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Source Identification and Health Risks Assessment of Toxic Metals in Rainwater and Groundwater in Eket and Esit Eket, Nigeria

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Abstract

Eket and Esit Eket in South-South Nigeria are oil producing local government areas. Oil exploration activities with the attendant gas flares and recurrent oil spillages have degraded the environment including water sources. To determine the safety of rainwater and groundwater potability, the levels of metals (Ni, Cd, Pb, Cu, Fe, Mn and Zn using atomic absorption spectrophometer), non-carcinogenic and lifetime carcinogenic health risks in adults through two pathways (ingestion and dermal absorption) based on USEPA model were evaluated. The levels of Ni, Cd, Pb, Fe, and Mn in rainwater and groundwater at all sites exceeded the Nigerian and WHO's quality guidelines while Cu and Zn were below. Esit Urua and Mkpok in Eket showed highest levels of metals in rainwater and groundwater, respectively. Multivariate analysis (correlation, cluster analysis and principal component analysis) identified the source of pollution as mixed anthropogenic (mainly oil and gas related activities, incineration of domestic and municipal wastes) and natural (lithogenic and entrained dust). Non-carcinogenic health quotients (HQ) and the combined hazard index (HI) were higher in groundwater than in rainwater via ingestion. The relative abundance of metals (for HQ and HI) followed the order: Zn<Fe<Ni<Cu<Mn<Pb<Cd (rainwater) and Zn<Ni<Fe<Cu<Cd<Mn<Pb (groundwater). The results indicated potential health hazards of rainwater and groundwater through ingestion; and Ni, Cd and Pb the main contributors to potential lifetime carcinogenic risks. Lifetime carcinogenic risks of metals increased in the order: Mn< Ni<Cd<Pb (both rainwater and groundwater) with values higher in rainwater, and revealed that rainwater through ingestion may pose much more lifetime carcinogenic risks than groundwater. Non-carcinogenic and lifetime carcinogenic risks of metals were not associated with rainwater and groundwater through dermal contacts for individual metals, at all sites.

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This study is essential for alerting government on the danger posed by consumption of rainwater and groundwater in Eket and Esit Eket, and the need for establishing suitable remediation method for the water sources for potable use.

Keywords: Exposure route; Groundwater; Rainwater; Risk assessment; Toxic metal pollution

1. Introduction

Water is fundamental, and a highly priced resource. Franks [1] refers to it as the "matrix of life". It is in such abundance that it covers 75% of the world's surface area. 97% of the earth's water is in the ocean, 2% locked up in polar ice caps and, only the 1% available as fresh water in rivers, lakes, streams and groundwater could be suitable for human use and consumption [2].

In the quest for improved living standard man, inadvertently, is impacting negatively on natural water sources. Issues of availability, quantity and quality therefore continue to define water sources across communities, nations and continents.

More than half of the world's population is estimated to use groundwater for drinking and other purposes [3]. Over exploitation and improper waste disposal as a result of rapid urbanisation however is reported to affect the availability and quality of groundwater especially in developing countries [4]. Aside availability, continuous water pollution due to sewage disposal, industrial and mining wastes also threatens to reduce the available quantity of usable water from ground and surface sources [5, 6]

Water being a universal solvent dissolves chemicals and carries a lot of impurities in suspension [7]. This characteristic is responsible for the abundance of toxic chemicals in drinking water, and which cause malfunctioning of the body, chronic illnesses and in some cases cancers [8] The trace elements some though essential to man, at elevated levels may impede growth, increase mortality and produce mutagenic effects [9, 10].

Rainwater, is also a source of water for drinking and other purposes in some communities especially in the developing countries, including Nigeria [7]. Indeed despite the seasonal pattern of rainfall in the Savannah and Sahel zones of Nigeria, rainwater is of tremendous importance as it supports our agriculture which is mainly rain-fed. The local government areas Eket and Esit Eket situate in the guinea climatic latitudinal zone (coast-8^{o}N) with rainfall virtually all the year round, peaking in the month of September and beginning its decline in October [11]. The two local government areas are oil producing, hence have witnessed oil exploitation activities/gas flares for many decades. Recurrent oil spillages have threatened surface water sources. The inhabitants of the area especially the rural dwellers and urban poor have no option than embrace groundwater (borehole) and rainwater for their water needs. Pipe borne water is not available to non-functional.

This work aims at assessing the quality of rainwater and groundwater in Eket and Esit Eket, in Akwa Ibom State of Nigeria by: determining the levels of metals at the various sites in the months of September and October; and,

evaluating the risk level of water using non-carcinogenic hazard (HQ and HI) and the lifetime carcinogenic risk models.

2. Materials and Methods

2.1. Study area

Eket and Esit-Eket Local Government Areas (LGAs) are located in Akwa Ibom State of Nigeria, and geographically situated between Latitude 4^{o} 38′ 28″ and 4^{o} 38′ 47″N and extend between 7^{o} 55′ 15″ N and (7^{o} 55′ 25″) E (Figure 1). The climate is humid with average rainfall of about 4.22 mm/year. Most of the rainfall occurs during six to seven months period (April to October). Eket LGA is bounded by Nsit Ubium to the North, Onna LGA to the West and Ibeno LGA to the South, while Esit Eket has boundaries with Ibeno, Eket and Nsit Atai local government areas. The landscape of Eket covers about 83 m^2 (214 m^2). The projected population of Eket and Esit-Eket is 288,980 and 117,300, respectively. The two LGAs are actively involved in the oil industry downstream operation [12, 13].

