0.0–6.31	1.62 + 0.25	1.8

Note: S.E.: standard error; T: total; TDS: total dissolved solids; TSS: total suspended solids; TS: total solids.
*Rir/Ffr.

(range = 0.00–22.64 mg l^{-1}), while ammonium occurred in traces (0.00–0.072 mg l^{-1}). Silica (SiO_2) the dominant nutrient compound occurred over the range of 0.0–32.1 mg l^{-1} with the mean value of 8.5 ± 3.9 mg l^{-1} and 16.3 ± 1.5 mg l^{-1} for the free-fall and roof-intercepted samples, respectively. Organic matter values were in the range of 0.0–6.31 mg l^{-1}, although the values for 70% of the samples were within the intermediate range of 0.5–3.0 mg l^{-1}.

3.2 *Rainwater quality over different roof types*

The mean composition of free-fall rainwater and those collected over the different roof types are indicated in table 3. Eleven of the 21 investigated parameters showed significant differences ($P \leq 0.05$) in their mean values. These include apparent colour, turbidity, conductivity, alkalinity, hardness, calcium, potassium, bicarbonate, chloride, sulphate and nitrate ions. The other parameters were not significantly different in their mean values for the six rain sample types considered (table 3). Considering only these 11 significantly different parameters, the six sample types could be separated into two clusters at both probability levels of 0.05 and 0.01 (comprising Adex and concrete roof samples as one cluster and the samples of other roof types as another cluster). The Adex–concrete roof-intercepted samples cluster was characterized by relatively high concentrations of calcium and bicarbonate ions but relatively low concentrations of the other major cations and anions. On the other hand, the members of the second clusters (free-fall, thatch, Fe–Zn and aluminium roof-intercepted samples) were characterized by relatively low concentrations of calcium and bicarbonate but relatively high levels of the other major ions (K^+, Cl^-, SO_4^{2-} and NO_3^-). The separation of the sample types into clusters was less distinct on the basis of all the 21 water quality parameters considered. For instance,

Table 3. Mean composition of bulk free-fall and roof-intercepted rainwater at Ile-Ife.

		Sample collection method/roof type of interception					
Parameter	Units	Free-fall	Thatch roof	Concrete roof	Aluminium roof	Fe–Zn roof	Adex roof
Colour	Pt–Co	45.29b	257.60a	72.99a,b	80.82ab	47.66b	25.94c
Turbidity	NTU	6.3b	24.7a	10.1ab	11.3ab	6.7b	6.4b
TSS	mg l^{-1}	23.04a	34.20a	42.57a	33.32a	44.09a	43.43a
pH	pH unit	6.68a	7.00a	7.45a	6.68a	6.77a	7.09a
Conductivity	μS cm^{-1}	10.4c	122.60a	84.13a	29.54b	19.46b	64.68a,b
T. acidity ($CaCO_3$)	mg l^{-1}	5.4a	12.5a	8.0a	16.1a	13.8a	8.0a
T. alkalinity ($CaCO_3$)	mg l^{-1}	4.4b	35.5a	34.7a	2.1b	5.8b	23.9a
T. hardness ($CaCO_3$)	mg l^{-1}	2.5b	21.9a	25.9a	4.3b	8.4b	15.9a
TDS	mg l^{-1}	19.33a	38.97a	44.49a	19.66a	24.42a	36.59a
TS	mg l^{-1}	42.37a	73.17a	87.05a	50.99a	68.51a	60.02a
Calcium (Ca^{2+})	mg l^{-1}	0.77b	6.12a	9.48a	1.29a	2.03a,b	5.84a
Magnesium (Mg^{2+})	mg l^{-1}	0.14b	1.61b	0.52b	0.27b	0.81b	0.31b
Sodium (Na^+)	mg l^{-1}	0.21a	0.31a	0.38a	0.52a	0.99a	0.31a
Potassium (K^+)	mg l^{-1}	0.06b	1.09a	0.14b	0.09b	0.31b	0.12b
Bicarbonate ($HCO3^-$)	mg l^{-1}	5.34b	43.08a	42.07a	2.56b	7.69b	28.99a
Chloride (Cl^-)	mg l^{-1}	1.66a	0.76b	2.63a	1.51a	4.48a	1.88a
Sulphate (SO_4^{2-})	mg l^{-1}	2.29b	1.49a	0.05a	2.69a	0.88a	0.41a
Ammonium (NH_4^+)	mg l^{-1}	0.05a	0.05a	0.05a	0.05a	0.06a	0.06a
Nitrate (NO_3^-)	mg l^{-1}	0.86a	4.13a	3.34a	6.18a	1.52a,b	2.26a,b
Silica (SiO_2)	mg l^{-1}	8.5a	7.3a	10.4a	10.2a	10.2a	10.9a
Organic matter (OM)	mg l^{-1}	0.916a	4.78a	2.10a	1.67a	1.24a	2.16a

Note: Values in the same row with the same letters are not significantly different ($P > 0.05$), while values with different letters are significantly different ($P < 0.05$).

the six sample types constitute a single cluster at $P = 0.05$ and were only separated into two clusters at the probability level of 0.01 when all the 21 water quality parameters were considered.

