

RESEARCH ARTICLE

SOURCE IDENTIFICATION AND VARIATION IN THE CHEMICAL COMPOSITION OF RAINWATER IN THE COASTAL AND INDUSTRIAL AREAS: A CASE STUDY OF IKOT ABASI, SOUTH-EASTERN NIGERIA

Etesin, Usoro Monday^a, George, Nyakno Jimmy^a, Ogbonna, Iniobong Joseph^c, Akpan, Itohowo Okon^a^a Department of Chemistry, Akwalbom State University, Ikot Akpaden, Mkpato Enin, Nigeria^b Department of Physics (Geophysics Research Group), Akwa Ibom State University, Ikot Akpaden, Mkpato Enin, Nigeria^c Environment and Safety Unit, Brass Fertilizer Company, Brass, Southeast Nigeria*Corresponding Author Email: nyaknogeorge@aksu.edu.ng

This is an open access journal distributed under the Creative Commons Attribution License CC BY 4.0, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited

ARTICLE DETAILS

Article History:

Received 05 December 2022

Revised 10 January 2023

Accepted 20 February 2023

Available online 23 February 2023

ABSTRACT

Studies on precipitation Chemistry were carried out with the aim to understand the nature and sources of rainwater at Utaewa (Location 1), a coastal village and Ikpetim, near Ibom Power Station (Location 2), all in Ikot Abasi Local Government Area, southern, Nigeria. These locations respectively represent the coastal and industrial regions. The rainwater samples, collected at these locations, were analyzed for major cations, anions, electrical conductivity and pH with the aim of identification of variation in the physiochemical compositions of the rainwater samples. The analysis of the rainwater samples gave a pH at locations 1 and 2 as 5.62 ± 0.26 and 5.77 ± 0.25 respectively during the wet season, while the pH of the rainwater at locations 1 and 2 during dry season were 5.41 ± 0.14 and 5.84 ± 0.21 respectively. The pH values indicated acidic water and were below the World Health Organisation (WHO) Standard of 6.5 to 8.5, but close to the World Meteorological Organisation (WMO) optimum pH value of 5.6 for rainwater from unpolluted continental areas. The predominance of Cl^- and Na^+ were observed in the coastal environment whereas, calcium, sulphate, nitrate and ammonium ions predominate in industrial environment where there are power generating plants, Aluminium smelting company and gas station. The total anion (37.9%) at Utaewa is less influenced by anthropogenic activities whereas total anion (72.5%) at Ikpetim, near Power Plant is influenced by pollutants emitted by anthropogenic activities. The ratio: $H^+/(NO_3^- + SO_4^{2-})$ was observed as 0.04 and 0.008 for Utaewa and Ikpetim respectively, which are close to zero, indicating that 99 % of acidity in the rainwater is neutralized in the study area with no consequence of acidity impact on the soil, surface waters and groundwater in the study area. Ca^{2+} , K^+ and Na^+ play important roles in neutralization of acidic ions in rainwater. For source identification, correlation matrix analysis was established, which showed that at locations 1 and 2, strong correlation exists between the acidic ions SO_4^{2-} and NO_3^- , indicating their origin from anthropogenic activities. This is viewed to be attributed to the similarity in their behaviour in precipitation and the co-emissions of their precursors, which are SO_2 and NO_2 . The major ion enrichment factors (EF) followed the order at location 1 during the dry season; Ca^{2+}/Na^+ (8.58) $> K^+/Na^+$ (4.32) $> SO_4^{2-}/Na^+$ (0.68) $> Cl^-/Na^+$ (0.11), while the enrichment factor (EF) during the wet season at location 1 followed the order, Ca^{2+}/Na^+ (11.92) $> K^+/Na^+$ (3.78) $> SO_4^{2-}/Na^+$ (0.88) $> Cl^-/Na^+$ (0.11).

KEYWORDS

Rainwater; Enrichment Factor; Anthropogenic Activities; Neutralisation Factor; Acid Potential

1. INTRODUCTION

With the noticeable fast economic and population growth in Nigeria in recent time, there is great concern on the global trend in wet precipitation Chemistry and its impact on the ecosystem. Long-term variation in the chemical pollutants characteristics of dry and wet depositions provides veritable data on the temporal evolution of atmospheric pollution, and can be engaged as a pertinent indicator to evaluate natural processes and anthropogenic activities (Tang et al., 2005; Yang et al., 2012). Wet deposition always play a more important role in flux compared to dry deposition, with chemical analyses of precipitation enabling a partial assessment of local air quality (O' zsoy et al., 2008). In Nigeria, acid deposition has been one of the most significant environmental issues since the discovery of oil decades ago (Etesin et al., 2013). Ikot Abasi is

located out of the south of the Niger Delta region impacted by oil bunkering and gas emissions from anthropogenic activities, which may likely cause acid rain in the area.

However, high concentrations of air pollutants in and around Niger Delta in Nigeria most likely lead to high loadings of various chemical species to the ecosystem through atmospheric wet depositions (Etesin et al., 2012). According to the average concentrations of sulphate and nitrate in fine particles, which are two dominant acidic species were much higher than those in some cities suffering severe acid deposition in southern China (Yang et al., 2011). Considering the fast economic and population growth, urbanisation, increased vehicular traffic, the trend in precipitation chemistry and its influence on the ecosystem are of great concern, globally. In developing countries, several sources contribute to the

Quick Response Code



Access this article online

Website:

www.earthsciencesmalaysia.com

DOI:

[10.26480/esmy.01.2023.66.74](https://doi.org/10.26480/esmy.01.2023.66.74)

presence of chemical pollutants in atmospheric air and precipitations such as, their natural resources, vehicular emissions, industrial and residential sources (Forehead and Huynh, 2018). Incidentally, poor air quality on people's behavioural factors and psychological health has resulted to low life expectancy in polluted areas (Qin et al., 2021).

The inhaled fine airborne particulate matters (PM_{2.5}) may likely settle in the lungs, having the potential to cause many health problems (Anderson, 2009). A five-year study of wet precipitation in Beijing, China, reported that the acidification of rainwater is evidently on the increase, especially under the background of complex air pollution (Dingetal., 1997; Wang and Zhang, 1997; Feng et al., 2001; Hu et al., 2005; Yang et al., 2012). Also, recent studies showed that pH and precipitation chemistry in Beijing were noticeably different before and after the year of 2000, which was likely related to the variations in atmospheric pollution type (Tang et al., 2005; Hu et al., 2005; Xu and Han, 2009). According to the reports, there are no studies that are based on long-term surface measurements to track the changing precipitation chemistry along with the changing emissions of acidic precursors and neutralizing substances in Beijing after 2000.

Many studies have investigated the contamination of environment and human health following bombing. A group researchers have determined trace metals in water samples from harvested rain water with health issues correlated with the contents of these contaminants (Alaani et al., 2011). Dissolved chemical compositions in rainwater have provided valuable information on the pollutant sources in the atmosphere and short-term environmental changes (Alaani et al., 2011; Thomas et al., 2020; Ekanem et al., 2021). There are evidences that are well documented which implicated flaring of gas as a serious contributor to acid-rain in the Niger Delta ,with environmental impacts such as vegetation damage , corrosion of roofing sheets and death of aquatic lives (Daily Trust Newspaper, 2008; Amadi et al., 2014 ; Amadi and Akobundu, 2014). Globally, the flaring of gas is estimated to be about 115 billion cubic meters of gas on annual basis (Stan, 2002).

