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Original Research Paper

Physicochemical properties, total concentration, geochemical fractions, and health risks of trace metals in oil-bearing soils of AkwaIbom State, Nigeria

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Abstract:
The physicochemical properties, total metal, metal fractions, and related human health problems of metals in oil-bearing soils of Akwa Ibom State were appraised using standard procedures. The study aimed at assessing the effects of crude oil and related activities on the properties of soil including metals (Cd, Cr, Ni, Pb and V), their fractions and associated health problems. Results showed that, levels of parameters were higher in the soils examined than in the control. The entire metals examined, apart from Cd, were within their acceptable limits however; higher than the limits for agricultural soils. Cd and Cr existed mainly in the readily available fraction, while Ni, Pb, and V occurred mainly in the reducible fraction in the studied soils. Conversely, these metals, except Cd, occurred principally in the inert fraction in the control. V/Ni ratio confirmed the soils as oil-forming continents and of organic matter origin. The natural factor, crude oil, and oil-related activities were major sources of soil contaminants. Anthropogenic proportions of metals were more in the soils investigated than in the background soil. The locations were contaminated with metals. Daily intake rates of metals were within their recommended doses except for Pb. The pollution status of the oil-bearing soils and the related human health risks have been revealed.

Keywords: Oil-bearing soil; multivariate analysis; soil pollution; metal speciation;trace metals

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1. Introduction

The discovery of crude oil in the South-South Region of Nigeria and the related industrial activities thereafter has caused serious environmental degradation in the area for years now. Reports have shown that the land, water, and air environments are under serious threat due to contaminants/pollutants from oil and oil-related activities (Bodo and Gimah, 2020; Julius, 2011; Singh *et al*., 2020). The existence of crude oil and oil-related activities within the studied region has led to the reduction in the population of fish and extinction of some species of living organisms in the area (Orisakwe, 2021; Ugochukwu and Ertel, 2008). It has also been reported that, the devastating effects of oil and oil-associated activities in the oil producing Region of the country has manifested in rooftops (Bodo and Gimah, 2020; Ismail and Umukoro (2012).

The physicochemical properties and soil nutrients within the oil producing Region are also impacted by the availability of crude oil and the associated oil activities (Atuma and Ojeh, 2013; Odjugo and Osemwenkhae, 2009; Ohanmu *et al*., 2018).

Naturally, Nigerian crude oil is known for having high level of toxic metals (Ahiamadu *et al*., 2021). Consequently, the soil that bears crude oil in Nigeria is expected to also contain elevated levels of these metals (Chinedu and Chukwuemeka, 2018; Thomas *et al*., 2021). Reports have shown that, oil-bearing soils and oil-related activities have considerable effect on total metals accumulation and speciation in the host soil environment (Borah and Deka, 2023; Duru *et al*., 2009; Ebong *et al*., 2022; Ogbo and Okhuoya (2011).

Metals associated with crude oil are both the essential and non-essential, but even the essential ones are dangerous to majority of biological species as well as human beings at levels higher their recommended limits (Slobodian *et al*., 2021). Ana *et al*. (2009) also opined that, the industrial activities within the Niger Delta Region have adverse effects on the health of the inhabitants. Crude oil bearing soil and associated activities have the potentials of increasing the levels of toxic substances in the environment (Ahiamadu *et al*., 202l; Thomas *et al*., 2021). Consequently, human beings in the oil producing Region of Nigeria are constantly exposed to high levels of toxic metals and their related human health implications either directly or indirectly (Amadi *et al*., 2021; Ordinioha and Brisibe, 2013).

Nevertheless, previous studies concentrated mainly on the effect of oil-related activities without investigating the status of the oil-bearing soils and the impact on the inhabitants of the communities. This study was carried out to close the gaps that were created by the research works done in the oil producing communities hitherto. This work evaluated the physicochemical properties, total metals and their geochemical fractions, pollution status, and related health risks of metals within oil-bearing soils. The Vanadium-nickel ratio was also assessed to confirm the source and type of crude oil in the studied soils. Hence, the results of this research will offer adequate and comprehensive information concerning the oil-bearing soils.

2. Materials and Methods

2.1 Description of study area

Akwa Ibom State lies between latitudes 4^{o} 32! and 5^{o} 33! North and longitudes 7^{o} 25! and 8^{o} 25! East of Nigeria. The state is one of the main oil producing region within Nigeria and the oil producing communities in the state border by the Atlantic Ocean. Accordingly, major oil activities are concentrated in these oil-bearing communities. The five locations studied are located within Eket, Esit Eket, and Ibeno local government areas (Figure 1). These are the major oil-bearing communities of the State. The control soil is located in Etinan LGA of Akwa Ibom State.