3.3 *Intraseasonal variation in bulk rainwater quality*

The composition and interrelationship between the six bulk rain sample types showed intraseasonal variation over the rainy season, and the six sample types could be separated into two distinct clusters ($P = 0.05$) during each of the three intraseasonal periods. However, the overall relationship among the six sample types was highest during the late rainy season (when the total rainfall was highest) and lowest during the mid-season period (when the total rainfall was lowest) suggesting that the relationship varied directly with the amount of rainfall. Similarly, roof-intercepted rain sample enrichment of each parameter/group of parameters showed a direct correlation with rainfall amount over the three periods of the season. For most of the parameters, roof sample enrichment was highest during the late rainy season (when total rainfall was highest) and lowest during mid-season, when the recorded rainfall was lowest. On the whole, the relationship between the amount of intra-season rainfall and roof sample enrichment was characterized by a significant positive correlation coefficient ($P < 0.05$).

Information on the mean composition of free-fall and all the roof-intercepted samples over the three periods of the rainy season is presented in table 4. Apparent colour and ammonium showed significant variations ($P < 0.05$) with rainfall amount over the three periods of the season, being highest during the late season (when the rainfall was highest) and lowest during the mid-season (when the rainfall was lowest). On the other hand, the concentrations of SiO_2, TDS, and SO_4^{2-} each showed a significant inverse relationship ($P < 0.05$) with rainfall amount (i.e. their values were lowest during the late season at the peak of rains and highest during the mid-season during the August dry spell). Turbidity, conductivity, acidity, TS, SO_4^{2-} and organic matter each showed a negative but non-significant correlation ($P > 0.05$) with rainfall amount over the three periods of the season.

The samples collected during the early rainy season could be grouped into two distinct clusters (comprising Adex and concrete samples as one cluster and the other samples as the second cluster). The Adex–concrete cluster samples were characterized by a relatively high alkalinity, bicarbonate, calcium, TDS and TS compared to samples of the other cluster. On the other hand, the Adex–concrete roof samples were characterized by relatively low values of acidity, sulphate and nitrate ions compared to samples of the other cluster. During the mid-season period, the six sample types could also be divided into two distinct clusters (comprising Adex and Fe–Zn samples as one cluster and the other samples as the second cluster). The Adex and Fe–Zn roof samples were characterized by relatively low values of apparent colour, conductivity, TDS, nitrate, SiO_2 and organic matter compared to samples of the other cluster (i.e. free-fall, thatch, concrete and aluminium roof-intercepted samples). The samples collected during the late rainy season also fell into two distinct clusters comprising Adex and aluminium roof-intercepted samples in one cluster and the other samples in the second cluster. The Adex and aluminium samples were characterized by relatively high values of apparent colour and nitrate compared with samples of the second cluster. Thus, Adex-intercepted samples always formed a separate cluster from most of the other samples over the season in terms of nutrient enrichment.

3.4 *Variation in roof-intercepted rainwater composition in relation to roof age*

This analysis was possible for only three of the roof types for which there was complete data (Adex, Fe–Zn and aluminium roof types). Variation in parameter enrichment factors with the

Table 4. Intra-seasonal variation in the mean composition of bulk rainwater at Ile-Ife.

