Chemical Sciences

Original article

Rainwater chemistry of a developing urban-industrial metropolis in Southeast Nigeria

Química del agua de lluvia de una metrópoli urbano-industrial en desarrollo en el sureste de Nigeria

Azubuike S. Ekwere

Department of Geology, University of Calabar, Calabar, Nigeria

Abstract

Rainwater (RW) over the Calabar metropolis was analyzed to establish its chemistry, influences, and agricultural suitability. Sampling was done in the rainy and dry seasonal cycles for three years (2018–2020). pH, electrical conductivity (EC), and major ions (Ca2+, Na+, Mg2+, K+, HCO3-, Cl-, and SO42-) were registered and the principal component analysis (PCA) and ionic ratios were used to establish relationships between ionic species and project their sources. RW suitability for agriculture was determined by calculating the sodium and magnesium absorption ratios. Results indicated a relative abundance trend of cations towards Ca2+ > Mg2+ > K+ > Na+ while HCO3- > SO42- > Cl- was the trend for anions. pH varied from 6.1 to 7.8 (mean = 6.60). This and the EC reflected influences from atmospheric gases and in-cloud dissolved solids. The volume-weighted mean (VWM) of ions (Ca2+, Mg2+, K+, Na+, HCO3-, SO42-, and Cl-) was 246 eq/l in the rainy season and 198 eq/l in the dry season indicating low-moderate atmospheric pollution. Wet deposition (WD) fluxes for total ionic contents in RW were higher in the rainy season indicating the impact of rainfall. The PCA and the ionic ratios showed that the ionic concentrations were of crustal and marine origins predominantly. RW chemical characteristics in the study area compared with the concentration ranges of other local and global locations with similar geologic settings and low to moderate pollution indices showed close similarity. The RW assessment for agricultural use based on sodium and magnesium absorption ratios indicated good levels of suitability.

Keywords: Rainwater; Chemical composition; Ionic ratios; Agriculture; Calabar; Nigeria.

Resumen

Se analizó el agua de lluvia en la metrópoli de Calabar para establecer sus características químicas y sus influencias e idoneidad para la agricultura. El muestreo se realizó durante los ciclos estacionales secos y de lluvias a lo largo de tres años (2018-2021). Se hicieron mediciones del pH, la conductividad eléctrica y los iones mayoritarios: Ca2+, Na+, Mg2+, K+, HCO3-, Cl- y SO42-. Se hizo un análisis de componentes principales y de proporciones iónicas para establecer las relaciones entre las especies iónicas y proyectar sus fuentes. La idoneidad del agua de lluvia para uso agrícola también se determinó mediante el cálculo de la proporción de absorción del sodio y el magnesio. Los resultados indicaron una tendencia de abundancia relativa de cationes de Ca > Mg > K > Na, en tanto que HCO3 > SO4 > Cl fue la tendencia de los aniones. El pH varió de 6,1 a 7,8 (con una media de 6,60), lo que conjuntamente con la conductividad eléctrica refleja las influencias de los gases atmosféricos y los sólidos disueltos en las nubes. La media ponderada por volumen de las especies iónicas fue de 246 eq/l para la estación húmeda y de 198 eq/l para la estación seca, lo que indica una contaminación atmosférica de baja a moderada. Los flujos de deposición húmeda para los contenidos iónicos totales en el agua de lluvia fueron más altos en la estación húmeda, lo que indica el impacto de la lluvia. El análisis de componentes principales y las proporciones iónicas evidenciaron que las concentraciones iónicas eran predominantemente de origen marino y de la corteza. Las características químicas del agua de lluvia en el área de estudio comparadas

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Corresponding autor:
Azubuike S. Ekwere;
zerratta77@yahoo.com

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con los intervalos de las concentraciones de otras ubicaciones con entornos geológicos similares e índices de contaminación de bajos a moderados fueron muy similares. La evaluación del agua de lluvia para uso agrícola basada en las proporciones de absorción de sodio y magnesio evidenció buenos niveles de idoneidad.

Palabras clave: Agua de lluvia; Composición química; Proporciones iónicas; Agricultura; Calabar; Nigeria.

Introduction

Rainfall is typically a slightly acidic, dilute solution, which generally contains a few parts per million dissolved solids, except where affected by air pollutants (**Berner & Berner**, 1996). **Langmuir** (1997) defines rainfall over continents as containing important amounts of Ca^{2+}, Na^{+}, NH_4^{+}, H^{+}, SO_4^{2-}, and NO_3^{-} with Ca^{2+} usually exceeding Na^{+}. Trace elements in rain are associated with particulates from the wash-out of windblown dust or aerosols, some volatile enough to exist as vapor in the atmosphere (**Langmuir**, 1997). However, the effects of tropospheric aerosols on climate are not quantitatively understood because of the limited information on their chemical composition, physical and optical properties, and geographical distribution (**Arimoto *et al*.**, 2004).

