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THE EFFECTS OF CRUDE OIL SPILL ON SOME SOIL PROPERTIES OF DIFFERENT SITES IN DUHOK GOVERNORATE - KURDISTAN REGION OF IRAQ

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ABSTRACT:

A study was conducted to investigate the impact of oil spillage on some properties of soils collected from Kashe and Nzarke sites in Duhok governorate, Kurdistan region of Iraq. Soil samples were taken from each site after one weak and then after three months at 0-15 cm and 15-35 cm depths with control samples approximately 500 m from outside oil spill area. The soil samples were analyzed using standards of routine laboratory methods to determine some soil properties. Based on results of the study the contaminated area has higher % TN (percentage total nitrogen) (0.34 and 0.28 %), % TOC (percentage total carbon) (4.84 and 5.81 %), Pb (lead) (1.59 and 2.28 mg L^{-1}) and Fe (Iron) (3.20 and 3.13 mg L^{-1}) for Kashe and Nzarke sites respectively than the control especially for 0-15 cm. Crude oil causes decrease in soil pH below 8.2 and also reduced the concentration of available phosphorus to a values of (18.40 and 15.20 mg L^{-1}) for Kashe and Nzarke soils respectively than the control (20.60 and 16.20 mg L^{-1}) for the two sites respectively. Higher values for EC (electrical conductivity), % TN, available phosphorous were found in Kashe site while Nzarke had higher % TOC, % OM (organic matter), CEC (cation exchange capacity), THC (total hydrocarbon) and available phosphorus.

KEYWORDS: Crude oil spill, Heavy metals, Soil properties, Total hydrocarbons.

1. INTRODUCTION

Spillage of crude oil is one of the major environmental problems in most oil-producing countries, and it has negative impacts on an organism ecosystem including human-being (Abdus et al., 2016). There are many studies have been carried out to estimate this type of pollution and their effect on humans, plants, and animals (Roseta and Ebomotei, 2011). Kurdistan region of Iraq considers one of the newest regions begin to produce oil in the Middle East, and like any other oil-producing countries, the effects of the oil spills began to appear on soil, water and environment (Barua et al., 2011). In most oil-rich countries, large amounts of oil have been released on farmland. One of the major sources of oil spills is related to human activities for instance exploration, storage, refining, and transportation, through this processes crude oil and its products have released to the soil. Furthermore, when the oil is separated from the water, oil spills also happen at the centers of oil collection. These spills may be either natural or accidental (Talukdar and Saikia, 2010). Products of Crude oil and refinery become a dangerous problem and it is mainly due to breakdowns of oil pipelines, wells and distribution of petroleum products (Song et al., 1990). In the rainy season, spillage of crude oil from tankers to the nearby forest or agricultural regions would cause soil and water pollution in the affected area (Atlas and Bartha, 1973). Contamination of soil and the aquatic environment by good explosion, sabotage, pipelines rupture and through oil carrier, as a result, these activities poses a hazardous to the agricultural land and living organisms. The release of Crude oil into the soil has alters the chemical properties of soil and it damages the soil fertility due to the destruction of habitats of microorganisms, fauna, and vegetation and causes the imbalance in nutrient recycling (Barua et al., 2011).

Refinery products of petroleum are complex mixtures of heavy metals, hydrocarbons, corrosion inhibitors, antioxidants and other additives (Essien and John, 2010). The most common sources of petroleum contamination of soil are oil spills from well blow-outs, disposal of oil base wastes, and pipeline ruptures (Reis, 1996). It was reported that oil spill hinders soil aeration as an oil film on the soil surface acts as a physical barrier between the soil and air thus affecting the chemical properties of the soil such as pH and nutrient status (Aghalino, 2000). There is a remarkable release of the heavy metals into soils caused by human activities (Salim and Spark, 2001). The total contents of heavy metals in soils are ordinarily used to indicate the contamination degree, but the most concentrations of heavy metal in the soil solution determine the actual environmental risks. Hence, it is necessary to measure the total concentration and chemical speciation in order to describe the behavior of heavy metals in soils (Tessier et al., 1979). The oil spillage impact on the environment is mostly evaluated by changes in the physical, chemical and biological components of the ecosystem. This impact on the soil environment is largely relies on the relative conditions of the soil and accumulated oil remains (Edwin and Albert, 2010). It has been indicated that the soil was affected by the crude oil spillage caused a decrease in soil moisture, porosity, water holding capacity, soil pH and extractable phosphorous, whereas the organic carbon, total nitrogen and exchangeable potassium of soil were increased (Barua et al., 2011). The present study investigated the toxic effects of oil contamination on some soil properties and heavy metal content of the contaminated soils, which is a major of risk evaluation, and also to estimate the damages caused by the oil spill on the soil environment.