		Early season rainwater			Mid-season rainwater			Late season rainfall		
Parameter	Unit	Free-fall (FFr)	Roof-intercept (Rir)	Enrichment	Free-fall (FFr)	Roof-intercept (Rir)	Enrichment	Free-fall (FFr)	Roof-intercept (Rir)	Enrichment
Colour	Pt–Co	20.0	74.8a	3.7	51.9	75.7a	1.5	11.2	96.75b	8.6
TSS	$\mathrm{mg\,l^{-1}}$	17.6	48.1a	2.7	36.1	38.8a	1.1	20.9	24.7a	1.8
Turbidity	NTU	2.9	9.3a	3.2	9.5	10.9a	1.1	8.1	6.5a	0.8
pH	pH unit	7.15	6.67b	0.9	6.55	6.78b	1.1	6.66	7.19a	1.1
Conductivity	$\mu\mathrm{S\,cm^{-1}}$	16.4	42.7a	2.6	11.2	47.7a	4.3	17.5	34.97a	2.0
T. Acidity	$\mathrm{mg\,l^{-1}}$	5.0	11.8a	2.4	6.0	12.1a	2.1	5.0	9.83a	1.97
T. Alkalinity	$\mathrm{mg\,l^{-1}}$	7.0	11.0a	1.6	6.0	16.2a	2.7	0.5	12.08a	24.2
T. Hardness	$\mathrm{mg\,l^{-1}}$	2.4	9.0a	3.8	2.7	11.3a	4.2	1.7	11.6a	6.8
TDS	$\mathrm{mg\,l^{-1}}$	10.4	15.8b	1.5	28.8	35.0a	1.2	9.1	29.09a	3.2
TS	$\mathrm{mg\,l^{-1}}$	28.0	64.0a	2.5	64.9	73.9a	1.1	30.0	53.81a	1.8
Calcium (Ca^{2+})	$\mathrm{mg\,l^{-1}}$	0.84	3.0a	3.5	0.8	3.4a	5.1	0.6	3.46a	5.7
Magnesium (Mg^{2+})	$\mathrm{mg\,l^{-1}}$	0.09	0.4a	4.4	0.2	0.4a	2.0	0.05	0.71a	15.8
Sodium (Na^{+})	$\mathrm{mg\,l^{-1}}$	0.18	0.2a	1.3	0.3	0.69a	1.7	0.1	0.74a	6.7
Potassium (K^{+})	$\mathrm{mg\,l^{-1}}$	0.05	0.2a	3.8	0.1	0.2a	1.9	0.1	0.24a	4.8
Bicarbonate (HCO_3^-)	$\mathrm{mg\,l^{-1}}$	8.50	13.3a	1.7	7.3	19.7a	2.7	0.5	14.7a	29.4
Chloride (Cl^-)	$\mathrm{mg\,l^{-1}}$	1.15	1.4a	1.2	3.0	3.0a	1.0	0.8	2.8a	3.6
Sulphate (SO_4^{2-})	$\mathrm{mg\,l^{-1}}$	0.28	0.4b	1.5	0.9	3.1a	3.5	0.5	0.3b	0.6
Ammonium (NH_4^+)	$\mathrm{mg\,l^{-1}}$	0.054	0.1b	0.9	0.03	0.05b	1.8	0.05	0.058a	1.3
Nitrate (NO_3^-)	$\mathrm{mg\,l^{-1}}$	2.07	2.3b	1.1	1.5	4.5a	2.9	0.5	7.0a	14.0
Silica (SiO_2)	$\mathrm{mg\,l^{-1}}$	0.50	1.2b	2.4	21.4	7.8a	0.4	7.5	5.6a	0.8
Organic matter (OM)	$\mathrm{mg\,l^{-1}}$	1.18	1.7a	1.4	0.9	1.9a	2.2	0.6	1.1a	1.6

Note: T: total; enrichment: Rir/FFr.
Values in the same row with the same letters are not significantly different ($P < 0.05$), while values with different letters are significantly different ($P < 0.05$).

age of roofing material is shown in table 5 for the 11 parameters known to vary significantly among the different roof-intercepted samples. Fifteen of the 21 investigated parameters showed an obvious increase in enrichment factors of parameters of roof-intercepted rainwater with roof age for Adex roofs as compared to nine such parameters for iron–zinc roofs and nine parameters for aluminium roofs. The five parameters that were common to all the three roof types were organic matter, total hardness, calcium, magnesium and nitrate (each of these five parameters showed a definite increase with the age of the three roof types). The increase in enrichment factor with roof age was much higher for hardness parameters than for the nutrient compounds (nitrate and organic matter). For most of the parameters, the change with roof age was most pronounced for samples over Adex roofs followed by iron–zinc roofs and least for aluminium roofs.

Compared to the other two roofing types, samples over relatively new Adex roofs were characterized by high values of hardness parameters which showed steady increase with age. On the other hand, they were characterized by low values of colour, turbidity, chloride and sulphate although these parameters also increased gradually with roof age. Rainwater over relatively new iron–zinc and aluminium roofs was generally characterized by low enrichment factors of 1.3 ± 0.2 and 1.1 ± 0.2, respectively). Solids, silica, turbidity, colour and hardness

Table 5. Variation in the enrichment factors of major parameters of rainwater samples collected over roofs of different ages at Ile-Ife.

