

EFFECTS OF CRUDE OIL SPILLAGE ON PHYSICO-CHEMICAL AND HEAVY METAL CONCENTRATIONS IN SOILS FROM ABLAGADA, NIGERIA

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ABSTRACT

The levels of heavy metals Cr, Cu, Cd, Ni and Pb, in soils after oil spillage were determined using atomic absorption spectrophotometer. The levels of some physicochemical parameters pH, texture, TOC, EC and THC of the soils were also determined with appropriate methods.

The results showed that soils in the area were predominantly clay and moderately acidic (pH = 5.32 and 5.96 for top and sub soils respectively). The mean concentrations of the metals in soils were Cu 11.21 ± 5.67 ; Pb 25.02 ± 7.18 ; Cr 28.75 ± 7.24 ; Ni 31.76 ± 26 ; Cd 1.19 ± 0.74 for top soils and Cu 9.12 ± 5.50 ; Pb 23.90 ± 6.58 ; Cr 23.43 ± 11.99 ; Ni 26.51 ± 8.44 ; Cd 0.77 ± 0.43 for sub soils. The results show that heavy metal pollution was highest at the topsoil. The metal levels exceeded typical levels found in unpolluted soils. In particular the levels of Pb at the impacted area exceeded permissible limit. The results also show that Cr and Pb are associated with the clay colloid of sub soil. The levels of metals at the impacted area were higher than levels at the control. Statistical analysis showed high correlation ($r = 0.9929$, $n = 130$, $P < 0.05$) between the topsoil and subsoil levels of heavy metals and physicochemical parameters in the study area. There was significant difference ($P < 0.05$) between the mean levels of heavy metals at the impacted and control areas. Similar observation was made in mean levels of physicochemical parameters. The levels of heavy metals and physicochemical parameters at the impacted area and the control showed significant correlation ($r = 0.7067$) at topsoil and ($r = 0.5885$) at subsoil.

The study revealed that the crude oil spillage that occurred in the area was the major source of the elevated concentrations of the metals and physicochemical parameters.

KEYWORDS: Heavy metal, soil, impacted, topsoil and subsoil, Ailagada, Nigeria

INTRODUCTION

In recent times, the occurrence of metal contamination resulting from rapid growth in population, increased urbanization, expansion of industrial activities, exploration and exploitation of natural resources, extension of immigration and other modern agricultural practices as well as lack of environmental regulations have become problems of increasing concern (Biney et al, 1994).

Heavy metal pollution can affect all facets of the environment but their effects are most long lasting in soils due to the relatively strong absorption of many metals onto humic and clay colloids in soil (Alloway and Arye 1994). A number of studies on the impact of crude oil spill on the Nigerian environment have been reported (Oteri, 1981; Idoniboye – Obu and Andy, 1985; Amajor, 1985; Odu et. al., 1985).

The major routes of heavy metal uptake by man are food, water and air. Although some heavy metals such as Cu, Zn and Mn are essential for the growth and well being of living organisms including man, they are toxic at higher concentrations. Other metals such as Pb, Cd and Hg are non-essential for metabolic activities and are toxic (Biney et al. 1994). Amajor (1985) reported that the Ejamah Ebubu oil spill incident near Eleme, Rivers State Nigeria in 1970 heavily impacted farmlands and swamps rendering the soils unfit for farming and streams unfit for fishing. He further observed that the lighter and low molecular weight hydrocarbons evaporated while the intermediate and heavier fractions permeated into the soil.

Heavy metals are associated with various soil components in different ways and these associations determine their mobility and availability (Kabala – Pendas and Pendas, 1992; Singh, 1997; Ahumada et. al., 1999)

Spillage occurs during the development, production, transportation and storage of crude oil and its derivatives. Since 1976 over 2.8 million barrels of crude oil have been released into the environment in over 550 reported cases of crude oil spillage in the Niger Delta (Odieta, 1999).

In Nigeria most oil fields and operations are located in the Niger Delta area. In 2003 there was an accidental spillage of crude oil in Ailagada community whose primary occupation is farming and fishing. There is paucity of information on the impact of oil spill and distribution of heavy metals in soils in this area. This study is therefore carried out to fill the gap by investigating the characteristic levels of Cr, Cu, Ni, Pb, Cd, pH, TOC, EC, CEC and THC in soils from impacted and non-impacted (control) soils within the community.