2. MATERIALS AND METHODS

The study area of the present research was around the local oil refinery in Kashe site (36°59' N latitude; 42°48' E longitude) and around oil-powered generators site in Nzarke site (36°50' N latitude; 43°1' E longitude) of Duhok Province in Kurdistan region of Iraq (Figures 1, 2), where both sites exposed to spillage of oil conducted by local petroleum companies. Duhok climate type is Mediterranean with a mean annual temperature of (19.2 °C) and mean annual precipitation of (539 mm) (Sulaiman et al., 2014). The soil of the area has low organic matter content (nearly 1.2-1.85 %). The bedrock beneath the soil in this area is calcareous (Fayadh, 2007).

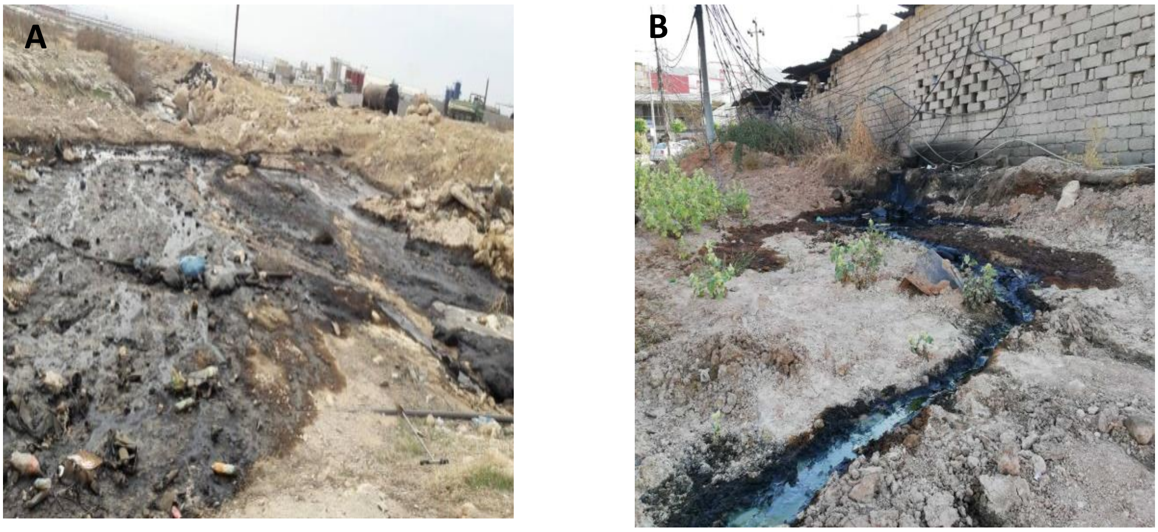


Figure 1. Photographs showing oil crude spillage in Kashe (A) and Nzarke areas (B).