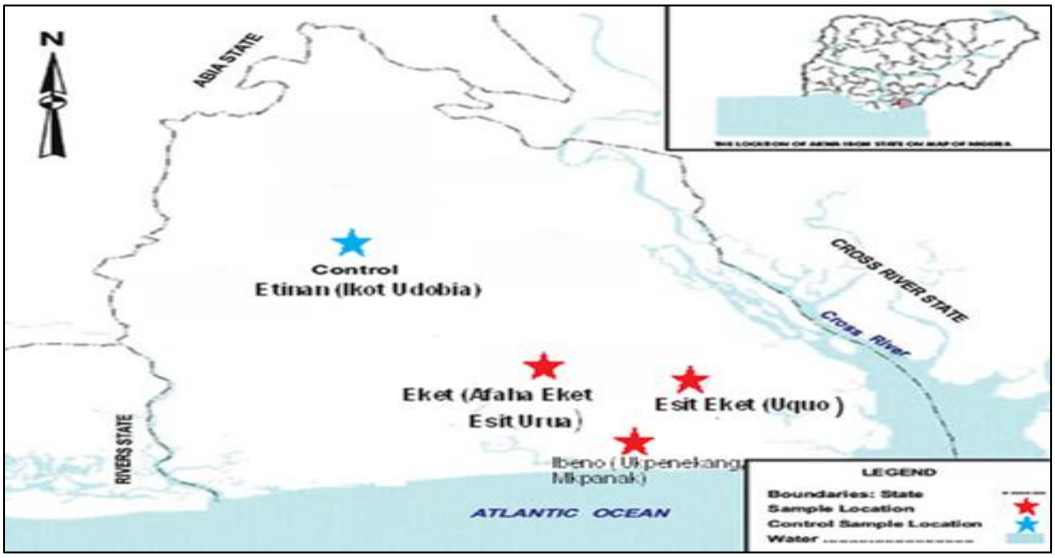


Figure 1: Map of Akwa Ibom State indicating the studied sites and control

2.2 Sample collection and treatment

Surface soil was collected from five (5) locations namely: AfahaEket, Esit Urua, Uquo, Upenekang, and Mkpanak in Akwa Ibom State, Nigeria using soil Augar following the procedures of Schroeder *et al*. (2007). Surface soil was also obtained from an uncontaminated area (lkot Udobia) and used as the control. The collection of samples was performed from January to March, 2017 for the dry season of the study area. A sum fifteen composite samples were obtained for the analysis. The samples were dried under the sun for three days, blended and sieved. The dried samples were digested using a hot plate using a mixture of HCl and HNO_3 in the ratio of 3:1 (*aqua regia*) and the filtrate stored in polyethylene containers for analysis. The background soil (control) was also treated, digested and analysed with the same methods used for the studied samples above.

2.3 Determination of the physicochemical properties of the soil

The pH was determined by mixing the soil with water to form a suspension following the methods of Van-Reeuwijk (1993). Organic matter contents of the soils investigated and the background soil (control) was determined by following the procedures of Walkley and Black (1934). Electrical conductivity was analysed by the use of a conductivity meter following the procedures of Burt (2004).

2.4 Metal speciation and analysis

The modified optimized Community Bureau of Reference (BCR) sequential extraction procedures of Rauret *et al*. (2000) were adopted for the determination of the different geochemical fractions of metals namely: readily available, reducible, oxidizable, and inert fractions. The total concentrations and their fractions were obtained in the mixtures from the aqua regia digestion and sequential extraction procedures by an inductively coupled plasma optical emission spectrometer (Perkin Elmer Optima 5300 DV, USA) following the procedures of Rauret *et al*. (1999).

2.5 Pollution status of the studied soils

2.5.1 Metal pollution index (MPI)

Metal pollution index (MPI) was utilized for the evaluation of the correlation among metals in the oil-bearing soils and the control (Lacatusu, 2000). MPI in this study was evaluated using Equation 1.

$$\text{MPI} = \frac{Concentration\ of\ metal\ in\ the\ studied\ soils}{Concentration\ of\ metal\ in\ the\ control\ site} \quad (1)$$

The different classes of MPI and their consequences in the environment as reported by Lacatusu (2000) are shown in Table 1.

Table1: Classes of pollution index of metals in the studied soils and their effects

MPI	Significance	Remark
<0.1	Very low contamination	No negative impact on the soil, plant and environment
0.1 – 0.25	Low contamination	No harmful impact on the soil, plant and environment
0.26 – 0.50	Modest contamination	No harmful impact on the soil, plant and environment
0.51 – 0.75	High contamination	No harmful impact on soil, plant and environment
0.76 – 1.00	Very high contamination	No harmful impact on the soil, plant and environment
1.10 – 2.00	Low pollution	Will cause harmful impact on the soil, plant and environment
2.10 – 4.00	Moderate pollution	Will cause harmful impact on the soil, plant and environment
4.10 – 8.00	Severe pollution	Will cause harmful impact on the soil, plant and environment
8.10 - 16	Very severe pollution	Will cause harmful impact on the soil, plant and environment
>16	Excessive pollution	Will cause harmful impact on the soil, plant and environment

2.5.2 *Level of site to site contamination (Cdeg)*

The Cdeg for each studied location was computed by the means of Equation 2.

$$\text{Cdeg} = \Sigma\text{MPI} \quad (2)$$

Where ΣMPI = the summation of metal pollution index for the entire metals determined at each location. The different degree of contamination and their environmental implications by Hakanson (1980) are: Cdeg< 8 stands for low degree of contamination; 8 <Cdeg< 16 denotes moderate degree of contamination; 16 <Cdeg< 32 indicates considerable degree of contamination; and 32 <Cdeg is very high degree of contamination.

Ecological risk index was employed for the appraisal of the risks related to the accumulation of metals in the studied locations using Equation 3 as reported by Hakanson (1980).

$$\mathrm{ERF} = \mathrm{Tr} \times \mathrm{MPI} \quad (3)$$

Tr signifies the toxic-response factor of the metals and MPI symbolizes the metal pollution index. The harmful response factors for each of the metals according to Hakanson (1980) are as follows: Cd (30.0), Cr (2.00), Ni (5.00), Pb (5.00), and V (2.00). The numerous classes of ecological risk factor according to Ren *et al*. (2007) are: ERF < 40 = low ecological risk; 40 < ERF≤ 80 signifies the moderate ecological risk; 80 < ERF ≤ 160 = appreciable ecological risk; 160 < ERF ≤ 320 = high ecological risk while; and ERF > 320 = severe ecological risk.

2.5.4 *Potential ecological risk index (RI)*

Potential ecological index was employed to evaluate the impact of trace metals on the different locations investigated. RI was calculated using Equation 4 following the methods of Cao *et al*. (2007).

$$\mathrm{RI} = \Sigma(ERF) \quad (4)$$

Where $\Sigma(ERF)$ stands for the sum of all the metals analysed for at each location. The various categories of potential ecological risk according to Ren *et al*. (2007) are: RI < 150 indicates low ecological risk, 150 < RI < 300 signifies moderate ecological risk, 300 < RI < 600 stands for the high ecological risk, and RI > 600 is significantly high ecological risk.

