
Impact of Seasonal Variations and Oil Activities on the Total Concentrations, Geochemical Fractions, And Human Health Problems of Trace Metals in Soils Within the Oil-Bearing Communities of South-South Region of Nigeria

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ABSTRACT: *The impacts of oil activities and seasonal variations on the total concentrations, geochemical fractions, and human health problems of trace metals in soils within oil-bearing communities of Akwa Ibom State, Nigeria were examined. Top soils were obtained from Eket, Onna, Esit Eket, and Ibeno local government areas between January and December, 2017. Samples were also collected from Etinan local government area of the State and used as the Control. The samples and Control were subjected to standard analytical procedures and analysed for their physicochemical properties and total metal concentrations. The modified BCR methods were employed for the speciation of metals. The findings revealed that the pH levels were higher during the dry season while, the electrical conductivity, organic matter, and cation exchange capacity of the studied soils were higher in the rainy season. The total mean concentrations of Pb, As, Cd, Cr, Fe, and V were higher in the dry season whereas, Ni was higher in the wet season. Though, their concentrations were within the acceptable limits. Generally, the concentrations of all the parameters in the studied soils were higher than at the control site. Pb, As, Ni, and V existed predominantly in the reducible fraction, Cd and Cr in acid extractable while, Fe existed mostly in the residual fraction in the studied soils. However, at the control site all the metals except Cd existed mainly in the residual fraction. The study showed that all the studied locations were highly contaminated with these metals and substantial seasonal variations were also recorded for the pollution indices. It was also noted that, seasonal changes and oil activities were the key factors affecting the quality of the studied soils. Daily intake rates for the metals through exposure to soil for both the young and old populations were within their required oral reference doses. The non-carcinogenic risks recorded for both populations were less than one. However, both populations were exposed to high Pb and the younger ones were more susceptible. The study revealed the influence of seasonal change and oil activities on the mobility and toxicity of metals in the studied soils.*

KEYWORDS: oil-bearing communities, trace metals, metal speciation, human health risks, soil pollution, multivariate analysis, Nigeria.

INTRODUCTION

The oil-bearing communities of Akwa Ibom State, Nigeria are inundated with different kinds of oil-related industries. The activities of these companies along with that of Mobil producing Nigeria Unlimited (MPNL) has impacted seriously on the host communities. The wastes generated by these companies are not properly managed hence; there are ecological imbalances in the environment (Appannagari, 2016). The current bad state of the environment within the Oil producing Area of Nigeria has a direct relationship with the discovery of crude oil in 1956 (Okotie *et al.*, 2018). The oil and oil –related activities in the region has resulted in the severe degradation of the air, land, and water environments. The oil exploration and exploitation activities, oil spillage, and gas flaring above all have decimated the environment with oil and oil-related waste materials (Kuch and Bavumiragira, 2019; Singh *et al.*, 2020). The devastating state of the communities investigated is evident in the damaged roof-tops, poor water and air quality, lack of soil nutrients, and extinction of some living organisms (Kennish, 2002; Anejionu *et al.*, 2015; Bodo and Gimah, 2020; Ebong *et al.*, 2022). Studies have shown that, crude oil and crude oil-impacted environment has elevated level of trace metals and could be transported into the human system (Chinedu and Chukwuemeka, 2018; Ahiamadu *et al.*, 2021; Thomas *et al.*, 2021). Gupta *et al.* (2014) and Chonokhuu *et al.* (2019) revealed that, a perfect understanding of the pollution status and health risks in an area, a multivariate analysis and speciation studies should be utilized. Nevertheless, previous studies concentrated on the physicochemical properties, total metals, and microbial load of the oil-bearing communities under investigation (Ndeh *et al.*, 2015; Udotong and Udotong, 2015; Etim *et al.*, 2016; Useh and Ikokoh, 2017; Wokocha and Aniebet, 2022). Hitherto, studies were also not based on the seasonal variations of the study area. However, findings have shown that change in seasons affects the physicochemical properties of soil, metal availability and toxicity (Shohunbi *et al.*, 2020; Madaniyazi *et al.*, 2022). Metal speciation and multivariate analysis techniques also provide a comprehensive information on the pollution status, mobility, and poisonous nature of trace metals in an area (Adebiyi *et al.*, 2019; Shehu and Koki, 2019; Valiallahi and Khaffaf, 2021). This study was undertaken to close the gap that was created in the previous researches carried out. Hence, the study assessed the impact of oil activities on the physicochemical properties, accumulation and bio-availability, health risks, and pollution status of trace elements in the environment within the studied communities during the dry and wet seasons.

MATERIALS AND METHODS

Description of study area

Akwa Ibom State is one of the major Oil-producing Areas in Nigeria situated in the Southern part (Fig 1). It lies between latitudes 4° 32' and 5° 33' North and longitudes 7° 25' and 8° 25' East. The State is situated within the tropical rain forest zone which makes it has sufficient rainfall with elevated temperature. The Oil-bearing communities in Akwa Ibom border by the Atlantic Ocean (Fig 1). The activities by the oil Companies are mostly concentrated in the oil-bearing communities

of Akwa Ibom State. These activities by the oil Companies and other downstream industries have caused serious environmental degradation in these communities.

A total of eight (8) locations covering four (4) local government areas within the Oil-bearing communities of Akwa Ibom State, Nigeria were used for this study. The locations are: (i) Sites 1 and 2 (Afaha Eket and Esit Urua, respectively) in Eket local government area, (ii) Sites 3 and 4, (Ndon Eyo and Ikot Akpatek, respectively) in Onna LGA, (iii) Sites 5 and 6 (Uquo and Edor, respectively) in Esit Eket LGA, (iv) Sites 7 and 8 (Upenekang and Mkpanak, respectively) in Ibeno LGA. An uncultivated area which has not been affected by the activities of Oil Companies in Ikot Udobia, Etinan local government area of Akwa Ibom State was used as the Control. During this study, the dry and wet seasons of the study area were covered. Samples were collected from the months of January to March and October to December, 2017 for the dry season; while the rainy season samples were obtained from April to September, 2017. Surface soil samples were obtained during the first week of each month for the entire period of sample collection.

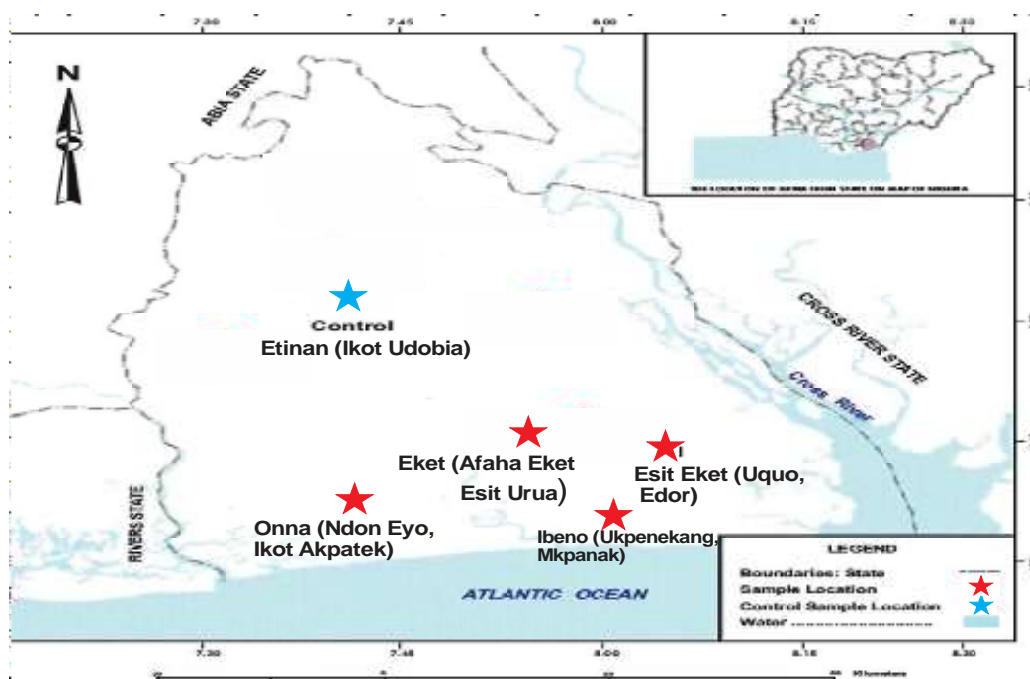


Fig.1. Map of Akwa Ibom State showing the studied locations and Control.

Sample collection and pretreatment

Sampling is a very important aspect of any analytical work hence; sampling procedures for this work were carefully planned in order to obtain reliable results (Radojevic and Bashkin, 2006). Samples collected were handled in such a way that quality and quantity of the component of interest present in the sample were not altered as reported by AWWA (1980). Top soil samples

were obtained at the depth of 0 -15cm from the eight (8) designated locations and the control site using soil Augar (Aydinalp, 2009). During sampling, soil samples were obtained from four different locations at each site bulked into one sample to obtain a composite sample for such location (Anake *et al.*, 2009). Sample collected were properly labeled and then taken to the laboratory for pretreatment and analysis. A total of one hundred and eight (108) composite samples were obtained. Samples for metal analysis were dried in air for three days in a plastic tray and homogenized by grinding using agate mortar and pestle. The samples were later on filtered through a 2mm Sieve, stored in a well-labeled polyethylene bags, and preserved for analysis (Radojevic and Bashkin, 2006).