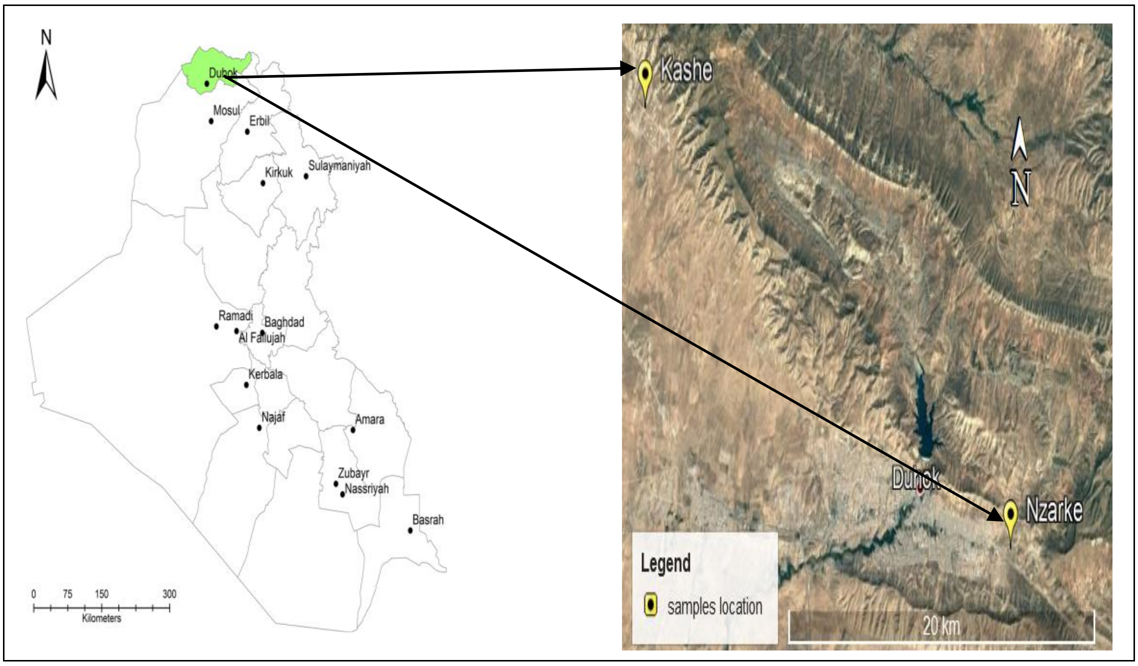


Figure 2. Location map showing the sampling sites.