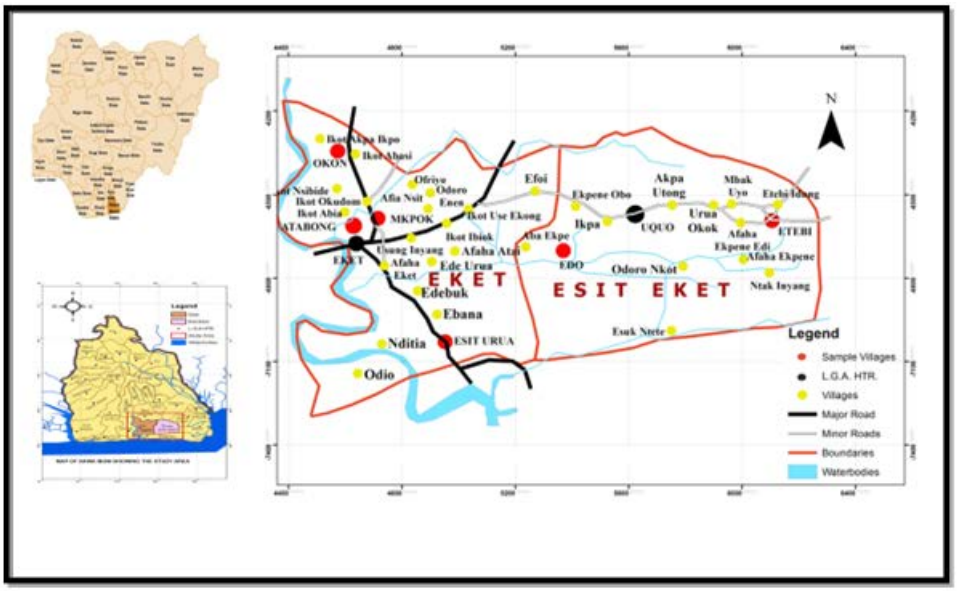


Figure 1: study area

2.2. Sampling and analysis

Rainwater and groundwater (borehole) samples were collected in six different locations, four from Eket LGA and two from Esit-Eket LGA, in duplicate (Figure 1, Table 1). Access to groundwater was hindered in Etebi (R3). The water samples were collected in clean plastic basins placed on a raised platform in open environment in order to eliminate water contamination with soil particles. Samples were transferred into pre-cleaned sample bottles and acidified with 1 ml conc. HNO_3/litre of sample. All samples were stored in ice coolers pending analysis. Toxic metals (Ni, Cd, Pb, Cu, Fe, Mn and Zn) levels in rainwater and groundwater were analysed using 210 VGP Buck Scientific atomic absorption spectrometer after digestion of 100 ml of sample with 5 ml of conc. HNO_3 on a hot plate.

Quality control was ensured at every stage, from sample collection to analyses. All reagents were of analytical grade from Sigma-Aldrich chemicals. Quality assurance included triplicate analysis, the use of reagent blanks and standard methods [14]. Calibration curves were used for instrument quality control (Table 2).

Table 1: Geographical positioning system (GPS) locations and description of study area

Site	Code	Coordinates		Altitude
		Longitude	Latitude	
Esit Eket LGA				
Edo	R1	4°32′65″N	8°01′31″E	250
Etebi	R2	4°36′26″N	8°11′53″E	252
Eket LGA				
Esit Urua	R3	4°35′21″N	7°57′59″E	159
Mkpok	R4	4°38′13″N	7°51′41″E	161
Atabong	R5	4°39′14″N	7°56′10″E	115
Okon	R6	4°41′29″N	7°54′45″E	151

Table 2: Summary of calibrations for quality control

Metal	Calibration Standard concentration (mg/l)		R^2	Wavelength
	Minimum	Maximum		
Ni	0.8	4	0.9978630	232.00
Cd	0.4	2	0.9991100	228.80
Pb	2	10	0.9879640	283.10
Cu	1.2	6	0.9995530	324.75
Fe	1.6	8	0.9987910	248.33
Mn	0.5	2.5	0.9855090	403.08
Zn	0.32	1.6	0.9880300	213.86

Analytical data were processed using IBM SPSS Statistics 20, Microsoft Excel and Statgraphic® Centurion XV statistical packages. Cluster analysis (CA) produced the dendrograms. The Ward's method in which the metric distance is Euclidean distance was used to create clusters [15]. The Clusters were generated from variables, and principal component analysis (PCA) performed by Equamax rotation with Kaiser Normalization for eigenvalue greater than one.

2.3. Human health risk assessment model

Human health risk assessment of toxic metals in rainwater and groundwater through ingestion and dermal absorption routes to inhabitants in Eket and Esit Eket for non-carcinogenic and carcinogenic effects were calculated using risk models [16-18]. The exposure doses were computed using equations 1 and 2 [19, 20].

$$Exp_{ing} = C_{water} \times \frac{IR \times ED \times EF}{BW \times AT} \quad \text{- - - - - -Equation 1}$$

$$Exp_{derm} = C_{water} \times \frac{SA \times K_p \times ABS \times ET \times CF \times ED \times EF}{BW \times AT} \quad \text{- -Equation 2}$$

where Exp_{ing} – exposure dose through ingestion of rainwater and groundwater (mg/kg/d); Exp_{derm} – exposure dose through dermal absorption (mg/kg/d); C_{water} – concentration of metals in rainwater and groundwater water mg/l; IR – water ingestion rate (L/d) is 2.0L; ED – exposure duration (year) = 30 year for non-carcinogenic and 70 year for carcinogenic; EF – Exposure frequency (days/year) = 350 days; BW – body weight (kg) = 70 kg; AT – Average times (days) =365 days; SA – Exposed skin area (cm^2) = 28,000 cm^2; K_p – Dermal permeability coefficient (cm/h) for Zn=6E-04, Pb=4E-03, Cr=2E-03, and 1E-03 for Cu, Mn, Fe and Cd; ABS – dermal absorption factor (unitless) = 1E-03; ET – exposure time (h/day) = 0.6 h; CF – conversion factor (L/cm^3) = 0.001 [16].

The Hazard quotient (HQ) for non-carcinogenic potential from the two pathways (ingestion and dermal) was computed using equation 3 [16].

$$HQ_{ing/derm} = \frac{Exp_{ing/derm}}{RfD_{ing/derm}} \quad \text{- - - - - - - -Equation 3}$$

where $HQ_{ing/derm}$ – hazard quotient via ingestion or dermal contact (no unit); $RfD_{ing/derm}$ – reference dose (mg/kg/d) [16, 19]

Hazard index (HI), the sum of the HQs from all pathways was used to calculate the overall potential for non-carcinogenic effect from all pathways applying equation 4 [16, 19]. HQ > 1 and HI > 1, indicate potential for non-carcinogenic adverse health effects on humans.

$$HI_{ing/derm} = \sum_{i=0}^{n} HQ_{ing/derm} \quad \text{- - - - - - - -Equation 4}$$

where $HI_{ing/derm}$ – hazard index via ingestion or dermal contact (no unit)

Carcinogenic risks (CR), the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen was estimated using equation 5. The acceptable range of carcinogenic risks is 1.00E-06 to 1.00E-04 [21]

$$CR_{ing/drem} = Exp_{ing/derm} \times SF \quad \text{- - - - - - -Equation 5}$$

where $CR_{ing/derm}$ is carcinogenic risk via ingestion or dermal route (unitless); $SF_{ing/derm}$ is slope factor via ingestion or dermal route $(mg/kg/d)^{-1}$ [16, 21].