Determination of properties of the studied soils and Control

Determination of the physicochemical properties of the studied soils and the Control

The physicochemical properties of the studied soils and Control were determined using the following standard methods: The pH was obtained in a soil/water suspension (1:2.5 v/v) using the procedures by Nabulo *et al.* (2008). Organic matter (OM) content was determined using the wet oxidation methods as reported Walkley and Black (2007). The cation exchange capacity (CEC) of soil was determined by the Spectrophotometric and summation of exchangeable bases methods of Hendershot and Duquette (1986). The use of electrical conductivity equipment as described by Rhoades *et al.* (1999) was employed for the determination of electrical conductivity while; particle size determination was done by Hydrometer methods as reported by Van Reeuwijk(1993).

Determination of total trace metal

One (1.0) gram of the soil was mixed with a3:1 ratio of HCl and HNO₃ and placed on a hot plate for digestion. The mixture was later filtered into a volumetric flask and filled to mark with distilled water. Total concentrations of lead, arsenic, Cadmium, nickel, chromium, iron and vanadium were analysed for in the filtrate using inductively coupled plasma optical emission spectrometer (Rauret *et al.*, 2000). The same procedures were applied to the soil from the control site.

Modified BCR sequential extraction of metals in the studied soils and Control

Sequential extraction of metals was done using the Optimized BCR methods of Rauret *et al.* (2000) which separates metals into the exchangeable (acid extractable), oxides of Fe and Mn (reducible), oxidizable (bound to organic matter and sulphide), and inert (residual) fractions as indicated below:

- (i) Fraction 1: Weak acid extractable: To 1 g of the dried soil, 40 ml of 0.11M acetic acid (CH₃COOH) solution was mixed in a 50ml polyethylene container. This was shaken on an automatic shaker at ambient temperature for 16 hours and the extract removed by centrifugation at 3000rpm for 20min. The extract obtained was stored in polyethylene container for analysis.
- (ii) Fraction bound to oxides of iron and manganese was obtained by mixing 40ml of 0.50M hydroxylammonium chloride solution (NH₂OH.HCl) containing 2.5ml 2M HNO₃ (pH = 1.5) with

the residue from the previous step. The mixture was shaken for 16 hours at ambient temperature and centrifuged to remove the filtrate from the residue.

(iii) The fraction bound to organic matter and sulphide was collected by treating the residue from step 2 with 10 ml of 8.8 M hydrogen peroxide (H_2O_2) in a 100 ml glass container. The container evaporated to dryness by heating at $85^\circ C$ for 1 hour. This was later cooled and 50ml of 11M ammonium acetate ($1\text{mol/dm}^3 NH_4OAc$) adjusted to pH of 2.0 with 2M HNO_3 was added, shaken for 16 hours at ambient temperature and filtered to eliminate the filtrate from the residue.

(iv) The inert fraction of the metals was obtained by combining the residue from the last step with a mixture of 5ml 16M trioxonitrate (V) acid and 15ml 12M hydrochloric acid and digested on a hot plate for 2 hours. This was cooled and filtered into a 100 mL volumetric flask and subsequently filled to the mark with distilled water. Concentrations of Pb, As, Cd, Ni, Cr, Fe, and V in the filtrate for each step were analyzed for using emission spectrometer.

Assessment of metal contamination/pollution in the studied soils

Some pollution models were employed to assess the extent of soil contamination/pollution by trace metals determined and to appraise the impacts of the natural and man-made factors on the metal load of the locations investigated. These models are as indicated below:

Contamination Factor (CF) of trace metals

Contamination factor of the metals in soil was computed with Equation 1 below as reported by Hakanson (1980) and Pekey *et al.* (2004).

$$CF = \frac{C_o-1}{C_n} \text{-----} (1)$$

Where C_{o-1} is the concentration of the element in the studied soil, C_n is the concentration of the metal in the background (control) soil. The various sets of contamination factor are indicated in Table 1.

Degree of Contamination (C_{deg})

The extent of site to site contamination of soils within the oil-bearing communities by metals was assessed by the aid of C_{deg} model indicated in Equation 2 according to Hakanson (1980) and Mmolawa *et al.* (2011).

$$C_{deg} = \Sigma \left(\frac{C_o-1}{C_n} \right) \text{-----} (2)$$

Where $\Sigma \left(\frac{C_o-1}{C_n} \right)$ = the summation of C_{deg} for the entire metals at each site. The diverse categories of C_{deg} are shown in Table 1.

Geo-accumulation index (I_{geo})

Geo-accumulation index was used to assess the extent of metal contamination in soils within the oil-bearing communities in comparison to the background (control) soil (Sutherland, 2000). Values obtained were multiplied by 1.5 so as to accumulate the variations of the elements in the soil likewise the anthropogenic factor (Loska *et al.*, 2003). Geo-accumulation index of metals in the studied soils was calculated by using Equation 3 as reported by Singh *et al.* (1997).

$$I_{geo} = \text{Log}_2 (C_n/1.5B_n) \text{-----} (3)$$

Where C_n denotes the measured concentration of trace metals in soil from the oil-bearing communities studied whereas, the concentration of trace metals in control site is indicated by B_n (Taylor and Maclean, 1985). Table 1 shows the different categories of I_{geo} used in this study according to Huu *et al.* (2010).

Ecological risk factor (E_r^i)

Ecological risk factor of metals was employed to assess the risk in the studied oil-bearing soils using Equation 4 according to the methods of Hakanson (1980).

$$E_r^i = \text{Tr} \times \text{CF} \text{-----} (4)$$

Tr indicates the toxic-response factor for each metal and CF denotes the contamination factor. The toxic response factors for the metals according to Hakanson (1980) are as follows: Pb (5.00), As (10.00), Cd (30.00), Ni (5.00), Cr (2.00), Fe (0.00), and V (2.00). According to Ren *et al.* (2007), the various categories of ecological risk factor are shown in Table 1 below.

Potential ecological risk index (RI)

The RI was determined in this study by the use of Equation 5 according to Cao *et al.* (2007).

$$RI = \sum(E_r^i) \text{-----} (5)$$

Where $\sum(E_r^i)$ = the summation of all the trace metals determined at a particular location. The Different classes of potential ecological risk as proposed by Ren *et al.* (2007).are indicated in Table 1 below.

Table 1 Various Classes of CF, Cdeg, I_{geo}, E_rⁱ, and RI as proposed by the respective authors.

	CF	Cdeg	I _{geo}	E _r ⁱ	RI
A	CF < 1 is low contamination	Cdeg < 8 is low degree of contamination	I _{geo} < 0 is unpolluted	E _r ⁱ < 5 is Low risk (LR)	RI < 30 is Low risk (LR)
B	1 < CF < 3 is moderate contamination	8 < Cdeg < 16 denotes moderate degree of contamination	0 – 1 is unpolluted to moderately polluted	5 ≤ E _r ⁱ < 10 is Moderate risk (MR)	30 ≤ RI ≤ 60 is Moderate risk (MR)
C	3 < CF < 6 is considerable contamination	16 < Cdeg < 32 denotes considerable degree of contamination	1 – 2 is moderately polluted	10 ≤ E _r ⁱ < 20 is Considerable risk (CR)	60 ≤ RI ≤ 120 is Considerable risk (CR)
D	6 < CF is very high contamination	32 < Cdeg is very high degree of contamination	2 – 3 is moderately to strongly polluted	20 ≤ E _r ⁱ < 40 is High risk (HR)	RI ≥ 120 is very high risk (VHR)
E			3 – 4 is strongly polluted	E _r ⁱ ≥ 40 is Very high risk (VHR)	
F			4 – 5 strongly to extremely		
G			I _{geo} > 5 is extremely polluted		

CF = Contamination Factor; Cdeg = Degree of Contamination; I_{geo} = Geoaccumulation Index; E_rⁱ = Ecological risk factor; RI = Potential Ecological Risk Index

2.5. Human health risk evaluation

The estimated daily intake rate (EDI), hazard quotient (HQ), and total chronic hazard index (THI) were used to assess the risks related to the contact to the trace elements in the oil-bearing communities as previously reported by USEPA (2000).

Estimated daily intake rate (EDI)

The estimated daily intake rate of trace elements via the ingestion of soil particles was calculated using Equation 6 as described by USEPA (2011).

$$EDI = \frac{C \times \text{IngR} \times EF \times ED}{BW \times AT} \text{----- (6)}$$

In the equation 6 above C is the concentration of the metal; IngR is the rate of soil ingestion rate by both the children and adult populations; EF indicates exposure rate per day per year, ED signifies the duration of exposure in twelve months; BW is mass of the body in kg while AT relates the average period for the non-carcinogens according to Grzetic and Ghariani (2008) and USEPA (2011). The values of the entire factors in Equation 6 are shown in Table 2.

