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Assessment of Heavy Metals in Soil around Leaking Underground Petroleum Facilities in Rivers State

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Abstract: *The concentrations of Pb, Cd, Ni, Cr, V and Fe in soil around leaking underground petroleum facilities were studied. The facilities are located in Idu community, near Port Harcourt, Rivers State, Nigeria. Sampling of soils was done at two depths (0 – 15 cm and 15 – 30 cm) quarterly (January, April, July and October) at ten (10) stations and one control point, established at 1.5 km from the sampling stations. AAS was used to analyze the heavy metals concentrations in soils. The results obtained showed that Pb was relatively high, Cr and Ni were very low, Cd and V were not detected while Fe was generally very high. The concentrations (mg/kg) recorded were Pb (1.08, 1.10, 0.73, 0.72 and 1.04, 1.14, 0.66, 0.66), Ni (0.02, 0.014, 0.02, 0.01 and 0.01, 0.00, 0.02, 0.01), Cr (0.01, and 0.00), Fe (1568.78, 1697.49, 2101.59, 2087.59, and 1509.03, 1572.69, 1849.77, 1893.81) in surface and subsurface soils in Q1, Q2, Q3 and Q4 respectively. The degree of heavy metals contamination of soil across the studied stations was in this order: SS 7 > SS 10 > SS 6 > SS 8 > SS 9 > SS 2 > SS 1 > SS 5 > SS 3 > SS 4. Pb is the major contributor to heavy metals contamination of soil in the area.*

Keywords: *Leaking Crude Oil Pipelines, Contamination, Pollution, Heavy Metals, Soils.*

I. Introduction

Storage and transportation of petroleum products in tanks and pipelines buried underground is an age-long practice. According to Australian Standard [1], underground storage tanks and pipes are those systems where the storage tank or pipe is either totally or partially installed below ground level. Nnah and Owei [2], noted that petroleum pipelines are essential modes of transportation and are infrastructures of highly specialized nature. It has been shown that oil and gas pipeline networks are the most economical and safest means of transporting crude oils and they fulfill a high demand for efficiency and reliability [3][4][5]. For example, the estimated deaths due to accidents per ton-mile of shipped petroleum products are 87%, 4% and 2.7% higher using truck, ship and rail respectively, compared to using pipelines [3][6]. However, Ogwu [7], argued that unlike other modes of transportation such as roads, pipelines do not improve access for people in communities through which they pass, rather they impose constraints on interactions and when located close to houses as observed in Nigeria, are potential hazards to life. Jia *et al* [8], in alignment, posited that transporting hazardous substances through miles-long using pipelines although has become popular across the globe in recent decades, the chances of critical accidents and contamination of the environment (from crude oil spills) due to pipeline failures have increased.

The causes of pipelines failures are either intentional (like vandalism or sabotage) or unintentional (like device/material failure and corrosion) damages [3][9][10]. Kadafa [11], attributed other causes of oil spill to leaking pipelines resulting from corrosion and old age as well as substandard equipment used by oil and gas industry operators. Odilinye [12], opined that equipment failure (from wellhead blow out, valves and flanges failure) and pipeline corrosion either through chemical or biological agent could cause oil spill in the environment. Ogwu [7], maintained that oil spills are due to failed pipelines which subsequently leak into the soil, rendering it unusable for agricultural and other purposes. Omofonwa and Odia [13], noted that aged and corroding pipeline is very common in many oil exploration fields in the Niger Delta region of Nigeria. The average life span of oil pipeline is between 20 and 30 years. However, Adebayo [14], noted that some pipelines in the Nigerian oil fields are over 30 years old. Most of the pipelines run across rivers, creeks, swamps and farmland in the Niger Delta, an environment that is wetland fragile, and highly sensitive to stress [7][15]. For example, the Shell Petroleum Development Company's 95 km trunk line runs from Nembe Creek field to Cawthorne Channel field passing through thirty five communities and transverse sixty rivers and creeks of various sizes along its route [7]. Achebe *et al* [16], maintained that the old age of the pipelines in Nigeria makes them prone to failures. Failed pipelines leak products such as naphthenic hydrocarbons, dye additives, antioxidants, alkanes, alkenes, alkynes, heavy metals, etc into the environment resulting in contamination and pollution.

Globally, heavy metals contamination of different matrices of the environment has been reported by many researchers. In Tehran, Iran, for example, a study on pollution and distribution of heavy metals in soils of South Pars Special Economic Zone using two indices of enrichment factor and geoaccumulation, showed that heavy metals pollution close to the industrial area had higher concentrations of cadmium, nickel and lead [17]. Afkhami *et al* [18], assessed heavy metals concentrations in soil around oil field in Persian Gulf, Western Asia, and reported higher concentrations of Arsenic, Cadmium and Vanadium. The higher values obtained in the study were attributed to the oil and gas activities in the area and the geological structures at different depths. Karbassi *et al* [19], studied the concentrations of lead (Pb), Vanadium (V), Zinc (Zn), Cadmium (Cd), Nickel (Ni), Copper (Cu), Cobalt (Co) and Molybdenum (Mo) in soils along oil pipelines in Iran, using Muller's geoaccumulation index to determine the degree of pollution. The results obtained ranged from 130 – 809 mg/kg, 14 – 82 mg, 68 – 552 mg/kg, 0.01 – 1.02 mg/kg, 19 – 97 mg/kg, 75 – 1378 mg/kg, 0.87 – 4.8 mg/kg and 50 – 574 mg/kg for V, Pb, Ni, Cd, Co, Zn, Mo and Cu respectively. Peng *et al* [20], carried out an assessment of ecological and human health risks of heavy metals (Cr, Cd, Cu, Ni, Pb and Zn) contamination of soils by pipeline construction in China, using Index of Geo-accumulation (*Igeo*) and Potential Ecological Risk Index (RI) values and human health risk to elucidate the level and spatial variation of heavy metal pollution risks. The results showed that the impact zone of pipeline installation on soil heavy metal contamination was restricted to pipeline right-of-way (RoW), which had higher *Igeo* of Cd, Cu, Ni and Pb than the samples collected at distances of 20 m and 50 m away from the pipelines. In another study, Qaiser *et al* [21], assessed the concentrations of heavy metals in drilling waste discharges of different oil and gas wells at Khyber Pakhtunkhwa, Pakistan. The representative soil samples were collected from seven oil and gas drilling waste discharges and the surrounding. The samples collected were analyzed for Ba, Pb Cr, Cd, Zn, Mn, and Ni by Atomic Absorption Spectrometry. The results showed that oil and gas well drilling operation waste is enriched with determined heavy metals. The high concentration of heavy metals, particularly Ba and Pb recorded in the study was found in the surrounding soil samples indicating anthropogenic influence. In particular, Ba concentration varied from 1050 to 4168 mg/kg with mean of 2077.43 mg/kg while Pb concentrations ranged from 720 to 1912 mg/kg with mean of 1015.76 mg/kg. Statistical correlation analysis depicted a common origin of the heavy metals in the soil.