In a similar report, also implicated the flaring of gas in Niger Delta, with attendant contribution to greenhouse gases more than all other sources in Sub-Saharan Africa combined (World Bank, 2004). Oil production in the Niger Delta of Nigeria started more than fifty years ago with the obnoxious practice of flaring associated gas. However, in the developed countries, the usual practice is re-injection of associated gas into the ground compared to the burning off into the atmosphere with no consideration of environmental and health consequences. Despite regulations introduced by the regulating agencies for more than 20 years to outlaw the practice, the associated gas is being flared by the oil companies with impunity, causing local pollution and contributing to climate change (Daily Trust Newspaper, 2008).

In this study, a precipitation monitoring program in Ikot Abasi is initiated in order to evaluate the magnitude as well as temporal trends and sources of acids and toxic substances in atmospheric depositions. Additionally, this study aims at summarizing the major findings with focus on the temporal variations in the precipitation chemistry and discusses possible mechanisms influencing these variations. Our hypothesis testing is that the acidity in the rainwater of the study area is increasing due to the combined effects of increasing SO₂ and NO₂ emissions from anthropogenic activities, beyond neutralizing ions in the rainwater compared with any other published data.

2. MATERIALS AND METHODS

2.1 The Study Area

The study area in Ikot Abasi lies within the Niger Delta zone in Nigeria (Figure 1). It is located between latitude 4.3111° and 4.4512°N and between longitude 7.5213° and 8.0219°E (Ikot Abasi: The Aluminium Town, 1997; Etesin and Iniemem, 2021). Ikot Abasi is a local government in Akwa Ibom State that hosts some major multinational companies, like Exxon Mobil, Aluminium Smelter Company of Nigeria (ALSCON), SEPTA gas station, Ibom Power Company Limited, Ikot Abasi and Oil Platforms close to Iko Town in Eastern Obolo. The study area is underlain by the sedimentary formation of the Late Tertiary and Holocene ages (Obianwu et al., 2011a, b, c; Etesin et al., 2013; Akpan et al., 2020a; George, 2020; Etesin and Iniemem, 2021). The climate of the area is characterized by distinct wet and dry seasons. The wet season begins in April and last still November, while the dry season begins in November till March. A short period of draught is usually experienced in July and August, while a period of harmattan characterized by cold dry winds and lower temperatures normally occurs between December and February (Moses, 1979; Enemugwem, 2009; Nduka and Orisakwe, 2010; Obianwu et al., 2011).

The study area is characterized by a humid tropical climate with rainfall

reaching about 3000 mm per annum (Evans et al., 2010; Ibanga and George, 2016; George et al., 2018; Igbemi et al., 2019; Ikpe et al., 2022; George, 2021; Ekanem et al., 2022). The mean annual daily evaporation of the area is 4.6 mm per day (Edet and Ntekim, 1996). Deposits of recent alluvium and beach ridge sands occur along the coast and the estuaries of the Imo and Qua Iboe Rivers and also along flood plains of creeks (Uwa et al., 2019; Umoh et al., 2022a). The study area consists of mainly of Coastal Plain sands. The sands are mature, coarse and moderately sorted. The Coastal Plain sands, otherwise known as the Benin Formation, overlie the Bende-Ameki Formation and dips south-westward (Mbonu and Ebeniro, 1991; Akankpo and Igbokwe, 2011; Ibuot et al., 2013; Obiara et al., 2015; Obiara et al., 2016; Akpan et al., 2020b; Inim et al. 2020; George et al., 2022). The landscape of Ikot Abasi comprises generally, low-lying plain and riverine areas with no portion exceeding 175 m above mean sea level. The physiography of the study area is that of a Beach Ridge Complex characterized by a succession of sub - parallel sand ridges (George et al., 2015; Ituen and Edem, 2016; Ibuot et al., 2017; Umoh et al., 2022b).

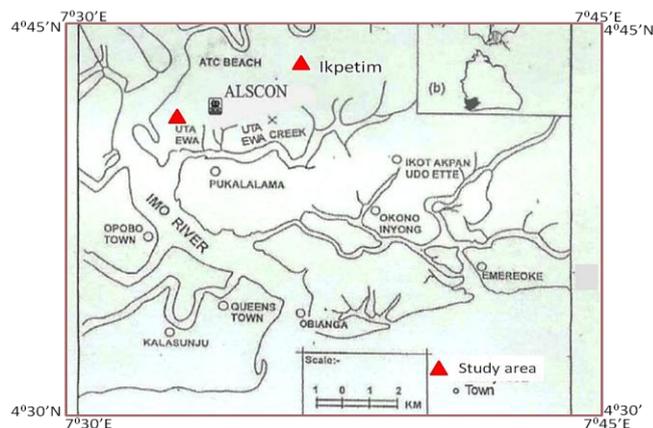


Figure 1: Map of study area showing Utaewa and Iketim, location of sample collections.

2.2 Collection of Rainwater Samples

The set up for the collection of rainwater samples is indicated in Figure 2 and the harvested samples were stored in polyethylene bottles in ice-cooled containers and transported to the Laboratory for chemical analyses. The rainwater samples were collected to cover dry season (October 2020 to March, 2021) and wet season (May to September, 2021). A total of four (4) rainwater samples were collected on event basis during the two seasons specified at two locations representing coastal area (Location 1 – Utaewa) and industrial area (Location 2 – Iketim, near Power Station), that were selected after field survey and were analysed for pH, conductivity, total dissolved solids , total petroleum hydrocarbons , temperature, dissolved oxygen, redox potentials, major anions (chloride, nitrate, sulphate , phosphate), major cations (calcium, sodium, potassium, ammonium) and heavy metals (iron, chromium, lead, cadmium, manganese, vanadium).



Figure 2: Diagram showing rainwater collection in the study area

2.3 Methods of Analyses

2.3.1 Physical Parameters of The Rain Waters

The rain water sampling and analyses were carried out in accordance with American Public Health Association, standard for sampling and analysis of water and wastewater (APHA, 2005). The physical parameters such as pH and conductivity, dissolved oxygen, temperature were determined on the field using a Gallenkamp pH meter and Hach conductivity meter WPA 400 digital model and dissolved oxygen meter respectively.

2.3.2 Analyses of Major Anions

Major anions (chloride, nitrate, sulphate, phosphate) were determined in accordance with American Public Health Association, standard for sampling and analysis of water and wastewater (APHA, 2005). Chloride content of the rain waters was determined by argentometric titration according to method No. 4500- Cl, B. of APHA, 2005. Sulphate content was determined by turbidimetric method, according to method No. 4500 SO₄ E of (APHA, 2005). Nitrate was determined by spectrophotometric method, according to method No. 4500 NO₃, B of (APHA, 2005). Phosphate content of the rainwater samples were determined by spectrophotometric method, according to method No.4500 - P, C of (APHA, 2005).

2.3.3 Analyses of Major Cations and Heavy Metals

Major cations (calcium, sodium, potassium, lead, cadmium, chromium, vanadium, manganese, iron) were determined in accordance with American Public Health Association, Standard Methods for sampling and analysis of water and wastewater (APHA, 2005). Calcium, sodium potassium, lead, cadmium, chromium, manganese, vanadium and iron were determined in the rainwater samples harvested by inductively coupled plasma – optical emission spectrometer (AGILENT 720 ICP-OES). The Agilent 720-ES with megapixel CCD detector was used, which provided simultaneous measurement while the Agilent SPS3 autosampler was used for sample introduction. Agilent Expert II Software was used to control the instrument and acquire data.