3. **Results and discussion**

3.1. Temporal and spatial distribution of toxic metals in rainwater and groundwater

Rainwater and groundwater are sources of drinking water in the study area (Figure 1). The levels of metals in rainwater and groundwater for the months of September and October are presented in Figure 2 for Esit Eket [Edo (R1) and Etebi (R2)], and Eket [Esit Urua (R3), Mkpok (R4), Atabong (R5) and Okon (R6)]. The mean values ± standard deviations are shown in Table 3. Higher levels of metals in rainwater are recorded in the months of September at most sites with a few exceptions like Ni and Pb in Mkpok, Pb, Fe, Mn and Zn in Etebi, Mn and Zn in Esit Urua and Fe in Okon, where higher levels are recorded in October. For rainwater samples, 100% of sites have Ni, Cd, Pb and Fe, and 50% of sites have Mn above the WHO's [22] limit for potable water.

3.1.1. Toxic metals (mg/l) in rainwater

In rainwater, the level (mg/l) of Ni range from 0.01 (Mkpok, Sept.) to 0.12 (Esit Urua, Sept.); Cd from 0.02 (Okon in Sept), Mkpok and Etebi in Oct.) to 0.07 (Edo, Sept.); Pb from 0.06 (Mkpok, Sept.) to 0.44 (Esit Urua, Sept.); Fe from 0.86 (Mkpok, Oct.) to 3.14 (Esit Urua, Sept.); Cu from 0.08 (Mkpok, Oct.) to 0.31 (Edo, Sept.); Zn from 0.22 (Mkpok, Oct.) to 0.74 (Esit Urua, Oct.); and Mn from 0.12 (Mkpok, Oct) to 0.52 (Etebi in Oct, Esit Urua in Oct., and Atabong in Sept.) (Figure 2). The levels of Cu and Zn at all sites and months did not exceed the Nigerian Standard and WHO's limits for drinking water. However, the values of Ni, Cd, Pb, Fe in rainwater was above both standards at all sites; while 83% of sites had Mn above the Nigerian Standard (NSDWQ, 2007) [23] and 50% above the WHO's [22] limit (R2, R3, and R6). This indicates rainwater pollution in Eket and Esit Eket. The relative abundance of metals increases in the order: Cd<Ni<Pb<Cu<Mn<Zn<Fe. The order of impact on site (total metals in mg/l = sum of all metals) was Mkpok (0.2629) < Atabong (0.5057) < Okon (0.5443) < Edo (0.5540) < Etebi (0.6021) < Esit Urua (0.6871). High metal content may be associated with oil/gas exploitation, vehicular emissions (diesel), and use of generators for electricity supply, incineration of municipal and domestic wastes.

3.1.2. Toxic metals (mg/l) in groundwater

Groundwater samples could not be collected from Etebi (R2) in Esit Eket. The range of measured levels (mg/l) of toxic metals in groundwater in all sites and months of sampling was: Ni from 0.02 (Atabong, Sept.) to 0.09 (Okon, Oct.); Cd from 0.01 (Mkpok, Sept.) to 0.04 (Esit Eket in Sept. and Atabong in Oct.); Pb from 0.07

(Atabong, Oct.) to 0.39 (Okon, Oct.); Fe from 2.14 (Atabong, Oct.) to 2.69 (Mkpok, Oct.); Mn from 0.50 (Atabong, Oct.) to 0.70 (Okon, Oct.); Cu from 0.12 (Atabong, Oct.) to 0.35 (Okon, Oct.); Zn from 0.32 (Atabong, Oct.) to 0.73 (Mkpok, Sept.). Like rainwater all sites have Cu and Zn below the Nigerian Standard and WHO's limits for drinking water (Figure 2 and Table 2) and, therefore, not indicative of pollution; while the levels of Ni, Cd, Pb, Fe and Mn exceed the Nigerian and WHO's limit for drinking water by 83%, 100%, 100%, 100% and 100%, respectively indicating pollution of groundwater systems in the area. Higher values of Mn, Zn and Fe in Edo, Mn in Esit Urua, Fe and Mn in Atabong, Pb, Cu, Fe, Mn and Zn in Okon, and Ni, Pb, Cu, Fe, Mn and Zn in Mkpok are recorded in groundwater compared to rainwater. In Mkpok, the levels of all metals except Cd exceeded those in rainwater. The relative abundance of metals increases in the order: Cd<Ni<Pb<Cu<Zn<Mn<Fe. The order of impact on site (total metals in mg/l) was Atabong (0.5129) < Edo (0.5510) < Okon (0.600) < Esit Urua (0.6036) < Mkpok (0.6257). Trace metals from agricultural sources and atmospheric deposition could reach the groundwater system through surface runoff or rainwater penetrating into the deep soil layers, and eventually threaten human life [24]. Higher metal levels in groundwater than in rainwater may be attributed to seepages from septic tanks, rain and surface water percolation; and which may contribute to the reduction in drinking water safety [24].