The composition of rainwater depends on the particulate or gaseous atmospheric constituents emitted by natural or anthropogenic sources locally or transported from distant sources (**Rao *et al*.**, 2016; **Majumdar & Adhikaryb**, 2022; **Li *et al*.**, 2022; **Ma *et al*.**, 2023). Consequently, the composition of rainfall can be both spatially and temporally variable across different environmental settings.

Rainfall has been shown to be a major scavenger for particulates and dissolved gaseous pollutants in the atmosphere. Its acidity, alkalinity, and ionic concentrations depend on the intensity of the constituent sources and their physical and chemical transformation and incorporation into the rainfall during cloud formation processes (**Rao *et al*.**, 2016; **Herrera *et al*.**, 2009). Rainfall composition is also the reflection of a series of processes within and below the cloud cover. The chemistry of rainfall is a major environmental concern, especially regarding acid deposition, eutrophication, trace metal deposition, health issues, and biogeochemical cycling (**Huang *et al*.**, 2010). According to **Casartelli *et al*.** (2008), the chemistry of rainfall is important in developing countries because it is an efficient mechanism of removing pollutants from the air.

The chemical composition of rainfall invariably gives an insight into the atmospheric quality in a specific region, which depends on the emission sources, the atmospheric chemistry, and the meteorological conditions (**Zunckel *et al*.**, 2003).

Long-term and frequent observation of rainwater chemistry provides an opportunity to explore the evolution of air pollutant emissions and the effectiveness of emission control measures (**Li *et al*.**, 2022; **Majumdar & Adhikaryb**, 2022; **Mazurkiewicz *et al*.**, 2022).

The study of the chemistry of rainfall and other forms of precipitation has been of great interest in recent times; it has focused on a better understanding of the environmental quality and the attendant effects of the resulting rainfall on the regional climate, the soil, the vegetation, and other natural cycles and systems, as evidenced by authors such as **Goncalves *et al*.** (2000), **Mouli *et al*.** (2005), **Rocha *et al*.** (2010), **Honorio** (2010), **Niu *et al*.** (2014), **Vet *et al*.** (2014), **Raimundo *et al*.** (2015), **Rao *et al*.** (2016), **Keresztesi *et al*.** (2019), **Keresztesi *et al*.** (2020), **Huang *et al*.** (2022), **Misawal *et al*.** (2022), and **Mazurkiewicz *et al*.** (2022).

The present study is part of a baseline research project on rainfall characteristics and the dynamics controlling its chemistry in the developing urban settlement of Calabar Metropolis, Nigeria. The study answers to recent somewhat visible increases in particulate matter content in rainwater over the area. There has also been a noticeable defacement in the aesthetics of public and private buildings and the infrastructure within the study area. These effects are assumed to be related to the rainfall regimes and chemical composition variations in recent times. Besides, it has been shown that RW recharge has a major influence on the contamination vulnerability of groundwater in the region (**Ekwere & Edet**, 2015). In this context, estimating rainfall composition, verifying possible sources of nutrients in wet precipitation, and projecting the possible effects of rain composition on the ecosystem are among the main objectives of the research project.

Materials and methods

Study area

Calabar Metropolis is located 4˚ 15´ -5˚ 1´5 North and 8˚ 15´ -8 ˚25´ East (**Figure 1**). It is a rapidly expanding modern city with increasing urbanization and industrialization within and around the city's environs over the last 30 years. Some of the major industries include limestone and cement processing and production facilities; wrought-iron smelting and processing factories; petroleum products and gas storage, and tank farms. More pollution is also expected with the increasing vehicular traffic and exhaust fume emissions within the city and adjoining suburbs.

Calabar is situated on the fringe of tropical rainforest vegetation of West Africa, which extends from the Oban hills into the Cameroon volcanic highlands and is bound to the south by the Atlantic Ocean.

The area is built on the Niger Delta basin Tertiary and Quaternary sediments (**Short & Stauble**, 1967) that consist of alternating sequences of gravel, sand, silt, clay, and alluvium. These sediments are primarily derived from the adjoining Precambrian basement (Oban Massif) complex and Cretaceous (Calabar Flank) rocks (**Ekwere *et al.***, 2021; **Ekwere & Elueze**, 2012). The basement complex is made up of gneisses, granites, schists, pegmatites, and a host of ultra-mafic suites (**Ekwere *et al.***, 2012) while the Cretaceous sedimentary unit is built up of limestone, sandstones, shales, and marls (**Reijers**, 1996). The soils and sediments on which the study area is domiciled represent a link between the fresh bedrock, the weathered profiles, and the soils that envelope the landscape of the lower Niger Delta basin. The soils are of the ultisol class characteristic of old landscape settings, i.e., lateritic (**Ekwere *et al.***, 2021).