2.5.2. Hazard index (HQ)

The hazard index otherwise known Non-carcinogenic risk of the metals was computed using the procedures of USEPA (2011) as shown in Equation 7.

$$HQ = \frac{DI}{Rfd} \text{----- (7)}$$

The HQ in equation 7 is the hazard quotient and Rfd represents the persistent reference dose for the metals. The values of the aforementioned parameters are indicated in Table 2 below.

Total chronic hazard index (THI)

The THI of the trace metals in the young and old populations was determined by the use of Equation 8 as reported by USEPA (2011).

$$THI = \Sigma HQ = HQ_{Pb} + HQ_{As} + HQ_{Cd} + HQ_{Ni} + HQ_{Cr} + HQ_{Fe} + HQ_V \text{ ----- (8)}$$

Where ΣHQ = the summation of all the individual hazard quotients (HQ) of the trace metals determined.

Table 2 Parameters employed for the determination of risks related with the ingestion of soil from the studied locations in human and their values

S/N	Parameter	Value	Source
A	Body weight (kg)	15 – child 70 – adult	USEPA (2000) and (2011)
B	Ingestion rate (kg/day)	0.0002 – child 0.0001 – adult	Grzetic and Ghariani (2008) USEPA (2011)
C	Exposure frequency (day/yr)	350	Wang <i>et al.</i> (2012)
D	Exposure period (yr)	6 – child, 30 – adult	Grzetic and Ghariani (2008)
E	Average time for non carcinogens (day/yr)	365	USEPA (2000)
F	Recommended reference dose (Rfd) (mg/kg/day)	Pb(0.0035), As(0.0003), Cd (0.001), Ni (0.02), Cr (1.5), Fe (0.70), and V (0.001)	USEPA (2010)

Statistical analysis

The statistical treatments of the data acquired were done with IBM SPSS Statistics 20 (IBM USA) model. Principal component analysis was performed using Varimax Factor analysis on eleven (11) parameters and values ranging from 0.476 and above were regarded as significant. The Hierarchical Cluster analysis was carried out with Dendrograms to recognize identical sets with familiar characteristics and source.

Table 3 Variation of total metals (mgkg⁻¹) in soils examined and Control in the dry and wet seasons

	Dry Season				Wet Season			
	Mean	SD	Min	Max	Mean	SD	Min	Max
pH	7.16	0.08	7.05	7.36	7.15	0.06	7.06	7.25
EC	1.115	0.507	0.175	1.485	1.193	0.504	0.251	1.497
OM	7.810	2.550	4.350	11.090	10.255	0.836	8.600	11.150
CEC	9.075	1.608	7.150	11.590	10.437	0.605	9.750	11.550
Pb	9.353	0.319	5.210	11.715	7.324	0.281	4.795	10.860
As	0.161	0.005	0.121	0.181	0.149	0.006	0.110	0.175
Cd	1.644	0.057	1.224	1.932	1.171	0.022	1.004	1.435
Ni	1.799	0.106	1.290	2.414	2.044	0.111	1.910	2.240
Cr	1.460	0.038	1.272	1.687	1.434	0.009	1.220	1.620
Fe	1494.640	29.379	1429.400	1581.120	1438.142	20.175	1281.410	1545.100
V	0.120	0.016	0.072	0.146	0.119	0.014	0.090	0.141
	Control				Control			
pH	5.93	0.42	5.31	6.31	6.45	0.20	6.28	6.80
EC	0.134	0.045	0.081	0.182	0.175	0.013	0.158	0.187
OM	4.990	1.700	3.150	6.740	6.588	0.284	6.15	6.84
CEC	4.857	0.672	4.020	5.610	5.333	0.127	5.13	5.47
Pb	2.250	0.357	1.550	2.525	1.562	0.283	1.205	1.940
As	0.126	0.008	0.115	0.132	0.114	0.009	0.101	0.128
Cd	0.803	0.356	0.425	1.255	1.085	0.077	1.001	1.185
Ni	1.193	0.216	1.010	1.517	1.119	0.043	1.073	1.202
Cr	0.761	0.397	0.380	1.175	1.058	0.044	1.002	1.110
Fe	1038.765	17.911	1027.200	1074.200	1028.880	25.928	998.400	1060.070
V	0.082	0.005	0.079	0.092	0.057	0.008	0.051	0.073

EC denotes Electrical conductivity; OM depicts Organic matter; CEC means Cation exchange capacity; SD is Standard deviation; Min stands for Minimum; Max is Maximum

RESULTS AND DISCUSSION

Physicochemical properties of the studied oil-bearing soils and Control between January and December, 2017 are shown in Table 3.

The overall pH of soil from the oil-bearing communities ranged from 7.05 to 7.36 as indicated in Table 3. The pH range obtained is similar to the results obtained by Ibrahim *et al.* (2011) however; higher than the range reported by Ogbonna *et al.* (2018). The pH range obtained encourages nutrients availability and plant yield in the area (Sanchez *et al.*, 2003). The mean pH level of the studied soils was higher in the dry than during the wet season (Table 3). This agrees with the results of Oyedele *et al.* (2008) and Jia *et al.* (2021) in their studies. This could be as a result of higher levels of EC and CEC obtained during the wet season (Agbaire and Emoyan, 2012; Ebong *et al.*, 2020). The pH of the control soil was more acidic whereas; those of the studied soils were slightly alkaline. This may be due to low OM and CEC levels reported in the background (control) soil.

Consequently, the oil and oil-related activities in the oil-bearing communities investigated may have impacted on the pH of the studied soils.

The results of EC in Table 3 indicate a general range of 0.175 dS/m - 1.497 dS/m for EC in the studied soils. The range of EC obtained in this study is lower than the one obtained by Akan *et al.* (2010) however; higher than that of Prabpai *et al.* (2007). The average EC value recorded in the wet season was higher than that reported for the dry season. This is similar to the findings by Bai *et al.* (2013) and Naeem & Begum (2020). The EC contents of the control soil were lower than the values recorded at the oil-bearing communities. This is consistent with the findings by Onweremadu (2008), and is an indication of anthropogenic impact on the EC levels of the studied soils. The relative higher EC levels of the studied soils as compared to the control soil could be as a result of the low CEC contents in the background soil (Chaudhari *et al.*, 2012).

Generally, the OM contents of soils the oil-bearing communities varied from 4.35 to 11.15 % (Table 3). The levels of OM in the studied soils are similar to the ones obtained by Ebong *et al.* (2014) although it was lower than values obtained by Oyelola and Babatunde (2008). The OM contents in soil from the oil-bearing communities were higher during the wet than in dry season as reported by Turner *et al.* (2015). This might be credited to the influence of rainfall on accumulation of organic matter in soils within the communities studied. The OM contents of the control soil were also lower than the levels obtained at the studied soils (Table 3). This relates closely with the results obtained by Musa *et al.* (2020) and it also indicates the impact of industrial activities on the OM contents in the oil-bearing communities.

The results in Table 3 show that, the overall CEC contents of the studied soils ranged from 7.150 to 11.590 Cmolkg⁻¹. The CEC values reported is higher than the ranges obtained by Fomenky *et al.* (2018) and Salem *et al.* (2020) although lower than the results obtained by Chukwulobe and Saeed (2014). The mean CEC value obtained in the rainy season was higher than values obtained during the dry season of the study area. This is consistent with the results reported by Olubunmi and Olorunsola (2011) and Nengi-Benwaria *et al.* (2021). This could be accredited to the higher OM contents of the soils from the oil-bearing communities during the wet than in dry season (Ebong *et al.*, 2014). The values of CEC recorded for soils from the oil-bearing communities were higher than the value reported for the control site. This agrees with the higher CEC results obtained in contaminated soils than the control site by Iwegbue *et al.* (2006). This study has shown that, the oil activities in the studied locations might have impacted negatively on the soil properties.

Total metals in soils from the oil-bearing communities and the control site

Table 3 shows the results of total metals in the soils from the oil-bearing communities and the Control between January and December, 2017(dry and wet seasons). Generally, the levels of total Pb in the studied soils varied between 4.795 and 11.715 mgkg⁻¹ (Table 3). The highest concentration was obtained in the dry season while the lowest was obtained in the rainy season. The range obtained is lower than 33.4 - 163.3gkg⁻¹ reported by Aydinalp and Marinova (2003) but higher than 0.96 - 7.69 mgkg⁻¹ obtained by Alimohammed-Kalhari *et al.* (2012) . The higher total Pb concentrations reported during the dry season is consistent with the results of Oluyemi *et al.*

(2008). This might be due to less rainfall, evaporation of water from the top soil, and low run-off which may increase the concentration of soil solution (Sparks, 2003; Yahaya *et al.*, 2009). The levels of total Pb in the oil-bearing communities were higher than those recorded in the background soil (Control). This indicates anthropogenic inputs of Pb into the studied soils by oil and oil-related activities in the studied communities as reported by Kuang *et al.* (2004). Consequently, there is a possibility of bioaccumulation of Pb in the tissues of organisms that feed on the plants and through the food chain can affect human beings (Akinola and Adededeji, 2007). However, the mean values of Pb obtained for the dry and wet seasons are lower than the 100.0 mgkg^{-1} acceptable limit by FAO (2001). Hence, the soils within the communities investigated are safe for agricultural and residential purposes (Onyegbule *et al.*, 2010). Though, as a toxic metal the level of accumulation in the environment ought to be consistently checked to avert health risks related to Pb toxicity.