MATERIALS AND METHODS

The study area Ailagada lies within longitudes $6^{\circ} 32' 43''$ and $6^{\circ} 38' 8''$ E and latitudes $5^{\circ} 38' 27''$ and $5^{\circ} 39' 9''$ N. It has annual rainfall range of 2540 – 3500mm and mean temperature of 30.5°C

Soil samples from 12 sampling stations within the impacted area (Fig. 1) and one control station were collected. At each station composite samples consisting of four random samples were collected at two depths (0 – 15cm and 15 –

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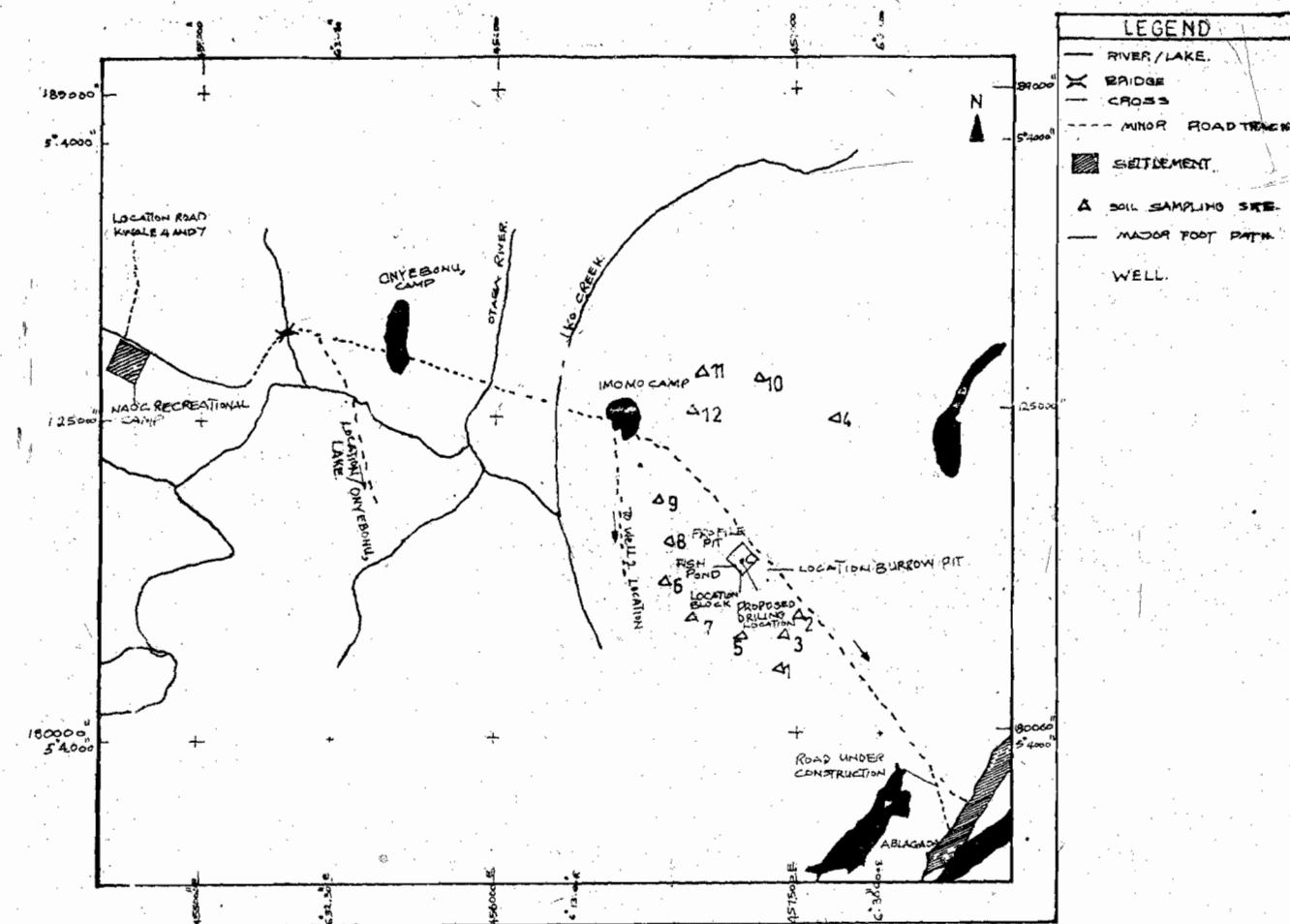


FIG1: MAP OF THE STUDY AREA SHOWING SAMPLING SITE.