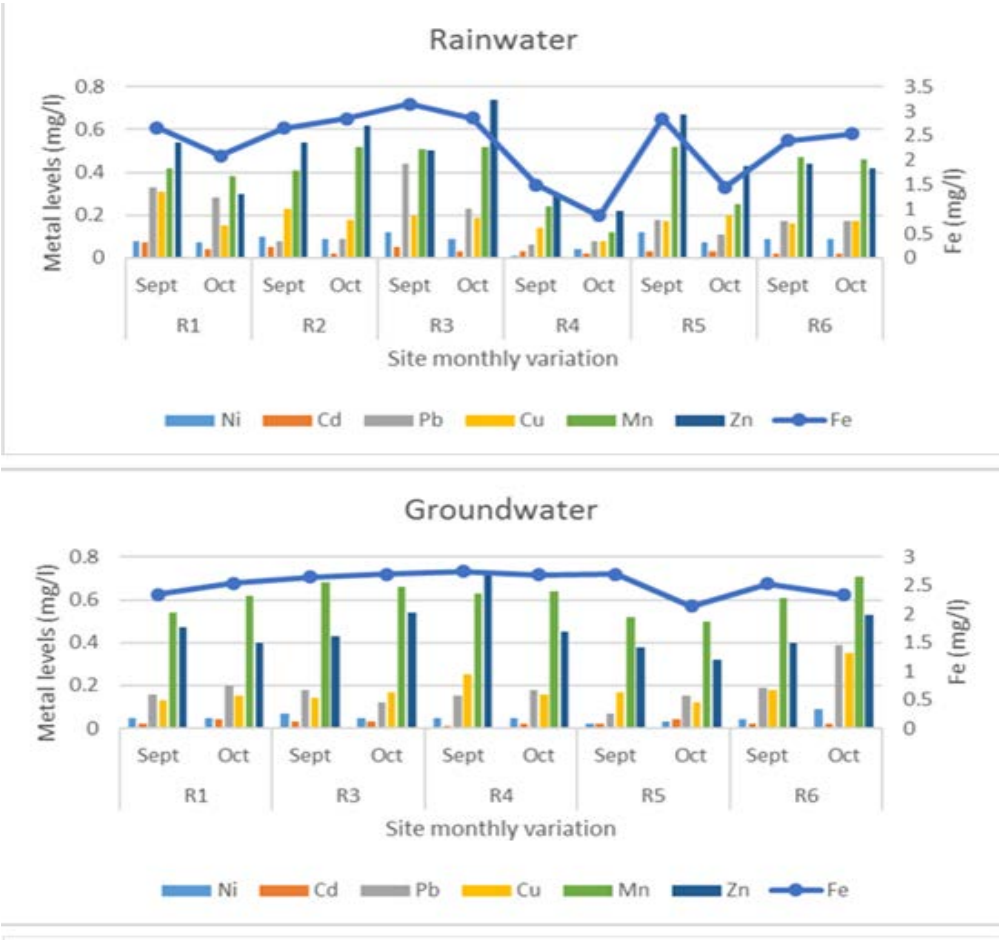


Figure 2: metals levels in rainwater and groundwater from Esit Eket and Eket Akwa

Table 3: Total mean metals in rainwater and groundwater

Metals	R1		R2		R3		R4		R5		R6		**WHO, 2011 (mg/l)**
	RW	GW	RW	GW	RW	GW	RW	GW	RW	GW	RW	GW	
Ni	0.075±0.005	0.050±0.00	0.095±0.020	NS	0.105±0.004	0.060±0.021	0.025±0.010	0.050±0.008	0.095±0.151	0.025±0.011	0.09±0.034	0.065±0.012	**0.020**
Cd	0.055±0.005	0.030±0.016	0.035±0.018	NS	0.040±0.020	0.030±0.016	0.025±0.035	0.015±0.004	0.030±0.009	0.03±0.015	0.02±0.027	0.020±0.017	**0.003**
Pb	0.305±0.009	0.180±0.020	0.085±0.079	NS	0.335±0.045	0.150±0.078	0.070±0.029	0.165±0.070	0.145±.0.019	0.11±0.074	0.17±0.019	0.290±0.044	**0.010**
Cu	0.230±0.000	0.14±0.002	0.205±0.005	NS	0.195±0.003	0.155±0.002	0.110±0.002	0.205±0.001	0.185±0.001	0.145±0.008	0.165±0.006	0.265±0.004	**2.000**
Fe	2.375±0.021	2.445±0.010	2.75±0.022	NS	3.000±0.019	2.675±0.210	1.175±0.011	2.72±0.013	2.15±0.010	2.420±0.016	2.470±0.011	2.435±0.034	**0.300**
Mn	0.400±0.005	0.580±0.029	0.465±0.049	NS	0.515±0.023	0.670±0.022	0.180±0.013	0.635±0.028	0.385±0.016	0.510±0.041	0.465±0.040	0.660±0.075	**0.400**
Zn	0.420±0.017	0.435±0.042	0.58±0.029	NS	0.620±0.039	0.485±0.039	0.255±0.023	0.590±0.013	0.550±0.013	0.350±0.053	0.430±0.049	0.465±0.010	**3.000**

NS=No sample, RW=Rainwater, GW=Groundwater, n=3

3.2. Source identification of toxic metals in rainwater and groundwater

Pearson's correlation coefficient, clusters analysis (CA) and principal component analysis (PCA) are used to identify the sources of toxic metals pollution in rainwater and groundwater. Pearson's correlation matric was computed to determine the inter-element relationships in rainwater and groundwater. A correlation coefficient of > 0.7 is interpreted as a strong relationship between two parameters while values between 0.5 and 0.7 represent a moderate relationship [25]; and only the significant correlations are extracted and discussion. There are significant correlations (** = ≤0.01 and * = ≤0.05, two-tailed) between metals in rainwater in the study area such as Pb versus Cd (r = 0.600**), Cu versus Cd (r = 0.793**), Fe versus Ni (r = 0.837**), Mn versus Ni (r = 0.822**) and Fe (0.969**), Zn versus Ni (r = 0.713**), Fe (0.800**) and Mn (0.798**).

In groundwater, strong correlation of Pb with Ni (r = 0.916**) could result from gas flares and vehicular emissions. Cu correlates with Ni (r = 0.832**) and Pb (r = 0.861**); the association of Cu/Pb has been reported [26]. Fe shows strong correlations with Ni (0.721**) and Cu (0.741**), and moderate correlations with Cd (0.679*) and Pb (0.615*). Mn correlates strongly with Ni (0.823**), Pb (0.772**), Cu (0.823**) and Fe (0.968**) and moderately with Cd (0.688*); while Zn correlates strongly with Ni (0.777**), Cu (0.844**) Fe (0.893**) and Mn (0.901**), and moderately with Pb (0.644*). The following relationships are obtained between metals in rainwater and groundwater: Positive correlation between Pb in rainwater and Cd in groundwater (r = 0.620**), and negative correlations between Cu rainwater versus Cu groundwater (r = -0.621*) and Zn rainwater versus Pb groundwater (r = -0.643*) indicates different sources of Cu contamination in rainwater and groundwater. Strong positive correlations signify the associated metals have common contamination sources. These results demonstrate that Ni, Zn and Pb have common sources as well as Cu, Ni, Cd, or that they interacted with one another to cause source of common pollution [27].