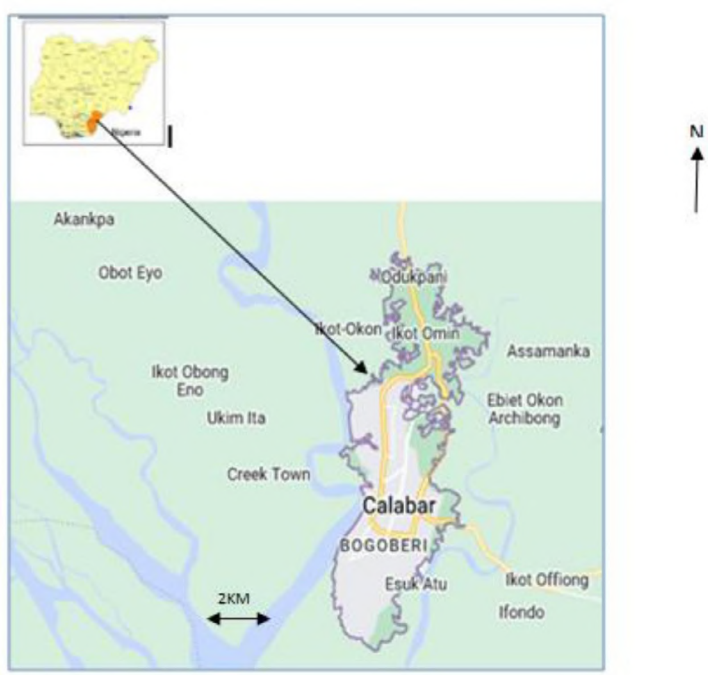

Figure 1. Map of the Study area, Calabar, metropolis: insert is map of Nigeria showing Calabar (adapted and modified from map data 2023).

The area receives an annual average rainfall of 2,300 mm within two distinct seasons: rainy and dry and is generally hot and humid all year round with mean annual temperatures and relative humidity of 26.8˚ C and 84.6%, respectively. The topographic variations extend from less than 10 m in the south to about 80 m in the north with highly and deeply weathered well-drained soil cover.

Sample collection

Rainwater (RW) samples were collected using precipitation samplers as modeled and adapted from **Raimundo *et al.*** (2015). This involved the use of 2-liter polyethylene bottles with a funnel of 120 mm in diameter to collect direct precipitation. Sixteen (16) plastic bottles were mounted on a mobile platform in an area devoid of any interfering substances that could contaminate the rainwater within the premises of the University of Calabar. Samples were collected from 2018 to 2020 during rainfall events within the period. Monthly rainfall was consolidated into composite samples (**Table 1**). The sample bottles were thoroughly rinsed with a few drops of antiseptic (chloroxylenol) to prevent the growth of microorganisms. The bottles were then rinsed several times with de-ionized water prior to use and wrapped in aluminium foil to prevent sunlight according to **Raimundo *et al.*** (2015). Complimentary rainfall data was also collected from the Nigerian Meteorological Agency (NIMET) station in Calabar, Cross River State.

The characteristic tropical climate that prevails during the rainy and dry seasons is controlled by the movement of the Inter Tropical Discontinuity (ITD), a zone separating the warm, humid maritime tropical air mass from the dry continental tropical air mass. The rainy season spans for about six months (May to October) and the dry season lasts from November to April. Temperatures are high with negligible diurnal and annual variations.

Analytical and interpretational techniques

The pH and conductivity values of rainwater were measured immediately after every collection using a standard water quality probe (PHT-027 multi-parameter probe). The water samples were filtered with a 0.45 µm filter paper. Selected nutrients, which included Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, HCO_3^{-}, Cl-, and SO_4^{2-}, were analyzed.

Na^{+} and K^{+} were determined using flame photometry, Mg^{2+} and Ca^{2+} by the titrimetric method using EDTA titration, SO_4^{2-} by the turbidimetric method, HCO_3^{-} by the titrimetric method, and chloride by the Brucine colorimetric method as in **Ademoroti** (1996) using a UNICAM UV2 spectrophotometer with a wavelength accuracy of ±1 nm and a transmittance accuracy of ±0.5% T.

The quality of the analytical data was tested by calculating the charge balances in the rainwater composition and the distribution of species. The charge balance is expressed as:

$$\frac{([\sum\text{anion} - \sum\text{cation}])}{([\sum\text{anion} + \sum\text{cation}])} \times 100$$

For all cases, there was a calculated negative charge ranging from -3.063×10^{-3} to -7.546×10^{-5} with a percentage error of 100^{*} (Cation – [Anion]) / Cation (Cation + [Anion]) ranging from -18.76 to 12.41.