30cm) into polythene bags. The samples were air-dried, ground and sieved to pass 2mm mesh.

Soil pH was determined in a 1:2.5 soil to water ratio using a glass electrode pH meter (Mclean, 1982). Particle size distribution was determined using the hydrometer method and the textural class determined from the "Textural Triangular Diagram (Loganathan, 1984). To determine Total Organic Carbon (TOC) 10ml, 1M potassium dichromate was added to 5g of soil sample and swirled. 20ml of concentrated H_2SO_4 was added and swirled. After 30 mins., 100ml distilled water was added followed by 3-4 drops of ferroin indicator and titrated with 0.5N ferrous sulphate solution. Blank titration was also carried out and the result divided by 1.729 (Bamgbose et al., 1999). The Electrical Conductivity (EC) of soil was determined in the filtrate from a mixture of 1:2.5 soil to water ratio using a conductivity meter (Loganathan 1984). The total hydrocarbon content (THC) was determined by refluxing 100g of soil sample with 100ml of methanol containing 3g KOH for 2.5 hours. The filtrate of the reflux mixture was extracted into two 2.5ml portions of redistilled hexane. The combined extract was evaporated to about 1ml and eluted with n-hexane (Onianwa and Essien, 1999).

1g of the soil sample was digested with a mixture of 5ml hydrofluoric, 5ml nitric and 5ml perchloric acid and diluted to 50ml with deionized water. (Allen et al., 1974; Basset et al., 1978). The sample solution was analyzed for Cr, Cu, Cd, Ni and Pb using air-acetylene flame atomic absorption spectrophotometer model Perkin Elmer A3100 with detection limit of 0.001mg/kg

RESULTS AND DISCUSSIONS

The levels of heavy metals and physicochemical parameters measured in the study area are presented in Tables 1 and 2

The particle size distribution was predominantly clay in both top and sub soils. The mean clay composition was 41.1% and 37.0% for the top and sub soils respectively. The levels of clay showed significant correlation with sand ($r = -0.578$ and -0.935 for top and sub soils respectively) and silt ($r = 0.667$ for sub soil). Both top and subsoils were moderately acidic with mean pH of 5.32 and 5.96 respectively. The pH of control topsoil and subsoil was 4.33 and 3.62 respectively. The pH value was predominantly higher in the 15-30cm depths except for few stations that have pH values lower than that of the topsoil. This observation indicates that crude oil raised the pH of the soil and is in line with reports of Kabala and Singh (2001). The moderately acidic to near neutral pH is typical of soils in the Niger Delta (Odu et al., 1985; Isirimah, 1987).

The mean levels of EC in the area were $1702.60\mu S/cm$ and $328.80\mu S/cm$ for topsoil and subsoil respectively. The EC levels at the topsoil were higher than those at the subsoil except at stations 3, 6 and 12. Elevated levels of EC $393.00\mu S/cm$ (station 1), $8740\mu S/cm$ (station 2), $1316\mu S/cm$ (station 5) and $9385\mu S/cm$ (station 4), at topsoil and $389\mu S/cm$ (station 1), $426\mu S/cm$ (station 2), $1814\mu S/cm$ (station 3) and $405\mu S/cm$ (station 4) at subsoil were obtained at heavily impacted areas. The EC values at stations 2 and 4 exceeded acceptable limit of $4000\mu S/cm$. The EC values in the area were higher than those at the control, $57.6\mu S/cm$ for