		Age of roof		
Roof type	Parameter	Relatively new	Middle age	Old age
Adex/asbestos	Apparent colour	0.3	0.7	0.7
	Turbidity	0.4	0.9	1.1
	Conductivity	4.8	4.9	9.0
	Alkalinity ($CaCO_3$)	3.9	4.9	7.1
	Hardness ($CaCO_3$)	4.9	5.2	8.9
	Calcium (Ca^{2+})	6.4	6.7	10.7
	Potassium (K^+)	2.3	1.2	2.7
	Bicarbonate (HCO_3^-)	3.9	4.9	7.1
	Chloride (Cl^-)	1.1	1.1	1.2
	Sulphate (SO_4^{2-})	1.1	1.3	1.3
	Nitrate (NO_3^-)	0.1	1.0	6.9
Aluminium	Apparent colour	1.0	2.8	1.5
	Turbidity	1.1	2.8	1.5
	Conductivity	1.8	5.0	1.8
	Alkalinity ($CaCO_3$)	0.5	0.4	0.7
	Hardness ($CaCO_3$)	1.4	1.8	2.3
	Calcium (Ca^{2+})	1.3	1.6	2.1
	Potassium (K^+)	1.0	1.7	1.8
	Bicarbonate (HCO_3^-)	0.4	0.5	0.6
	Chloride (Cl^-)	1.1	0.9	0.85
	Sulphate (SO_4^{2-})	0.9	6.4	9.6
	Nitrate (NO_3^-)	2.5	8.5	10.5
Iron-zinc	Apparent colour	0.3	0.4	2.6
	Turbidity	0.3	0.4	2.6
	Conductivity	1.0	2.1	2.6
	Alkalinity ($CaCO_3$)	1.8	1.1	1.4
	Hardness ($CaCO_3$)	0.8	1.5	7.7
	Calcium (Ca^{2+})	1.0	1.5	5.4
	Potassium (K^+)	2.2	2.7	1.7
	Bicarbonate (HCO_3^-)	1.8	1.1	1.4
	Chloride (Cl^-)	1.3	5.3	1.4
	Sulphate (SO_4^{2-})	2.5	1.1	2.4
	Nitrate (NO_3^-)	1.0	2.1	2.3

parameters were generally low in relatively new iron–zinc roof-intercepted samples but of relatively high acidity. On the whole, sample pH and ammonium ions seemed to be the least affected by roof age of all the investigated water-quality parameters.

3.5 *THB abundances and characterization of culturable bacterial isolates in rainwater*

Total heterotrophic bacterial (THB) counts for all the samples were in the range of 1×10^2–9×10^5 cfu ml^{-1}. The all-season range and mean ± standard deviation were 5×10^2–9×10^4 ($31.4 \times 10^3 \pm 244 \times 10^3$) cfu ml^{-1} for free-fall rain and 1×10^2–9×10^5 ($217.3 \times 10^3 \pm 65.9 \times 10^3$) cfu ml^{-1} for all the roof-intercepted rain types, respectively. The all-season averages for the respective types of samples were 1.10×10^5 cfu ml^{-1} for the aluminium roof rain 1.38×10^5 cfu ml^{-1} for Adex roofs, 2.19×10^5 cfu ml^{-1} for slate-roof rain, 2.76×10^5 cfu ml^{-1} for iron–zinc rain, and 3.43×10^5 cfu ml^{-1} for thatch-roof rain samples. Thus, the average enrichment in THB counts of roof-intercepted rains (relative to the free-fall abundance) was lowest in aluminium-roof samples (3.5) and highest in thatch-roof samples (10.9), while others were intermediate (4.4 for Adex roof samples, 7.0 for slate roof samples and 8.8 for iron–zinc roof samples).

Whereas THB counts fell from early rains (9.0×10^4 cfu ml^{-1}) through mid rains (3.7×10^3 cfu ml^{-1}) to a minimum in late rains (5×10^2 cfu ml^{-1}) for free-fall rain, for most of the roof-intercepted rains the highest and lowest counts were recorded for early and mid-season rains respectively. The average for the entire roof-intercepted samples being 4.88×10^5 cfu ml^{-1} for early rain 0.6×10^5 cfu ml^{-1} for mid-season samples and 1.04×10^5 cfu ml^{-1} for late season samples respectively.