Table 1. Monthly rainfall across the study period (values in mm)

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2018	27.1	25.5	222.9	248.1	328.3	387.3	343.3	522.9	293.5	341.0	148.3	85.1
2019	7.1	48.2	262.9	184.9	216.8	272.9	115.0	241.5	265.3	176.5	104.8	0.00
2020	30.5	35.4	107.8	316.2	246.3	314.6	390.2	539.3	380.2	299.5	56.4	0.00
Annual mean	21.57	36.37	197.87	249.73	263.80	324.93	282.83	434.57	313.00	272.33	103.17	28.37

The selected nutrients were chosen as their presence and interrelationships define the basic nature and origin of water chemistry and possible controlling influences (**Keresztesi *et al.***, 2019; **Keresztesi *et al.***, 2020; **Ekwere & Edet**, 2021; **Majumdar & Adhikaryb**, 2022).

The volume-weighted mean and the wet deposition fluxes were calculated to estimate intrinsic rainwater characteristics using the following formula.

Volume Weighted Mean (*VWM*) of rainwater ionic constituents:

$VWM\ (\mu eq/l) = \sum_{i=1}^{N} C_iP_i \,/\, \sum_{i=1}^{N} P_i$ where C_i is the ionic concentration of individual components (μeq/l) and P_i and N are the rain amounts for each rainy event (in mm) and the total number of rainfall events (**Akpo *et al.***, 2015).

Wet Depositional (*WD*) fluxes were calculated as:

WD (kg/ha/yr) = VWM (mg/l) multiplied by RF/100 with seasonal rainfall (RF) expressed in mm.

Analytical data were also statistically analyzed and the average constituent concentrations in RW were compared to established standards and concentrations from other parts of the world. Principal component analysis (PCA) and ionic ratios were used to assess interrelationships between ions and their concentrations and to determine factors controlling ion concentration data variability and sourcing. RW suitability for agricultural use in irrigation was also assessed.

Results and discussion

Rainfall in the rainy seasons during the study period (defined here as a monthly volume not less than 200 mm according to **Raimundo *et al.***, 2015) had an average total quantity of 2,964 mm within the study period with a minimum of 249.7 mm (April) and a maximum of 434.7 mm (August).

In the dry seasons, the total average volume was 387.3 mm with a minimum of 28.3 mm (December) and a maximum of 197.9 mm (March). It is obvious then that about 92% of the total annual precipitation during the study period fell within the rainy season, well within the range of 90-95% reported by the Nigerian Meteorological Agency (NIMET) for the region.

pH and electrical conductivity

The measurements showed that the pH ranged from 6.1 to 7.8 across seasons during the study period. The mean pH values for dry and rainy seasons within each year of monitoring (2018-2020) did not show any significant differences (**Tables 2, 3, 4**). The mean pH value

Table 2. Results of measured parameters in rainwater in 2018 (units are in mg/l)

Month	K^+	Mg^{2+}	Ca^{2+}	Na^+	Cl^-	SO_4^{2+}	pH	EC(μs/cm)
JAN	2.25	0.75	1.76	0.36	0.25	0.85	6.7	48.3
FEB	1.85	0.63	2.24	0.52	0.42	0.74	6.6	37.5
MAR	0.95	0.82	1.85	0.55	0.55	0.55	6.1	45.8
APR	1.15	0.09	2.04	0.23	0.36	0.84	6.5	40.7
MAY	0.87	1.14	1.05	0.63	0.24	0.62	6.4	42.8
JUN	1.68	0.86	1.55	0.77	0.75	0.77	6.7	56.0
JUL	0.95	0.75	2.08	0.15	0.64	0.56	7.3	38.5
AUG	1.28	0.92	2.26	0.75	0.56	0.85	6.8	66.7
SEP	1.06	1.05	1.85	0.66	0.72	0.72	6.2	38.5
OCT	2.18	0.75	2.46	0.32	0.45	0.82	6.7	47.5
NOV	1.97	0.88	1.87	0.42	0.19	0.73	6.5	56.8
DEC	0.75	1.18	1.56	0.47	0.53	0.66	6.2	64.6
Dry mean	1.66	0.84	1.96	0.44	0.40	0.73	6.47	50.08
Rainy mean	1.24	0.81	1.83	0.52	0.52	0.73	6.62	47.61

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Table 3. Results of measured parameters in rainwater in 2019 (units are in mg/l)

Month	K^+	Mg^{2+}	Ca^{2+}	Na^+	Cl^-	SO_4^{2+}	pH	EC(µs/cm)
JAN	1.68	0.62	1.08	0.42	0.54	0.78	6.8	37.4
FEB	0.67	0.54	1.02	0.74	0.66	0.78	6.5	48.6
MAR	0.64	0.74	2.02	0.53	0.71	0.74	6.8	52.5
APR	2.04	0.65	1.16	0.28	0.36	0.81	6.4	70.4
MAY	0.85	0.56	1.25	0.75	0.54	1.03	6.8	45.6
JUN	1.23	1.05	2.14	0.82	0.66	0.72	7.8	37.2
JUL	1.05	1.26	1.75	0.41	0.18	0.80	6.6	74.5
AUG	0.77	0.78	1.06	0.70	0.55	0.60	6.7	45.5
SEP	2.36	1.14	1.08	1.03	0.28	0.35	6.6	63.0
OCT	1.14	0.62	1.35	0.68	0.34	0.78	6.5	54.7
NOV	1.08	0.74	1.56	0.52	0.25	0.84	6.7	62.0
DEC	0.82	1.12	2.01	0.58	0.37	0.65	6.6	52.4
Dry mean	1.01	0.73	1.51	0.58	0.48	0.76	6.65	51.27
Rainy mean	1.38	0.91	1.41	0.67	0.43	0.72	6.82	56.03