2.5.5 *Pollution intensity (Ipoll)*

The Ipoll which serves as a technique for the complete assessment of the extent of contamination according to Kowalska *et al*. (2018) was obtained using Equation 5 according to Karbassi *et al*. (2008).

$$\mathrm{Ipoll} = \mathrm{Log2}\ (\mathrm{Bc}/\mathrm{Lp}) \quad (5)$$

Where Bc represents the total concentration while Lp signifies the geogenic portion from results of metal speciation (Karbassi *et al*., 2008). The classes of Ipoll based on Karbassi *et al.* (2008) are as follows: <0-1 stands for unpolluted, 1 - 2 indicates lowly polluted, 2 -3 signifies moderately polluted, 3 - 4 stands for the highly polluted, 4 -5 is strongly polluted, while >5 indicates extremely polluted.

2.5.6 *Pollution load index (PLI)*

The pollution load index was employed for the assessment of the status of soils (Rabee*et al*., 2011). Pollution load index of the soils investigated was computed using Equation 6.

$$\mathrm{PLI} = (\mathrm{MPICd} \times \mathrm{MPICr} \times \mathrm{MPINi} \times \mathrm{MPIPb} \times \mathrm{MPIV})^{1/5} \quad (6)$$

MPI signifies the metal pollution index at each location. The various classes of pollution load index and their related environmental implications as recommended by Tomilson *et al*. (1980) are indicated as: PLI < 1 indicates no pollution, 1 < PLI < 2 signifies moderate pollution, 2 < PLI < 3 stands for heavy pollution and 3 < PLI indicates extremely heavy pollution.

2.5.7 *Assessment of anthropogenic fraction (AF)*

The anthropogenic fraction of the metals represents the proportion of the metal emanated from man-made source; it was obtained by the use of Equation 7 recommended by Ghaderi *et al*. (2012).

$$\mathrm{AF} = \frac{F1+F2+F3}{TM} \mathrm{X}\ 100) \quad (7)$$

Where F1 indicates the readily available fraction, F2 is the fraction bound to oxides and hydroxides of Fe and Mn, F3 signifies the fraction bound to sulphide and organic matter, and TM signifies the overall metal concentrations.

2.5.7 *Determination of lithogenic fraction (LF)*

Lithogenic portion of the metals denotes the proportion of the metals derived from the normal soil forming procedures and was obtained with Equation 8 according to Ghaderi *et al*. (2012).

$$\mathrm{LF} = 100 - \mathrm{AF} \tag{8}$$

AF represents the man-made fraction of the metals within the oil-bearing locations investigated.

2.6 *Determination of percentage recovery of the metals*

The percentage recovered of the metals was calculated by the use of Equation 9.

$$\text{Percentage of recovery} = \frac{\sum \mathrm{n}\ \text{BCR speciation method}}{\text{Digestion with Aqua regia}} \times 100 \tag{9}$$

Where $\sum \mathrm{n}$ BCR extraction method signifies the F1, F2, F3 as well as F4 geochemical fractions of the speciation method, while Digestion using Aqua regia is the total metal concentration of each element.

2.7 *Evaluation of human risk associated with the exposure to the metal*

The daily intake rate (DI), hazard quotient (HQ), and the total hazard index (THI) of the metals in the studied soils as related to human health were assessed following the methods by USEPA (2000).

2.7.1 *Daily intake rate (DI)*

The day by day intake rate of metals through the exposure to soil particles in the locations investigated was estimated with Equation 10 according to the methods of USEPA (2011).

$$\mathrm{DI} = \frac{C \times \mathrm{IngR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{10}$$

In the above equation, C = the concentration of the metal; IngR = the rate of soil ingestion rate by both the children and adult populations; EF shows exposure rate for each day per year, ED = the duration of contact for twelve months; BW = mass of the body expressed as kg while AT = the mean period for the non-carcinogenic risks (Grzetic and Ghariani, 2008and USEPA, 2010). The numerical rates of all the parameters in Equation 10 are indicated in Table 2.

2.7.2 Hazard *index (HQ)*

The non-carcinogenic hazard otherwise called hazard index of the metals was calculated using Equation 11 as recommended by USEPA (2011).

$$\mathrm{HQ} = \frac{\mathrm{DI}}{\mathrm{Rfd}} \tag{11}$$

Where the DI represents daily intake rate of the metals while, Rfd symbolizes the recommended reference dose of the metals (Table 2).

2.7.3 *Total hazard index (THI)*

The total hazard index of the metals in the oil-bearing soils with regards to human health was computed using Equation 12 as proposed by USEPA (2011).

$$\mathrm{THI} = \Sigma \mathrm{HQ} = \mathrm{HQCd} + \mathrm{HQCr} + \mathrm{HQNi} + \mathrm{HQPb} + \mathrm{HQV} \quad (12)$$

Where ΣHQ indicates the summary of all the hazard quotients (HQ) of the metals analysed for in the studied soils.

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
1	Body weight (kg)	Child (15), Adult (70)	USEPA (2000) and (2011)
2	Ingestion rate (mg/day)	Child (100), Adult (50)	Grzetic and Ghariani (2008) USEPA (2011)
3	Exposure frequency (day/yr)	350	Wang *et al*. (2012)
4	Exposure period (yr)	Child (6), Adult (30)	Grzetic and Ghariani (2008)
5	Average time for non-carcinogens (day/yr)	365	USEPA (2000)
6	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)

2.8 *Statistical analysis*

The statistical analysis of results obtained was performed using IBM SPSS Statistics 20 (IBM USA) model. Principal component analyses were done with Varimax Factor analysis on nine (9) parameters and numerical values starting from 0.419 and beyond were regarded as important. Hierarchical Cluster study was performed with Dendrograms to recognize the parameters with common properties and source.