Nwankwoala and Ememu [22], assessed the anthropogenic influences on soil quality around filling stations in Okpoko, Anambra State, Nigeria, using Contamination Index (CI), Pollution Load Index (PLI), modified Contamination Degree (mCD), geo-accumulation Index (Igeo) and Nemerow Integrated Pollution Index (NIPI) models. The results showed that the soils are heavily polluted from the activities at the various fuel filling and service stations in the area which included pollution arising from gasoline combustion exhausts, lubricating oil spills, and other chemical inputs to automobile operations. The anthropogenic percentage contribution of each metal are in the order; Cd > Pb > Zn > Cu > Fe > Ni > Mn. Cadmium, lead, zinc and copper are the major contributors to soil pollution in the area, and are usually associated with activities done at fuel filling and service stations and mechanic workshops. Radulescu *et al* [23], studied the concentrations of heavy metals including Pb, Cd, Cr, Cu and Zn in crude oil contaminated soil samples collected from five oil extraction parks of Dambovita County, Romania. The samples were collected in November 2011, at two depths (0-5 cm and 30 cm) and were analyzed by Energy Dispersive X-ray Fluorescence (EDXRF) technique. They found out that the concentrations of Pb, Cd, Cu, Cr and Zn in the contaminated soil samples exceeded the values specified in Romanian legislation. They noted that the risk associated with the presence of metals in soil depends on their ability to infiltrate the groundwater or taken up by plants. It was concluded that heavy metals can cause pollution of soil with dangerous implication on the environment and health. Hence, they recommended routine monitoring of soil around oil and gas facilities for heavy metals and other contaminants to prevent harm to the biophysical and health environments. Although a handful of heavy metals including zinc, iron, copper, boron, manganese, cobalt, etc are essential to plant and animal metabolism in trace amounts, others such as lead, cadmium, arsenic, mercury, chromium etc play little or no role in plant development. At high concentrations, they can lead to poisoning. Human exposure at higher concentration has been reported to cause serious health effects, including reduced growth and development, organ and nervous system damage and in extreme cases, death [24][25]. Against this backdrop, it is imperative to monitor and inform the public about the concentrations of these killer elements in the environment.

II. Materials And Methods

2.1 THE STUDY AREA

This study was carried out in Idu (Lat 5°15'0.64"N, Long 6°35'43.68"E) communities in Ogba/Egbema/Ndoni Local Government Area of Rivers State, Nigeria. Geographically, Idu Communities are located about 60km Northwest of Port Harcourt, Rivers State. Ecologically, the study area lies within the swamp forest of the Niger Delta region of Nigeria. The communities within the study area are Idu Obosi-Uku and Idu Osobile. The area is characterized by streams and floodplain. The vegetation type is typical of freshwater with diverse and rich floristic composition. The climate is tropical with rainy season between the Months of April and October and dry season between the Months of November and March. Temperature range in the area is between 25^0C and 32^0C. Farming and fishing are the major occupation of the people. The major water body in the area is the Orashi River. The general language spoken in the communities is Ogba**.** The communities are blessed with land resources that the dwellers utilize for farming activities. The two communities play host to two international oil companies. There are farms in and around the area. The inhabitants are people of different income class. Besides oil and gas activities in the area, there are other visible businesses owned by artisans and petty traders in the two communities. The general settlement pattern is dispersed with some linear characteristics identifiable in the location of houses along access roads and internal streets. Fig. 1 is the map of Nigeria showing the Local Government Area (Ogba/Egbema/Ndoni) in Rivers State where the study was carried out.

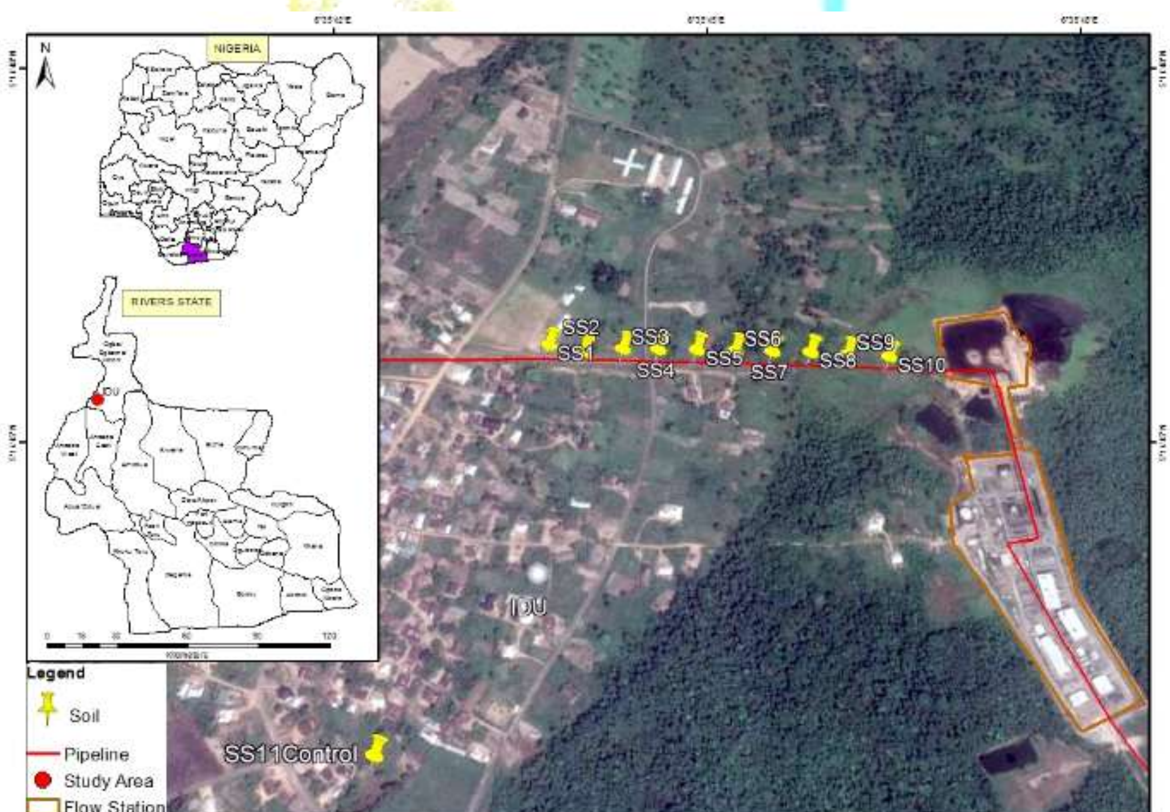

Fig. 1: The map of Nigeria showing the Local Government Area (Ogba/Egbema/Ndoni) in Rivers State where the study was carried out**.**