Table 4. Results of measured parameters in rainwater in 2019 (units are in mg/l)

Month	K^+	Mg^{2+}	Ca^{2+}	Na^+	Cl^-	SO_4^{2+}	pH	EC(µs/cm)
JAN	1.88	0.52	2.14	0.48	0.46	0.64	6.5	47.8
FEB	0.85	0.76	2.05	0.45	0.55	0.58	6.4	51.2
MAR	1.77	0.98	2.17	0.48	0.24	0.64	6.5	60.8
APR	0.55	0.88	1.87	0.57	0.51	0.69	6.7	56.6
MAY	1.18	1.08	2.10	0.76	0.86	0.66	6.8	47.2
JUN	0.95	0.75	2.08	0.15	0.64	0.76	7.6	44.5
JUL	1.28	0.86	1.76	0.58	0.56	1.05	6.6	66.8
AUG	1.24	0.98	1.85	0.46	0.84	0.92	6.2	48.5
SEP	2.38	0.77	2.46	0.32	0.56	0.84	6.6	37.5
OCT	0.92	1.04	2.11	0.58	0.42	0.65	6.6	52.4
NOV	1.09	0.62	1.15	0.78	0.44	0.78	6.7	64.2
DEC	0.87	1.12	1.34	0.53	0.64	0.76	6.4	60.6
Dry mean	1.23	0.84	1.83	0.55	0.46	0.68	6.52	56.17
Rainy mean	1.26	0.89	2.02	0.47	0.66	0.82	6.75	50.18

during the wet seasons was 6.66 ± 0.42 and 6.60 ± 0.07 during the dry seasons indicating a slight decrease in acidity from the dry to the rainy seasons. Rainfall within the study area was generally within the acceptable pH limits of 6.5-8.5 for potable water (**WHO**, 2008). Under clean atmospheric conditions, RW is expected to have a pH of ~5.6 due to the dissolution of CO_2 in rain droplets (**Rao *et al.***, 2016). Values below this indicate acid rain (**Oliveira *et al.***, 2012), therefore, RW in the study area showed no acidity threats. Alkaline species concentrations in the atmosphere may result in RW acidity neutralization and a somewhat basic nature (**Chughtai *et al.***, 2014).

Rainwater conductivity was measured with a multi-parameter water probe (model PHT-027). Conductivity values ranged from 74.5 to 37.2 µs/cm across seasons during the study period with a mean value of 51.48 µs/cm for the rainy seasons and of 50.88 µs/cm for the dry ones, i.e., very similar to those reported by **Abeng & Idim** (2019). Conductivity is generally an indicator of total dissolved solids in precipitation (**Gioda *et al.***, 2013).

Mean conductivity values were higher during 2018 and 2020 dry seasons than during the rainy seasons but lower in 2019. However, there were no marked significant differences in the range of values across seasons during the study period. This may reflect the combined effects of the variations in the atmospheric quality during the dry seasons and a greater scavenging of particulates and aerosols during the rainy seasons due to more rainfall. The variations within seasons may also reflect differences in air mass transport over the coastal area. During dry seasons, winds generally blow from the northeast trans-Sahara belt across the dominantly agrarian landmass of north and central Nigeria and are laden with dust particles. The air masses in the rainy seasons are trans-Atlantic south-east winds blowing across the dominantly industrial coastal states with reported high pollution levels. Similar high conductivity RW has been reported in areas with high levels of pollution (**Kaskaoutis *et al.***, 2014; **Tiwari *et al.***, 2015).

Rainwater nutrients

The parameter averages measured during monthly rainfall events and the mean values across seasons for the three-year monitoring period are presented in **tables 2, 3,** and **4**. The means of the parameters measured across seasons for individual years within the monitoring period indicated a general increase in ionic species during the rainy seasons. Higher K+, Mg2+, and Ca2+ values during the dry season were recorded only in 2018, which confirms the scavenging of particulates and aerosols during the rainy seasons. Across seasons during the study period, the relative abundance of cationic and anionic contents in rainwater showed $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$ and $HCO_3^{+} > SO_4^{2-} > Cl^{-}$ trends, respectively. **Figure 2** shows the percentage distribution of inorganic chemical species in rainwater during the study period, and **figure 3** the statistical distribution of chemical species data variation trends.

The total ionic species *VWM* was 246 µeq/l in the rainy season and 198 µeq/l in the dry season. These values indicate low to moderate atmospheric pollution over the metropolis.