The overall results indicated that, the levels of total As in the studied soils varied between 0.110 mgkg^{-1} and 0.181 mgkg^{-1} . The obtained range is lower than $0.00 - 13.04 \text{ mgkg}^{-1}$ recorded by Yahaya *et al.* (2010) and $0.012 - 3.814 \text{ mgkg}^{-1}$ by Okoye *et al.* (2022). Higher mean levels of total As were recorded in the dry than in the rainy season. The results in Table 3 also indicate that; average values of total As in soils from the oil-bearing communities are higher than those reported in the background soil (Control). This could be credited to the effect of the activities by the oil Companies in the communities examined. Nevertheless; mean concentrations of total As obtained in the studied soils in the dry and rainy seasons are lower than 20.0 mgkg^{-1} recommended by FAO (2001). Notwithstanding the relative lower total As concentrations reported, results of total concentration could be misleading in terms of potential risks hence, the speciation result is more reliable (Pongratz, 1998).

The concentrations of total Cd within soils in the oil-bearing communities varied between 1.004 and 1.932 mgkg^{-1} (Table 3). The highest level of total Cd was obtained during the dry season while the lowest level was reported during the rainy season. This is in conformity with the report by Oluyemi *et al.* (2008) but unlike that of Yahaya *et al.* (2010) who recorded higher Cd concentrations in soils during the rainy season. Wong *et al.* (2005) opined that, this could be caused by run-off effect, dilution of soil solution and leaching into the sub soil by rainwater. The range of total Cd obtained is above the $0.09 - 0.56 \text{ mgkg}^{-1}$ reported by Olowoyo *et al.* (2013) however; the range is below the $2.0 - 5.5 \text{ mgkg}^{-1}$ obtained by Umoren and Onianwa (2005). Concentrations of total Cd in soils from the oil-bearing communities were relatively high compared to the concentrations recorded at the background soil (Control). This conforms to the values obtained by Jaradat and Momani (1999) and Bai *et al.* (2008). This shows anthropogenic inputs of Cd into the studied soils by oil and oil related activities within these oil-bearing communities. Though, the concentrations of total Cd obtained during the two seasons are within the permissible limit of 3.0 mgkg^{-1} by FAO (2001). Cadmium is highly toxic and can easily be taken up by plants hence; it may constitute a possible health hazard to those in contact with the soil from the studied locations (Kashem *et al.*, 2007). Thus, a careful and timely assessment of the accumulation of the metal along the food chain should be emphasized.

Generally, total Ni in the studied oil-bearing soils varied between 1.290 and 2.414 mgkg⁻¹ (Table 3). The average value of total Ni in soils from the oil-bearing communities in the rainy season was higher than the one obtained during the dry season of the area. This is similar to the results obtained in contaminated soils by Fagbote and Olanipekun (2010). The range reported in Table 3 is higher than 0.04 - 0.21 µg/g recorded by Mmolawa *et al.* (2011) but; lower than 0.02 - 22.80 mgkg⁻¹ obtained by Edet *et al.* (2014). The total Ni concentrations obtained in the oil-bearing soils were higher than those reported in the control plot. This could be credited to the impacts of oil and oil-related activities within the communities investigated. Nevertheless, the average values of total Ni obtained in the dry and wet seasons were lower than the 50.0 mgkg⁻¹ limit stipulated by FAO (2001). Hence, the levels of Ni reported in the studied soils may not be a potential threat to those exposed to it. Nevertheless, the reported levels should be properly assessed since bioavailability and toxicity depends on metal speciation not on the total concentration (Ebong *et al.*, 2018).

Table 3 shows that, the concentrations total Cr in the studied soils generally ranged from 1.220 to 1.687 mgkg⁻¹. The highest level of total Cr was obtained during the dry season while the lowest was in the rainy season. This agrees with the results obtained by Onweremadu *et al.* (2007) and Yahaya *et al.* (2009) in their researches. The range of total Cr obtained is lower than 15.19 - 57.65 µg/g obtained by Wang *et al.* (2002). However, the mean values of total Cr for both the dry and wet seasons are higher than 0.60 µg/g reported by Udosen *et al.* (2010) (Table 3). Table 3 also shows that, the total Cr contents in soils from the oil-bearing communities are higher than those obtained in the control plot. This signifies the negative impact of oil and oil-related activities on Ni accumulation in the oil-bearing communities studied. Nevertheless, the concentrations of Cr in soils within the communities studied are lower than the 100.0 mgkg⁻¹ proposed by FAO (2001). Thus, the concentrations of total Cr recorded in soils from the oil-bearing communities might be essential for normal metabolic activities in plants and animals (Samantaray *et al.*, 1998; Snitynskyi *et al.*, 1999). Though, the trend should be observed to avoid bio-accumulation and attendant effects along the food chain as reported by Panda and Choudhury (2005).

Total Fe ranged from 1281.410 to 1581.120 mgkg⁻¹ in soils within the oil-bearing communities examined (Table 3). The highest level of total Fe was recorded during the dry season while the lowest was in the rainy season. The obtained range is higher than 48.947 - 51.584 mgkg⁻¹ obtained by Oluyemi *et al.* (2008) nevertheless; it was less than 34.100 - 4541.00 µgkg⁻¹ obtained by Onyegbule *et al.* (2010). Higher concentrations of total Fe were recorded at the oil-bearing communities than in Control. This might be accredited to the widespread utilization of Fe in industries and high traffic density at the oil-bearing communities (Adachi and Tainosho, 2004; Olowoyo *et al.*, 2013). Total Fe had the highest concentration among the metals determined which is consistent with the findings by Onyedika (2015) who attributed this to the prevalent of Fe and Fe-containing wastes in the region. The average values of total Fe obtained in the studied soils in the dry and rainy seasons are lower than 50,000.00 mgkg⁻¹ stipulated for soil by FAO (2001). Although Fe is not a toxic metal, it has been reported that its concentration and chemical form can influence the bioavailability and toxicity of Pb (Adriano, 2001). Hence, the accumulation of total Fe in the studied soils should be strictly observed to prevent harmful effects of high Pb on human health.

The concentrations of Total V in soils from the oil-bearing communities varied from 0.072 to 0.146 mgkg⁻¹ (Table 3). The mean concentration of V was higher in the dry than during the rainy season. This is a deviation from the higher wet season total V obtained in contaminated soils by Fagbote and Olanipekun (2010) and Lokeshwary and Chandrappa (2006). The range of V reported in the oil-bearing soils is less than 0.00 – 1.13 mgkg⁻¹ obtained by Nwadinigwe *et al.* (2014). The concentrations of total V in the oil-bearing communities investigated were above the values recorded for the control site. Consequently there might be artificial inputs of V in the studied communities possibly from the industrial activities. However, the concentrations of total V obtained in the studied soils are below the recommended limit of 10.83mgkg⁻¹ by WHO (2006). Consequently, the levels of total V reported in the studied oil-bearing communities may not be hazardous to those exposed to it.

Table 4 Results of Speciation of trace metals in the studied soils and Control

	Pb	As	Cd	Ni	Cr	Fe	V
STUDIED SOILS (DRY)							
Aex	23.57	24.76	55.06	17.10	32.22	11.02	21.18
Red	38.78	40.73	20.72	50.80	26.59	14.68	42.26
Ox	21.58	12.56	13.78	22.02	19.13	18.41	19.45
Res	16.07	21.95	10.44	10.08	22.06	55.89	17.11
STUDIED SOILS (WET)							
Aex	23.19	24.70	53.71	14.51	31.76	10.34	20.75
Red	36.65	41.97	21.06	51.53	27.84	13.27	43.67
Ox	22.82	13.19	14.00	21.40	18.59	18.56	18.90
Res	17.34	20.14	11.23	12.56	21.81	57.83	16.68
CONTROL SOIL (DRY)							
Aex	22.64	19.95	41.31	13.97	16.17	14.12	19.50
Red	13.37	24.24	26.88	22.76	19.33	17.43	21.68
Ox	19.17	12.75	20.20	10.55	21.22	21.63	15.37
Res	44.82	43.06	11.61	52.72	43.28	46.82	43.45
CONTROL SOIL (WET)							
Aex	22.71	20.34	40.75	14.39	15.66	13.64	18.52
Red	17.24	25.13	27.91	21.76	17.18	18.86	20.70
Ox	20.46	13.37	18.80	12.47	20.42	20.93	16.88
Res	39.59	41.16	12.54	51.38	46.74	46.57	43.90

Aex denotes Acid extractable fraction; Red is Reducible fraction; Ox signifies Oxidisable fraction; Res indicates the Residual fraction

Speciation of trace metals in the studied soils and Control

The results for the speciation of metals in soils from the oil-bearing communities and the background soil (Control) are indicated in Table 4.