Calibration and Quality Control (QC) solutions were prepared from the following reference materials:

- Accustandard QCSTD-27 multi-element solution AG-QCS27-ASC-1
- Agilent Calibration Mix Majors 6610030700
- Agilent Calibration Mix2 6610030600
- Agilent ICMS Internal Standard Solution 6610030400
- Ultrapure Merck Lichrosolv water was used for dilution of standards and quality calibration solutions.

These were also stabilized in high purity 2% v/v concentrated nitric acid (HNO₃). Appropriate concentrations ranges of working standards from the multi-elements stock standard were prepared through serial dilution method. A new worksheet was created from the ICP-OES Expert software into which was programmed the individual sample codes as well as the method with the parameters set according to the Manufacturer's manual. Ammonium ion was determined by macrojeldahl method according to method No.4500 NH₃ B and Cof APHA, 2005, which will involve distillation and titration of the liberated ammonia.

2.3.4 Data Analysis and Calculations

The total cation percent and total anion percent were calculated based on the major cations, Ca²⁺, Na⁺, K⁺, NH₄⁺ and major anions, SO₄²⁻, Cl⁻, NO₃⁻

determined. The ratio of the total anions and total cations was calculated as Total anions / Total cations, to indicate the predominance of the ions in the atmosphere (Xing et al., 2017).

The neutralization factors (NF) were calculated using the following equation for the base cations:

$$NF_i = \frac{X_i}{[(SO_4^{2-}) + NO_3^-]} \quad (1)$$

where, X_i is the base cation of interest, i.e., NH₄⁺, Ca²⁺, Na⁺, K⁺

The acidifying potential (AP) of the acidic anions were calculated to indicate the acidifying capacity of gaseous oxides in the atmosphere as:

$$AP = [SO_4^{2-}] + [NO_3^-] \quad (2)$$

The neutralising potential (NP) was calculated to indicate the neutralising capacity of base cations in the atmosphere as:

$$NP = [NH_4^+ + Ca^{2+}] \quad (3)$$

The ratio of NP / AP, will be calculated and compared to the optimum value of 1.2, indicating the predominance of base cations in the atmosphere to neutralise the acidic anions (Hontoria et al., 2003; Xing et al., 2017; Salve et al., 2008). Ratios such as (NO₃⁻ + Cl⁻) / SO₄²⁻, NH₄⁺/NO₃⁻, NH₄⁺/SO₄²⁻ and Cl⁻/Na⁺ are calculated to indicate the possible predominance of these ions in the atmosphere. The enrichment factor (EF) was calculated for each element in the atmosphere by comparing the ratios of the elements measured in precipitation versus the ratios of elements present in standard seawater. In this study, the sodium ion (Na⁺) was chosen as the reference element for the marine origin elements (Xing et al., 2017). The equation for the enrichment factor calculation can be expressed as:

$$EF_{(X)} = \frac{\left[\frac{X}{Na^+}\right]_{Rainwater}}{\left[\frac{X}{Na^+}\right]_{Marine}} \quad (4)$$

where, X is the concentration of a specific ion (µeq/L). [X/Na⁺]_{marine} is the ratio of seawater reported (Keene et al., 1986). Also to show similar sources of chemical species, Pearson's correlations were calculated between major rainwater ions determined.

2.3.5 H⁺/(NO₃⁻+SO₄²⁻) ratio

The ratio of H⁺/(NO₃⁻+SO₄²⁻) in ueq/L as observed by is also an indicator for the determination of the extent of neutralization process in rainwater (Seinfeld, 1986). The ratio close to zero indicates extensive neutralization whereas values close to one indicate lack of neutralization in rainwater (Salve et al., 2012).

3. RESULTS AND DISCUSSION

The results of analyses of the rainwater samples from Ikot Abasi, Akwa Ibom State, Nigeria are presented in Tables 1 and 2 for the wet and dry Seasons respectively.

Table 1: Results of Physicochemical Analyses of Rain Water From Ikot Abasi, Nigeria, During Wet Season

Parameter	Unit	Mean		WHO Standard
		Location 1	Location 2	
p H		5.62 ± 0.26	5.77 ± 0.25	6.50 - 8.50
Elec. Cond.	(µ S/cm)	8.78 ± 0.78	8.45 ± 0.63	50.00
Redox Potential	(m V)	81.00 ± 2.19	89.00 ± 3.05	
Temperature	° C	28.70 ± 0.66	28.70 ± 0.92	25
Salinity	‰	0	0	
Total Diss. Solid	(mg/L)	4.30 ± 0.53	4.45 ± 0.36	1000
Dissolved Oxygen	(mg/L)	3.74 ± 0.02	3.64 ± 0.05	9.00
Oxygen Sat.	(%)	47.90 ± 0.39	47.5 ± 0.56	100
Total Hydrocarbon	(mg / cm3)	0.52 ± 0.04	0.73 ± 0.02	0.70
Iron (Fe)	(mg/L)	0.017 ± 0.05	0.049 ± 0.07	0.3
Chromium	(mg/L)	0.012 ± 0.006	0.059 ± 0.007	0.05
Phosphate	(mg/L)	1.41 ± 0.09	0.347 ± 0.004	
Sulphate	(mg/L)	1.066 ± 0.05	2.011 ± 0.32	
Nitrate	(mg/L)	0.412 ± 0.013	0.91 ± 0.045	
Chloride	(mg/L)	0.57 ± 0.042	0.71 ± 0.026	
Calcium	(mg/L)	2.75 ± 0.62	1.93 ± 0.051	
Potassium	(mg/L)	0.83 ± 0.049	0.57 ± 0.006	
Sodium	(mg/L)	3.07 ± 0.054	2.92 ± 0.11	
Ammonium	(mg/L)	0.27 ± 0.04	0.41 ± 0.07	

Table 2: Results of Physicochemical Analysis of Rainwater from Ikot Abasi, Nigeria During Dry Season				
Parameter	Unit	Mean	Mean	WHO
		Location 1	Location 2	Standard
pH		5.41 ± 0.14	5.84 ± 0.21	6.50 - 8.50
Elec. Cond.	(μ S/cm)	10.19 ± 0.25	12.65 ± 0.06	50.00
Redox Potential	(mV)	92.00 ± 1.15	87.00 ± 2.05	
Temperature	° C	29.10 ± 0.27	29.50 ± 0.52	25
Salinity	‰	0	0	-
Total Diss. Solid	(mg/L)	7.260 ± 0.23	6.99 ± 0.21	1000.00
Dissolved Oxygen	(mg/L)	5.56 ± 0.07	4.87 ± 0.07	9.00
Oxygen Sat.	(%)	46.31 ± 0.42	67.5 ± 0.53	100.00
Total Hydrocarbon	(mg /cm ³)	0.67 ± 0.06	0.71 ± 0.06	0.70
Iron (Fe)	(mg/L)	0.019 ± 0.05	0.091 ± 0.03	0.30
Chromium	(mg/L)	0.014 ± 0.02	0.073 ± 0.02	0.05
Phosphate	(mg/L)	2.05 ± 0.06	1.22 ± 0.04	
Sulphate	(mg/L)	1.46± 0.07	2.65± 0.16	500.00
Nitrate	(mg/L)	0.36± 0.05	0.73± 0.05	-
Chloride	(mg/L)	1.15± 0.07	1.06 ± 0.03	-
Calcium	(mg/L)	3.99 ± 0.17	2.76± 0.07	-
Potassium	(mg/L)	0.78± 0.08	0.77± 0.05	-
Sodium	(mg/L)	3.21± 0.051	3.41 ± 0.14	-
Ammonium	(mg/L)	0.42± 0.06	0.63± 0.12	-