The bacteriological flora of samples comprised a total of nine bacterial species isolates belonging to the four genera *Pseudomonas* (Pseudomonadales: Pseudomonadaceae), *Klebsiella* and *Proteus* (Enterobacteriales: Enterobacteriaceae) and *Actinomyces* (Actinomycetales: Actinomycetaceae). The occurrence of the respective isolates over the three periods of the rainy season for the six rain sample types is shown in table 6 (based on both free-fall and roof samples). The total recorded isolates per sample type varied from five species each for free-fall and thatch-roof-intercepted rain through four species for slate-intercepted rain, three species each for aluminium-intercepted and iron–zinc-intercepted rain, to two species for Adex-intercepted rain samples. *Pseudomonas aeruginosa* and the coliform *Klebsiella pneumoniae* occurred in all the rain sample types with an overall occurrence frequency of 100% and 78%, respectively, in the individual samples. The other species were each characterized by an occurrence frequency of less than 20% and were restricted in distribution either with regard to rain sample type or the period of the rainy season. For instance, *Pseudomonas fluorescens* was recorded only in iron–zinc-intercepted samples, while *Pseudomonas povonacea* and *Klebsiella edwardsii* occurred only in thatch rain samples. Similarly, *Actinomyces bovis* occurred only in free-fall rain, while *Proteus morganella* occurred only in slate-intercepted rain samples. Five of the nine recorded isolates, viz *Pseudomonas fluorescens*, *Pseudomonas povonacea*, *Klebsiella edwardsii*, *Proteus morganella* and *Actinomyces bovis*, were recorded only from roof-intercepted samples, while *Pseudomonas pseudomallei* was the only isolate restricted to free-fall rain samples. Thus, only three isolates namely, *Pseudomonas pseudomallei, Pseudomonas aeruginosa* and *Klebsiella pneumoniae*, occurred commonly in all the six rain sample types considered.

The total recorded isolates for all samples increased from four species in early rain to five species in mid-season rain to six species in late rain samples, i.e. more isolates were detected as the season progressed (although the number of isolates per individual sample tended to decrease from early rain to mid/late rains). Similarly, the number of non-coliform bacterial

Table 6. Occurrence of bacterial species isolates and (THB) counts in rainwater samples from Ile-Ife, Nigeria.

	Early-season samples						Mid-season samples						Late-season samples						Occurrence frequency
Bacterial isolate	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	(%)
Pseudomonas aeruginosa	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	100.0
Pseudomonas fluorescens	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	+	−	5.6
Pseudomonas povonacea	−	−	−	−	−	−	−	−	+	−	−	−	−	−	+	−	−	−	11.1
Pseudomonas pseudomallei	−	−	−	+	−	−	+	−	−	−	−	−	−	−	−	−	−	−	11.1
Klebsiella edwardsii	−	−	−	−	−	−	−	−	+	−	−	−	−	−	−	−	−	−	5.6
Klebsiella ozoenae	+	+	+	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	16.7
Klebsiella pneumoniae	+	+	+	+	+	+	+	−	+	+	+	−	−	+	+	+	+	−	77.8
Proteus morganella	−	−	−	−	−	−	−	−	−	−	−	−	−	+	−	−	−	−	5.6
Actinomyces bovis	−	−	−	−	−	−	−	−	−	−	−	−	+	−	−	−	−	−	5.6
THB (10^4 cfu ml^{-1})	9	38	90	10	65	41	0.37	0.75	6.0	16.0	7.0	0.16	0.05	27.0	8.0	7.0	11.0	0.01	

Note: THB: total heterotrophic bacteria; +: present; −: absent; 1: free-fall rainwater; 2: concrete/slate roof intercepted rainwater; 3: thatch roof-intercepted rainwater; 4: aluminium roof-intercepted roof rainwater; 5: iron-zinc roof-intercepted rainwater; 6: asbestos/Adex roof-intercepted rainwater.

species (i.e. *Pseudomonas*, *Proteus*, and *Actinomyces* species) for all samples increased from two species in early rain to three species in mid rain to four species in late rain, whereas the corresponding number for coliform bacteria species (i.e. *Klebsiella* species) remained as two species throughout the three periods of the season. The coliform *Klebsiella ozoenae* occurred only in early rain samples, while *Klebsiella edwardsii* and *Pseudomonas povonacae* occurred only in mid-season rain samples. On the other hand, *Actinomyces bovis*, *Pseudomonas fluorescens* and *Proteus morganella* were recorded only during the late rainy season.

Based on the occurrence of the recorded bacterial species over the entire period of the rainy season, the six rain sources fall into two clusters ($P < 0.001$). The first cluster (I) comprised free-fall and thatch-roof samples, while the other four rain sample types (aluminium, iron–zinc, Adex and slate roof-intercepted samples) made up the second cluster (II). Species richness was generally higher in cluster I (free-fall and thatch samples) than in the cluster II samples. For instant, the total recorded species was at least five per sample in cluster I as opposed to at most four per sample in cluster II over the entire season. The number of recorded species isolates per sample per period of the rainy season was also higher among members of cluster I (with average of three species isolates) than for members of cluster II with the average of two isolates. Similarly, the total number of recorded coliform bacterial isolates per sample type was also higher for members of cluster I (two isolates) than for those of cluster II (one isolate).