Agglomeration schedule of cluster analysis (CA) was performed on data based on the Ward's method and Euclidean distance as a measure of proximity between variables, in order to detect spatial similarity for groupings in relation to measured metals in rainwater and groundwater. The results of CA are displayed in Figures 3 and 4 for rainwater and groundwater, respectively.

Clustering generated two distinct groups for metals in rainwater. Cluster 1 includes Cd, Cu, Pb, and Zn. These metals are associated with anthropogenic activities such as crude combustion, vehicular emissions and agricultural activities. The grouping of Zn in cluster 1 did not stand out since there is no correlation with any of the metals in cluster, but Cd correlates with Pb* and Cu** indicating common source in rainwater. Cluster 2 includes Fe, Mn and Ni. Close relationships are obtained among all metals in this cluster. Source of pollution could be both anthropogenic and lithogenic (from entrain dust from roads containing Fe and Mn). Cluster analysis produced three clusters of metals for groundwater. Cluster 1 contains Cd and Fe. The metals are anthropogenic in origin and Fe could originate from mixed (anthropogenic and lithogenic) sources. Cluster 2 contains metals (Cu, Pb and Ni) that have very strong association with each other. Pb is strongly associated with vehicular emissions, Ni and Cu are associated with oil and gas activities. Cluster 3 contains Mn and Zn. Zinc is associated with various industrial processes [28].

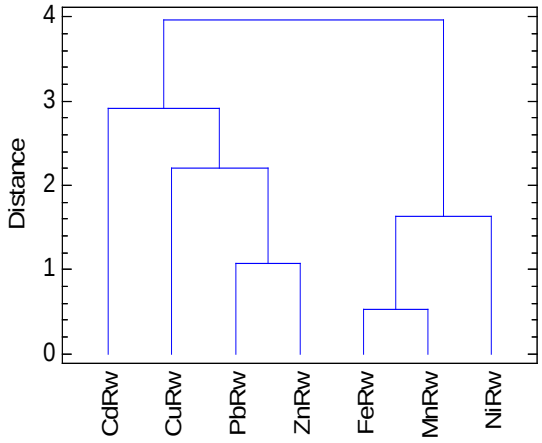


Figure 3: Dendrogram showing clustering of toxic metals for rainwater

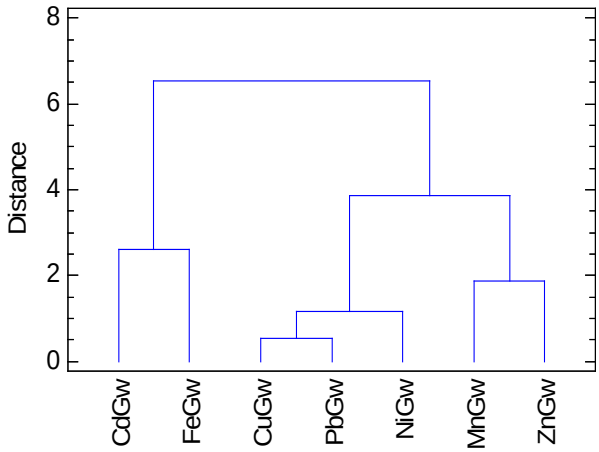


Figure 4: Dendrogram showing clustering of toxic metals for groundwater

Principal component analysis was performed to establish source apportionment of toxic metals in rainwater and groundwater. Extraction was based on Equamax rotation with Kaiser Normalization with eigenvalue greater than or equal to one. The result of principal component analysis suggests two factors that control toxic metals contamination of rainwater and groundwater in the study area (Figures 5 and 6). The two principal components (PCs) extracted for rainwater account for 83.156% of the variability in the original data. PC1 accounts for 61.944% of variability. It shows high loading on Zn, Mn, Ni and Fe. Ni is associated with oil and gas activities like gas flaring in Esit Eket and Eket, and Fe and Mn from entrained dust from roads, domestic and municipal

waste. PC2 accounts for 21.212% of variability and is characterized by high loadings on Pb, Cd and Cu. These are associated with vehicular emissions, domestic and municipal waste, incineration of waste, and may be responsible for increased levels of these metals in rainwater.

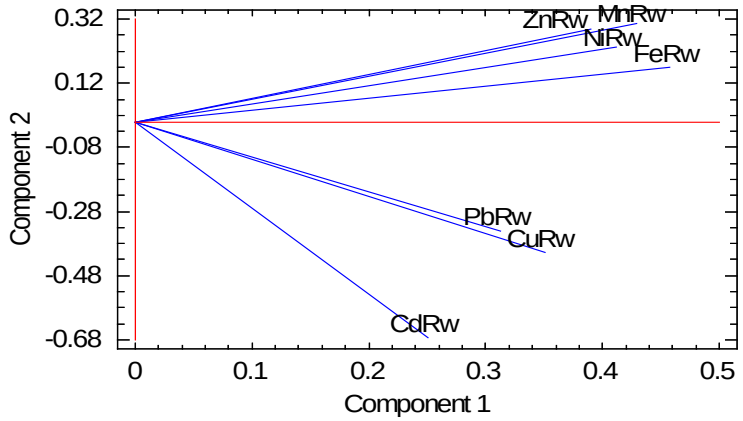


Figure 5: Plot of component weights of toxic metals in rainwater

For groundwater, the two PCs extracted account for 78.424% variability. PC1 accounts for 51.005% of variability with loadings on Fe, Zn, Mn, Cu, Ni and Pb; the six metals are strongly loaded on PC1 and may indicate homoplastic sources of pollution, including vehicular emissions, gas flares, and penetrations of toxic elements into the groundwater table [27, 29]. PC 2 has only one metal Cd and explains 27.4195% of the total data variance. Cd is derived from industrial activities, automobiles and dumpsites [30]. Crude oil combustion could result in Cd and Ni pollution.