3.1 Results and Discussion

3.1 Physicochemical properties of the oil-bearing soils and control

The results of the physicochemical constituents' of the oil-bearing soils and control site are shown in Table 3. The pH of the oil-bearing soils varied from5.76 to 6.25 with average value of 5.99±0.22. The range is below 5.65 – 6.92 reported in oil-impacted soils by Nnaji and Egwu (2020). The pH of the oil-bearing soils was more acidic and lower than the pH of the control soil (Table 3). This agrees with the result obtained by Chukwuemeka *et al*. (2017) as well as Nwaogu and Onyeze (2010) in oil-impacted soils. The acidic nature of the oil-impacted soils could alter the normal metabolic activities in the soil and make toxic metals readily available (Li *et al*., 2022; Olaniran *et al*., 2013).

The range and mean value of organic matter (OM) contents of the oil-bearing soils are 5.78 - 7.56% and 6.33±0.70%, respectively. This range is higher than 4.14 – 4.63% reported by Chukwuemeka *et al*. (2017) within the oil-bearing soils. The OM contents of the studied soils were high above those of the background soil (control) (Table 3). The result reported is similar to that obtained by Ezeigbo *et al*. (2013) in oil-impacted soils. This could be related to the metabolic processes associated with crude oil that aids in addition of organic carbon from the hydrocarbon to the oil-impacted soils (Osuji and Onojake, 2006).

The values of electrical conductivity (EC) reported for the studied soils ranged between 1.97 and 2.62μS/cm with an average value of 2.34 ± 0.26 μS/cm. The obtained EC range is lower than 2.45 - 10.60 μS/cm reported in oil-contaminated soils by Onwuka *et al*. (2021). The EC values recorded for the studied soils were greater than those obtained at the background soil (Table 3). This is similar to the findings by Onojake and Osuji (2012) and Osuji *et al*. (2006) in oil-contaminated soils. The higher EC values of the studied soils can be related to the elevated crude oil salts in the studied soils due to anthropogenic activities (Zahermand *et al*., 2020).

Table 3: Physicochemical properties and total metal concentrations within oil-bearing locations and control

	pH	OM	EC	CEC	Cd	Cr	Ni	Pb	V	V/Ni
S1	5.84	6.16	2.42	5.73	3.54	1.51	2.22	16.62	1.74	0.78
S2	6.20	5.78	2.50	5.67	3.58	1.50	2.16	14.90	1.75	0.81
S3	5.76	7.56	1.97	4.96	3.41	1.41	2.11	16.74	1.72	0.82
S4	6.25	6.12	2.621	6.37	3.23	1.46	1.98	15.51	1.74	0.88
S5	5.90	6.05	2.18	6.34	2.88	1.48	1.93	15.95	1.66	0.86
Min	5.76	5.78	1.97	5.67	2.88	1.41	1.93	14.90	1.66	0.78
Max	6.25	7.56	2.62	6.37	3.58	1.51	2.22	16.74	1.75	0.88
Mean	5.99	6.33	2.34	5.81	3.33	1.47	2.08	15.94	1.72	0.83
SD	0.22	0.70	0.26	0.58	0.29	0.04	0.12	0.77	0.04	0.04
CV	3.7	11.0	11.1	3.1	8.7	2.7	5.8	4.8	2.3	4.8
Con.	6.94	4.26	0.647	8.66	1.06	0.85	1.76	2.31	0.69	0.12

S1 = AfahaEket; Site S2 = EsitUrua; Site S3 = Uquo; Site S4 = Upenekang; Site S5 = Mkpanak Min = Minimum; Max is Maximum; SD denotes Standard deviation; CV signifies Coefficient of variation; Con. = Control (lkotUdobia).

Cation exchange capacity (CEC) of the oil-bearing soils varied from 5.67 to 6.37cmolkg^{-1} with an average value of 5.81±0.58 cmolkg^{-1}. The CEC range obtained in this study is lower than 12.56 – 16.73 cmolkg^{-1} obtained in oil-impacted soils by Zahermand *et al.* (2020). Table 3 indicates that, the CEC values for the oil-bearings soils are lower than the value obtained in the control soil. This is similar to the results obtained by Nnaji and Egwu (2020). This could be accredited to the higher pH level of the control soil as the CEC of the soil is directly related to the pH (Domingues *et al.*, 2020; Martinsen *et al.*, 2015). Consequently, the intensive human activities within the studied areas may have resulted in the low CEC levels recorded and may affect the metabolic processes in the soil environment (Ebulue *et al.*, 2017).

Consequently, this study has shown that, crude oil availability in soil can influence the quality of the host soil environment. The low coefficient of variation (CV) recorded for the soil properties reveals low spatiotemporal variability exhibited by these properties Su *et al*. (2018).

3.2 *Total metals in the oil-bearing soils*

Table 3 shows the results for the total metals in the oil-bearing soils. Cadmium (Cd) varied between 2.88 and 3.58 mgkg^{-1} with a mean value of 3.33±0.29 in the studied soils. The range is higher than 1.82 – 2.87 mgkg^{-1} reported by Radulescu *et al*. (2012). Total chromium (Cr) indicated a range and average values of 1.41 – 1.51 mgkg^{-1} and 1.47±0.04 mgkg^{-1}, respectively. The range obtained is below 4.02 – 29.19 mgkg^{-1} reported by Ahiamadu *et al*. (2021). Total nickel (Ni) in the studied soils varied between 1.93 and 2.22 mgkg^{-1} with a mean value of 2.08±0.12 mgkg^{-1}. This is below the 0.15 – 1.65mgkg^{-1} reported in oil-contaminated soils reported by Osuji and Adesiyan (2005). Lead (Pb) in the oil-bearing soils varied between 4.90 and 16.74mgkg^{-1} with an average of 15.94±0.77 mgkg^{-1}. This range is higher than 0.22 – 9.79 mgkg^{-1} obtained by Onwuka *et al*. (2021). Total vanadium (V) varied between 1.66 - 1.75 mgkg^{-1} with an average of 1.72±0.04 mgkg^{-1}. The recorded range is lower than 2.699–7.708 mgkg^{-1} reported by Mohammed *et al*. (2022) in oil-impacted soils.

The average concentrations of the entire metals within the oil-bearing locations were higher than their values in the background soil. The obtained results are consistent with the findings by Adesina and Adelasoye (2014) and Eze *et al*. (2022) in their studies. This could be attributed to the oil existence, oil-related activities, and low pH in the studied soils (Wei *et al*., 2020).