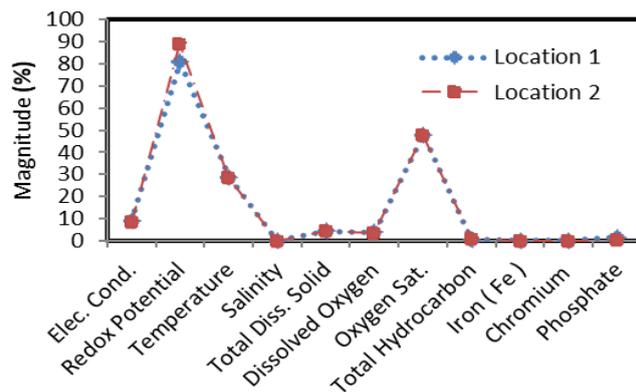


Figure 3: Plot of Physicochemical Parameters during Wet Season

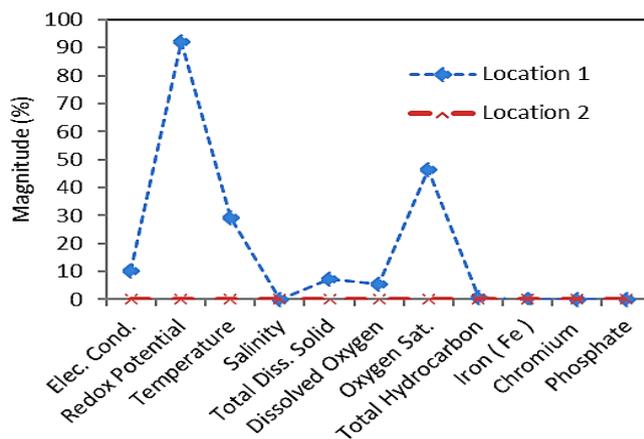


Figure 4: Plot of Physicochemical Parameters during Dry Season

3.1 pH and Electrical Conductivity of Rainwater

The pH of the rainwater at locations 1 and 2 were 5.62 ± 0.26 and 5.77 ± 0.25 respectively during the wet season (Table 1), while the pH of the rainwater at locations 1 and 2 were 5.41 ± 0.14 and 5.84 ± 0.21 during the dry season respectively (Table 2). The pH values indicated acidic water and were below the WHO Standard of 6.5 to 8.5, but close to the WMO optimum pH value of 5.6 for rainwater from unpolluted continental areas

(Tang et al., 2000; Berner and Berner, 2012). The electrical conductivity of the rainwater at locations 1 and 2 were 8.78 ± 0.78 and 8.45 ± 0.68 respectively during the wet season (Table 1), while the electrical conductivity of the rainwater at locations 1 and 2 were 10.19 ± 0.25 and 12.65 ± 0.06 during the dry season respectively (Table 2). The electrical conductivities were below the WHO Standard of 50 uS/cm, but close to the WMO optimum value of 14.6 for rainwater (Tang et al., 2000).

3.2 Total Cations and Anions

The total cations obtained during the dry season at locations 1 and 2 were 62.6 % and 57.2 % respectively, while the total anions obtained during the wet season at locations 1 and 2 were 37.4 % and 42.8 % respectively. The total cations obtained during the wet season at locations 1 and 2 were 66.7 % and 59.8 % respectively, while the total anions obtained during wet season at locations 1 and 2 were 33.3 % and 40.22 % respectively. Locations 1 and 2 show increase in total cations than total anions during both seasons.

3.3 Total Anion and Total Cation Ratio

The ratios of total anion/total cation of the rainwater were 0.61 and 0.75 at locations 1 and 2 respectively during the dry season, while the ratios of total anions /total cations were 0.51 and 0.67 respectively at locations 1 and 2. Overall, the ratio of total anions /total cations were less than one, suggesting an anion deficiency ascribed to some unmeasured anions such as carbonates and short chain organic acids as observed (Hontoria et al., 2013).

Table 3: Rain Water Parameters for Wet Season and Dry Season

Parameter	Unit	Dry Season		Wet Season	
		Location 1	Location 2	Location 1	Location 2
Total Cations	%	62.6	57.22	66.7	59.78
Total Anions	%	37.4	42.78	33.3	40.22
Totalanions / Total cations		0.61	0.75	0.51	0.67
		(< 1)	(< 1)	(< 1)	(< 1)
Cl^-/Na^+		0.35	0.31	0.19	0.24
$NO_3^- + Cl^-/SO_4^{2-}$		1.03	0.66	0.92	0.81
NH_4^+/NO_3^-		1.17	0.86	0.66	0.45
NH_4^+/SO_4^{2-}		0.28	0.24	0.25	0.21
NO_3^-/SO_4^{2-} (NSS)		0.25	0.51	0.39	0.45
SO_4^{2-}/Na^+		0.45	0.78	0.35	0.69
Ca^{2+}/Na^+		1.24	0.81	0.90	0.66
K^+/Na^+		0.24	0.22	0.27	0.21
NP	mg/L	4.41	3.39	3.02	2.34
AP	mg/L	1.82	3.38	1.48	2.92
NP / AP		2.42	1.00	2.04	0.81

3.4 Neutralisation Factor (NF)

Neutralisation Factor for the base cations during the dry season at location1 (Table 4) follows the order NF_{Ca} (2.19) > NF_{Na} (1.76) > NF_K (0.38) > NF_{NH_4} (0.23), and at location 2, follows the order NF_{Na} (1.01) > NF_{Ca} (0.82) > NF_K (0.23) > NF_{NH_4} (0.22). Neutralisation Factors for the base cations during the wet season at location 1 (Table 4) follows the order NF_{Na} (2.08) > NF_{Ca} (1.86) > NF_K (0.56) > NF_{NH_4} (0.18) and at location 2 follows the order NF_{Na} (1.00) > NF_{Ca} (0.66) > NF_K (0.21) > NF_{NH_4} (0.14).

Table 4: Neutralization Factor of Base Cations

Neutralisation Factor (NF)	Dry Season		Rainy Season	
	Location 1	Location 2	Location 1	Location 2
NF (Ca)	2.19	0.82	1.86	0.66
NF (Na)	1.76	1.01	2.08	1.00
NF (K)	0.38	0.23	0.56	0.21
NF (NH4)	0.23	0.22	0.18	0.14

3.5 Cl^-/Na^+ Ratio

The ratios of Cl^-/Na^+ of the rainwater during the dry season at locations 1 and 2 were 0.35 and 0.31 respectively, while the ratio of Cl^-/Na^+ of the rainwater during the wet season at locations 1 and 2, were 0.19 and 0.24 respectively (Table 3). The values of the Cl^-/Na^+ ratio at locations 1 and 2 during the dry and wet seasons were less than one as compared to Cl^-/Na^+ ratio of 1.16 for seawater by the WMO (Tang et al., 2000). The results indicated the high sodium ion contribution to the atmosphere from the seawater due to the proximity of the study area to the Atlantic Ocean. ($NO_3^- + Cl^-/SO_4^{2-}$ Ratio. The ratio of ($NO_3^- + Cl^-/SO_4^{2-}$) (Table 3) gave values of 1.03 and 0.66 at locations 1 and 2 respectively during the dry season, and 0.92 and 0.81 at locations 1 and 2 respectively during the wet season. The results indicated equal contribution of the NO_3^- , Cl^- and SO_4^{2-} anions from anthropogenic activities in the study area to the acidity of the rainwater at location 1 during the dry season. However, the wet season results indicated the increase in the concentration of sulphur oxides from anthropogenic activities to the acidity of the atmosphere, which culminated in the increase of sulphate ion in the rainwater.