Lead existed predominantly in the reducible fraction (oxides of Fe and Mn) in soils from the oil-bearing communities in the dry and rainy seasons. The distribution of Pb into the various fractions in the oil-bearing soils for both seasons is Red > Aex > Ox > Res. This shows that, a higher

proportion of Pb in the soils within the studied locations was in the non-residual fraction during both seasons. This is similar to the results obtained for Pb in contaminated soils by Andreas and Zhang (2016). However, Pb occurred mainly in the residual fraction in the background soil as reported by Asmoay *et al.* (2019). Consequently, considerable quantity of Pb in soils from the oil-bearing communities may have initiated by the anthropogenic source (Hu and Cheng, 2016). Thus, Pb may have been highly available in the oil-bearing communities but relatively unavailable at the control site (Hacısalıhoğlu and Karaer, 2016; Malsiu *et al.*, 2020). Hence, the food chain has been exposed to Pb toxicity and the associated risks in the study area.

Results in Table 4 indicate that, As also occurred mostly in the reducible fraction in the oil-bearing soils both in the dry and wet seasons. This is similar to the result obtained consistent in contaminated soils by Kalyvas *et al.* (2022). The trend for the distribution of As in the studied soils for both seasons is Red > Aex > Res > Ox. This shows the bioavailability of As in the studied soils as reported by Malsiu *et al.* (2020). Conversely, As existed principally in the inert (residual) fraction within the control plot indicating its unavailability and toxicity as opined by Wang *et al.* (2018) and Álvarez-Quintana *et al.* (2020). It also confirms that As could emanated mostly from the anthropogenic source in the studied soils but, from the lithogenic source at the control site (Cao *et al.*, 2015; Hu and Cheng, 2016).

Cd occurred predominantly in the readily available (acid extractable) fraction in both the oil-bearing communities and the background soil during both seasons. This agrees with the findings by Emurotu (2020) Nimyel and Chundusu (2021) in contaminated soils. Though, the proportions of Cd in the acid extractable fraction were higher in soils from the oil-bearing communities than at the background soil. Acid extractable fraction of Cd contributed 55.06 and 53.71% in the dry and rainy seasons, correspondingly but lower proportions of this fraction were recorded in the control site during both seasons (Table 4). The sequence of Cd in the studied soils for both seasons is Aex > Red > Ox > Res, similar to that reported by Özyaytekin and Dedeoğlu (2022). This reveals the high mobility and bioavailability of Cd in the oil-bearing communities (Kubier *et al.*, 2019; Dutta *et al.*, 2020). The elevated percentage of the metal in the highly mobile fraction could be attributed to the oil activities within the oil-bearing communities (Hu and Cheng, 2016). Considering the high toxicity of Cd, the trend supposed to be strictly observed to forestall the risks related to high Cd along the food chain (Balali-Mood *et al.*, 2021).

Ni occurred mostly in the reducible fraction in the studied soils in the dry and wet seasons. This is in agrees with the results obtained by Tamunobereton-ari *et al.* (2011) and Wali *et al.* (2014). The sequence for the distribution of Ni in the dry and rainy seasons is Red > Ox > Aex > Res. This observation could be attributed to the oil and oil-related activities in the oil-bearing communities as Ni is highly related to crude oil (Osuji and Adesiyan, 2005; Osuji and Achugasim, 2010). On the contrary, Ni occurred mainly in the residual fraction in the background soil during both seasons (Ayodele and Mohammed, 2011; Asmoay *et al.*, 2019). Consequently, Ni might have emanated from the anthropogenic source in soils from the oil-bearing communities but from the geogenic source in the control site (Hu and Cheng, 2016). Apparently, Ni could be more bio-available in the oil-bearing communities than in the background soil (Wang *et al.*, 2018).

Table 4 shows that Cr existed primarily in the acid extractable fraction in soils from the oil-bearing communities during the dry and wet seasons (Table 4). This conforms with the results obtained by Katana *et al.* (2013) in contaminated soils. The trend for the distribution of Cr into the different soil fractions is Red > Aex > Res > Ox. Accordingly, higher quantities of non-residual Cr were obtained in the studied area. This could be attributed to the impact of anthropogenic source in the oil-bearing communities and may result in high mobility and bioavailability of Cr in these communities (Osuji and Achugasim, 2010; Mandal *et al.*, 2011). Nonetheless, Cr existed basically in the inert (residual) fraction at the control site during both seasons as reported by Ayeni and Adebiyi (2021) and Zhang *et al.* (2021). This indicates that Cr is unavailable and may originate mainly from the natural source in the control site (Cao *et al.*, 2015; Hacısalıhoğlu and Karaer, 2016).

The residual fraction of Fe was the major proportion in the studied oil-bearing communities in the dry and rainy seasons. This compares with the reports of Borgese *et al.* (2013) and Osakwe and Okolie (2015) in contaminated soil environment. The speciation of Fe followed the order Res > Ox > Aex > Red. This shows the unavailable nature of essential Fe in the studied soils. This also corroborates with the findings by Cluster analysis that, Fe in soils from the oil-bearing communities may have originated mainly from the natural factor. Fe also occurred chiefly in the inert (residual) fraction in the control site in the dry and rainy seasons. Hence, Fe is naturally available in the study area as reported by Ebong & Ekong (2015) and Ekwule *et al.* (2021). Apparently, the industrial activities carried out within the studied oil-bearing communities may not have impacted significantly on the accumulation of Fe in the area.

Table 4 indicates that, V occurred mostly as oxides of Fe and Mn in the studied soils in the dry and rainy seasons. This is similar to the results obtained by Agnieszka and Barbara (2012) and Fayiga and Nwoke (2017). The separation of V into the various soil fractions varied as follows: Red > Aex > Ox > Res. This reveals that the non-residual fractions of V were higher in the studied soils in both seasons. This also shows the high mobility and bioavailability of V in soils within the oil-bearing communities. This could be related to the oil activities in the area since V is closely linked to crude oil in soil (López and Mónaco, 2017). On the contrast, V existed principally in the inert fraction in the background soil (Control). This agrees with the results obtained by Yang *et al.* (2013) and Shi *et al.* (2010). Thus, V may not be readily available in the control site and it may have originated mostly from the lithogenic processes of the soil. Consequently, V in the control site may not pose a serious threat to those exposed to it.

Generally, the forms of Pb, As, Cd, and Cr were higher during the wet season than in the dry while; those of Ni, Fe, and V were higher in the rainy season. This could be credited to the variations in soil properties, season, and total concentrations of the trace metals (Ebong *et al.*, 2014; Osobamiro and Adewuyi, 2015).

Table 5 The Contamination factor, geo-accumulation index, and ecological risk factor of trace metals in soils from the oil-bearing communities

Pollution Model	Elements													
	Pb	As	Cd	Ni	Cr	Fe	V	Pb	As	Cd	Ni	Cr	Fe	V
	Dry Season							Wet Season						
CF														
Min	4.00	1.2	1.9	1.4	1.8	1.4	1.1	4.5	1.2	1.0	1.7	1.3	1.3	1.6
		5	8	1	5	0	3	1	3	6	3	5	7	8
Max	4.29	1.3	2.1	1.6	1.9	1.4	1.6	4.9	1.3	1.1	1.9	1.3	1.4	2.2
		3	1	3	7	7	3	0	5	0	4	6	1	5
Mean	4.15	1.2	2.0	1.5	1.9	1.4	1.4	4.6	1.3	1.0	1.8	1.3	1.4	2.0
		8	5	1	3	4	7	9	0	8	3	6	0	8
Igeo														
Min	1.41	-	0.3	-	0.3	-	-	1.5	-	-	0.2	-	-	0.1
		0.2	9	0.0	0	0.0	0.3	9	0.2	0.5	0	0.1	0.1	0
		7		9		9	6		9	2		5	4	
Max	1.51	-	0.4		0.3	-		1.7	-	-	0.3	-	-	0.5
		0.1	9	0.1	9	0.0	0.1	1	0.1	0.4	7	0.1	0.0	1
		8		1		3	6		4	5		5	9	
Mean	1.47	-	0.4	0.0	0.3	-	-	1.6	-	-	0.2	-	-	0.3
		0.2	5	0.4	6	0.0	0.0	5	0.2	0.4	8	0.1	0.1	9
		4				5	1		0	8		5	0	
E_r^i														
Min	20.0	12.	59.	7.0	3.7	0.0	2.2	22.	12.	31.	8.6	2.7	0.0	3.3
		5	4	5	0	0	6	55	30	80	5	0	0	6
Max	21.4	13.	63.	8.1	3.9	0.0	3.2	24.	13.	33.	9.7	2.7	0.0	4.5
	5	30	3	5	4	0	6	50	50	00		2	0	0
Mean	20.7	12.	61.	7.5	3.8	0.0	2.9	23.	13.	32.	9.1	2.7	0.0	4.1
	6	79	50	4	6	0	3	45	04	44	4	1	0	6

Pollution Status of soils from the oil-bearing communities and the Control

The contamination factors (CF) of trace metals in soils from the oil-bearing communities for the dry and rainy seasons are displayed in Table 5. The CF ranges of the metals are as follows: 4.00 - 4.90, 1.23 – 1.35, 1.06 – 2.11, 1.41 – 1.94, 1.35 – 1.97, 1.37 – 1.47, and, 1.13 – 2.25 for Pb, As, Cd, Ni, Cr, Fe, and V, respectively. Accordingly, all the metals except Pb are in the moderate contamination class (Pekey *et al.*, 2004). Pb with the highest CF values for both seasons belongs to the considerable contamination class as reported by Jimoh *et al.* (2020). The high CF values of the elements during both the dry and wet seasons could be credited to the oil and oil-related activities in the studied communities. However, the mean CF values of the Cd, Cr, and Fe were higher in the dry season while those of Pb, As, Ni, and V were relatively higher during the rainy

season. This is attributed to the seasonal variation as reported by Edokpayi *et al.* (2017) in their study. The sequence for the CF of trace metals during the dry and wet seasons are Pb>Cd>Cr>Ni>V>Fe>As and Pb>V>Ni>Fe>Cr>As>Cd, respectively. This shows different levels of metals enrichment in the studied soils for different seasons.