Levels of Cr, Ni, as well as Pb were within their recommended limits of 100.00 mgkg^{-1}, 35.00 mgkg^{-1}, and 85.00mgkg^{-1}, respectively for unpolluted soil in Nigeria soil according to FEPA (1999). Total V is within the regulatory limit of 129.00mgkg^{-1} by Kabata-Pendia (2011). However, total Cd is above the stipulated 0.80 mgkg^{-1} (FEPA, 1999). Consequently, Cr, Ni, Pb, and V may not pose serious threat but, Cd could be a potential threat to the environment. Nevertheless, the average values of Cd, Cr, Ni, as well as Pb exceed 0.003, 0.10, 0.05, and 0.10mgkg^{-1}recommended by World health organization for agricultural soil (Kinuthia *et al*., 2020; Sallau *et al*., 2017). Accordingly, crude oil availability in soil may render the host environment unsuitable for agricultural purposes. The low CV values recorded for the metals in Table 3 indicate the low degree of variability exhibited by these metals.

3.3 *Vanadium-nickel ratio in the studied oil-bearing soils*

The vanadium-nickel ratio was used as an indicator for oil pollution and the source of crude oil within the studied soils (Barwise, 1990; Mirza *et al*., 2013; Oluwole et *al*., 1993). The V/Ni ratio ranged from 0.78 in Afaha Eket and 0.88 at Upenekang (Table 3). The range is lower than 0.66 - 1.24 obtained by Branga *et al*. (2019) in oil-impacted sites. This range of V/Ni ratio reveals that, crude oil in the studied soils originated from organic matter and it belongs to the light crude oil residue (Barwise, 1990; Ogunlaja *et al*., 2014). The low V/Ni ratio recorded within the control site signifies that, the studied locations belong to the oil-forming continent. The low coefficient of variation recorded for V/Ni ratios in this study depicts the common source of crude oil (Lu *et al*., 2010).

3.4 *Speciation of metals in the oil-bearing and the background soils*

The results speciation of trace metals in Table 4 indicate that Cd occurred mostly in the acid extractable (Aex) fraction within the oil-bearing soils and Control. The result is consistent with that obtained by Nimyel and Chundusu (2021) in contaminated soils. However, a higher proportion of Cd existed in the Aex fraction in the oil-bearing soils than in the background soil. This might be caused by the existence of crude oil and the associated anthropogenic activities in the oil-bearing soils. Cr occurred mainly in the Aex fraction within the oil-bearing soils as reported by Katana *et al*. (2013). However, the metal existed principally in the residual fraction in the control site as reported by Adebiyi and Ayeni (2021).Ni existed predominantly in the reducible (Red) fraction within the oil-bearing soils as previously reported by Wali *et al*. (2015). Conversely, in the control site the greatest proportion of Ni was found in the inert fraction as obtained by Asmoay *et al*. (2019). Pb occurred mostly as oxides and hydroxides of Fe and Mn (reducible fraction) in the oil-bearing soils. This is in agreement with the findings by Andreas and Zhang (2016). But, Pb existed mainly in the inert phase within the Control as reported by Asmoay *et al*. (2019). V existed primarily as the reducible fraction in the oil-bearing soils which is consistent with the result of Agnieszka and Barbara (2012). On the contrary, V occurred mostly in the residual fraction in the background soil (control) similar to the reported of Shi *et al*. (2010). Consequently, the existence of crude in the oil-bearing soils might have impacted on the geochemical fraction of the metals. The high percentage of recovery reported indicates high degree of accuracy and consistency of the results achieved

3.5 *Manmade and natural fractions of trace metals*

Table 4 indicates the values for the anthropogenic and lithogenic parts of the metals in the studied soils and Control. Anthropogenic factor contributed greater proportions of the metals in the oil-bearing soils than in the background soil (control). This finding agrees with that of Ghaderi *et al*. (2012) in contaminated soils. Nonetheless, higher percentages of the metals in the control site originated from the natural source (Table 4). This is in conformity with the result obtained by Meena *et al*. (2011). This confirms that, the existence of crude oil and the related anthropogenic activities in the oil-bearing locations might have added considerable quantity of metals to the environment.

Table 4: Fractions, total metal, percentage composition, percentage recovery, anthropogenic as well as lithogenic factors of metals

	Aex	Red	Ox	Res	TF	TM	% REC	AF	LF
					Studied Soils				
Cd	7.12	3.78	2.75	2.03	15.68	16.64	94.0	82	18
Cr	3.16	1.63	1.29	0.75	6.83	7.36	93.0	83	17
Ni	2.35	4.72	1.43	1.16	9.66	10.40	93.0	82	18
Pb	18.05	33.60	12.20	8.24	72.09	79.72	90.0	80	20
V	1.47	3.36	2.03	0.81	7.67	8.61	89.0	80	20
					Control				
Cd	0.31	0.19	0.13	0.28	0.95	1.06	86.0	59	41
Cr	0.04	0.06	0.11	0.56	0.77	0.85	91.0	27	73
Ni	0.19	0.25	0.28	0.89	1.61	1.76	92.0	41	59
Pb	0.27	0.36	0.23	1.34	2.20	2.31	95.0	37	63
V	0.06	0.08	0.10	0.38	0.62	0.69	90.0	35	65

Aex denotes Acid extractable; Red depicts the Reducible; Ox is the Oxidisable; Res indicates Residual; TF = Total fraction, TM = Total metal, %REC signifies the percentage recovery, AF = Anthropogenic factor; LF = Lithogenic factor.