2.2 COLLECTION OF SOIL SAMPLES

Soil samples were collected from ten stations quarterly for one year (twelve months). The samples were collected precisely on the 2nd January, 2019, 2nd April, 2019, 2nd July, 2019 and 2nd October, 2019 respectively. Soil samples were also collected at 1.5 km away from the pipeline quarterly as control. A total of eighty eight (88) soil samples were collected across the study stations and control. Soils were collected at two depths (0-15 cm and 15 – 30 cm depths) at each sampling station using the soil Auger. The collection of samples was done by taking 2-3 auger borings of soil at each sampling station with a Dutch Auger and bulked together to make a composite sample. At each quarterly sampling, the samples were collected in well-labeled ziploc bags and taken to the laboratory for analysis. In the laboratory, the samples were air-dried at room temperature, crushed and passed through 2 mm mesh sieve and later stored in clean plastic bags with proper labeling. The soil samples were analysed for Pb, Cd, Ni, V, Zn and Fe content.

2.3 CHEMICAL ANALYSIS

Soil samples (1 g) each was introduced into digesting tubes following the addition of 10 ml concentrated HNO_3. The samples were placed in the digester for 8 h at 96°C with intermittent stirring. Upon complete digestion, the samples were filtered into 100 ml volumetric flasks using Whatman no. 42 filter paper. The samples were made up to the 100 ml mark in the volumetric flask using distilled or deionised water. The concentrations of Pb, Cd, Ni, V, Zn and Fe in the supernatant solutions were determined using atomic absorption spectrophotometer (AAS). All the analyses were done in duplicates. The concentration of heavy metals (mg/kg) =

$$\frac{\text{Instrument Reading x Slope Reciprocal x Volume of Extract}}{\text{Weight of sample}} \qquad \text{Equation 1}$$

2.4 STATISTICAL ANALYSIS

Means, standard deviations and Analysis of Variance (ANOVA) as well as Duncan multiple range test of the heavy metals in soil were calculated. Pollution assessment models such as geoaccumulation (Igeo) and pollution load indices were used to assess the presence and degree of contamination of soil with the heavy metals.

$$\text{Geoaccumulation Index } (I_{geo}) = \text{Log}_2 \text{ (Cn/1.5 x Bn)} \qquad \text{Equation 2}$$

Where Cn = Concentration of heavy metals in the studied soil, Bn = Background concentration (control soil) of heavy metal and 1.5 is the background correction factor.

The PLI is obtained using [26] approach as follows:

$$\text{PLI} = [\text{CF1} \times \text{CF2} \times \text{CF3} \times \ldots\ldots \times \text{C n}]\ 1/n \qquad \text{Equation 3}$$

where, CF= contamination factor; and n = specific number of contaminants studied.

2.5 Quality Assurance and Control

Quality assurance/quality control was an integral part of the research work. Basically, the quality assurance and control programme ensured that the integrity of the samples was not compromised. Specifically, we ensured that;

- Contamination of samples was avoided by use of clean sampling material
- Samples were correctly labeled and preserved;
- Field and equipment blanks were collected as appropriate.

Table 1: Environmental Guidelines and Standards for Soil for the Petroleum Industry in Nigeria (EGASPIN) (2018 Revised)

PARAMETER	Target Values (DPR, 2018) (mg/Kg)	Intervention Values (DPR, 2018) (mg/Kg)
Nickel (mg/Kg)	35	210
Iron (mg/Kg)	-	-
Chromium (mg/Kg)	100	380
Cadmium (mg/Kg)	0.8	12
Zinc (mg/Kg)	140	720
Lead (mg/Kg)	85	530
Copper (mg/Kg)	36	190
Barium (mg/Kg)	200	625
Mercury (mg/Kg)	0.3	10
Vanadium(mg/Kg)	-	-

Source: [27]

Table 2: Summary of Heavy Metal Concentrations in Soil (mg/kg)

Metal	**Soil**
Pb	42.9 - 1833.5
Cd	-
Cr	12.2 – 480.5
Ni	12.5 – 131.9
Fe	-
Cu	11.0-186.6
Zn	26.9 – 882.1

Source: *Maximum permissible concentrations as defined by [28]

III. Results And Discussion

3.1. Results

Table 3: Summary of Heavy Metals Characteristics of Soil in the Study Area

PARAMETERS	STUDY STATIONS (0 – 15 cm)											
	1st Quarter			2nd Quarter			3rd Quarter			4th Quarter		
	Range	Mean ± SD	Control	Range	Mean ± SD	Control	Range	Mean ± SD	Control	Range	Mean ± SD	Control
Nickel (mg/Kg)	<0.001-0.07	0.02 ± 0.022^{a}	<0.001	<0.001-0.04	0.01 ± 0.014^{a}	<0.001	<0.001-0.04	0.02 ± 0.014^{a}	<0.001	<0.001-0.07	0.01 ± 0.022^{a}	<0.001
Iron (mg/Kg)	651.97-2244.87	1568.78 ± 470.25^{a}	1494.41	913.54-2936.21	1697.49 ± 524.88^{a}	1532.70	1249.31 - 3103.23	2101.59 ± 617.49^{a}	2843.13	1742.27 - 2963.20	2087.59 ± 364.445^{a}	2183.25
Chromium (mg/Kg)	<0.001	0.01 ± 0.028^{a}	<0.001	<0.001-0.09	0.01 ± 0.027^{a}	<0.001	<0.001-0.05	$<0.001 \pm 0.017^{a}$	<0.001	<0.001-0.09	0.01 ± 0.028^{a}	<0.001
Cadmium (mg/Kg)	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.00^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001
Lead (mg/Kg)	<0.001-4.91	1.08 ± 1.802^{ab}	0.24	<0.001-5.13	1.10 ± 1.662^{ab}	0.020	0.2-1.893	0.73 ± 0.300^{a}	0.386	0.05-2.85	0.72 ± 0.785^{a}	0.421
Vanadium (mg/Kg)	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001