Table 1. heavy metal concentrations (mg/kg) in soils at the sampling sites

Station	Depth	Cr	Cu	Cd	Ni	Pb
1 HI	(0-15cm)	23.05	5.26	1.66	24.69	21.08
	(15-30cm)	21.19	7.59	1.66	24.89	24.46
2 HI	(0-15cm)	36.03	23.41	1.59	42.25	14.32
	(15-30cm)	31.70	8.05	1.39	20.55	14.32
3 HI	(0-15cm)	21.19	6.19	1.12	24.89	14.32
	(15-30cm)	34.18	17.36	0.05	33.57	21.08
4 HI	(0-15cm)	18.72	15.04	3.01	29.23	31.22
	(15-30cm)	0.02	0.02	0.59	11.87	21.08
5 HI	(0-15cm)	31.70	16.34	1.39	33.57	27.84
	(15-30cm)	31.09	7.59	0.59	24.89	24.46
6 UI	(0-15cm)	11.31	0.59	37.91	31.22	31.22
	(15-30cm)	10.85	0.59	37.91	24.46	24.46
7 UI	(0-15cm)	22.43	3.86	0.32	20.55	24.46
	(15-30cm)	30.47	5.73	0.59	24.89	31.22
8 UI	(0-15cm)	26.76	6.66	1.12	29.23	27.84
	(15-30cm)	0.02	0.02	0.59	16.21	14.32
9 MI	(0-15cm)	29.23	9.92	0.86	33.57	17.70
	(15-30cm)	21.81	10.38	0.59	29.23	37.98
10 MI	(0-15cm)	27.38	11.31	1.12	33.75	25.46
	(15-30cm)	19.95	12.24	0.59	29.23	24.46
11 MI	(0-15cm)	28.61	8.98	0.59	33.57	37.98
	(15-30cm)	30.47	15.97	0.86	37.91	21.08
12 MI	(0-15cm)	44.07	16.43	1.93	37.91	27.84
	(15-30cm)	34.18	13.64	1.12	37.91	27.84
Control	(0-15cm)	11.00	4.10	0.59	7.00	2.00
	(15-30cm)	15.00	7.00	0.85	7.00	3.00

HI = Heavily impacted
 MI = Moderately impacted
 UI = Unimpacted

Table 2. Levels of physicochemical parameters in soils at the sampling sites

Station	Depth	pH	EC (μ S/cm)	TOC (%)	THC (mg/kg)	Sand (%)	Silt (%)	Clay (%)	Texture
1 HI	(0-15cm)	5.26	393	11.21	865.64	12.6	34	53.4	Clay Clay Loam
	(15-30cm)	6.71	389	15.11	876	40.7	23.7	35.6	
2 HI	(0-15cm)	7.24	8740	2.91	78.97	23.4	24.2	52.4	Clay Sandy Clay Loam
	(15-30cm)	6.91	426	1.02	5.37	54.2	11.9	33.9	
3 HI	(0-15cm)	5.21	72.5	2.00	12.99	61.5	11.5	26.9	Sandy Clay Loam Sandy Clay Loam
	(15-30cm)	7.83	1814	1.71	22.29	56.7	10.4	33.9	
4 HI	(0-15cm)	6.39	9385	38.03	117.88	54.8	12.9	32.3	Sandy Clay Loam Sandy Clay Loam
	(15-30cm)	6.07	405	0.15	2.84	82.1	5.3	12.6	
5 HI	(0-15cm)	5.75	1316	40.37	12.99	37.8	23.7	38.5	Sandy Clay Loam Sandy Loam
	(15-30cm)	5.5	160.8	1.00	1.99	41.3	20.2	38.4	
6 UI	(0-15cm)	5.33	63.6	1.22	0.02	23	28	49	Clay Clay
	(15-30cm)	5.17	236	3.95	6.22	23.4	30.6	46	
7 UI	(0-15cm)	4.95	140	2.88	0.02	38.2	18	43.8	Clay Clay
	(15-30cm)	4.64	207	0.30	1.15	20.2	18	61.1	
8 UI	(0-15cm)	4.93	103.3	2.68	0.02	45.7	3.6	50.6	Sandy Clay Sandy
	(15-30cm)	5.63	73.8	0.22	6.22	88.9	2.2	8.9	
9 MI	(0-15cm)	5.2	58	1.7	67.97	48.7	20.5	30.8	Sandy Clay Loam Sandy Clay Loam
	(15-30cm)	7.57	57.3	0.15	5.37	63.3	8	28.2	
10 MI	(0-15cm)	4.83	75.2	0.96	3.68	39.1	23.8	37	clay loam clay loam
	(15-30cm)	5	41.9	0.46	7.91	49.9	20	30.1	
11 MI	(0-15cm)	5.19	58.5	0.89	5.37	46.5	12.6	40.9	Sandy clay clay
	(15-30cm)	5.13	45.6	0.36	0.02	23.1	15.5	61.5	
12 MI	(0-15cm)	4.82	55.4	1.3	0.30	10.1	52.4	37.5	Silty Clay loam Clay
	(15-30cm)	5.19	89.22	1.00	0.02	20.6	25.4	54	
Control	(0-15cm)	4.33	57.6	15.8	12.4	38.9	23.5	36.4	Clay loam Clay loam
	(15-30cm)	3.62	17.8	4.1	12.0	43.5	20.0	34.8	