3.6 *Pollution status of the studied soils*

Results for the metal pollution index (MPI) of trace metals in oil-bearing soils are indicated in Table 5. The values in Table 5 show an average MPI value for Cd as 3.14. Cr and Ni had mean MPI values of 1.73 and 1.18, respectively. The mean MPI value recorded for Pb is 6.90 while, 2.50 was reported as the mean MPI value for V. Accordingly, Cd and V belong to the moderate pollution class. Cr and Ni are in the slight pollution category while, Pb belongs to the severe pollution class (Lacatusu, 2000). Consequently, all the metals will pose negative effect on the studied soils, available plants, and the environment. Hence, the existence of crude oil and the associated anthropogenic activities have elevated the metals from the contamination to pollution status within the studied soils.

The ecological risk factors (ERF) in Table 5 indicate that, Cd range between 81.6 and 101.4. The ERF values for other metals varied as follows: 3.32 – 3.56, 5.50 – 6.30, 32.3 – 36.0, and 4.82 – 5.08 for Cr, Ni, Pb, and V, respectively. Thus, based on the Ren *et al*. (2007) classifications, Cd belong to the appreciable environmental risk class, whereas other metals belong to the low environmental risk group. This confirms that, those exposed to soil particles from the oil-bearing soils could be vulnerable to elevated Cd level and the related health risks.

Results of the pollution index (Ipoll) of trace metals within the oil-bearing soils are indicated in Table 5. The mean Ipoll values for the metals obtained in the oil-bearing soils are as follows: 3.04, 3.29, 3.17, 3.28, and 3.41 for Cd, Cr, Ni, Pb, as well as V, correspondingly. The Highest average Ipoll value was recorded for V while the lowest was Cd. Nevertheless, all the metals belong to the highly polluted class according to the Karbassi *et al.* (2008) classifications. Consequently, considerable quantity of these metals may have been released to the studied soils via crude oil-related activities within the area.

Table 5: Metal pollution index (MPI), ecological risk index (E^i_r) and pollution intensity of metals in the oil-bearing soils

		Cd	Cr	Ni	Pb	V
MPI	Min	2.72	1.66	1.10	6.45	2.41
	Max	3.38	1.78	1.26	7.25	2.54
	Mean	3.14	1.73	1.18	6.90	2.50
E_r^i	Min	81.6	3.32	5.50	32.3	4.82
	Max	101.4	3.56	6.30	36.0	5.08
	Mean	94.3	3.50	5.92	34.6	4.99
Ipoll	Mean	3.04	3.29	3.17	3.28	3.41

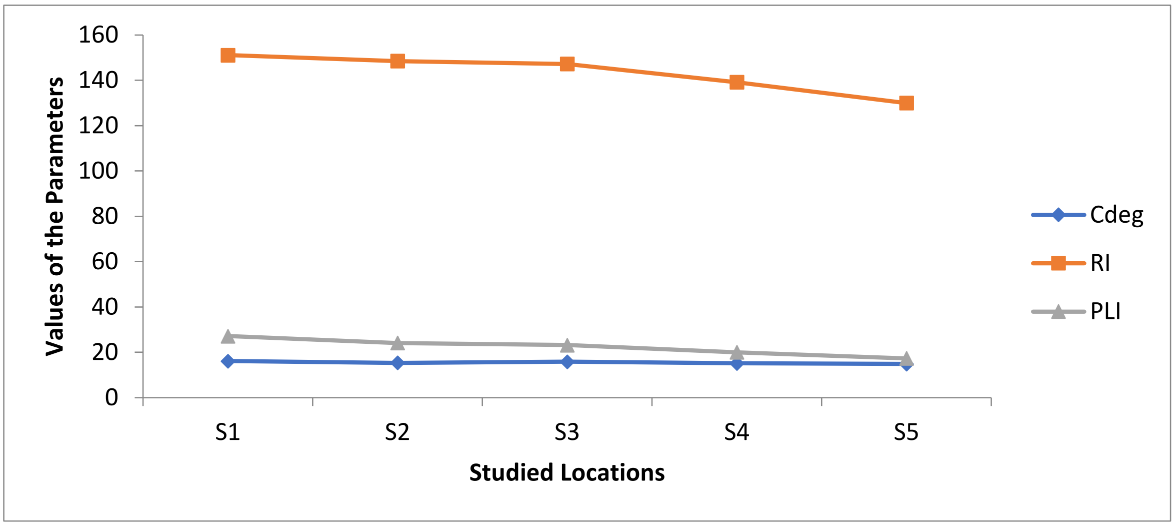


Figure 2: Values of degree of contamination (C_{deg}), potential ecological risk index (RI), and pollution load index (PLI).

The degrees of contamination (Cdeg) of the locations are illustrated in Figure 2. The values for the Cdeg of the studied oil-bearing soils varied from 14.88 in Mkpanak to 16.10 in Afaha Eket. The mean Cdeg values for other locations are as follows: 15.37, 15.82, and 15.13 for EsitUrua, Uquo, and Upenekang, respectively. This shows that apart from Afaha Eket that is in the substantial degree of contamination, all the other locations belong to the moderate degree of contamination (Hakanson, 1980).

The potential ecological hazard indices (RI) in Figure 2 varied between 130.0 in Mkpanak and 151.1 in Afaha Eket. This shows that the potential ecological risk index of Afaha Eket belongs to the reasonable ecological risk class (Ren*et al*., 2007). The other studied locations belong to the low ecological risk category. Hence, the level of soil pollution at Afaha Eket calls for concern as high RI values of metals correlate directly with the health of human (Mugosa *et al*., 2016).

Pollution load index (PLI) of trace metals within the oil-bearing soils are illustrated in Figure 2. The results of the PLI values varied from 17.34 in Mkpanak to 27.18 in Afaha Eket. The PLI values for other locations are 24.11, 23.16, and 20.05 for Esit Urua, Uquo, and Upenekang, respectively. Thus, the entire studied locations belong to the extremely heavy pollution class (Tomilson *et al*., 1980). The results of PLI corroborate the findings from metal pollution index and pollution intensity of metals in soils investigated. The pollution status of the studied soils has confirmed that, metals are natural constituents of crude oil. Hence, crude oil in addition to the associated human activities are the main causes of soil contamination/pollution within the areas studied (Chinedu and Chukwuemeka, 2018; Osuji and Onojake, 2004).