Mean ± S.D across the columns with different superscript were significantly different at 5% with a>b>c. Mean separation done by Duncan multiple range test

Table 4: Summary of Heavy Metals Characteristics of Soil in the Study Area

PARAMETERS	STUDY STATIONS (15 – 30 cm)											
	1st Quarter			2nd Quarter			3rd Quarter			4th Quarter		
	Range	Mean ± SD	Control	Range	Mean ± SD	Control	Range	Mean ± SD	Control	Range	Mean ± SD	Control
Nickel (mg/Kg)	<0.001-0.03	0.01 ± 0.010^{a}	<0.001	<0.001-0.01	0.00 ± 0.004^{a}	<0.001	<0.001-0.13	0.02 ± 0.040^{a}	<0.001	<0.001-0.05	0.01 ± 0.017^{a}	<0.001
Iron (mg/Kg)	699.20-2003.36	1509.03 ± 443.490^{a}	1856.22	890.12-2753.88	1572.69 ± 542.420^{a}	1593.40	1110.13-2993.11	1849.77 ± 631.9^{a}	2743.28	1538.75-2583.38	1893.81 ± 310.160^{a}	2121.91
Chromium (mg/Kg)	<0.001-0.04	0.00 ± 0.012^{a}	<0.001	<0.001-0.04	0.00 ± 0.012^{a}	<0.001	<0.001-0.02	$<0.001 \pm 0.007^{a}$	<0.001	<0.001-0.04	0.00 ± 0.012^{a}	<0.001
Cadmium (mg/Kg)	<0.001	$<0.01 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001
Lead (mg/Kg)	<0.001-4.56	1.04 ± 1.704^{ab}	0.191	<0.001-5.72	1.14 ± 1.838^{ab}	0.013	0.20-1.69	0.66 ± 0.467^{a}	0.299	0.30-2.33	0.66 ± 0.606^{ab}	0.392
Vanadium (mg/Kg)	<0.001	$<0.01 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001	<0.001	$<0.001 \pm 0.001^{a}$	<0.001

Mean ± S.D across the columns with different superscript were significantly different at 5% with a>b>c. Mean separation done by Duncan multiple range test

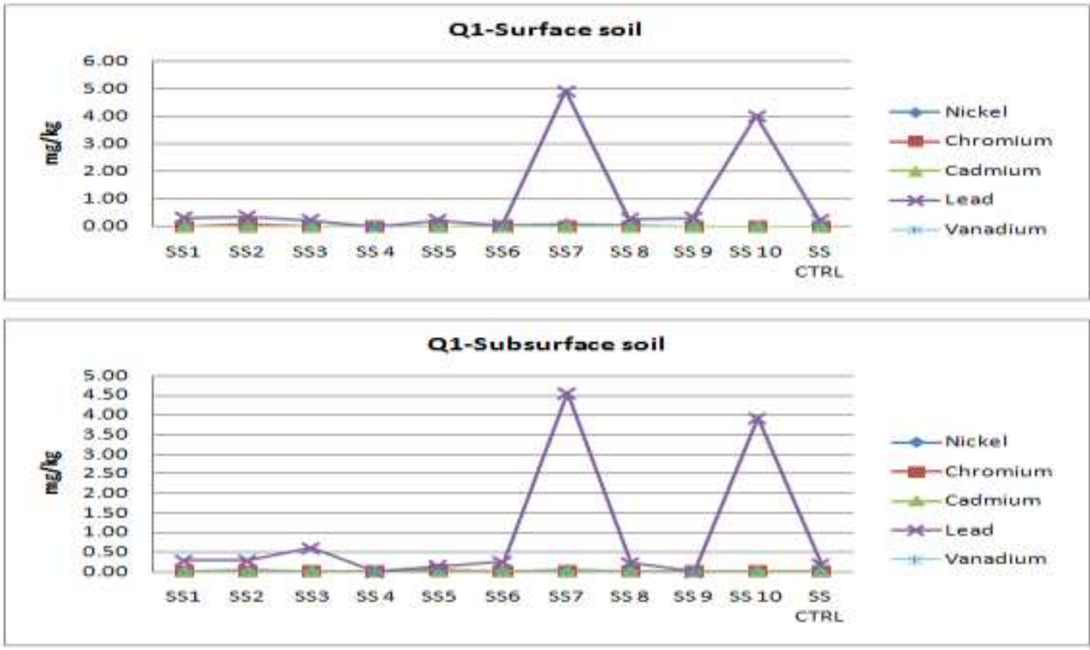

Fig. 2: Heavy Metals Concentrations across Study Stations in Surface and Subsurface Soils in 1st Quarter (Q1) (January, 2019)

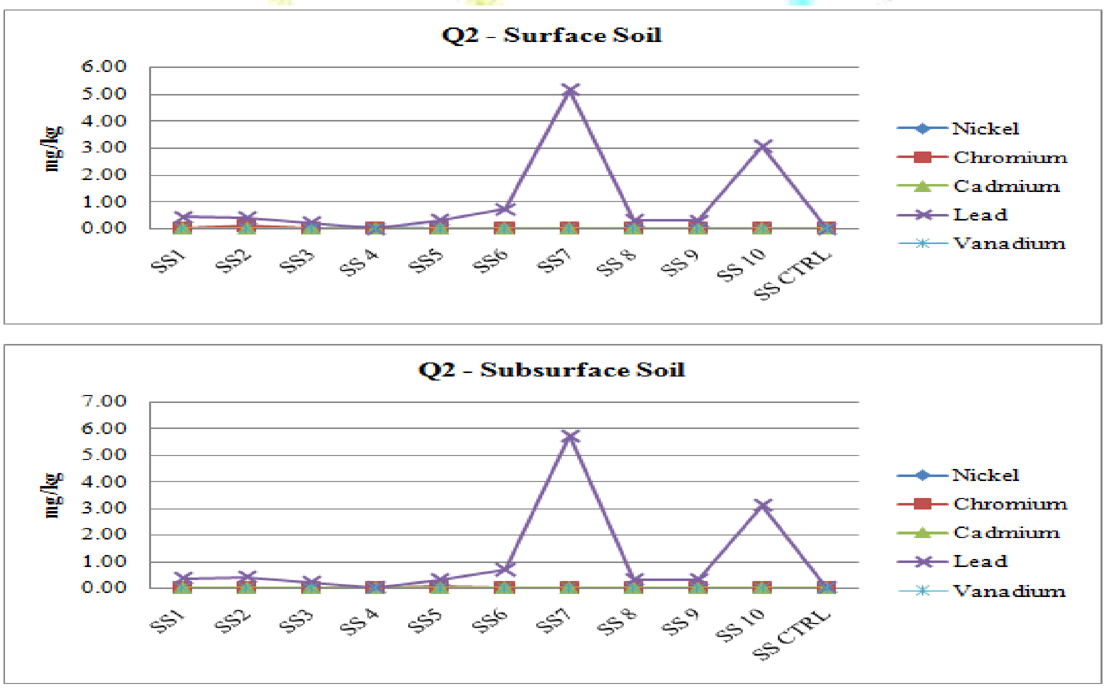

Fig. 3: Heavy Metals Concentrations across Study Stations in Surface and Subsurface soils in 2nd Quarter (Q2) (April, 2019)