topsoil and 17.8 μ s/cm or subsoil. The EC levels showed significant correlation with pH ($r = 0.913$ and 0.40 for topsoil and subsoil respectively). The high levels of EC indicate increased amount of soluble salts in the soils, which could adversely affect plant growth.

The total hydrocarbon content (THC) in soils at the area varied from 0.02 – 865.64mg/kg at top soil and 0.02 – 22.29mg/kg at sub soil. The values at topsoil were generally higher than those at subsoil. The THC values at the heavily impacted areas were higher than the values at the control, 12.4mg/kg at topsoil and 12.0mg/kg at subsoil. The remarkably low levels of THC measured at stations 6, 7 and 8 (unimpacted areas) could be attributed to the absence of spilled oil. The high level of THC at station 9 (moderately impacted area) could be attributed to gradual flow and settlement of oil owing to the topography of the area. Similar observation at stations 10 and 11 could probably be due to wine blown aerosol during spillage. The levels of total organic carbon (TOC) in the area ranged from 0.89% to 40.37% with mean of 8.84 for topsoil and 0.15% to 15.11% with mean of 1.82 for subsoil. The levels of TOC decreased with depth except at stations 1 and 6. Heavily impacted areas, stations 2, 4 and 5 had high TOC values of 11.30%, 38.03% and 40.37% respectively. The levels of TOC at the impacted areas were higher than those at the control (15.8% and 4.1% for top and sub soils respectively). The levels of TOC showed no significant correlation with other parameters. These observations indicate that despite drainage of oil to surrounding water bodies by run-off and other factors substantial amount of oil remain in the soil. However, the oil does not penetrate to greater depths. The elevated levels of THC and TOC in the area could be attributed to the spilled crude oil, which is a complex mixture of hydrocarbons. These levels could impair the fertility of the soil leading to poor crop yield.

The concentrations of Cr in this study ranged from 18.72 – 44.07mg/kg and 0.02 – 34.18mg/kg for top soil and subsoil respectively. This indicates that the topsoil accumulated more Cr than the subsoil. The trend at the control was different with values of 11mg/kg and 15mg/kg for the top and subsoil respectively. Compared with the control levels the levels of Cr in the impacted area increased by 3 and 2 folds for the top and sub soils respectively. The levels of Cr showed significant correlation with sand ($r = -0.654$) and Cu ($r = 0.600$) at topsoil and sand ($r = -0.783$), clay ($r = 0.802$) and Cu ($r = 0.776$) at sub soil. The concentrations of copper in the study area ranged from 2.86mg/kg – 23.14mg/kg for the topsoil and 0.02 – 15.97mg/kg for the subsoil. The levels of Cu at the control site were 4mg/kg and 7mg/kg at top and sub soils respectively. Heavily impacted sites showed significantly higher concentrations of Cu than other sites. The concentrations of Cu were below typical levels 40mg/kg found in unpolluted soils. Comparing with the control data, the levels of Cu in soil obtained in this study increased by 2.8 and 1.3 folds for topsoil and subsoil respectively. However, the levels of Cu in this study were lower than levels reported for other contaminated sites (Ma and Rao 1997; Kabah and Singh 2001). The levels of Cu showed significant correlation with pH ($r = 0.726$) and EC ($r = 0.666$) at topsoil and sand ($r = -0.633$) and clay ($r = 0.594$) at sub soil. The levels of Cd in the area ranged from 0.59 – 3.01mg/kg for topsoil and 0.05 – 1.66mg/kg for subsoil. The levels of Cd at the topsoil were higher than those at the subsoil. The levels of Cd in the area were lower than levels reported by Ma and Roa (1997) for contaminated soils. The levels of Cd showed significant correlation with TOC ($r = 0.650$) at topsoil and TOC ($r = 0.686$) at subsoil.