3.6 *Physico-chemical parameters in relation to bacteriological composition*

Each of the investigated physico-chemical rain quality parameters was correlated with the bacteriological quality of the samples (THB counts, number of species isolates and number of coliform species isolates). Potassium (K^+), organic matter, total acidity, TSS and magnesium (Mg^{2+}) all showed varying degree of positive correlation with total bacterial counts (THB) and species isolates number per sample. On the other hand, sulphate (SO_4^{2-}), chloride (Cl^-) and silica (SiO_2) all showed a negative correlation with the same parameters. The THB counts of the samples showed a significant correlation ($P < 0.05$) only with apparent colour, potassium (K^+) and electrical conductivity. A highly significant correlation ($P < 0.001$) could thus be obtained from the multiple correlations of these three parameters with THB counts. Overall, all the major cations showed a positive but weak correlation with THB while all the major anions (except nitrate) showed negative but weak correlation with it.

The number of total bacterial species isolates per sample showed a significant negative correlation ($P < 0.05$) with sodium (Na^+) and chloride (Cl^-) but a rather weak positive correlation with potassium (K^+) and magnesium (Mg^{2+}). Similarly, the number of coliform bacterial species isolates per sample showed a significant negative correlation ($P < 0.05$) only with chloride ion (Cl^-).

4. Discussion

The study of atmospheric precipitation, especially the chemistry of rainwater, has continued to attract the attention of many workers for a wide range of reasons, some of which are considered in the present study. In general, air and precipitation chemistry provides a means of gaining insight into some of the natural processes (e.g. chemical reactions, material transport and the removal by scavenging of gases and aerosols) that take place in the atmosphere and the effects of some anthropogenic activities and urbanization on the general environment. Raindrops absorb atmospheric gases (including trace pollutant gases) and dissolve aerosols and other particulates through the two major processes of incloud rainout and subcloud washout thus cleaning the Earth's atmosphere. However, the cleansing of the air by precipitation scavenging often leads to some detrimental environmental and/or health effects, as is associated with the problems of acid rain in many industrialized countries of the world. It follows from the general knowledge of rain formation [29], precipitation scavenging [30] and the great ability of water as a solvent, that rainwater, even in pristine and/or non-industrialized environments, is rarely the same as distilled or deionized water, as sometimes assumed by members of the general public. The composition and salinity of rainwater depend on a wide range of variables (including climate type, the prevailing meteorological conditions, the relative effectiveness or efficiencies of atmospheric scavenging, concentration of pollutants, etc.); hence, free-fall rain events can be quite variable in nature. However, low salinity values are usually associated with uncontaminated continental rains; hence, they often compare well with the dilute freshwater sources (notably rivers and lakes) in their environment.

The generally low values of salinity parameters (conductivity, TDS and the sum of major ions) observed in the present study portray bulk free-fall rainwater in the study area as very dilute, i.e. poor in electrolytes. This is confirmed by the fact that the range and mean conductivity values for the free-fall samples obtained occurred only within the lowest 10% dilution range, that of Opa Reservoir surface water (range = $150\text{–}309\,\mu\mathrm{S\,cm}^{-1}$, $203 \pm 30\,\mu\mathrm{S\,cm}^{-1}$), the reservoir draining most of the rivers and streams in the study area [31]. Detailed comparison with Opa reservoir shows that bulk free-fall rainwater in the study area is relatively rich in organic matter, silica and TSS, which are most probably scavenged from airborne suspended particulate matter (SPM) in the area via below-cloud washout mechanisms. An earlier study [8] has revealed that the major sources of outdoor air SPM in the area are remobilized dust produced by motor vehicle traffic on unpaved roads (1445 tonnes yr^{-1}) and agricultural bush burning (750 tonnes yr^{-1}). This suggests that the relatively high contents of TSS, SiO_2 and organic matter, which altogether accounted for 84.3% of the mean total solids (TS) of free-fall rainwater and 80.4% of roof-intercepted rainwater in the study area (see table 2), are mainly of terrestrial origin. This is so because dwelling houses are located very close to the kerbs along road corridors in the study area, and about 80% of these roads are unpaved, such that vehicles generate a considerable amount of dust as they pass by [8]. Such remobilized dust often contains decomposed or decomposing organic materials and dry sludge (a probable source of pathogenic micro-organisms) originating from the cleaning of open drains into nearby unpaved surfaces. The animal component of such wastes is a possible source of atmospheric ammonium-nitrogen and ammonia via volatilization [32] just as ammonia volatilization can also result from nitrogenous fertilizers applied to soil and denitrification processes.