The total WD fluxes of total ions were 72.91 kg/ha/yr during the rainy seasons and 6.7 kg/ha/yr during the dry seasons. The WD in the rainy seasons was greater than that in the dry season by a factor of 10.8 showing the impact of rainfall on deposition over the study area. WD values in the study area were within the reported ranges in India (**Rao *et al.***, 2016) during similar seasonal regimes.

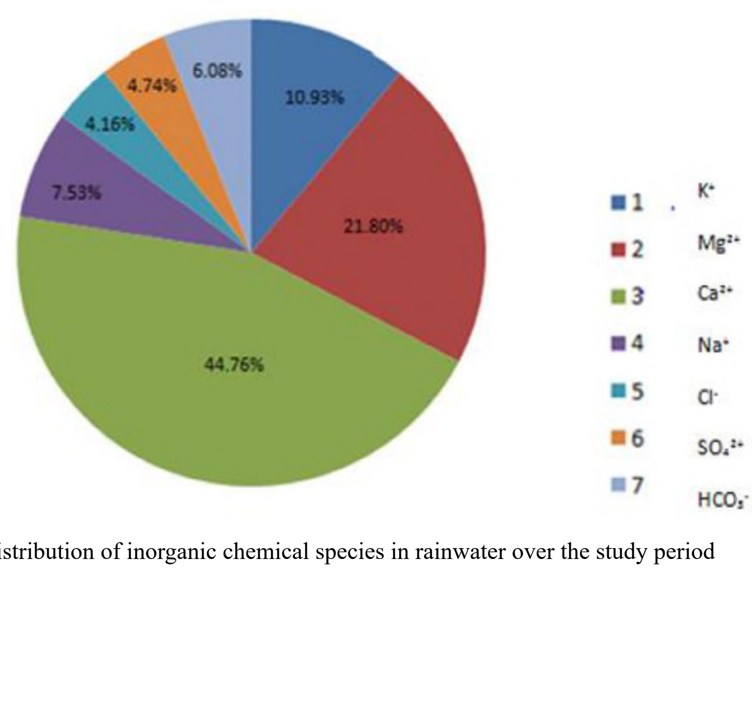

Figure 2. Distribution of inorganic chemical species in rainwater over the study period

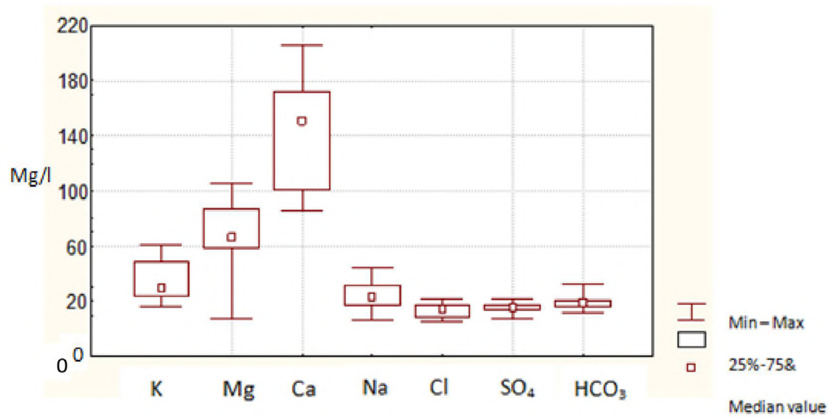

Figure 3. Statistical distribution diagram of measured concentration (Box and whisker diagram)

The monthly composite nutrient averages for the three-year period are presented in **Tables 2-4**. There were no significant variations in monthly concentration levels. However, the bulk comparison of seasonal variations in concentration levels over the period showed some notable variations. Calcium concentration ranged between 1.05 and 2.46 mg/l with a mean of 1.72 mg/l and a standard deviation of 0.44. The other cations had the following ranges, means, and standard deviations: Mg [(0.09 - 1.26) mg/l, 0.83mg/l, 0.27], Na [(0.15 - 1.03) mg/l, 0.55mg/l, 0.22], and K [(0.64 - 2.36) mg/l, 1.35mg/l, 0.56].

As for the anions, HCO_3^- ranged from 0.38–1.03 mg/l with a mean of 0.61 mg/l and a standard deviation of 0.15. Chloride (Cl^-) had range, mean, and standard deviation of 0.18–0.75 mg/l, 0.46 mg/l, and 0.18, respectively. Sulphate (SO_4^{2-}) had a range of 0.35–1.03mg/l, a mean of 0.73mg/l, and a standard deviation of 0.14.

Calcium (Ca^{2+}) and bicarbonate (HCO_3^-) were the dominant ions accounting for 52.65% and 40.59% of total cations and anions, respectively.

Generally, the highest concentrations of cations and anions were registered during the wet seasons highlighting the significance of climatic conditions and the scavenging properties of precipitation. Only Na^+ and K^+ showed higher values at the onset of the dry seasons (November), which may be related to the abrupt temperature variation usually experienced around that period in the region.