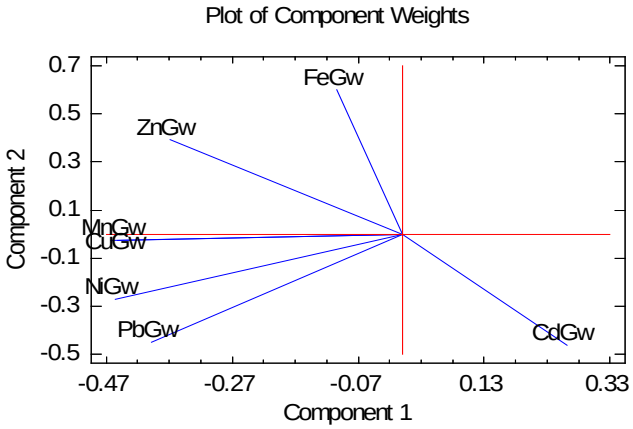


Figure 6: Plot of component weights of toxic metals for groundwater

3.3. Human health risk assessment of toxic metals in rainwater and groundwater

Non-carcinogenic and carcinogenic health risk through ingestion and dermal absorption of rainwater and groundwater are assessed and presented in Figures 7 and 8, Table 4. Health quotients (HQ) and Health Index (HI) values greater than one indicate potential for non-carcinogenic adverse health effect to occur or the need for further study [31]. Carcinogenic risk value greater than 1.00E-06 are generally considered unacceptable [21, 31]; however, values as high as 1.00E-04 has been accepted as safety threshold by some nations [31-33].

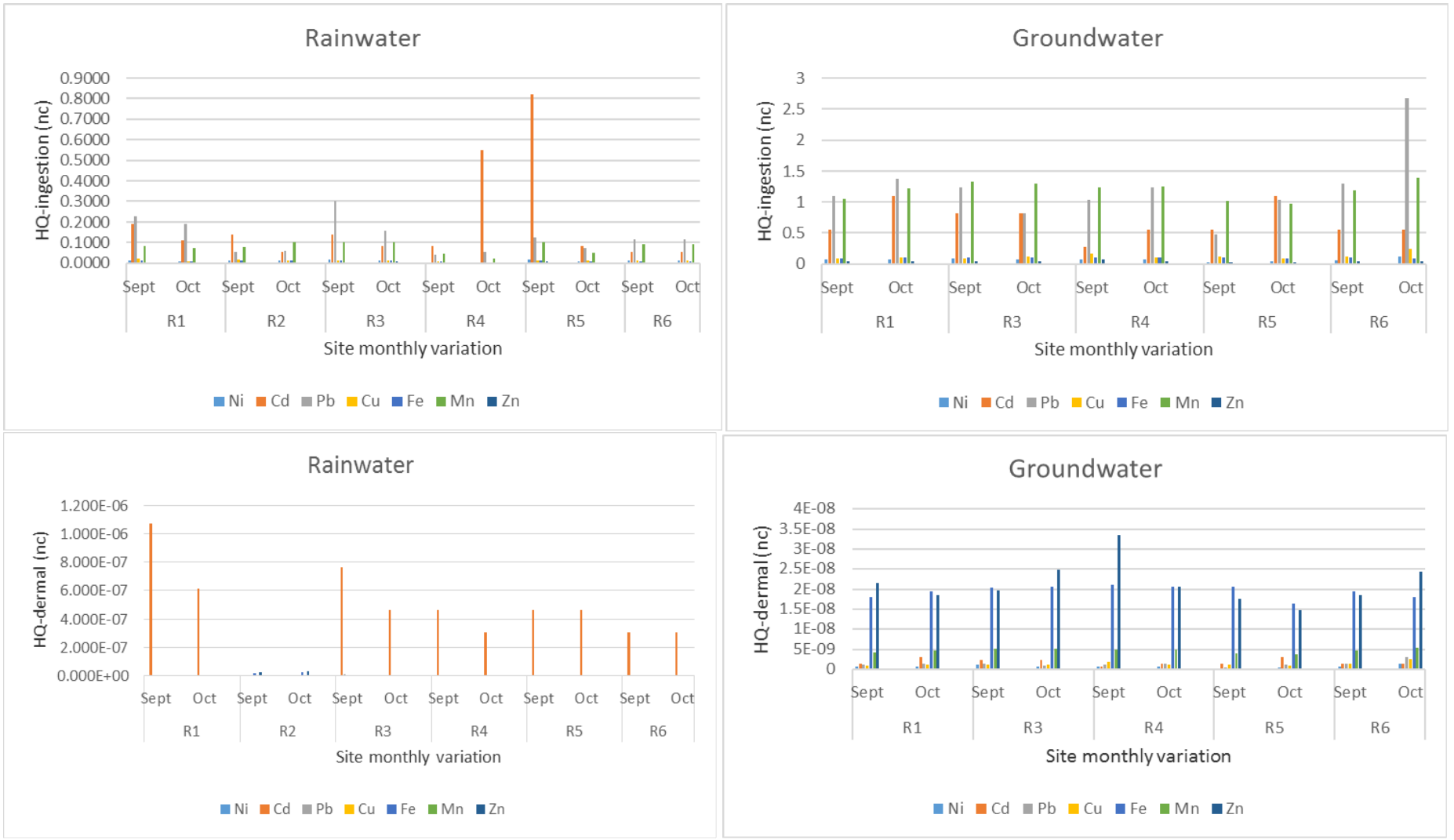
3.3.1. Adult non-carcinogenic Hazard

Figure 7 displays sites and months variations of non-carcinogenic hazards for oral and dermal routes of exposure to toxic metals (Ni, Cd, Pb, Cu, Fe, Mn, and Zn) for rainwater and groundwater. The HQ_{ing} and HQ_{derm} of rainwater for individual metals at individual locations and month of sampling are below the safe limit (HQ<1) and could be considered to pose no health threat. However, the sum of the HQs via ingestion (Table 4) of rainwater revealed potential threat from the presence of Cd, Pb and Mn (HQ>1). On the other hand, the sum of the HQs via dermal absorption (Table 4) were much lower than the safe limit (HQ<<1) in rainwater, hence contact through dermal route is considered safe for all metals. The health risk distribution pattern (Table 4) in increasing order for rainwater through ingestion is Zn<Fe<Ni<Cu<Mn<Pb<Cd and in the range 0.05215 to 1.5205, and Ni<Cu<Pb<Fe<Mn<Zn<Cd through dermal contact with range 5.1312E-09 to 5.6882E-08.