2.1 Collection of soil samples:

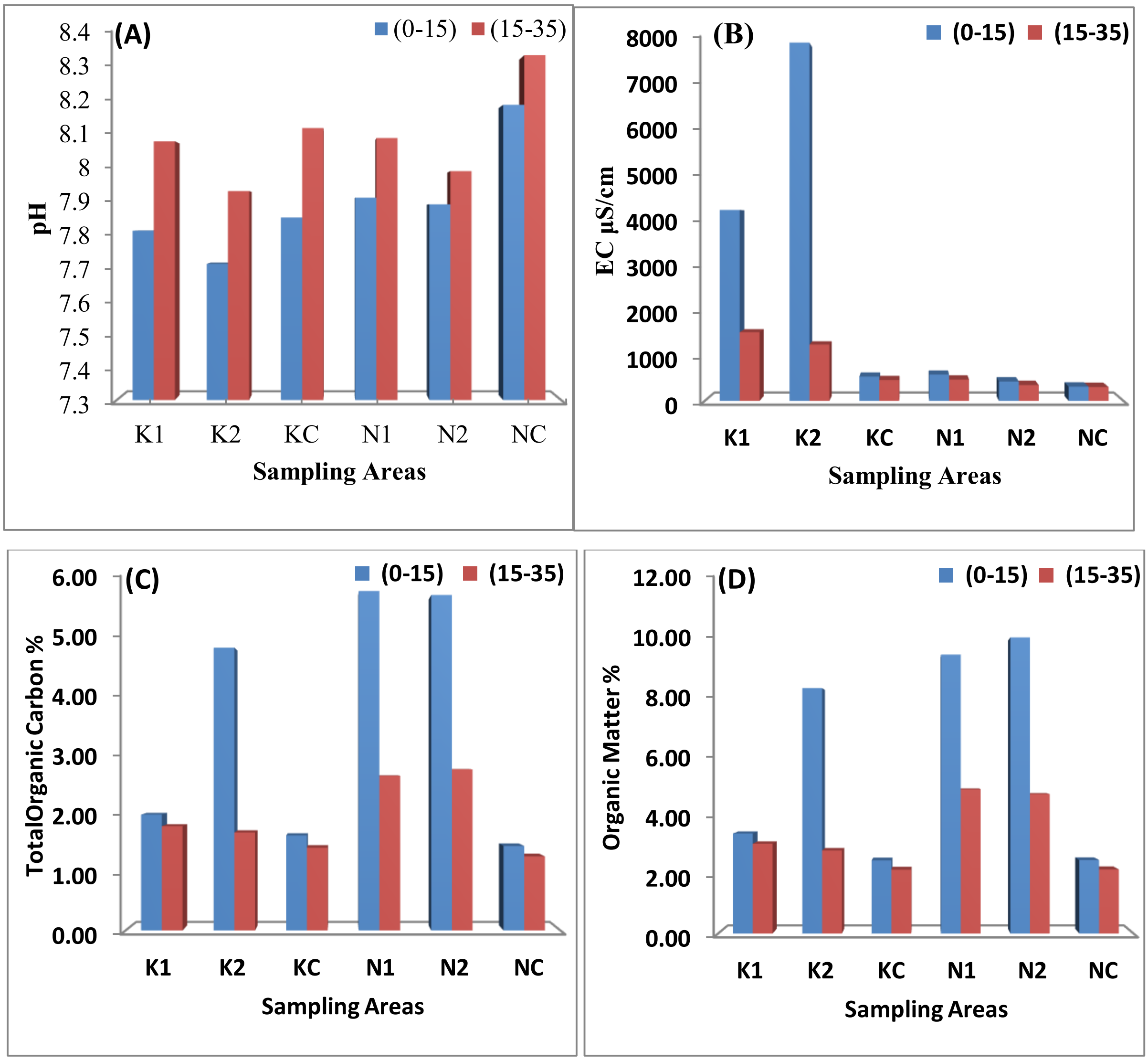
Two sampling sites were selected for each area; one was taken after one week (K1, Kashe site; N1, Nzarke site) and the other after three months Kashe site (K2) and Nzarke site (N2) after exposed to spillage oil. Soil samples were collected at surface (0-15 cm) and subsurface (15-35 cm) depths using soil auger equipment. The control samples Kashe site (KC) and Nzarke site (NC) were taken outside the contamination area up to approximately 500 m from the polluted sources. The collected soil samples were spread on a piece of nylon, it was individually air dried at room temperature, stones or debris were removed by hand and then the soil samples were broken and sieved through a 2.0 mm. The samples were then kept in clean polyethylene bags until analysis. Three replicates were used. All the test materials were immediately transferred for analysis.

2.2 Laboratory Analysis:

Standard routine laboratory methods were used to determine the following soil properties: The particle size distribution was determined by hydrometer method according to the procedures of (Gee and Or, 2002), Bulk density was measured by core method (Grossman and Reinch, 2002). Porosity was computed from bulk density and particle density (Brady and Weil, 1999). Soil pH was determined potentiometrically from the slurry of 1:25 soil-water ratio, before taking the measurements, the pH meter was calibrated using buffer solution of pH 7 and pH 4 (Jackson, 1958). Electrical conductivity was determined by EC meter in 1:25 soil: water suspension (Hanlon, 1993).The Cation exchange capacity was measured by extraction with ammonia acetate (1N) NH_4OAC according to the method of (Jackson, 1958). Total Organic carbon was measured according to the method described by (Walkley and Black, 1934) then the organic matter content calculated by multiple organic carbon results by 1.724. Total available phosphorus was measured by the ammonium molybdate in ascorbic acid blue colour method (Olsen and Dean, 1965). Total Nitrogen was measured using the Kjeldahl digestion method (Bremner, 1965). Total Hydrocarbon was carried out using the procedure described by (Ijah and Ukpe, 1992). Heavy metal analysis was conducted after digesting 1 g of soil using concentrated perchloric acid ($HClO_4$). The digested soil samples were left to cool, then filtered through Whatman No.42 filter papers in a 100 mL volumetric flask and then supplemented to the mark with distilled water. Atomic Absorption spectrophotometer GBC932AA model in Agriculture College laboratory of Duhok University was used for determination of heavy metals