These ion concentrations in RW are a clear indication of calcareous soil suspensions, windblown dust, material anthropogenic processing (cement), and possible contributions from sea salt.

The mean concentrations of chemical constituents in the study area were compared with those from other areas locally and worldwide (**Table 5**). The ionic concentration of the major reported acidic species (SO_4^{2-}) in the current study was higher than the maximum range of values reported by **Abeng & Idim** (2019) for Calabar. The values were also higher than the ranges reported by **Okoya *et al.*** (2017) for the Ile-Ife area in southwestern Nigeria but lower than those registered in China, Mexico, Spain, Delhi, Belgium, and Jordan. Acidic species concentrations can be attributed to anthropogenic emissions, particularly from gas flaring and other industrial sources in the region (**Ekwere & Edet**, 2023). As for the soil-derived components K, Ca, and Mg (**Rao *et al.***, 2016; **Majumdar & Adhikaryb**, 2022), the study area had greater concentrations than Benin, Brazil, Mexico, and Belgium. These high concentrations would originate from the dust particulates associated with intensive rock aggregate quarrying in the Oban Massif and the limestone quarrying in the Mfamosing Karst formation (**Rauf *et al.***, 2022; **Ekwere & Edet**, 2021; **Ekwere *et al.***, 2012), which have been shown to be rich in calcite (**Ekwere & Edet**, 2021).

Table 5. Mean and range concentrations of chemical and physical parameter analysis of rainwater (units are in mg/l except for pH)

Month	K^+	Mg^{2+}	Ca^{2+}	Na^+	Cl^-	SO_4^{2+}	HCO_3^-	pH	References
Calabar	24.64	69.09	141.91	23.87	13.20	15.02	19.28	6.7	Present study
Calabar	-	-	-	15.6-80.4	15.8-93.64	0.01-5.15	-	5.4-8.0	**Abeng & Idim**, 2019
Ile-Ife	0.09-0.17	0.07-0.10	0.09-0.15	0.12-0.21	-	0.15-0.17	4.5-18.8	6.13-6.62	**Okoya *et al.***, 2017
Djougou, Benin	1.85	0.63	2.24	-	-	0.74	-	5.19	**Akpo *et al.***, 2015
Beijing, China	9.17	30.5	273	-	-	357	-	4.85	**Xu *et al.***, 2015
Brazil	1.15	0.09	2.04	-	-	0.84	-	6.5	**Mimura *et al.***, 2016
Mexico	2.04	63.7	70.0	-	-	76.7	-	-	**Baez *et al.***, 2007
Coruńa, Spain	15.1	53.7	121.7	-	-	72.5	-	5.55	**Moreda-Piñeiro *et al.***, 2014
Delhi, India	5.3	69.2	198.6	-	-	91.6	-	6.35	**Rao *et al.***, 2016
Belgium	2.0	9.3	28.9	-	-	47.3	-	5.19	**Staelens *et al.***, 2005
Jordan	85.2	93.1	165.3	-	-	112.4	-	6.91	**Le Bolloch & Guerzon,** 1995

Principal component analysis (PCA)

A correlation analysis was conducted for both chemical and physical RW parameters to establish the interrelations between them (**Table 6**). The results showed positive correlations between Na–Mg–Ca indicating the presence of ionic chemical species of crustal (soil) origin (**Rao *et al.***, 2016). A positive correlation was also detected between Na–K–Cl indicating marine sourcing of the ionic species, especially during the wet seasons, and common soil sourcing during the dry seasons (**Safai *et al.***, 2004; **Tiwari *et al.***, 2012; **Majumdar & Adhikaryb**, 2022). The correlation between soil-derived Ca^{2+} and Mg^{2+} with acidic species of SO_4 could be related to atmospheric HSO_4 chemical reactions with alkaline species and carbonate materials present as windblown particulate matter (**Rao *et al.***, 2016).

The factor analysis (**Table 7**) showed two possible dominant factors responsible for data variation. Only the factors with scores greater than 0.30 (moderate significance) were considered significant in determining the major parameters in the factor loadings. The two established factor loadings accounted for 53.29% of the data variability. Factor 1 (31.85%) consisted of HCO_3, Mg, Ca, Na, and SO_4 and indicated a mixture of inputs from debris and dust particulates mainly of crustal or environmental origin. Factor 2 was composed of K, Ca, and Cl (21.44%) and appeared to have a geogenic origin related to mineral salt.

Table 6. Correlation coefficient matrix of measured parameters

	K	Mg	Ca	Na	Cl	SO_4	HCO_3	pH	EC
K	1								
Mg	-0.04	1							
Ca	0.10	-0.13	1						
Na	-0.03	0.50	0.47	1					
Cl	0.52	-0.02	0.30	0.42	1				
SO_4	-0.01	0.50	0.49	-0.27	0.04	1			
HCO_3	-0.11	0.23	-0.14	0.51	0.02	-0.24	1		
pH	-0.01	-0.01	0.42	0.11	0.41	0.10	0.43	1	
EC	0.20	0.46	-0.27	0.05	-0.35	0.03	0.04	-0.29	1

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Table 7. Factor loadings (normalized). Clusters of loadings are in bold.