The fact that higher values of rainwater contents and nutrient enrichment were recorded at the beginning and late periods of the rainy season (when both TSS and SiO_2 were also very high) than during the mid-season period suggests that rainwater nutrients are mainly of soil origin. During the early and late rains, there is both dry and wet deposition, whereas during the mid-season, wet deposition is the significant form of deposition. Dry deposition during the early rainy season is mainly derived from the accumulation of suspended particles and gaseous aerosols in the atmosphere from the preceding harmattan dust. This trend of higher concentrations of nutrients in rainwater has been reported in previous work in the study area and elsewhere in Nigeria [4, 33] and tends to confirm the fact that the amount and time of precipitation during certain periods of an annual cycle can influence the amount of nutrients in the precipitation [34].

The probability that free-fall rainwater contents in the study area are mainly of terrestrial origin is also strongly supported by the close similarity exhibited in the ranking orders of the mass concentrations of most of the investigated elements and compounds (especially the major ions) in the rainwater samples compared to that of Opa Reservoir [31] and the world average freshwater [35]. Common to the ranking orders of these waterbodies and the typical Earth crust material [36] is the predominance of SiO_2, HCO_3^-, CO_3^{2-}, Al_2O_3, Fe_2O_3 and Ca^{2+} and the relatively low ranking of Cl^-, Na^+ and SO_4^{2-} which predominate in seawater and water sources of sea origin [37]. Water bodies in which terrigenous materials predominate are almost invariably members of the bicarbonate group of waters of the world in which bicarbonate salts of calcium often dominate the ions [29]. Bicarbonate ions predominate in this group of world waters because silica, aluminium and iron, which usually dominate their salinity, are very poorly ionized and thus make very little or no contribution to the total ionic content or conductivity of the water. Thus, bicarbonate waters are typically characterized by a relatively high proportion of TDS/conductivity values which, for waters of normal composition, occur within the range of 0.55–0.75 [29, 38, 39]. This explanation may account for the relatively high mean proportion of TDS/conductivity values recorded for free-fall rain samples in the present study (1.03–1.85), as can be estimated from table 2.

A major objective of the present study was to assess the impact of the different roofing materials considered on the quality of rainwater drained over them. The major findings on this issue (tables 2–5) show that roof interception causes a slight increase in rainwater pH (due to the relatively high enrichment of base cations) and enrichment (compared to free-fall rainwater) in virtually all the water quality parameters considered. Available evidence suggests that enrichment due to nutrient yield from roofing materials most probably resulted both from direct leaching (by weathering) of the roof materials and from the accumulated deposits of particulates and associated flora on them by event rains which were mostly acidic. Aluminium and iron–zinc roof-intercepted rainwater showed a weak correlation ($P > 0.05$) with corresponding bicarbonate surface waters, suggesting that nutrient enrichment in rainwater over the two roof types was mainly from the direct leaching of roof materials by chemical reactions and possibly also by microbial activities (depending on roof types). This may explain why nutrient enrichment was generally higher in rainwater collected over Adex, concrete and thatch roofs than for rains collected over aluminium and iron–zinc roofs. Again, concrete and Adex roofs are more predisposed to being colonized by a wide range of plants, notably mosses, other bryophytes, algal crust and lichens. In the study area, a luxuriant carpet of green mosses is a common feature on many old concrete and Adex roofs. These plants are known to maintain high moisture levels in the outer layer of concrete tiles and asbestos roofing materials, and often this leads to flaking or cracking of the roofing materials under freezing conditions in the winter [40]. Such an effect may result in the release of asbestos into the intercepted waters. A major effect of most micro-epiphytes on roof substrates is the softening of the hard outline of building and roofing materials and subsequent leaching and release of nutrients to intercepted rainwater. Williams and Rudolph [41] have observed that because of the weakly acidic properties of lichen thalli and the metal complexing ability of their surface hyphae, these properties can even participate in the weathering of rock materials and deposition of trapped particles. The composition (carbonation), rough surface texture and the great ability to retain moisture make concrete slate tiles and asbestos/Adex roofs much more susceptible to plant colonization than either aluminium or iron–zinc roofs. The strong combination of direct weathering by acidic individual events rainwater and the weathering activities of associated microflora on Adex and concrete roofs are probably responsible for the pronounced enrichment of rain intercepted over them with the age of the roof.

The primary purpose of rainfall harvesting in the study area and most parts of Nigeria is for various domestic applications and possibly for drinking. To a lesser extent, the supply also serves self-supplied and small-scale industrial establishments. In terms of the population served, roof-harvested rainwater constitutes an important component of the Nigerian public water-supply system, especially in rural and semi-urban areas of the country, hence the need

Table 7. Water quality of bulk rainwater at Ile-Ife compared with set guideline for drinking-water.