3.6 NH_4^+/NO_3^- Ratio

The ratio of NH_4^+/NO_3^- ions were 1.17 and 0.86 at locations 1 and 2 respectively during the dry season (Table 3), while the ratio were 0.66 and 0.45 at locations 1 and 2 respectively during the wet season. All the values

were less than one, except at location 1 during the dry season, indicating the predominance of NH_4NO_3 in the atmosphere in the study area from anthropogenic activities.

3.7 NH_4^+/SO_4^{2-} Ratio

The ratio of NH_4^+/SO_4^{2-} at locations 1 and 2 were 0.28 and 0.24 respectively during the dry season, while the ratio at locations 1 and 2 were 0.25 and 0.21 respectively during the wet season (Table 3). All the values at locations 1 and 2 were less than one during the dry and wet seasons, indicating the predominance of $(NH_4)_2SO_4$ in the atmosphere from anthropogenic activities, in the study area.

3.8 NO_3^-/SO_4^{2-} (nss) Ratio

The non-sea salt ratio of NO_3^-/SO_4^{2-} (nss) in the rainwater were 0.25 and 0.51 at locations 1 and 2 respectively during the dry season, and were 0.39 and 0.45 at locations 1 and 2 respectively during the wet season (Table 3). All the values were less than one, indicating that the precipitating acidity is predominantly from non-sea salt sulphur oxides as emissions from anthropogenic activities, and progressively substituted by nitrogen oxides NO_x (Pradeep et al., 2012).

3.9 Ca^{2+}/Na^+ Ratio

The ratio of Ca^{2+}/Na^+ ions in the rainwater at locations 1 and 2 were 1.24 and 0.81 respectively during the dry season, while the wet season values at locations 1 and 2 were 0.90 and 0.66 respectively (Table 3). The value at location 1 during the dry season was greater than one, indicating the predominance of calcium ion in the atmosphere as a result of crustal components abundance. However, other locations had values that were less than one, indicating the predominance of sodium ion in the atmosphere which may have been influenced by the sea salt water from the Atlantic Ocean by proximity (Yang et al., 2012).

3.10 Neutralisation Potential / Acidification Potential Ratio (NP/AP)

NP/AP ratio of the rainwater at locations 1 and 2 were 2.42 and 1.00 respectively during the dry season (Table 3), while the NP/AP ratio of the rainwater at locations 1 and 2 were 2.04 and 0.81 respectively during the wet season. The NP/AP ratio values at location 1 were higher during dry and wet seasons than the optimum value of 1.2, indicating the predominance of neutralising potential of the wet precipitation (Salve et al., 2008). The NP/AP ratio values greater than the optimum value of 1.2, correlates with higher concentration of calcium ion in the study area as a major acid neutralising factor in the atmosphere (Xing et al., 2017).

3.11 Correlation Matrices

Pearson's correlation matrix of major ions in the rainwater is presented in Table 5. pH values of the rainwater correlates with sulphate ion (R = 0.64) and very strongly with nitrate ion (R = 0.86), but not correlate with

chloride ion (R = -0.26), Calcium ion (R = -0.02), potassium ion (R = -1.27), sodium (R = 0.023) and less with ammonium ion (R = 0.38), indicating strong contributions of sulphate and nitrate ions to the acidification of the acid rain (Salve et al., 2012).

Table 5: Pearson Correlation of Rain Water Parameters

Parameters	pH	Sulphate	Nitrate	Chloride	Calcium	Potassium	Sodium	Ammonium
pH	1							
Sulphate	0.64	1						
Nitrate	0.86	0.72	1					
Chloride	-0.26	0.73	0.47	1				
Calcium	-0.82	-0.29	-0.82	0.607	1			
Potassium	-1.27	-1.13	-0.27	0.18	0.65	1		
Sodium	0.083	0.511	-0.23	0.75	0.511	0.61	1	
Ammonium	0.38	0.94	0.44	0.71	0.067	-0.11	0.75	1

The value of sulphate ion determined in the rainwater correlates strongly with nitrate (R = 0.72), and ammonium ion (R = 0.94), indicating same source contribution from anthropogenic activities, mostly emission of sulphur (IV) oxide and NO_x gases, and also strongly with chloride (R = 0.73) and less with sodium ion (R = 0.51), indicating possible contribution from marine source by proximity. The value of chloride determined in the rainwater correlates with calcium ion (R = 0.61), sodium ion (R = 0.75) and ammonium ion (R = 0.71), indicating same source contribution from marine and crustal abundance. The value of calcium ion determined in the rainwater correlates less with sodium ion (R = 0.51) and potassium (R = 0.65), indicating different sources contribution to acid neutralisation from marine and terrestrial origins (Salve et al., 2012).

3.12 Major Ion Ratios and Enrichment Factor (EF)

The major ion enrichment factor (EF) by micro equivalent per litre (ueq/L) followed the order at location 1 during the dry season; Ca²⁺ / Na⁺ (8.58) > K⁺ / Na⁺ (4.32) > SO₄²⁻ / Na⁺ (0.68) > Cl⁻ / Na⁺ (0.11), while

the enrichment factor (EF) during the wet season at location 1 follow the order Ca²⁺ / Na⁺ (11.92) > K⁺ / Na⁺ (3.78) > SO₄²⁻ / Na⁺ (0.88) > Cl⁻ / Na⁺ (0.11), (Table 6). The sea salt fraction for Ca²⁺ / Na⁺ was 11.65 percent, and non-sea salt fraction was 88.35 per cent at location 1 during the dry season, while K⁺ / Na⁺ had sea salt fraction and non-sea salt fraction of 23.13 percent and 76.87 percent respectively (Table 6), indicating the sources of calcium and potassium ions from crustal abundance. The sea salt and non-sea salt fractions of Cl⁻ / Na⁺ had values of more than 100 percent and less than zero percent respectively, during the dry and wet season at location 1, indicating the source of chloride ion in the rainwater from sea salt evaporation. At location 1 during the wet season, The sea salt fraction for Ca²⁺ / Na⁺ was 8.39 percent, and non-sea salt fraction was 91.61 percent, while K⁺ / Na⁺ had sea salt fraction and non-sea salt fraction of 26.43 percent and 73.57 percent respectively (Table 6), which indicated same source contribution for calcium and potassium ions from crustal abundance in both seasons, as compared to the sea salt and non-sea salt fractions of more than 100 percent and less than zero per cent respectively for Cl⁻ / Na⁺ ratio.