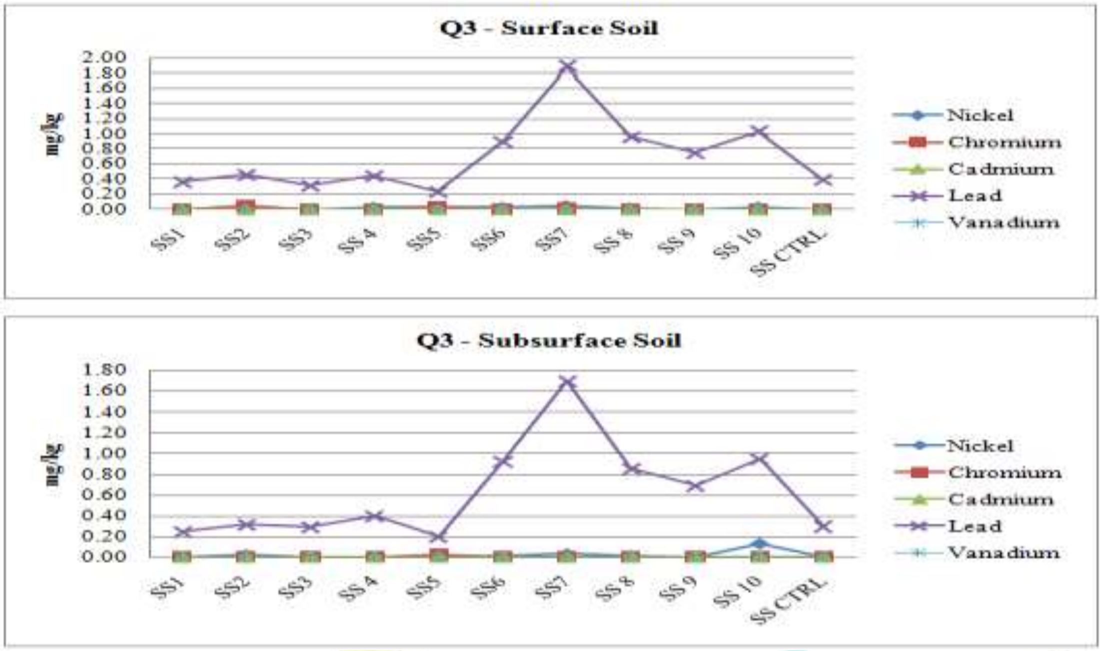

Fig. 4: Heavy Metals Concentrations across Study Stations in Surface and Subsurface soils in 3rd Quarter (Q3) (July, 2019)

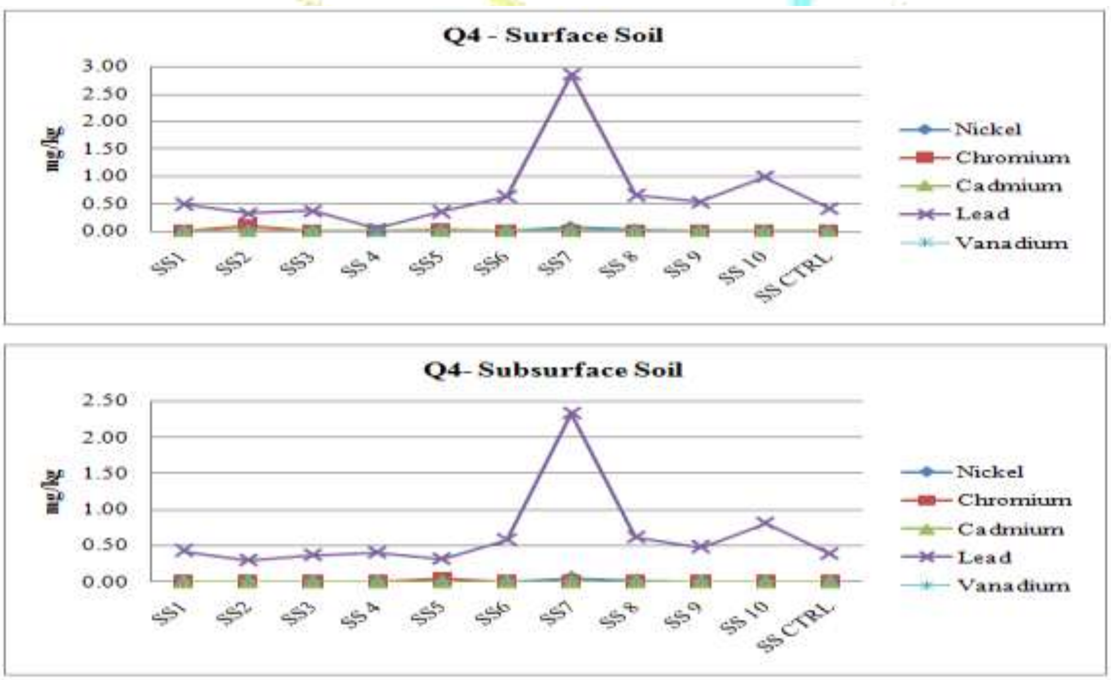

Fig. 5: Heavy Metals Concentrations across Study Stations in Surface and Subsurface soils in 4rd Quarter (Q4) (October, 2019)