Results for the geo-accumulation index (I_{geo}) of metals for both seasons are in Table 5. The overall I_{geo} values for the trace metals during both Seasons ranged as follows: (1.41 – 1.71) Pb, (-0.29 - -0.14) As, (-0.52 – 0.49) Cd, (-0.09 – 0.37) Ni, (-0.15 – 0.39) Cr, (-0.14 - -0.03) Fe, and (-0.36 – 0.51) V. This reveals that, Pb, Cd, Ni, Cr, and V are in the unpolluted to moderately polluted class while As and Fe are in the unpolluted category (Huu *et al.*, 2010). The mean I_{geo} values of Cd, Cr, and Fe were comparatively higher in dry season while, those of Pb, As, Ni, and V were higher in the rainy season. The observed seasonal variation in the I_{geo} values between the two seasons corroborates the results obtained by Roy *et al.* (2018) and Zubair *et al.* (2021). This also confirms the observations by contamination factor that, change in seasons can also affect the enrichments of metals in soils within the oil-bearing communities.

Generally, the ecological risk factor (E_r^i) of the metals for the two seasons in soils within the studied oil-bearing communities fluctuates as follows: Pb (20.00 - 24.50), As (12.30 – 13.50), Cd (31.80 – 63.30), Ni (7.05 – 9.70), Cr (2.70 – 3.90), Fe (0.00 - 0.00), and V (2.26 – 4.50) (Table 5). Thus, Pb is in the high risk category, As is in the considerable risk class, Cd in the very high class, Ni belongs to the moderate risk class, while, Cr and V are in the low risk class (Ren *et al.*, 2007). Fe is not regarded as a toxic metal hence; no toxic response factor was allocated to it thus, it has a zero ecological risk factor. The ecological risk factor of trace metals in soils from the oil-bearing communities in the dry and rainy seasons showed some degree of disparity as observed by Mirzaei *et al.* (2020) and Hong *et al.* (2021). The general results of ecological risk factor indicated that, the mean values for Cd and Cr were comparatively higher during the dry season while the ones for Pb, As, Ni, and V were higher during the rainy season. The high E_r^i of most of the trace metals in soils from the oil-bearing communities could be credited to the oil activities carried out in the area. Consequently, remediation process is encouraged to control the quantity of these metals in the area especially the highly toxic ones like Pb and Cd.

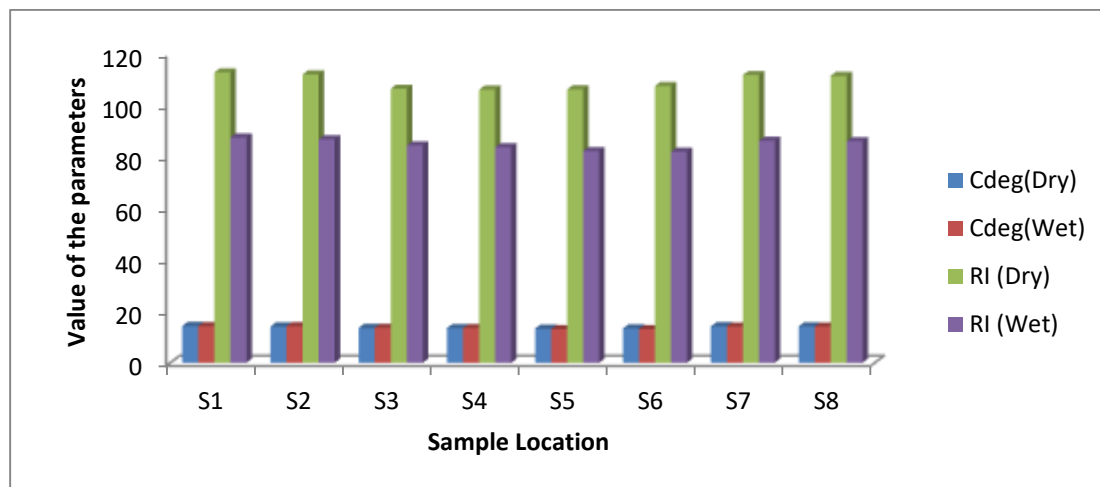


Fig. 2. Results of degree of contamination (Cdeg) and ecological risk index (RI).

The degree of contamination (Cdeg) of the different communities investigated in the dry and rainy seasons are illustrated in Fig 2. The overall a Cdeg values varied as follows: 13.07 - 14.31 in the studied oil-bearing communities for both seasons. The highest Cdeg value was obtained at Afaha Eket (S1) while the lowest was recorded at Uquo (S5) and Edor (S6). The degree of variability among the different locations was very low during the dry and wet seasons with Coefficient of variation (CV) values of 3.11 and 3.59%, respectively. This could be credited to the common source of metal contaminants (oil and oil-related activities) at all the studied communities (Ayenimo *et al.*, 2005; Lu *et al.*, 2010). However, the mean values of Cdeg of the different studied locations during the dry and wet seasons demonstrated some variations as reported by Nwankwo *et al.* (2019). This could be credited to the disparity in the atmospheric deposition, runoff, and soil properties among the different sites investigated between the dry and wet seasons (Gunawardena *et al.*, 2013; Biswas *et al.* 2018; Gunes, 2022). The major contributors to the Cdeg during the dry season were Pb, Cd, and Cr while, Pb, Ni, and V were the main contributors during the wet season.

The potential ecological risk index of the trace metals in the different communities investigated are demonstrated in Fig 2. The mean RI values in the studied soils varied between 106.19 and 112.92 during the dry season but between 82.04 and 87.54 in the wet season. The observed variation between the dry and wet seasons is consistent with the report by Mirzaei *et al.* (2020). Consequently; higher mean RI values were obtained in the dry than in the rainy season. The higher mean RI values in the dry season reported agree with the results obtained by Nwankwo *et al.* (2019). This could be credited to the dilution and leaching of metal concentrations in soil during the rainy season and the concentration of metal concentrations by evaporation in the dry season. The average RI values obtained in both seasons belong to the considerable risk class according Ren *et al.* (2007). It has been opined that, high RI values of metals in soil are closely related to

several human health problems. Thus; the high mean RI values obtained in soils from the different communities investigated is an indication of the existence of health risks associated with their toxicities in these areas. This should not be overlooked as it may result in severe human and environmental problems within these communities.

Table 6 Total variance clarified for the parameters obtained in soils from the oil-bearing communities.

Component	Initial Eigen values			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
DRY SEASON									
1	6.57	59.72	59.72	6.57	59.72	59.72	4.76	43.26	43.26
2	2.97	26.96	86.68	2.97	26.96	86.68	4.22	38.37	81.63
3	1.08	9.79	96.48	1.08	9.79	96.48	1.63	14.85	96.48
WET SEASON									
1	5.41	49.16	49.16	5.41	49.16	49.16	5.06	46.01	46.01
2	2.66	24.18	73.34	2.66	24.18	73.34	2.53	23.02	69.03
3	1.42	12.87	86.21	1.42	12.87	86.21	1.63	14.77	83.80
4	1.12	10.16	96.37	1.12	10.16	96.37	1.38	12.57	96.37

Table 7: Total variance for the parameters obtained in soils from the oil-bearing communities explained

	Component							
	Dry Season			Wet Season				
	1	2	3	1	2	3	4	
Ni	0.977	0.178	-0.108	0.951	0.063	0.200	0.207	
Cd	0.976	-0.087	0.011	0.241	0.916	-0.312	-0.053	
OM	-0.936	-0.324	0.105	-0.992	0.021	-0.046	0.025	
Pb	0.857	0.490	0.093	0.962	0.153	-0.068	0.184	
pH	-0.853	0.386	-0.322	-0.315	-0.367	-0.836	-0.015	
AS	0.736	0.453	0.179	0.800	-0.538	0.151	-0.066	
Fe	0.686	-0.512	0.489	0.454	0.859	0.223	0.052	
V	0.439	0.867	0.147	0.649	0.712	0.089	0.240	
Cr	0.559	-0.813	-0.154	0.304	0.256	0.155	-0.867	
CEC	-0.644	0.733	0.199	-0.703	0.183	0.318	0.447	
EC	-0.626	-0.127	0.765	-0.763	0.149	0.606	-0.144	