Table 6: Major ion ratio in rainwater at Location 1

Major ion ratio	SO ₄ ²⁻ / Na ⁺	Ca ²⁺ / Na ⁺	K ⁺ / Na ⁺	Cl ⁻ / Na ⁺
Location 1 (DS)				
Sea water	0.25	0.12	0.037	1.16
Rainwater	0.17	1.03	0.16	0.12
Sea salt (%)	> 100	11.65	23.13	> 100
Non-sea salt (%)	< 0	88.35	76.87	< 0
Enrichment Factor (EF)	0.68	8.58	4.32	0.11
Location 1 (WS)				
Sea water	0.25	0.12	0.037	1.16
Rainwater	0.22	1.43	0.14	0.13
Sea salt (%)	> 100	8.39	26.43	> 100
Non-sea salt (%)	< 0	91.61	73.57	< 0
Enrichment Factor (EF)	0.88	11.92	3.78	0.11
(EF)				

Table 7: Major ion ratio in rainwater at Location 2

Major ion ratio	SO ₄ ²⁻ / Na ⁺	Ca ²⁺ / Na ⁺	K ⁺ / Na ⁺	Cl ⁻ / Na ⁺
Location 2 (DS)				
Sea water	0.25	0.12	0.037	1.16
Rainwater	0.33	0.76	0.12	0.09
Sea salt (%)	75.76	15.79	30.83	> 100
Non-sea salt (%)	24.24	84.21	69.17	< 0
Enrichment Factor (EF)	1.32	6.33	3.24	0.08
Location 2 (WS)				
Sea water	0.25	0.12	0.037	1.16
Rainwater	0.37	0.93	0.13	0.21
Sea salt (%)	67.57	12.91	28.46	> 100
Non-sea salt (%)	32.43	87.09	71.54	< 0
Enrichment Factor (EF)	1.48	7.75	3.51	0.18
(EF)				

At location 2 during the dry season, the enrichment factor for the major ions in the rainwater had the following order, Ca^{2+} / Na^{+} (6.33) $> K^{+} / Na^{+}$ (3.24) $> SO_4^{2-} / Na^{+}$ (1.32) $> Cl^{-} / Na^{+}$ (0.08), (Table 7). In comparison with the values obtained during the wet season, the order were, Ca^{2+} / Na^{+} (7.75) $> K^{+} / Na^{+}$ (3.51) $> SO_4^{2-} / Na^{+}$ (1.48) $> Cl^{-} / Na^{+}$ (0.18), (Table 7), indicating the dominance of calcium, potassium and sulphate ions in the rainwater from anthropogenic activities and crustal abundance. At location 2 during the dry season, Ca^{2+} / Na^{+} had sea salt and non-sea salt fractions of 15.79 per cent and 84.21 per cent respectively; K^{+} / Na^{+} had sea salt and non-sea salt fractions of 30.83 per cent and 69.17 percent respectively; SO_4^{2-} / Na^{+} had sea salt and non-sea salt fractions of 75.76 per cent and 24.24 per cent respectively; Cl^{-} / Na^{+} had sea salt and non-sea salt fractions of greater than 100 per cent and less than zero respectively (Table 7). In comparison during the wet season, Ca^{2+} / Na^{+} had sea salt and non-sea salt fractions of 12.91 per cent and 87.09 per cent respectively; K^{+} / Na^{+} had sea salt and non-sea salt fractions of 28.46 per cent and 71.54 per cent respectively; SO_4^{2-} / Na^{+} had sea salt and non-sea salt fractions of 67.57 per cent and 32.43 per cent respectively; Cl^{-} / Na^{+} had sea salt and non-sea salt fractions of greater than 100 percent and less than zero respectively (Table 7). The results of major ions

obtained during both seasons indicated that calcium and potassium ions are dominant in the rainwater from the study area from terrestrial origin; chloride ion is not dominant in the rainwater from the marine origin, while sulphate ion is however, dominant in the rainwater from anthropogenic activities in the study area.

3.13 $H^{+} / (NO_3^{-} + SO_4^{2-})$

The ratio of $H^{+} / (NO_3^{-} + SO_4^{2-})$ in ueq/L as observed by is also an indicator for the determination of the extent of neutralization process in rainwater (Seinfeld, 1986). In this study the values determined at location 1 for dry and wet seasons were 0.08 and 0.11 respectively, while the values determined for Location 2 were 0.03 and 0.02 during the dry and wet seasons respectively (Table 8). The ratio close to zero indicates extensive neutralization whereas values close to one indicate lack of neutralization in rainwater (Al-Chessman, 2005; Salve et al., 2012). The ratios determined for all the locations in both seasons were close to zero, indicating that 99 % of acidity in the rainwater is neutralized in the study area. The results corroborate the observations by in acid rain study in Warri and Port Harcourt, Niger Delta (Efe and Mogborukor, 2012).

Table 8: Major Ion Concentration in Micro Equivalent Per Litre

Ion concentration in (ueq/L)	Location 1	Location 2	Location 1	Location 2
	Dry season	Dry season	Wet season	Wet season
Hydrogen ion (ueq/L)	2.41	1.70	3.90	1.45
Sulphate (ueq/L)	22.19	41.86	30.39	55.16
Nitrate (ueq/L)	6.64	14.68	5.81	11.77
Chloride (ueq/L)	16.08	11.45	18.55	29.9
Calcium (ueq/L)	137.2	96.31	199.1	137.7
Potassium (ueq/L)	21.23	14.58	19.95	19.69
Sodium (ueq/L)	133.5	127.1	139.6	148.3
Ammonium (ueq/L)	14.96	22.71	23.27	34.9
$H^{+} / (SO_4^{2-} + NO_3^{-})$	0.084	0.03	0.11	0.021

4. CONCLUSION

This study investigated the concentration and composition of major ions in rainwater at Utaewa (Location 1) and Ikpetim (Location 2), in Ikot Abasi, southern part of Niger Delta, with an aim to characterize the chemical composition of rainwater and identify possible sources. The pH of the rain waters in the two locations had values in the acidic range in both seasons; some values were less than the optimum pH of 5.6 for rainwater. In all locations in both seasons, the ratio of Total anions to Total cations were less than one, which clearly indicated major anion deficit. Neutralisation Factor for the base cations during the dry season at Location 1 follows the order $NF_{Ca} > NF_{Na} > NF_K > NF_{NH_4}$, and at location 2, follows the order $NF_{Na} > NF_{Ca} > NF_K > NF_{NH_4}$, and same sequence repeated during the wet season. Significantly, the major neutralisation base cations were calcium ion, sodium ion, potassium ion. The correlation matrix showed a strong correlation between sulphate, nitrate and ammonium ions, which shows a common source of the ions from anthropogenic activities like the emissions from the Power Plant in the study area. Sodium ion correlates strongly with chloride ion, which shows a common source from sea salt spray ferried by wind from the Atlantic Ocean due to proximity to the study area. The ratio of $H^{+} / (NO_3^{-} + SO_4^{2-})$ measured in ueq/L in both locations and seasons were less than one, which indicated complete neutralisation of the acidity in rainwater in the study area with no consequence of acidity impact of the soil, surface water and groundwater. This observation is corroborated by the significant enrichment of the base cations from the Enrichment Factor measured.

FUNDING

The project was funded by the authors

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

HUMAN AND ANIMAL RIGHTS

This article does not contain studies with human or animal subjects.