In the case of groundwater, the non-carcinogenic hazards through dermal route is negligible and considered safe (HQ_{derm}<<1) (Figure 7 and Table 4) despite their concentrations (Ni, Pb, Cd, Mn, Fe) in groundwater being above the safety limit [22] guideline (Table 2). HQ_{derm} range from 7.6712E-09 to 2.1403E-07 and followed the pattern: Ni<Pb<Cu<Cd<Mn<Fe<Zn.

The individual HQs for Cd, Pb and Mn in some locations are greater than one, and could constitute non-carcinogenic risk to adults in these areas. HQ>1 are recorded at sites R1 (Edo in Esit Eket) and R5 (Atabong in Eket) in Oct. for Cd; R1, R4 and R6 (Edo in Esit Eket, Mkpok and Okon in Eket) in Sept. and Oct., also R3 (Esit Urua) in Sept. and R5 (Atabong in Eket) in Oct. for Pb; R1, R3, R4 and R6 (Edo in Esit Eket; Esit Urua, Mkpok and Okon in Eket) in Sept. and Oct., also R5 (Atabong in Eket) in Sept. for Mn (Figure 7). All these areas are associated with high traffic, gas flare (from crude combustion), corrosion/burning of municipal domestic/wastes. The sum of the HQs via ingestion (HQ_{ing}) for individual metals from all sites ranges from 0.4247 to 12.2603, and followed the pattern - Zn<Ni<Fe<Cu<Cd<Mn<Pb.

The combined HQs through oral and dermal routes known as hazard index (HI) range from 0.0521 to 2.3561 and 0.4246 to 12.260 for rainwater and groundwater, respectively. HI increased in the order: Zn<Fe<Ni<Cu<Mn<Pb<Cd (rainwater) and Zn<Ni<Fe<Cu<Cd<Mn<Pb (groundwater). The main route of exposure to non-carcinogenic risks is through the oral route for adults residing in Eket and Esit Eket, and is due to the presence of Cd, Pb and Mn. The overall HI in groundwater for individual elements were higher than in rainwater. The non-carcinogenic risk elements Cd, Pb and Mn are 3-, 8- and 13-folds in groundwater greater than in rainwater.



HQ = Hazard quotient nc = Non-carcinogenic

Figure 7: Non-carcinogenic hazard quotients for individual metals and sites-monthly variations through oral and dermal routes

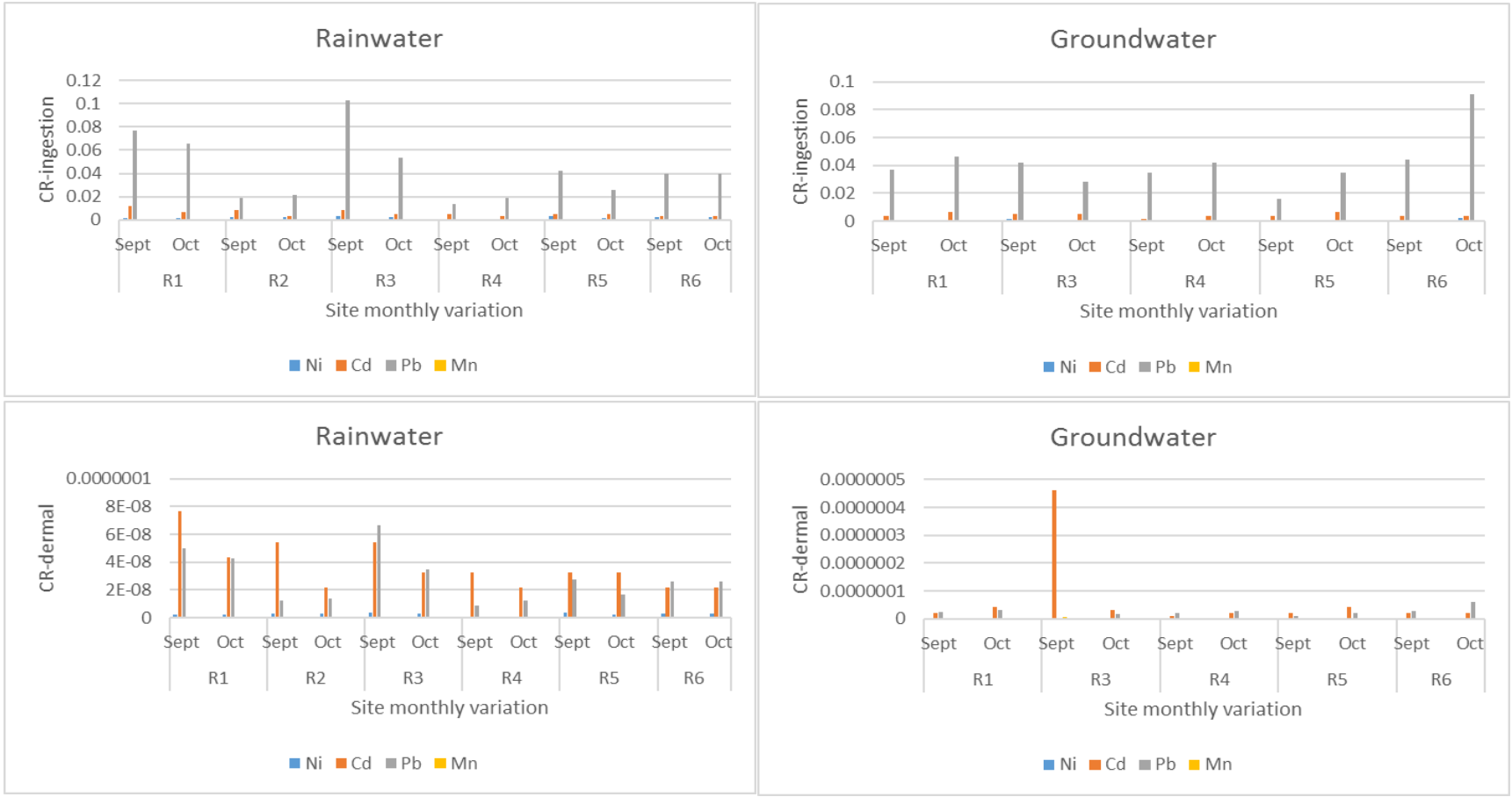
Table 4: Cumulative non-carcinogenic hazards and carcinogenic risk of toxic metals form different exposure routes**.**