3.7 *Multivariate analysis*

3.7.1 *Principal component analysis (PCA) of the soil properties*

This study employed PCA and Hierarchical cluster analysis for the detection of the factors responsible for the parameters determined in the studied soils and their relationships (Kahangwa, 2022; Wu and Kuo, 2012). Results of PCA analysis in Table 6 reveals three (3) key factors that are responsible for the parameters determined. These factors have Eigen values higher than one and 95.5% total variance. The first factor (PC1) contributed 47.9% to the entire variance with significant positive correlations between pH, EC, CEC, as well as Cr although, with significant negative loadings on OM in addition to Pb. This represents the artificial and natural factors on the status of the soils (Chibuike and Obiora, 2014). The second factor (PC2) added 35.0% to the whole variance with strong positive correlations between Cd, Ni, and V however, with significant negative loading on CEC. This signifies unambiguously the effects of anthropogenic factor over the quality of the soils investigated according to Ebong *et al*. (2020) along with Olabanji *et al*. (2015). Factor three (PC3) donated 12.6% to the whole variance with significant positive loading on Cr and significant negative loading on pH. This signifies the effects of industrial activities on the quality of the soils examined (ATSDR, 2000; Lin *et al.*, 2010; Saha *et al*., 2011).

3.7.2 *Hierarchical cluster analysis (HCA) of parameters*

The general associations existing between the parameters determined in the studied oil-bearing soils are illustrated in Figure 3. The Figure shows three (3) major clusters namely: (i) Cluster one joining Cr, V, EC, Ni, and Cd together. (ii) Cluster two correlates pH, CEC, and OM. Cluster three shows a linkage to Pb only. This also reveals the source of these parameters in the studied soils as indicated by the principal component analysis.

Table 6: Result of principal component analysis demonstrating comparative loading for metals and other properties of the soil investigated

Variable	PC1	PC2	PC3
pH	0.876	0.055	-0.479
OM	-0.930	0.089	-0.341
EC	0.917	0.255	-0.065
CEC	0.732	-0.614	0.129
Cd	0.001	0.999	-0.022
Cr	0.704	0.179	0.682
Ni	-0.136	0.935	0.320
Pb	-0.837	0.010	0.343
V	0.290	0.889	-0.282
% Total Variance	47.9	35.0	12.6
Cumulative %			95.5%
Eigen value	4.3	4.2	1.1

PC: Principal component

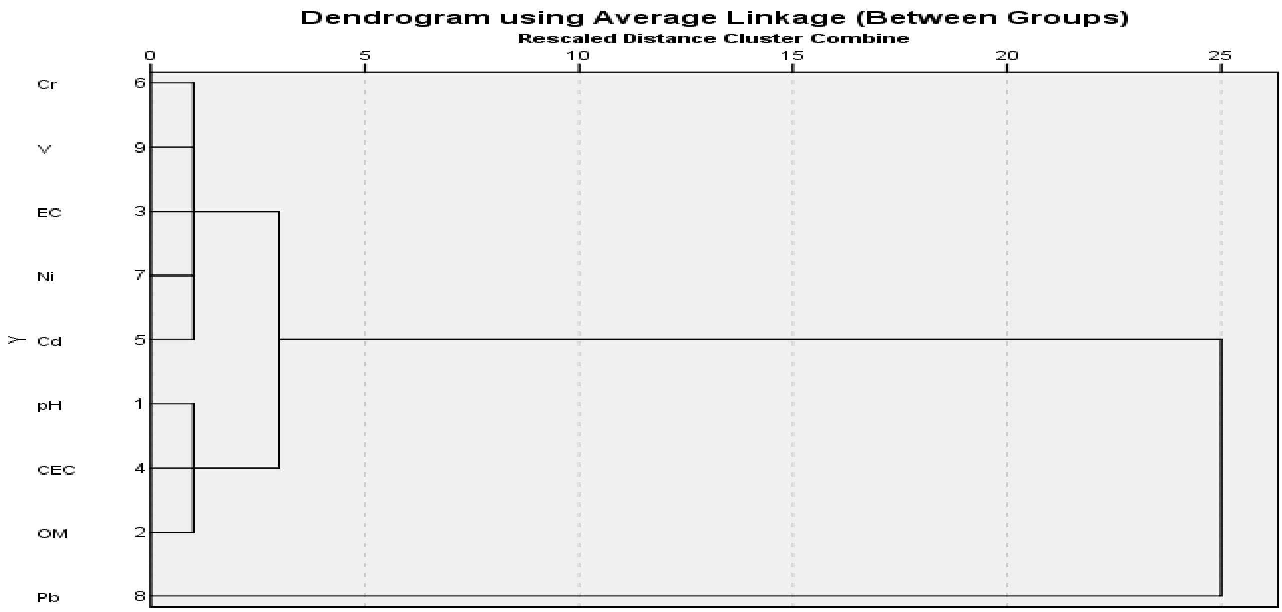


Figure 3: Hierarchical clusters for the soil properties in the oil-bearing locations.

3.8 *Results for health risk appraisal*

3.8.1 *Daily intake rate*

The day by day intake rate of metals through the exposure to the studied soils by both the young and old populations are indicated in Table 6. The daily intake rate of all the metals apart from Pb in children was within their proposed oral reference dose (Rfds) by USEPA (2010). Thus, the children population exposed to soil from the locations investigated is susceptible to Pb toxicity and the related health implications as reported by USEPA (2004). The elevated daily intake rate of Pb in the children population reported is compatible with the reports by Song *et al*. (2015). The overall results for the day by day ingestion rate of the metals for both the young and adult populations followed the sequence: Pb> Cd > Ni > V > Cr. Hence, the day by day ingestion rate of Cr was the lowest but it should not be overlooked as it may bio-accumulate and result in health consequences reported by ATSDR (2000).