REFERENCES

- Akpan, A.S., Obiora, D.N., Okeke, F.N., Ibuot, J.C., and George, N.J., 2020. Influence of wavelet phase rotation on post stack model based seismic inversion: A case study of X-field, Niger Delta, Nigeria. *Journal of Petroleum and Gas Engineering*, 11 (1), Pp. 57-67. DOI: 10.5897/JPGE2019.0320.
- Akpan, A.S., Okeke, F.N., Obiora, D.N., and George, N.J., 2020. Modelling and mapping hydrocarbon saturated sand reservoir using Poisson's impedance (PI) inversion: a case study of Bonna field, Niger Delta swamp deponent, Nigeria. *Journal of Petroleum Exploration and Production Technology*, Pp. 117-132. <https://doi.org/10.1007/s13202-020-01027-8>
- Al-Khashman, O.A., 2005. Study of chemical composition in wet atmospheric precipitation in Eshidiya area, Jordan. *Atmos. Environ.*, 39, Pp. 6175-6183.
- Aluminium Smelting Company of Nigeria (ALSCON) IkotAbasi, 1997. *The Aluminium Town: Socio- economic Transformation of a Nigerian Community*.
- Anderson, L.G., 2009. Ethanol fuel use in Brazil: air quality impacts. *Energy & Environmental Science*, 2, Pp. 1015 - 1037.
- Berner, E.K., Berner, R.A., 1987. *The global water cycles. Geochemistry and environment*. Prentice-Hall, New York, Pp. 394.
- Ding, G., Xu, X., Fang, X., Jin, Shu., Xu, X., Tang, J., Liu, Q., Wang, S., and Wang, W., 1997. The status and trend of acidic rain in China. *Chinese Sci. Bulletin*, 42, Pp. 169-173.
- Edet, A.E., and Ntekim, E.U., 1996. Heavy metal distribution in ground water from Akwa Ibom State, Eastern Niger Delta, Nigeria. A preliminary pollution assessment. *Global Journal of Pure and Applied Science*, 2 (1), Pp. 67 - 77.
- Efe, S.I., and Mogborukor, J.O.A., 2012. Acid Rain in Niger Delta Region: Implication on Water Resources Quality and Crisis. *International Journal of Science and Technology Bahir Dar, Ethiopia*, 1 (1), Pp. 17-46

- Ekanem, A.M., Akpan, A.E., George, N.J., Thomas, J.E., 2021. Appraisal of protectivity and corrosivity of surficial hydrogeological units via geo-sounding measurements. *Environ Monit. Assess.*, 193 (11), Pp. 718. doi: 10.1007/s10661-021-09518-9. PMID: 34642861.
- Ekanem, K.R., George, N.J., Ekanem, A.M., 2022. Parametric characterization, protectivity and potentiality of shallow hydrogeological units of a medium-sized housing estate, Shelter Afrique, Akwa Ibom State, Southern Nigeria. *Acta Geophys.* <https://doi.org/10.1007/s11600-022-00737-3>
- Enemugwem, J.H., 2009. Oil Pollution and Eastern Obolo Human Ecology, 1957 – 2007. *International Multidisciplinary Journal*, 3 (1), Pp. 136 – 151.
- Etesin, U., Enewan, U., and Thomas, H., 2013. Seasonal Variation of Physicochemical Parameters of Water and Sediments from IkoRiver, Nigeria. *Journal of Environment and Earth Science*, 3 (8), Pp. 2224-3216.
- Etesin, U.M., and Iniemem, J.I., 2021. Hydrochemical study of shallow ground water in IkotAbasi Coastal Aquifer. *Communication in Physical Sciences*, 7 (3), Pp. 218-228.
- Evans, U.F., Akpan, A.E., George, N.J., Obot, I.B., Ikot, A.N., 2010. A Study of the Superficial Sediments and Aquifers in Parts of Uyo Local Government Area, Akwa Ibom State, Southern Nigeria Using Electrical Sounding Method. *E-journal of Chemistry, India*, 7 (3), Pp. 1016-1022.
- Feng, Z., Huang, Y., Feng, Y., Ogura, N., and Zhang, F., 2001. Chemical composition of precipitation in Beijing area, Northern China. *Water, Air, and Soil Pollut.*, 125, Pp. 345–356,
- Forehead, H., and Nicolas H., 2018. Review of modelling air pollution from traffic at street-level - The state of the science. *Environmental pollution*, 241, Pp. 775 – 786.
- George, N.J., 2020. Modelling the trends of resistivity DOI:dient in hydrogeological units: a case study of alluvial environment, *Model. Earth Syst. Environ.*, 7, Pp. 95–104. DOI 10.1007/s40808-020-01021-3.
- George, N.J., 2021. Integrating hydrogeological and second-order geoelectric indices in groundwater vulnerability mapping: A case study of alluvial environments. *Applied Water Science*, 11 (123), <https://doi.org/10.1007/s13201-021-01437-x>
- George, N.J., Ibuot, J.C., Ekanem, A.M., George, A.M., 2018. Estimating the indices of inter-transmissibility magnitude of active surficial hydrogeologic units in Itu, Akwa Ibom State, southern, *Arabian Journal Geosciences, Saudi Arabia*, 11 (6), Pp. 1-16. DOI 10.1007/s12517-018-3475-9.
- George, N.J., Umoh, J.A., Ekanem, A.M., Agbasi, O.E., Asfahani, J., Thomas, J.E., 2022. Geophysical-laboratory data integration for estimation of groundwater volumetric reserve of a coastal hinterland through optimized interpolation of interconnected geo-pore architecture, *J. Coastal Conservation*, DOI : 10.1007/s11852-022-00902-2.
- Hontoria, C., Saa, A., Almorox, J., Cuadra, L., S'anchez, A., and Gascó, J.M., 2003. The chemical composition of precipitation in Madrid. *Water, Air, Soil Pollut.*, 146, Pp. 35–54.
- Hu, M., Zhang, J., and Wu, Z., 2005. Chemical compositions of precipitation and scavenging of particles in Beijing. *Sci. in China. Chem.*, 48, Pp. 265–272.
- Ibanga, J.I., George, N.J., 2016. Estimating Geo hydraulic parameters, protective strength, and corrosivity of hydrogeological units: a case study of ALSCON, Ikot Abasi, Southern Nigeria. *Arab J. Geosci.*, 9, Pp. 363. <https://doi.org/10.1007/s12517-016-2390-1>.
- Ibuot, J.C., Akpabio, G.T., George, N.J., 2013. A survey of the repository of groundwater potential and distribution using geoelectrical resistivity method in Itu Local Government Area (L.G.A), Akwa Ibom State, southern Nigeria. *Central European Journal of Geosciences, USA*, 5 (4), Pp. 538-547. DOI10.2478/s13533-012-0152-5.
- Ibuot, J.C., Ibuot, Okeke, F.N., George, N.J., Obiora, D.N., 2017. Geophysical and physicochemical characterization of organic waste contamination of hydro lithofacies in the coastal dumpsite of Akwa Ibom State, southern Nigeria. *Science & Technology: Water Supply*, 17 (6), Pp. 1626-1637. doi: 10.2166/ws.2017.066.
- Igbemi, A.I., Nwaogazie, I.L., Akaranta, O., Abu, G.O., 2019. Water Quality Assessment by Pollution Indices in Eastern Obolo Coastline Communities of Nigeria. *American Journal of Water Resources*, 7 (3), Pp. 111-120.
- Inim, I.J., Udosen, N.I., Tijani, M.N., Afia, U.E., George, N.J., 2020. Time-lapse electrical resistivity investigation of seawater intrusion in coastal aquifer of Ibeno, Southeastern Nigeria, *Applied Water Science*, 10, Pp. 232. <https://doi.org/10.1007/s13201-020-01316-x>
- Ituen, U., Atser, J., Edem, S.N., 2016. Analysis and Depiction of Accessibility Levels of water Supply Schemes in Rural Akwalbom State, Nigeria. *Iranian Journal of Health, Safety & Environment*, 3 (2), Pp. 518-527.
- Keene, W.C., Pszeny, A.P., Galloway, J.N., Hawley, M.E., 1986. Sea salt correction and interpretations of constituents ratios in marine precipitation. *J. Geophys. Res.*, 91, Pp. 6647–6658.
- Mbonu, D.D.C., Ebeniro, J.O., Ofoegbu, C.O., and Ekine, A.S., 1991. Geoelectrical Sounding for Determination of Aquifer Characteristics in Parts of Umuahia Area of Nigeria. *Geophysics*, 56 (5), Pp. 284-291.
- Moses, B.S., 1979. The Cross River, Nigeria- its ecology and fisheries. In proceedings of the International Conference on Kanji Lake and River Basin Development in Africa. Kanji Lake Research Institute, New Bussa, Nigeria. Pp. 335 – 370.
- Nduka, J.K.C., and Orisakwe, O.E., 2010. Precipitation chemistry and occurrence of acid rain over the oil-producing Niger Delta Region of Nigeria. *The Scientific World Journal*, 10, Pp. 528–534. DOI 10.1100/tsw.2010.61.
- O' zsoy, T., Tu' rker, P., and O' rnektekin, S., 2008. Precipitation chemistry as an indicator of urban air quality in Mersin, North-Eastern Mediterranean Region. *Water, Air, Soil Pollut.*, 189, Pp. 69–83.
- Obianwu, V.I., Chimezie, I.C., Akpan, A.E., George, N.J., 2011a. Estimation of Aquifer Secondary Parameter Distributions from Surficial Geophysical Measurements of Primary Parameters. A case Study of Ngor-Okpala Area of Imo State. *Journal of Applied Physics Research, Canada*, 3 (2), Pp. 67-80.
- Obianwu, V.I., Chimezie, I.C., Akpan, A.E., George, N.J., 2011c. Surficial Geophysical Deduction of the Geomaterial and Aquifer Distribution at Ngor-Okpala Local Government Area of Imo State, Southern Eastern Nigeria. *Central European Journal of Geosciences*, 3 (4), Pp. 368-374. USA, Doi: 10.2478/S13533-011-0011-0033-1.
- Obianwu, V.I., George, N.J., Okiwelu, A.A., 2011b. Preliminary Geophysical Deduction of Lithological and Hydrological Conditions of the North-Eastern Sector of Akwa Ibom State, Southern Nigeria, *Research Journal of Applied Sciences, Engineering and Technology*, 3 (8), Pp. 806-811.
- Obinawu, V.I., George, N.J., Udofia, K.M., 2011d. Estimation of aquifer hydraulic conductivity and effective porosity distributions using laboratory measurements on core samples in the Niger Delta, Southern Nigeria. *International Review of Physics, Praise Worthy Prize, Italy*, 5 (1), Pp. 19–24.
- Obiora, D.N., Ibuot, J.C., George, N.J., Solomo, U.O., 2016. Delineation of Groundwater Saturation Indicators and their Distributions in the Complex Argillaceous Geological Units of Ezra North Local Government Area of Ebonyi State, Nigeria. *Journal of current Science*, 110 (4), doi: 10.18520/cs/v110/i4/701-708
- Obiora, D.N., Ibuot, J.C., George, N.J., 2015. Evaluation of aquifer potential, geoelectric and hydraulic parameters in Ezza North, southeastern Nigeria, uses geoelectric sounding. *Int. J. Sci. Technol.*, <https://doi.org/10.1007/s13762-015-0886-y>
- Pradeep, V., Deepika, C., Urvi, G., and Hitesh, S., 2012. Water quality analysis of an organically polluted lake by investigating different physical and chemical parameters. *Int. J. Res. Chem. Environ*, 2 (1), Pp. 105-111.
- Qin, G., Niu, Z., Yu, J., Li, Z., Ma, J., and Xiang, P., 2021. Soil heavy metal pollution and food safety in China: effects, sources and removing