	Non-carcinogenic hazard					
	Rainwater			Groundwater		
Metals	HQ_{ing}	HQ_{derm}	**HI**	HQ_{ing}	HQ_{derm}	**HI**
Ni	0.1328	5.13E-09	0.1328	0.6849	7.67E-09	0.6849
Cd	2.3561	5.22E-06	2.3561	6.8493	1.91E-08	6.8493
Pb	1.5205	3.87E-08	1.5205	12.260	1.37E-08	12.260
Cu	0.1493	4.27E-09	0.1493	1.2465	1.39E-08	1.2465
Fe	0.1089	4.34E-08	0.1089	0.9937	1.94E-07	0.9937
Mn	0.9432	4.44E-08	0.9432	11.956	4.68E-08	11.956
Zn	0.0521	5.68E-08	0.0521	0.4246	2.14E-07	0.4246
Sum	5.2632	5.41E-06	5.2632	34.416	5.10E-07	34.416
	Carcinogenic risk					
	Rainwater			Groundwater		
Metals	CR_{ing}	CR_{derm}	$\mathbf{CR_{tot}}$	CR_{ing}	CR_{derm}	$\mathbf{CR_{tot}}$
Ni	0.0223	2.91E-08	0.0223	0.0115	1.31E-08	0.0115
Cd	0.0685	4.47E-07	0.0685	0.0417	7.00E-07	0.0417
Pb	0.5169	3.37E-07	0.5169	0.4168	2.48E-07	0.4168
Mn	1.88E-06	1.23E-12	1.88E-06	2.39E-06	6.52E-09	2.40E-06
Sum	0.6078	8.14E-07	0.6078	0.4701	9.68E-07	0.4701

3.3.2. Lifetime carcinogenic risk

The lifetime oral and dermal risks are computed for Ni, Cd, Pb and Mn only and presented in Figure 8. The lifetime carcinogenic risk via ingestion and dermal routes in rainwater and groundwater from Eket and Esit Eket are presented in Figure 8 and Table 4. The carcinogenic risks (CR) through ingestion (CR_{ing}) and dermal absorption (CR_{derm}) range from 1.88E-06 to 0.5169 and 1.23E-12 to 4.47E-07, respectively in rainwater, and 2.39E-06 to 0.0417 and 6.52E-09 to 7.00E-07, respectively in groundwater. The lifetime carcinogenic distribution patterns for the study are: Mn<Ni<Cd<Pb and Mn<Ni<Pb<Cd for ingestion and dermal routes, respectively for rainwater. Groundwater also has similar pattern. The distribution pattern for all metals and for all routes (CR_{tot}) is: Mn<Ni<Cd<Pb and ranges from 1.88E-06 to 0.5169 (rainwater) and 2.40E-06 to 0.417 (groundwater).

Ni, Cd and Pb exceeded the acceptable limit for lifetime carcinogenic effect in adults through oral route while Mn is within the acceptable range of 1.0E-06 to 1.0E-04 [21]. This suggests that Ni, Cd and Pb could cause or contribute to cancer in adults.



CR =Carcinogenic risk

Figure 8: Carcinogenic lifetime risk quotients for individual metals and sites-monthly variations through oral and dermal routes

Exposure through dermal contact was safe at all sites, for all metals. CR_{tot} was less than the acceptable limit, suggesting the possibility of developing skin cancer through contact with rainwater and groundwater is nonexistent.

Mn is below the lifetime carcinogenic risk limit (1.0E-06 to 1.0E-04) [21, 34]. The result reveals that Ni, Cd and Pb are main contributors to carcinogenic risk through the ingestion pathway. Therefore, drinking rainwater and groundwater could expose the local residents in Eket and Esit Eket to health risk. The values of Cd and Pb in this study are higher than reported previously [16]. The CR_{tot} follows the same pattern observed for CR_{ing} indicating rainwater and groundwater ingestion as potential exposure route to carcinogens. Comparing the CR_{tot} in rainwater and groundwater for individual metals, the rainwater values are 1-2-folds higher than those for groundwater, hence rainwater poses more carcinogenic risk through oral route than groundwater.

4. Conclusion

This study gives some understanding into the quality, non-carcinogenic and carcinogenic risks levels of metals (Ni, Cd, Pb, Cu, Fe, Mn and Zn) in rainwater and groundwater in Eket and Esit Eket local government areas in Akwa Ibom State, Nigeria through the ingestion and dermal pathways. Metal levels in rainwater and groundwater exceed the Nigerian and WHO's limits except for Cu and Zn and, therefore, need purification to be suitable for drinking purposes. Elevated levels of metals are observed in Esit Urua (R3) and Mkpok (R4) in rainwater and groundwater, respectively.

Multivariate analysis, such as Pearson's correlation coefficients, cluster analysis (CA) and principal component analysis (PCA), simplifies the complex multivariate relationships among the metals. Majority of the extracted components with their high loadings of metals association indicate anthropogenic sources – from oil and gas related activities like gas flare, vehicular and generator emissions; and some attributed to natural sources (lithogenic). The principal components extracted are supported by cluster analysis and Pearson's correlation coefficients.

Human health risk computed for non-carcinogenic health hazard (HQ and HI) and the lifetime carcinogenic risks reveals that rainwater and groundwater pose no threat to humans through dermal route ($HQ<<1$ and $HI<<1$) at all sites, in the months of sampling. On the other hand, lifetime carcinogenic risk of toxic metals through ingestion is observed, the main contributors being Cd, Pb and Ni. This points to the fact that the main route of exposure to carcinogens in Eket and Esit Eket is through ingestion of rainwater and groundwater.

It behoves on government, through its health agency, to create public awareness to the effect that untreated rainwater and groundwater sources are unsafe for drinking; and for the long term, provide pipe borne water to the communities.

It is recommended that other compounds such as polyaromatic hydrocarbons (PAHs), arsenic, among others should be investigated for their health risks.

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