3. RESULTS AND DISCUSSION

The chemical properties and heavy metals results were calculated at 95 % confidence limits using Microsoft Excel software. Figure.3. (A) shows small differences in pH values between locations and time of sampling; however, the values were higher in 15-35 cm depth. Soil pH values of the contaminated soil samples were less than the control, this may be attributed to petroleum hydrocarbon pollution which increase the acidity of the soil (Dutta et al., 2017). EC of Kashe was higher in top soils. The values vary from 7946.0 µS cm^{-1} to 4228.0 µS cm^{-1} for 0-15 cm and from 1519.3 µS cm^{-1} to 1245.3 µS cm^{-1} for 15-35 cm depth (Figure.3. B). After three months EC values were greater than after one week for 0-15 cm depth.



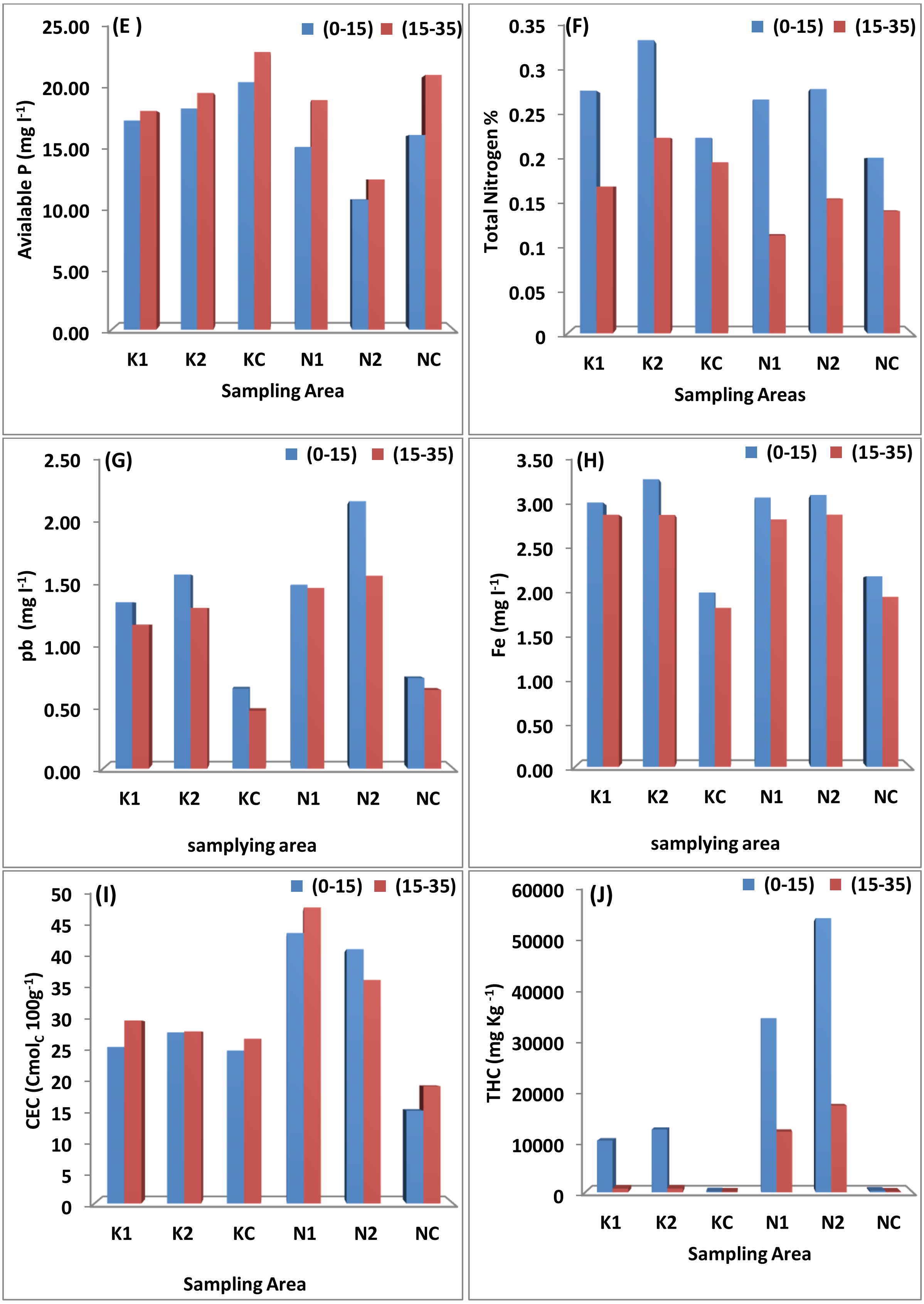


Figure.3. Shows the study of different parameters including: (A) pH, (B) Electrical conductivity, (C) Total organic carbon, (D) Organic Matter, (E) Available phosphorus ,(F) Total Nitrogen, (G) lead, (H) Iron, (I) cation exchange capacity, and (J) total hydrocarbon in soil samples at different areas and depths.

Small differences were found between samples of Nzarke contaminated samples and were small compared with control. Considering the two areas, large differences were observed between Kashe and Nzarke samples. The reason responsible for the above variation could be attributed to the different type of crude oil in the two areas. Figure.3. (C, D) show the same trend for % total organic carbon and % organic matter for all treatments and depths. Generally, Nzarke values were higher than Kashe area. This may be related to the above reason. For both sites, samples taken after one week were higher. The percentage of organic matter is used as an indicator because of its effect on other physical, chemical and biological properties of soil (Dutta et al., 2017).