- technology. *Chemosphere*, 267, Pp. 129- 205.
- Salve, P.R., Maurya, A., Wate, S.R., Devotta, S., 2008. Chemical composition of rainwater in an urban environment. *Bull. Environ. Contam.Toxicol.*, 80, Pp. 242–246.
- Seinfeld, J.H., 1986. *Atmospheric chemistry and physics of air pollution*, 219. Wiley, New York
- Tang, A., Zhuang, G., Wang, Y., Sun, Y., Yuan, H., and Sun, Y., 2005. The chemistry of precipitation and its relation to aerosol in Beijing. *Atmos. Environ.*, 39, Pp. 3397–3406.
- Tang, J., Xu, X., Ba, J., and Wang, S., 2010. Trends of the precipitation acidity over China during 1992–2006. *Chinese. Sci. Bul.*, 5, Pp. 1800–1807.
- Tang, J., Xue, H., Yu, X., Cheng, H., Xu, X., Zhang, X., and Ji, J., 2000. The preliminary study on chemical characteristics of precipitation at Mt. Waliguan. *ACTA Sci. Circumstantiate*, 20, Pp. 420–425.
- The Guardian, Editorial, 2008. Gas flaring, end of a moving target? Tuesday January 15, 2008 http://www.guardiannewsngr.com/editorial_opinion/article01/indexn2
- Thomas, J.E., George, N.J., Ekanem, A.M., Nsikak, E.E., 2020. Electro stratigraphy and hydro geochemistry of hyporheic zone and water-bearing caches in the littoral shorefront of Akwa Ibom State University, Southern Nigeria. *Environ Monit Assess.*, 192, Pp. 505. <https://doi.org/10.1007/s10661-020-08436-6>
- Umoh, J.A., George, N.J., Ekanem, A.M., and Emah, J.B., 2022a. Characterization of hydro-sand beds and their hydraulic low units by integrating surface measurements and ground truth data in parts of the shorefront of Akwa Ibom State, Southern Nigeria. *International Journal of Energy and Water Resources* <https://doi.org/10.1007/s42108-022-00215-y>
- Umoh, J.A., George, N.J., Ekanem, A.M., Thomas, J.E., Emah, J.B., 2023b. Approximate delineation of groundwater yield capacity and vulnerability via secondary geo-electric indices and rock-water interaction hydrodynamic coefficients in a coastal environment, 29 *Researchers Journal of Science and Technology*, 2 (3), Pp. 28 – 54.
- Uwa, U.E., Akpabio, G.T., George, N.J., 2019. Geohydrodynamic parameters and their implications on the coastal conservation: A case study of Abak Local Government Area (LGA), Akwa Ibom State, Southern Nigeria, *Nat Resour Res., Switzerland*, 28 (2), Pp. 349-367. <https://doi.org/10.1007/s11053-018-9391-6>
- Wang, Y., Liu, X.H., Li, H.L., Wang, W.X., 2007. Appropriate range of quality control limit for wet deposition monitoring. *Environ. Monit. Assess.*, 132, Pp. 45–51.
- World Bank. 2004. *Global gas flaring reduction initiative: report No.3: regulation of associated gas flaring and venting – a global overview and lessons*, Pp. 64.
- Xing, J.J., Song, H., Yuan, X., Li, N., Li, L., Duan, B., Qu, Q., Wang, X., Kang, 2017. Chemical characteristics, deposition fluxes and source apportionment of precipitation components in the Jiaozhou Bay, North China. *Atmos. Res.*, 190, Pp. 10-20.
- Xu, Z.F., and Han, G.L., 2009. Chemical and strontium isotope characterization of rainwater in Beijing, China. *Atmos. Environ.*, 43, Pp. 1954–1961.
- Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., Chen G., and Zhao, Q., 2011. Characteristics of PM_{2.5} speciation in representative megacities and across China, *Atmos. Chem. Phys.*, 11, Pp. 5207–5219. doi: 10.5194/acp-11-5207-
- Yang, F.J., Tan, Z.B., Shi, Y., Cai, K., He, Y., Ma, F., Duan, T., Okuda, S., Tanaka, and Chen, G., 2012. Five-year record of atmospheric precipitation chemistry in urban Beijing, China. *Atmos. Chem. Phys.*, 12, Pp. 2025–2035.