3.8.2 *Hazard quotient (HQ)*

The non-cancer risk otherwise known as hazard quotient (HQ) of the metals for both children and adult populations are shown in Table 6. The average HQ value for each of the metals was less than one (1). Accordingly, the metals determined might not cause severe health problems to those in contact with them irrespective of the source. The highest mean HQ value for both the children and adult populations was recorded for Pb. This is in agreement with the findings by Etuk *et al*. (2022) in contaminated soil environment. The outcome of the research as well revealed that, the younger ones were more vulnerable to the Pb toxicity and the attendants' human health problems. Although the THI is less than one, the children and adult populations could still be exposed to non-carcinogenic problems which has direct implications as the values of THI (Man *et al*., 2010). The average HQ values of the metals for both populations varied as follows: Pb> Cd > V > Ni >Cr.

3.8.3 *Total hazard index (THI)*

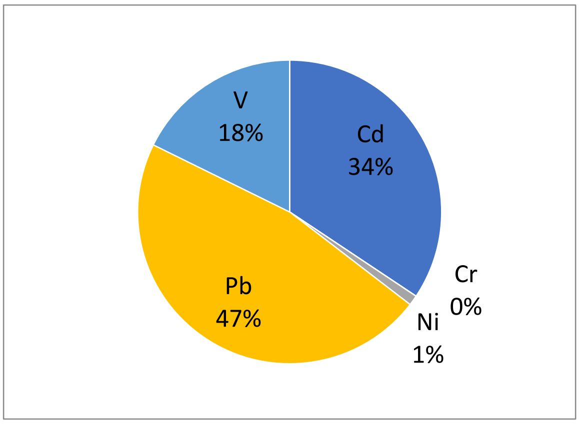
The overall chronic hazard index (THI) of oral contact to metals through exposure to soil particles at the locations investigated by the children and adult populations are indicated in Table 6. The values of THI for the metals varied as follows: 7.20E-5 - 3.66E-1 and 3.87E-5 - 1.97E-1 for the children and adult populations, respectively. Thus, the values of THI recorded for the children were greater than those reported for the elderly. Accordingly, the children population was more susceptible to health issues associated with the exposure to high levels of these metals than the adult. This is consistent with the results of Singh *et al*. (2010) in a similar study. The results obtained also revealed that, Pb contributed 47% to the THI for both the children and adult populations. Accordingly, Cd, Cr, Ni, as well as V added a sum of 53% towards the THI in both populations.

3.9 Policy implications and future work

This study has shown the effects of crude oil existence within the soil, the environmental and human health problems related to the discovery and exploitation processes. Thus, standard rules and regulations should be strictly adhered to by oil companies and their workers to preserve the environment and human beings. Standard and recommended methods used for the management of wastes should be implemented for the treatment of waste materials generated. Future studies in a similar environment should be extended to embrace other techniques as well as models related to the environment not employed here. Soil parameters not included here should be captured in future work. Edible plants, aquatic ecosystem and living organisms should be closely monitored to identify and established the negative impacts of crude oil availability and related activities on these media.

Table 6: Daily intake rate and non-carcinogenic risks of trace metal in the studied soils.

		DI		HQ	
Metal	Outline	Child	Adult	Child	Adult
	Min	2.21E-4	1.18E-4	2.21E-1	1.18E-1
Cd	Max	2.75E-4	1.47E-4	2.75E-1	1.47E-1
	Mean	2.56E-4	1.37E-4	2.56E-1	1.37E-1
Cr	Min	1.08E-4	5.80E-5	7.20E-5	3.87E-5
	Max	1.16E-4	6.21E-5	7.73E-5	4.14E-5
	Mean	1.13E-4	6.05E-5	7.53E-5	4.05E-5
Ni	Min	1.48E-4	7.93E-5	7.40E-3	3.97E-3
	Max	1.70E-4	9.12E-5	8.50E-3	4.56E-3
	Mean	1.60E-4	8.55E-5	7.98E-3	4.28E-3
	Min	1.14E-3	6.12E-4	3.26E-1	1.75E-1
Pb	Max	1.28E-3	6.88E-4	3.66E-1	1.97E-1
	Mean	1.22E-3	6.55E-4	3.49E-1	1.87E-1
	Min	1.27E-4	6.82E-5	1.27E-1	6.82E-2
V	Max	1.34E-4	7.19E-5	1.34E-1	7.19E-2
	Mean	1.32E-4	7.08E-5	1.32E-1	7.08E-2
THI (Children)	7.20E-5 - 3.66E-1				
THI (Adult)	3.87E-5 - 1.97E-1				



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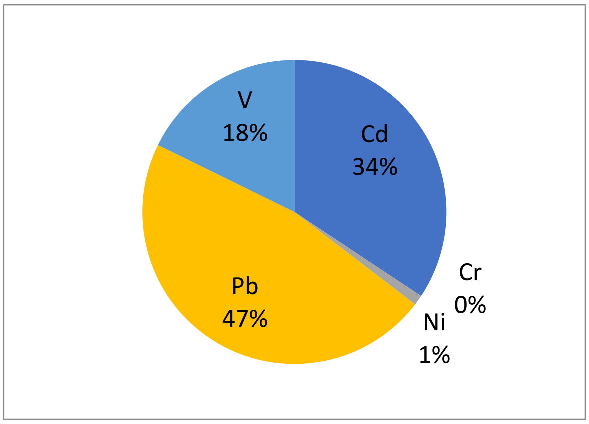

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Figure 4: Mean hazard index for the children (A) and Adult (B) populations.

4. Conclusion

The outcome of this research has revealed the pollution status of the oil-bearing soils in Akwa Ibom State and the human health associated with exposure to soil particles from these locations. The crude oil-related activities have been identified as one of the major sources of soil contaminants to the areas investigated. The study has also indicated that, the availability of crude oil in soil has the potential to influence the total concentrations of the metals and their geochemical fractions. The anthropogenic factors of the metals in the oil-bearing soils were relatively higher than values obtained in the control site. The entire locations studied were highly contaminated with trace metals based on the outcome of pollution studies conducted. The health risk evaluation has indicated at, both the children and adult populations in the studied locations are being exposed to Pb toxicity however; the children are more susceptible.

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