Multivariate analysis of the parameters in the studied soils

The principal component analysis (PCA) was employed to identify the factors accountable for the buildup of parameters determined in soils from the oil-bearing communities (Wu and Kuo, 2012). The results in Table 6 indicate three factors that are accountable for the availability of parameters analyzed for in soils within the oil-bearing communities during the dry season. These three (3) key factors with Eigen values greater than one contributed a significant 96.48% to the entire variance during the period. Factor one donated 59.72% of the total variance with significant positive loadings on Ni, Cd, Pb, As, Fe, Cr, and considerable negative loadings on OM, pH, CEC, and EC (Table 7). This represents the influence of the anthropogenic and natural factors on the buildup of these parameters in soils from the studied communities (Zhang and Wang, 2020; Soltani-Gerdefaramarzi *et al.*, 2021). Factor two added 26.96% of the overall variance with significant positive loadings on Pb, V, CEC, but strong negative loadings on Fe and Cr (Table 7). This proposes the negative effects of industrial (man-made) activities on soil within the oil-bearing communities investigated (Mugoša *et al.*, 2016; Ebong *et al.*, 2020). Factor three added 9.79% to the total variance with significant positive loadings on Fe and EC (Table 7). Thus; reveals the impact of lithogenic factor on the value of the studied soils (Xu *et al.*, 2022). However; during the wet season four principal factors with Eigen values higher than one were identified, these factors contributed 96.36% of the total variance (Table 6). Factor one donated 49.16% to the overall variance with significant positive loadings on Ni, Pb, As, V, and strong negative loadings on OM, CEC, and EC (Table 7). This signifies the strong anthropogenic impact on the quality of the studied soils. Factor two added 24.18% of the entire variance with considerable positive loadings on Cd, Fe, V, and significant negative loading on As (Table 7). This implies the effects of both the natural and man-made influence on the current state of the studied soils. Factor three donated 12.87% to the overall variance with strong positive loading on EC and significant negative loading on pH. This could be the impact of natural influence such as rainfall on the studied soil environment (Brevik *et al.*, 2006; Bai *et al.*, 2013). Factor four contributed 10.16% of the entire variance with significant negative loading on Cr however, fair positive loadings on Ni, Pb, V, and CEC. This suggests the modest negative of aerial deposition and runoff on the quality of the studied soils (Viard *et al.*, 2004; Steffan *et al.*, 2018).

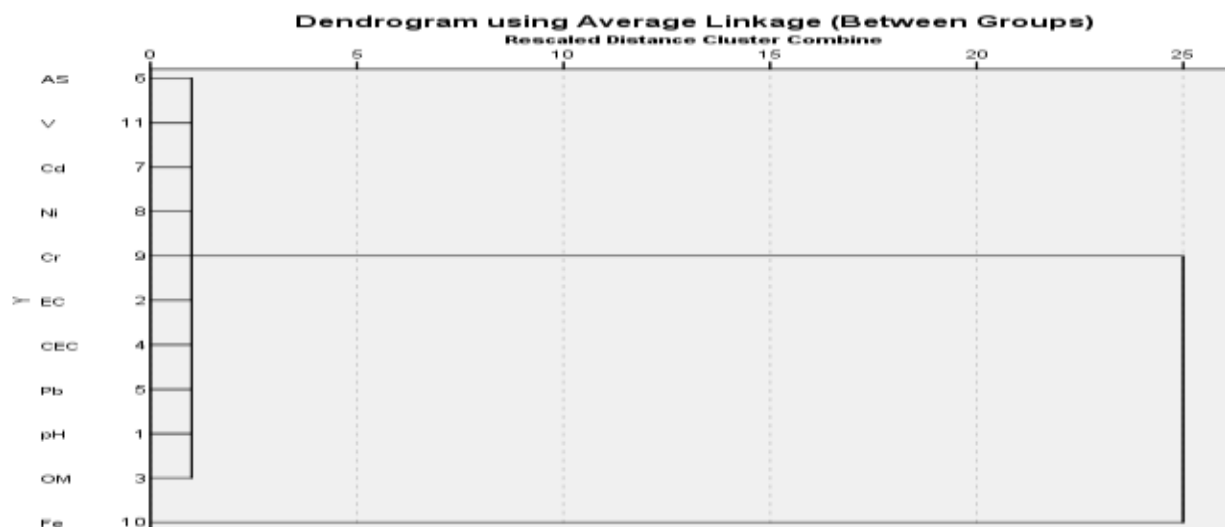


Fig. 3. Hierarchical clusters formed among the parameters in the studied soils.

The divisive Cluster method was used to identify parameters with common source and properties (Ebong *et al.*, 2019; Kahangwa, 2022). The Hierarchical cluster analysis (HCA) for the parameters in the dry and rainy seasons resulted in a common cluster as shown in Fig 3. The pair wise association that existed between the parameters analyzed for in soils from the oil-bearing communities for the two seasons is displayed in Fig 3. Fig 3. illustrates two major clusters namely: Cluster one relating As,V, Cd, Ni, Cr, Ec, CEC, Pb, pH, and OM together and cluster two connecting only Fe. This indicates a common source (anthropogenic) for a significant amount of all the parameters determined in the studied soils apart from Fe (Al-Khashman and Shawabkeh, 2006, Yang *et al.*, 2011). The results of HCA also revealed that, majority of Fe could have originated from the natural source which is different from the other parameters as indicated by Ebong *et al.* (2019).

Table 8: Non-carcinogenic health risks for each trace metal and the contact route.

Metal	Summary	DI		HQ					
		Dry Season		Rainy Season		Dry Season		Rainy Season	
		Child	Adult	Child	Adult	Child	Adult	Child	Adult
Pb	Min	4.00E-4	2.14E-4	3.63E-4	1.97E-4	0.11	0.06	0.10	0.06
	Max	8.99E-4	4.81E-4	8.33E-4	4.46E-4	0.26	0.14	0.24	0.13
	Mean	7.18E-4	3.84E-4	5.62E-4	3.01E-4	0.21	0.11	0.16	0.09
As	Min	9.28 E-6	4.97E-6	8.44E-6	4.52E-6	0.03	0.02	0.03	0.02
	Max	1.39 E-5	7.44E-6	1.34E-5	7.19E-6	0.05	0.03	0.05	0.02
	Mean	1.25E-5	6.62E-6	1.14E-5	6.12E-6	0.04	0.02	0.05	0.02
Cd	Min	9.39 E-5	5.03E-5	7.70E-5	4.12E-5	0.09	0.05	0.08	0.04
	Max	1.48E-4	7.94E-5	1.10E-4	5.90E-5	0.15	0.08	0.11	0.06
	Mean	1.26E-4	6.76E-5	8.98E-5	4.81E-5	0.13	0.07	0.09	0.05
Ni	Min	9.90 E-5	5.50E-5	1.47E-4	7.85E-5	0.01	0.003	0.01	0.004
	Max	1.85E-4	9.92E-5	1.72E-4	9.21E-5	0.01	0.01	0.01	0.01
	Mean	1.38E-4	7.85E-5	1.57E-4	8.40E-5	0.01	0.004	0.01	0.004
Cr	Min	9.76 E-5	5.23E-5	9.36E-5	5.01E-5	6.51E-5	3.49E-5	6.24E-5	3.34E-5
	Max	1.29E-4	6.93E-5	1.24E-4	6.66E-5	8.60E-5	4.62E-5	8.26E-5	4.44E-5
	Mean	1.12 E-4	6.00E-5	1.10E-5	5.89E-5	7.47E-5	4.00E-5	7.33E-6	3.93E-5
Fe	Min	1.10 E-1	5.87E-2	9.83E-2	5.27E-2	0.16	0.08	0.14	0.08
	Max	1.21 E-1	6.50E-2	1.19E-1	6.35E-2	0.17	0.09	0.17	0.09
	Mean	1.15E-1	6.00E-2	1.10E-1	5.91E-2	0.16	0.09	0.16	0.08
V	Min	5.52 E-6	2.96E-6	6.90E-6	3.70E-6	0.01	0.003	0.01	0.004
	Max	1.12 E-5	6.00E-6	1.08E-5	5.80E-6	0.01	0.01	0.01	0.01
	Mean	9.21E-6	4.93E-6	9.13E-6	4.89E-6	0.01	0.01	0.01	0.01
Mean THI (Children) 0.56						Mean THI (Children) 0.48			
Mean THI (Adults) 0.30						Mean THI (Adults) 0.25			

Health risks assessment

Risks related to the human contact with metals are directly related to the daily intake rate (DI) of the metals (Ebong *et al.*, 2020). The mean values for the estimated daily intake rate (EDI), hazard quotient, and total chronic hazard index are presented in Table 8. The mean DI values for all the trace metals obtained during both seasons were lower than their limits for the oral reference doses (RfDs) specified by USEPA (2010). Accordingly, the exposure to metals by both the young and old populations during the dry and wet seasons may not result in harmful effect immediately. The mean DI values for all the metals were higher in the young than in the adults' population apart from Cr. This shows that the young ones were more exposed to metal toxicity and their related problems than the older ones. Table 8 also signifies that, the average DI values of the entire metals except Ni were higher in the dry season than during the wet season. The variation in the values of DI of the metals between the dry and wet seasons is consistent with the report by Mandindi *et al.* (2022) and Moruf (2022). The highest and lowest mean DI values obtained for both populations and seasons were Fe and V, respectively. The highest mean DI value recorded for Fe is similar to that report by Ebong *et al.* (2019) in contaminated soils. The DI values of Fe reported may not result in harmful effect given that, it is an essential metal. However, it should be assessed periodically to forestall bio-accumulation and related problems in the studied communities (Goyer,

1995). The low mean DI values of Pb, As, Cd, and Ni ought not to be ignored since these metals are highly toxic even at their minimal concentrations (ATSDR, 2007; Tchounwou *et al.*, 2012).