The concentrations of Ni ranged from 20.55 – 42.25mg/kg and 11.87 – 37.91mg/kg for topsoil and sub soils respectively. The level of Ni, 7mg/kg at the control site did not vary at both depths. Compared with the control, levels of Ni increased by 4.5 and 3.8 folds for the topsoil and sub soil

respectively as a result of the oil spill. The levels of Ni showed significant correlation with Cu ($r = 0.821$) and Cr ($r = 0.816$) at top soil and sand ($r = -0.789$), silt ($r = 0.634$), clay ($r = 0.720$), Cu ($r = 0.894$) and Cr ($r = 0.717$) at subsoil. The levels of Pb in soils ranged from 14.32 – 37.98mg/kg and 14.32 – 37.98mg/kg for the top and sub soils respectively. This indicates higher Pb levels in the topsoil than in the sub soil. The levels of Pb in soils were higher than the levels in the control site, 2mg/kg for topsoil and 3mg/kg for sub soil. The levels of Pb in the impacted area increased by 12.5 and 11.7 folds at topsoil and subsoil respectively. The levels of Pb in the area were lower than levels reported by Lavado et al (1998) and Kabala and Singh (2001) for contaminated sites. The levels of Pb showed no significant correlation with any other parameter. The lower levels of metals in the study area compared to levels reported by other studies for contaminated site could be attributed to differences in the magnitude of the spillage as well as the composition of the oil.

Within the impacted area there were spatial variations as a result of topography and differences in settling or accumulation of crude oil. The mean concentrations of all the heavy metals in both top and sub soils were higher than the concentrations measured at the control and levels (Pb 0.17 – 0.31ppm, Cu 0.13 – 6.3ppm, Cd 0.0003 – 0.027ppm and Cr 0.00023 – 0.640ppm) of heavy metals in crude oil (Magee et al., 1973 and Valković, 1978). This indicates that the crude oil contributed to the concentrations of the metals since the control soils had no record of oil spill. In addition other effluents from industrial and domestic sources contributed to the levels of the metals. The concentrations of most heavy metals at both impacted and non-impacted (control) areas were found to be below permissible limits. The maximum recommended heavy metal concentrations in soils are 300 μ g/g As, 3 μ g/g Cd, 1000 μ g/g Cr and Pb, 250 μ g/g Cu and 100 μ g/g Ni (Brady, 1974). Also, the Federal Ministry of Environment (FMEnv, 1991 and the Rivers State Ministry of Environment and Natural Resources (RSMENR, 2002) recommended permissible limits of < 1 μ g/g Cd, 10 - 200 μ g/g Cr, 2 - 100 μ g/g Cu, 5 - 500 μ g/g Ni and 2 - 200 μ g/g Pb. However the concentrations of Pb at the impacted area exceeded the permissible limit. Statistical analysis showed high correlation ($r = 0.9929$, $P < 0.05$) between the topsoil and subsoil levels of heavy metals and physicochemical parameters in the study area. The difference between the levels of heavy metals and physicochemical parameters at the impacted area and the control was significant ($P < 0.05$) with high correlation ($r = 0.7067$) at topsoil and ($r = 0.5885$) at subsoil. The positive correlation of most metals with clay indicates possible retention and hence minimal plant uptake. These metals are generally toxic to plants. Thus the significant correlation at the topsoil could adversely affect crop yield.

CONCLUSION

The distribution pattern of heavy metals was in the order Ni > Cr > Pb > Cu > Cd and Ni > Pb = Cr > Cu > Cd for the top and sub soils respectively. The concentrations of metals increased when compared with control concentrations. Heavily impacted areas showed significant levels of physicochemical parameters. The acidic nature of the soil indicate high tendency for metal availability. Heavy metal contamination is limited to the topsoil and did not penetrate to greater depths. The levels of metals measured at the study sites were higher than those at the control. The study revealed that in addition to the crude oil spillage that occurred in the area industrial and domestic effluents also contributed to the elevated levels of heavy metals and physicochemical parameters measured in the area.

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