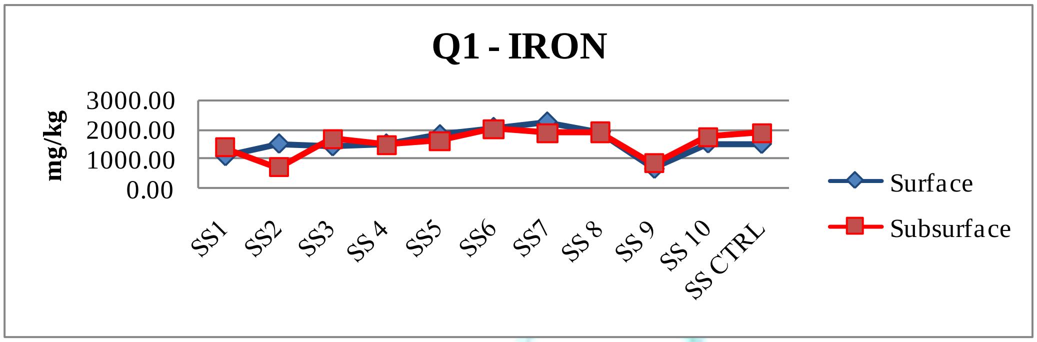

Fig. 6: Iron Concentrations across Study Stations in Surface and Subsurface Soil in 1st Quarter (Q1) (January, 2019)

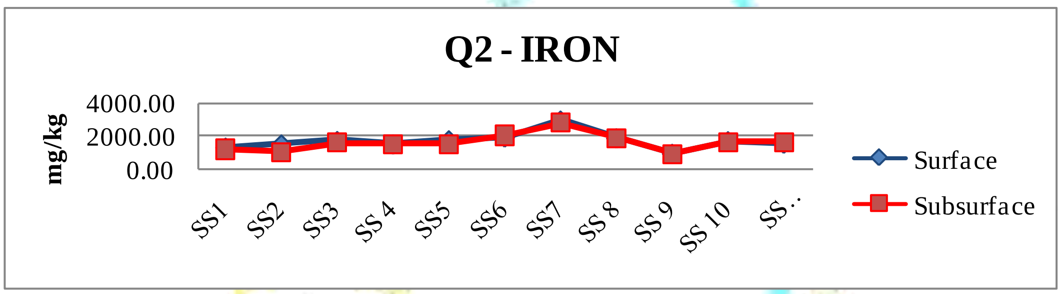

Fig. 7: Iron Concentrations across Study Stations in Surface and Subsurface Soil in 2nd Quarter (Q2) (April, 2019)

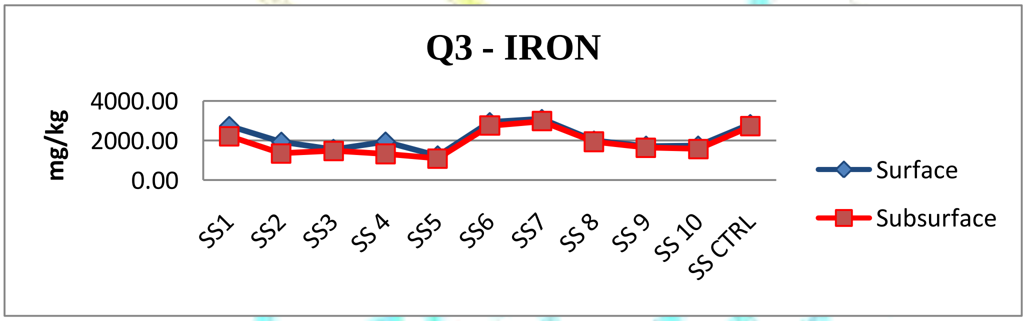

Fig. 8: Iron Concentrations across Study Stations in Surface and Subsurface Soil in 3rd Quarter (Q3) (July, 2019)

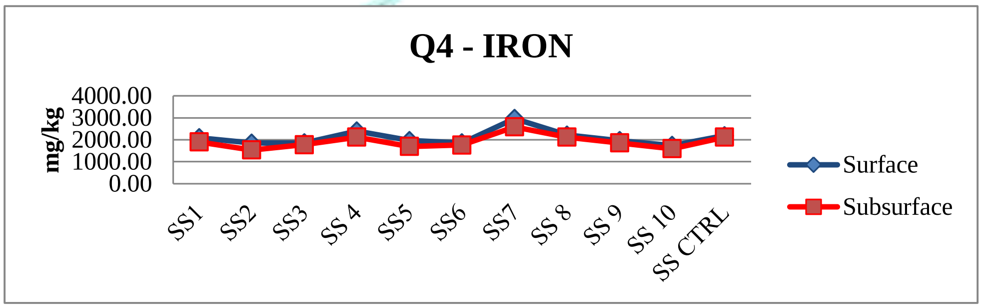

Fig. 9: Iron Concentrations across Study Stations in Surface and Subsurface Soil in 4th Quarter (Q4) (October, 2019)

Table 5: Assessment of Heavy Metals in Ten (10) Study Stations using Geoaccumulation Index (I_{geo})

Study Station (SS1)	I_{geo}											
	Surface Soil (0 – 15 cm)						Subsurface Soil (15 – 30 cm)					
	Ni	Fe	Cr	Cd	Pb	V	Ni	Fe	Cr	Cd	Pb	V
SS1	-19.35	21.20	-19.35	-19.35	-3.76	-19.35	-19.35	21.14	-19.35	-19.35	-4.33	-19.35
SS2	-15.61	21.12	-20.85	-19.35	-3.83	-19.35	-23.83	20.60	-19.35	-19.35	-4.37	-19.35
SS3	-19.35	21.06	-19.35	-19.35	-4.31	-19.35	-19.35	21.10	-19.35	-19.35	-4.20	-19.35
SS4	-22.87	21.23	-19.35	-19.35	-5.42	-19.35	0	21.08	-19.35	-19.35	-5.02	-19.35
SS5	-23.83	21.11	-22.87	-21.87	-4.26	-19.35	-19.35	20.96	-21.87	-21.87	-4.82	-19.35
SS6	-22.87	21.49	-19.35	-19.35	-3.26	-19.35	-23.83	21.49	-19.35	-19.35	-3.48	-19.35
SS7	-14.89	21.85	-23.85	-19.35	0.93	-19.35	-15.61	21.75	-19.35	-19.35	0.59	-19.35
SS8	-23.83	21.35	-19.35	-19.35	-3.31	-19.35	-23.83	21.37	-19.35	-19.35	-3.77	-19.35
SS9	-19.35	20.75	-19.35	-19.35	-3.53	-19.35	-19.35	20.78	-19.35	-19.35	-4.20	-19.35
SS10	-23.83	21.10	-19.35	-19.35	-1.29	-19.35	-15.61	21.10	-19.35	-19.35	-1.63	-19.35