Table 8 presents the values of the non-carcinogenic hazard indicated as hazard quotient. The general results revealed that, the HQ of each of the metals is lower than one (1). Accordingly, these metals might not be of immediate severe threat to both the young and old populations. The highest mean HQ value was recorded for Pb while, Cr showed the lowest for both populations and seasons. Nevertheless, the highest mean value was recorded in the dry season while the lowest was reported during the rainy season. This seasonal variation in the mean HQ values of metals in both the children and adults' populations reported is consistent with the reports by Mandindi *et al.* (2022). The mean HQ values of children were higher than those of the elderly indicating the higher vulnerability of children to metal toxicity than the adults' population. The sequence for the mean HQ values for both populations and seasons is: Pb > Fe > Cd > Pb > As > Ni = V > Cr. Hence, high susceptibility of both the children and adults populations to Pb toxicity and the associated health implications in the dry and rainy seasons has been exposed. According to the results in Table 8, the children population is more vulnerable to the Pb toxicity and related problems as reported by Reagan & Silbergeld (1989). Even though the mean THI values obtained for both populations and seasons are below one (1), there is still a propensity of the people in these communities being disposed to the non-carcinogenic risks which is directly proportional to the values of total chronic hazard index according to Man *et al.* (2010).

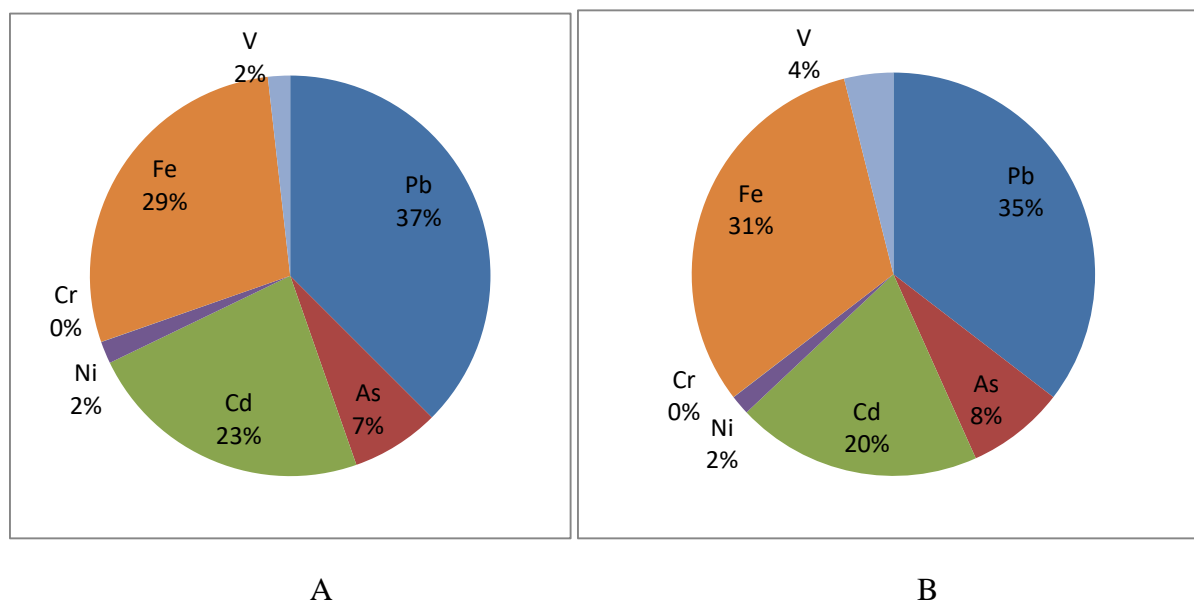


Fig. 4. Mean hazard quotient for the young (A) and old (B) during the Dry season.

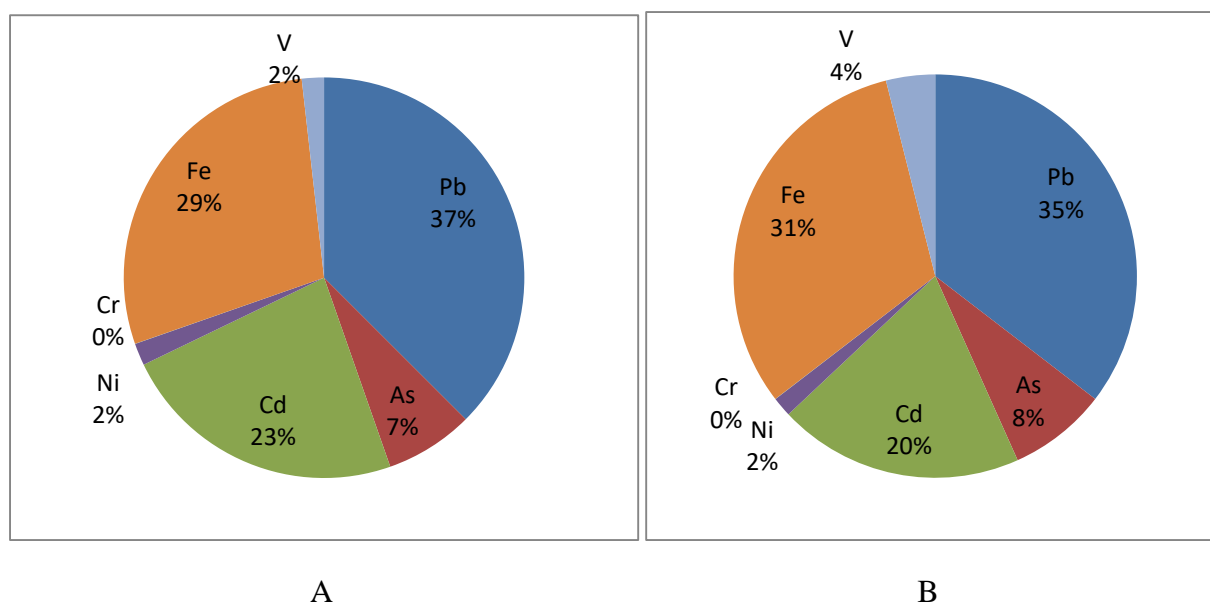


Fig. 5. Mean hazard quotient for the young (A) and old (B) during the Dry season.

The mean values of total chronic hazard index (THI) for the children and the elderly populations during the dry and rainy seasons are indicated in Table 8. The mean THI values for the young and old populations during the dry season are 0.56 and 0.30, respectively. Whereas, during the wet season the mean THI values for the young and old were 0.48 and 0.25, respectively. Accordingly, the average THI value for the young ones was higher than the value recorded for the old population. The mean THI values recorded for the dry season were also higher than in the rainy season. The relative higher mean THI values reported for the dry season is comparable with the results obtained by Zhang *et al.* (2018). The relatively higher mean THI value reported for the young population consents to the findings by Singh *et al.* (2010). Thus, the children populations within the studied communities are more susceptible to health problem associated with metal toxicity than the adults and the tendency is higher in the dry than during the rainy season (Zhang *et al.*, 2018). Fig 4. illustrates that the average HQ values recorded for Pb and Fe in the young population contributed 37 and 29 %, respectively but, 35 and 31%, respectively in the adults to the total chronic hazard index in the dry season. However, during the rainy season the average HQ values of Pb and Fe contributed 35 and 31%, respectively for both the children and adults populations to the total chronic hazard (Fig 5).

CONCLUSION

The study has revealed that, the industrial activities carried out within the oil-bearing communities of Akwa Ibom State have impacted negatively on the soil properties and trace metals accumulation in the host environment. It has also indicated that, the effect of seasonal changes on the

physicochemical properties and metals accumulation in soils within the oil-bearing communities. The multivariate analysis has also identified the oil and oil-related activities with the communities studied as the major factor affecting the soil environment. The change in season has significant implications on the pollution condition of the studied soil environment, and exposure to health risks. Thus, all activities should be done according to the recommended standards and wastes emanating from these activities should be properly managed.

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