Organic carbon %, total nitrogen % and available phosphorous are important indexes for a soil fertility evaluation. In this study, an increase in % total organic carbon and % total nitrogen was observed when compared to control for the two locations and depths. % total organic carbon was higher for Nzarke area, while % total nitrogen was higher for Kashe area; it may be related to the lower consumption of nitrogen by organisms in Kashe area (Debojit and Sarada, 2011). A decrease in available P was noticed in the contaminated samples compared to control (Figure .3. E). Comparing the two locations, Kashe had higher available phosphorous than Nzarke; this may be attributed to the effect of crude oil on microorganism activity (Uzoho and Oti, 2004). Heavy metals (Pb and Fe) concentration in both polluted locations and control were shown in Figure.3. (G, H). The analysis of samples indicated a higher concentration of Pb and Fe in the contaminated area than control for the two depths. The increase in the concentration of these metals in the topsoil indicates the large effect of the crude oil on the properties of soil. Crude oil contains a substantial amount of heavy metals and therefore crude oil may be contributed to the high concentration of metals in the nearby area (Aneliefo and Vwioko, 1995). It has been reported that heavy metals from oil are potential environmental pollutants and many of them are toxic even at very low concentration (Kumar et al., 2016). Considering the two locations, higher concentrations of Pb were found in Nzarke area for the two depths and control, while Fe concentrations were nearly similar. The concentration of Pb increased 2-2.5 and 2-3 times than the control for Kashe and Nzarke area respectively. Cation exchange capacity and total hydrocarbon values (Figure.3. I and J) were directly related to clay content and % organic matter of the samples. Higher values for cation exchange capacity were obtained in Nzarke area for both depths because of higher % organic matter and clay content (Okoro et al., 2011). Generally, increase trend with 0-15 cm depth was observed for cation exchange capacity of the two locations.

Table1. Physical characteristics of soils impacted by oil spill at two depths.