Table 6: Heavy Metals Contamination and Pollution Load Index of Soil in the Study Area

STUDY STATIONS	PARAMETERS			
	Total Metal Conc. (Ni + Cr + Cd + Pb + V)	CF	DC	PLI
SS1	0.758	1.52		
SS2	0.845	1.70		
SS3	0.658	1.32		
SS4	0.367	0.74		
SS5	0.683	1.40		
SS6	1.226	2.50	36.99	2.06
SS7	7.375	14.81		
SS8	1.086	2.18		
SS9	0.858	1.72		
SS10	4.516	9.10		
SSCTR	0.498	1		

3.2. Discussion

The World Health Organisation does not have soil quality guidelines or standard for heavy metals in soil. Therefore, comparisons made in this study were based on concentrations of the control soils, target and intervention limits of the Department of Petroleum Resources (DPR) enshrined in Environmental Guidelines and Standards for Soil for the Petroleum Industry in Nigeria (EGASPIN) (2018 Revised), universally accepted safe range for tropical soil and Canadian Council of Ministers of the Environment (CCME) limits.

3.2.1 Lead

The mean concentrations of lead obtained were 1.08 mg/kg, 1.10mg/kg, 0.73 mg/kg, 0.72 mg/kg, and 1.04 mg/kg, 1.14 mg/kg, 0.66 mg/kg and 0.66 mg/kg in Q1, Q2, Q3 and Q4 in surface and subsurface soils respectively. The highest concentration of lead recorded (5.721mg/kg) was at study station 7 (SS 7) in subsurface soil in Q2 (April) followed by 4.913 mg/kg at SS 7 in surface soil in Q1 (January) at the same sampling station. This result showed that lead concentrations were higher in dry season (January) and during transition period (2nd April) than the wet season (July), indicating slight seasonal variation. This could be attributed to differences in solubility, pH, leaching by acidic rain during the wet season and topography of the area [29]. Heavy rain has the potential of enhancing leaching of heavy metals and other contaminants especially in sand dominated soils as recorded in this study. This finding is in agreement with similar studies conducted by [30][31][32][33][34][35][36][37][38], in Nigeria, [39], in Ghana, and [40], in Bangladesh.

In this study, higher concentrations of lead were obtained at sampling station 7 (SS 7) and (SS 10) than other stations along the same pipeline route. This observation indicates point source of contamination, suggesting that the pipeline might be leaking at these points. The suspected pipeline leakage at SS 7 and SS 10 could be attributed to pressure on the connecting branches as these two sampling stations were close to the flow station in the area. Pipeline transportation of crude oil from the pump or flow station begins with major force, and loses forward momentum over time and distance. Klass [41], had noted earlier that pressure wave may occur in pipeline transporting product if the velocity of the flowing liquid suddenly changes. This probably explains the higher concentrations of heavy metals and hydrocarbons recorded at these two study stations. Besides, the suspected leakage could be attributed to corrosion due to the old age of the pipeline. According to Omofonwa and Odia [13], aged and corroding pipeline is very common in many oil exploration fields in the Niger Delta region where this study was conducted. The average life span of oil pipeline is between 20 and 30 years. The pipelines in the study area were unarguably installed in the 1970's, indicating that they are over 30 years old. This observation agreed with Adebayo [14], who noted that some pipelines in the Nigerian oil fields are over 30 years old. Ogon [15], conducted an analysis of oil pipelines in the Niger Delta region and reported that large number of the oil pipelines in the area were put into operation in the 1960s and 1970's.

The concentrations of lead obtained in this study including 5.721mg/kg and 4.913 mg/kg recorded at study stations 7 and 10 were lower than the Department of Petroleum Resources (DPR) target value of 85 mg/kg for crude oil polluted soil, minimum permissible concentration of 42.9 mg/kg defined by the Canadian Council of Minister of Environment (CCME) however, higher than the values recorded at the control points. This suggests that anthropogenic activities including oil and gas exploration in the area might have contributed to the concentrations of lead obtained. These findings were in consonance with the work of [42][43][44], who reported that oil contaminated soils had higher concentrations of lead than the control points. Although the concentrations of Pb obtained in this study were within the permissible limit in tropical soil, the study sites especially sampling station 7 is contaminated with Pb. Lead is undesirable to humans because of its health hazards. A notable serious health effect of lead toxicity is its tetratogenicity [45]. Lead poisoning also causes inhibition of the synthesis of haemoglobin, dysfunctions in kidney, joints and damage to the central nervous system [46].

3.2.2 Iron

In this study, Fe concentrations were high in all the stations including control points in the four quarters of the year (January, April, July and October, 2019). This finding was expected because Fe is the most common element (by mass) forming much of Earth's outer and inner core. Besides, Fe has been reported to occur in high concentrations in Nigerian soil environment [46]. In this study, higher concentrations of Fe were recorded in surface than subsurface soils, and at sampling station 7 (SS 7) in all the quarters of the year. The values obtained were 2244.87 mg/kg, 2936.21 mg/kg, 3103.23 mg/kg and 2963.20 mg/kg in Q1, Q2, Q3 and Q4 in surface and subsurface soils respectively. Whilst Fe is naturally abundant in soil particularly in the tropics, the higher concentrations recorded in SS 7 indicated a point source of contamination. This result was expected because, among the ten sampling stations along the pipeline route in the study area, SS 7 had the highest concentrations of both heavy metals and hydrocarbons, suggesting anthropogenic influence. Leakage due to corrosion was suspected at this sampling point. [15], had earlier noted that the old age of the pipelines in Nigeria makes them prone to failures due to rupture and corrosion. This probably explains the higher concentrations of Fe at this station. Furthermore, the organic carbon values recorded at study station 7 (SS 7) were 1.29 %, 1.54 %, 1.67 % and 1.83 % in Q1, Q2, Q3, and Q4 in surface soil, which suggested that the soil is relatively rich in organic matter. In an earlier study, [24], noted that organic matter improves iron availability by combining with iron, thereby reducing chemical fixation or precipitation of iron as ferric hydroxides. According to Schulte [47], this reduction in fixation and precipitation results in higher Fe concentrations remaining in the soil. This could be the reason Fe concentrations were generally high in the study sites and control points. The Fe concentrations obtained in this study were far lower than 36186 – 108054 mg/kg, and 23016.4 – 38458 mg/kg reported by [29] in Nigeria, and [40], in Bangladesh respectively however, higher than 706 mg/kg reported by [48]. Plants need Fe to make chlorophyll but excess of it can cause stunted growth, bronzing of leaves and general poor health. In addition, excess concentrations of Fe in soil can interfere with plants ability to utilize manganese, which can exhibit symptoms similar to deficiencies of Fe. Although Fe is generally not considered as a soil pollutant because of its abundance on earth [49][50], the high concentrations obtained in this study in all the stations calls for serious concern. Excessive exposure to Fe can cause serious health problems such as vomiting, upper abdominal pain, pallor, cyanosis, diarrhea, dizziness, shock, heamochromatosis, diabetes, liver, lungs and kidney diseases, haepatoma and cardinomyopathy [51][52][46].