		WHO International Guideline [9]		EC Directive [10]		Ile-Ife bulk rainwater*	
Parameter	Unit	Acceptable	Allowable	Guide level	MAC	Range	% C
Colour	Pt–Co	5	50	1	20	0.5–310.5	54
Turbidity	mg SiO_2	5	25	1	10	0.2–38.3	95
Conductivity @ 25 °C	$\mu S\ cm^{-1}$	n.d.	n.d.	400	n.d.	4.5–174.2	100
pH	pH unit	7.0–8.5	6.5–9.2	6.5–8.5	n.d.	6.1–8.4	78
TDS	$mg\ l^{-1}$	500	1500	n.d.	n.d.	1.0–79.8	100
Calcium (Ca^{2+})	$mg\ l^{-1}$	75	200	100	n.d.	0.5–16.7	100
Magnesium (Mg^{2+})	$mg\ l^{-1}$	50	150	30	50	0.1–5.7	100
Sulphate (SO_4^{2-})	$mg\ l^{-1}$	200	400	25	250	0.0–10.5	100
Chloride (Cl^-)	$mg\ l^{-1}$	200	600	n.d.	n.d.	0.0–21.2	100
Sodium (Na^+)	$mg\ l^{-1}$	n.d.	n.d.	20	50	0.1–7.0	100
Potassium (K^+)	$mg\ l^{-1}$	n.d.	n.d.	10	12	0.0–2.0	100
Nitrate (NO_3^-)	$mg\ l^{-1}$	n.d.	30	25	50	0.0–22.6	100

Note: MAC: maximum acceptable contribution; % C: percent compliance with allowable level; na: not applicable, n.d.: no data.
*This study.

for assessing the potability of the supply. Based on the general physico-chemical parameters considered (table 7), the potability of bulk rainwater sources in the study area did not fall completely within the allowable guidelines of most international organizations [9, 10], the two main affected physico-chemical parameters in the list considered being apparent colour and pH (table 7). Apparent colour had 46% of its values above the WHO [9] allowable guide level, while pH had 22% of its values below the lower limit of 6.5. All the rainwater types (both free-fall and roof-harvested samples) were affected to varying extents by the non-compliant levels of both colour and pH values.

There is also evidence of non-compliance of the rainwater sources with set drinking guideline in terms of bacteriological quality (table 6). Although the presence of *E. coli* and other well-known faecal coliforms were not detected, the occurrence of other coliforms (notably *Klebsiella* spp.) and non-coliform pathogenic bacteria was confirmed in virtually all the sample types. The US National Academy of Sciences [42] has reviewed the bacterial agents that cause human intestinal diseases that are disseminated by drinking-water. One of these bacterial isolates, viz *Pseudomonas aeruginosa*, occurred widely distributed in the investigated rainwater samples, while the second isolate, *Proteus* sp., was rare. *Pseudomonas aeruginosa* is reported to cause various infectious, while *Proteus* sp. and other genera of the Enterobacteriaceae (coliform) are associated with gastroenteritis [43]. In view of this and the poor compliance with respect to both colour and pH, the bulk rainwater supply in the study area is not considered potable without the applicable treatment.

In addition to the above considerations, there are potential risks in drinking untreated rainwater collected over Adex/asbestos roofs. Asbestos is among the known synthetic inorganic materials with equivocal evidence of carcinogenicity [43]. Although the concentrations of asbestos in the investigated bulk samples were not determined, the probability of the compound occurring in detectable levels in asbestos roof-intercepted rainwater, especially in the samples collected over old asbestos roofs (which were characterized by relatively high enrichment factors; see table 5), does exist. Such risks, as well as those relating to the probable leaching of heavy metals, deserve in-depth multidisciplinary investigations on the potability of rainwater supply in the study area. While the potability of raw roof-intercepted rainwater is in question, there is no doubt that the supply can be used for a number of other domestic applications such as washing, laundry and other applications, in which water poor in electrolytes or of a poor quality is suitable.

5. Conclusions

Bulk free-fall rainwater in the study area is poor in electrolytes but relatively rich in organic matter, silica, total suspended solids and other airborne materials of terrigenous origin, which are most probably scavenged from the lower atmosphere through subcloud processes. Roof-interception of rainwater leads to a slight increase in pH and about two- to threefold enrichment in most of its water-quality parameters. Rainwater enrichment over roofing materials results from both direct weathering of the roof material and the leaching of the accumulated deposits of particulate matter and associated flora on them. The extent of nutrient enrichment depends on the type of roofing material (being highest over Adex/asbestos roofs and lowest over aluminium roofs) and its age (generally higher over old roofs than new roofs). It is also directly correlated with the amount of rainfall, being higher during early and late rains than during the mid-season rains. In view of the chemical nature of some of the roofing materials (notably asbestos, a well-known carcinogen) and the fact that some coliform and pathogenic bacteria were recorded in the rainwater samples, roof-intercepted rainwater appears not to be potable without necessary treatment. They are, however, suitable for a wide range of other domestic applications.

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