	Factor 1	Factor 2
HCO_3	**0.6588**	-0.1195
K	0.1609	**0.7037**
Mg	**0.6522**	0.0485
Ca	**0.5382**	**0.3661**
Na	**0.8019**	-0.1506
Cl	-0.0438	**0.8918**
SO_4	**0.6398**	-0.1923
% total variance	31.85	21.44
Cumul. % variance	31.85	53.29

Table 8. The ratio of Na to other elements as sourcing indicator

Ratio	Mean Ratio	Seawater Ratio
Cl/Na	0.67	1.80
SO_4/Na	0.75	0.25
K/Na	1.78	0.12
Mg/Na	3.19	0.12
Ca/Na	4.47	0.04

Ionic ratios

The ratio of Na^+ to an element X (values expressed in milliequivalents, mEq) can be used to assess the likelihood of such an element originating from a marine source (**Casartelli *et al.***, 2008). Such equity in the ratio indicates that the element is of marine origin. Higher ratios point to other important contributing sources. Based on these assumptions, the possibility of inputs from marine sourcing was calculated for the ions (**Table 8**). The Cl-/Na+ ratio was lower than the average for seawater indicating possible marine sourcing (**Majumdar & Adhikaryb**, 2022). Other element ratios were higher than the average seawater ratios indicating that other sources also contribute.

Atmospheric precipitation and deposition, especially in coastal settings like the study area, are usually from marine salts and mineral particulates. The particulates are basically from soil dust or mining and earth excavation work. In the proximity of the study area, there is intensive rock and aggregate quarrying in the crystalline basement of the Oban Massif, as well as limestone quarrying and cement processing within the adjacent Mfamosing karst country. Thus, contributions from other elements may come from rock mass quarrying and processing. The burning of dried foliage and agricultural debris can also contribute, particularly due to high SO_4^{2-} and K^+ to Na^+ ratios.

Suitability assessment of rainwater for agricultural use

In view of the common practice of the local population of harvesting rainwater for small-scale seasonal farming, especially during somewhat dry climatic spells, the study also assessed RW suitability for agricultural use based on the sodium absorption ratio (SAR) and that of magnesium (MAR).

SAR was calculated using the following formula:

$SAR = Na+ / \sqrt{½ (Ca2+ + Mg2+)}$ *with ionic contents expressed in meq/l.*

Higher SAR indicates a higher potential for long-term damage to the soil. Values of less than 3 are safe, while values of >9 cause severe permeability problems on textured soils, e.g., silty-clay and loam (**Baride *et al*.**, 2014), although it has less effect on coarse sandy soils.

SAR calculations for rainwater within the study period ranged from 0.03 to 0.24 with an average value of 0.13. These values were far below the risk value of 9 indicating rainwater suitability for agricultural use within the area.

Calcium and magnesium are usually in equilibrium in water. High Mg adversely affects crop yield and soil quality.

The magnesium absorption ratio (MAR) is computed as:

$$MAR = \frac{\text{Mg}}{\text{Mg+Ca}} \times 100$$

Values greater than 50% indicate the water is poisonous for agricultural use (**Mizra *et al*.**, 2017). Calculated rainfall MAR values within the study area ranged from 0.74–9.50% posing no threat to agricultural use.

Conclusions

Major ionic species analysis, PCA-based interpretations, and ionic ratios were used to determine the hydrochemical characteristics and possible sources of ionic species in rainwater within the Calabar Metropolis.

Rainfall in the study area generally lies within the potable and permissible pH limits of 6.5-8.5. The trend of nutrients in rainwater was Ca > Mg > K > Na and HCO_3 > SO_4 > Cl for cations and anions, respectively, with both sets of nutrients reaching the highest values in the rainy season. The higher nutrient concentration in the rainy season arises from the scavenging influence of more rain within the period. Principal component analyses and ionic ratios indicated that the rainfall composition was controlled by crustal-derived particulates and marine salts, which are geogenic with minimal anthropogenic inputs. The chemical composition of rainfall within the study area was within the concentration range of other world locations with similar geological settings and low to moderate pollution incidences.

Based on sodium and magnesium absorption ratio indices, rainwater within the study area was deemed suitable for agricultural purposes and uses currently.

The present study provides baseline data for the study area, although it only covers a three-year period, and the variability of rainfall and its constituents is considerable over time. Therefore, it is advisable to conduct continuous monitoring and assessment of rainwater in the area over time to check for possible variations, especially from anthropogenic sources. Future studies may also incorporate isotope studies of rainfall constituents for more definitive projections.

Conflicts of interest

There is no conflict of interest as concerns the development of this research through to the production of this manuscript.

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