3.2.3 Chromium

The range of Cr concentrations obtained in this study was generally very low, ranging from minute values to below equipment detection limit of <0.001 mg/kg across the stations in all the seasons (January, April, July and October, 2019). There was no significant difference ($p>0.05$) in season and across the sampling stations. The low Cr concentrations recorded in this study is attributed to the fact that the metal is unstable and short lived in the biological system [53]. Exposure to high dose of chromium can cause respiratory irritation, kidney damage, liver damage, pulmonary congestion and edema, upper abdominal pain, nose irritation and damage, respiratory cancer, skin irritation, and erosion and discoloration of the teeth [54].

3.2.4 Nickel

The range of Ni concentrations obtained was generally very low, ranging from minute values to below equipment detection limit of <0.001 mg/kg across the stations in all the season. There was no significant difference ($p>0.05$) in season and across the sampling stations. Nickel is a potent skin sensitiser which implies that, it could cause allergic reaction in human [55]. Soluble nickel salts and the mixture of nickel sulphides and oxides present in refinery dust have been reported to be carcinogenic to the lung and nasal tissues in humans [55].

3.2.5 Cadmium

The concentrations of Cd obtained in this study were below equipment detection limit of <0.001 mg/kg across the sampling stations in all the seasons (January, April, July and October, 2019). The very low concentrations obtained for cadmium in this study can be attributed to the physical and chemical properties of the soil in the area. Cadmium is a metal with unknown essential function in higher plants [56] and animals. Long term exposure to Cd either through inhalation or ingestion has been reported to be highly toxic to humans especially kidney and bones and with the potential to cause cancer of the lungs [55]. Cd build up in the body over a time period also affects vitamin D metabolism, disturbing the calcium balance within the body which may lead to a decrease in the mineral content within the bones, resulting in Osteoporosis and Osteomalacia [55].

3.2.6 Vanadium

The concentrations of V obtained in this study were below equipment detection limit of <0.001 mg/kg across the sampling stations in all the seasons (January, April, July and October, 2019). Nevertheless, concentrations of 0.04 mg/kg, 24.05 mg/kg in soil were earlier reported by [33][29], respectively in similar studies. The very low concentrations obtained for vanadium in the study can be attributed to the composition of other trace metals in soil such as iron and manganese as well as pH and soil texture. The studies conducted by [57][58][59][60], have shown that the adsorption of vanadium is dependent on soil pH, the presence of iron and manganese oxides and soil texture. According to Agniezka and Barbara [61]; Gabbler *et al* [59]; Terzano *et al* [62], sandy soil has lower sorption ability for vanadium due to the occurrence of ion-exchange sites and low oxalate soluble Fe, Mn and Al concentrations. This probably provides further explanation for very low concentrations of vanadium obtained in this study.

3.3 Geoaccumulation Studies of the Soil Stations

Geoaccumulation Index was used to assess the degree of heavy metals contamination of the studied environment. Based on Forstner [63] classification, the degree of contamination in all the stations may be classified between uncontaminated, moderately and very strongly contaminated. In this study, the ten sampling stations were practically uncontaminated ($I_{geo}< 0$) with Cr, Ni, Cd and V, uncontaminated/moderately contaminated ($I_{geo}<0<0.94$)

with Pb and very strongly contaminated (I_{geo}<20) with Fe in both surface and subsurface soils. The strongly contamination of the sampling stations with Fe as recorded in this study was expected. Fe is very abundant on earth, and highly distributed in soil in the Niger Delta region of Nigeria. Apart from Fe, the study area was not contaminated with other metals however, sampling station 7 was moderately contaminated with Pb, suggesting a point source due to anthropogenic activities in the area. The pipeline was suspected to be leaking crude oil into the soil at this point. This finding is in agreement with earlier studies conducted by [14][15][13], who reported that pipelines in the Nigerian oil field are old and prone to leakages at different points. The geoaccumulation indices of Cr, Ni, V and Cd were negative, indicating that the soil in the study area was practically uncontaminated with these metals. This finding is in consonance with the reports of [64][65], in Niger Delta region, [66] in Vietnam; [67][68] in Poland; [69], in Norway.

3.4 Degree of Contamination (DCI) and Pollution Load Index of Soil

The order of heavy metals contamination of soil is SS 7 > SS 10 > SS 6 > SS 8 > SS 9 > SS 2 > SS 1 > SS 5 > SS 3 > SS 4. In this study, it was observed that Pb was the major contributor to the overall heavy metals load in the area. Pb occurs naturally in the environment however, anthropogenic activities including oil and gas exploration in the study area might have contributed to the release of relatively high concentrations obtained. The degree of heavy metals contamination (36.99) and pollution load (2.06) indices recorded in this study indicated that the soils were highly contaminated nevertheless, the pollution load was minimal. The heavy metals pollution load showed a localized pattern, evidenced by higher concentrations of Pb obtained at sampling station 7 than other stations. This suggests a point source of contamination suspected to come from pipeline leakage due to operational failure or corrosion.

IV. Summary and Conclusion

The results obtained in this study showed that Pb was relatively high, Cr and Ni were very low, Cd and V were not detected while Fe was generally very high across the sampling stations in all the seasons. Except Pb and Fe, the geoaccumulation indices of Cr, Ni, V and Cd were negative, indicating that the soil in the study area was practically uncontaminated with these metals. Nevertheless, Pb and Fe were relatively high. The degree of heavy metals contamination was in this order: SS 7 > SS 10 > SS 6 > SS 8 > SS 9 > SS 2 > SS 1 > SS 5 > SS 3 > SS 4. Pb was the major contributor to the overall heavy metal load in the study area. The study has established the degree of heavy metals contamination in the area and has identified underground petroleum storage facilities such as pipelines, service and flow stations as major sources of heavy metals contamination of the environment. Monitoring of heavy metals in soils around these facilities is recommended to avoid fauna and flora contamination via food chain.

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