Sample	Depth	% Sand	% Silt	% Clay	Texture	Bulk density ($g\ cm^{-3}$)	% Porosity
K1	0-15	27.3	30.0	42.7	CL	1.75	33.96
	15-35	22.5	30.0	47.5	CL	1.67	36.98
K2	0-15	22.5	35.0	42.5	CL	1.81	31.70
	15-35	25.0	32.5	42.5	CL	1.78	32.83
KC	0-15	22.0	38.0	40.0	CL	1.33	49.81
	15-35	19.5	33.0	47.5	CL	1.37	48.30
N1	0-15	22.0	35.4	42.6	CL	1.47	44.53
	15-35	27.0	25.4	47.6	CL	1.43	46.04
N2	0-15	27.0	27.9	45.1	CL	1.55	41.51
	15-35	22.0	27.8	50.2	CL	1.62	38.87
NC	0-15	32.0	31.0	37.0	CLL	1.42	46.42
	15-35	29.5	36.0	34.5	CLL	1.40	47.17

***CL-** Clay **CLL-** Clay Loam

3.1 Soil Texture:

Table (1) shows the percentage of sand, silt, clay and texture of the soils used in the study. There were no significant changes in particle size distribution for studied soils. Both Kashe and Nzarke sites have roughly balanced values of sand, silt and clay with the lowest amount of sand content. Nzarke has a slightly higher amount of clay content.

3.2 Bulk Density:

Soil compaction is measuring by bulk density. Generally, the greater the bulk density the less pore space for water infiltration into the soil, root growth, soil aeration, and seed germination. From table (1), in Kashe the values of the average bulk density obtained for the two depths for K1, K2 and KC areas were 1.71 g/cm^3, 1.80 g/cm^3 and 1.35 g/cm^3 respectively, whereas in Nzarke for N1, N2 and NC areas were 1.45 g/cm^3, 1.59 g/cm^3 and 1.42 g/cm^3 respectively. It has been found that the oil spill affected slightly on the bulk density of both sites as compared with control. This indicates that oil spillage increases the bulk density of the investigated soils corroborating with (Chikezie et al., 2009).

3.3 Soil Porosity:

The mean values difference in percentage porosity for the two depths between control and polluted area K1, K2 and KC were 35.47 %, 32.26 % and 49.05 % respectively, whereas in Nzarke area were 45.28 %, 40.19 % and 46.80 % for N1, N2 and NC respectively. The lower values of porosity in the crude oil spilled areas could be attributed to the formation of thick crude oil in which coating the soil surface might have resulted in compactness of soil particles and consequently reduces the porosity of soils contaminated by crude oil (Debojit et al., 2011). Statistical analysis Pearson's correlation coefficient was also used for assessing the significant relationship between physical and chemical properties of soil. Statistical analysis was performed using the Minitab software package 17.

Table 2. The correlation (r) between studied parameters.

	pH	EC	TOC	OM	TN	Av. P	Pb	Fe
EC	-0.624**							
TOC	-0.532**	0.264						
OM	-0.527**	0.273	0.988**					
TN	-0.748**	0.666**	0.571**	0.548				
Av. P	0.286	0.075	-0.631**	-0.661**	-0.240			
pd	-0.542**	0.258	0.774**	0.805**	0.379*	-0.771**		
Fe	-0.637**	0.498**	0.678**	0.697**	0.472**	-0.586**	0.892**	
THC	-0.379*	-0.047	0.884**	0.892**	0.389*	-0.795**	0.808**	0.574**
*Correlation significant at P< *0.05*. **Correlation significant at P< *0.01*.								

EC- Electrical conductivity **TOC**- Total organic carbon **OM**- Organic matter

There was a strong negative correlation among pH and other measured parameters include EC, TOC, OM, TN, Pb, Fe and THC at 0.01 significant levels, while there is a weak correlation between pH and available phosphorous ($P > 0.05$). Moreover, there were a strongly positive correlation among EC with TN and Fe r = 0.666 and 0.498 respectively, ($P<0.01$). TOC was positively correlated with OM, TN, Pb, Fe and THC ($P<0.01$). Strong significant negative effect were also found among TOC, OM and available phosphorous r = -0.631 and -0.661 at $P < 0.01$ respectively. Pb correlated positively with Fe and THC r = 0.892 and 0.808 at $P < 0.01$ respectively while Fe positively correlated with THC r = 0.574 at $P < 0.01$ (Table 2).

4. CONCLUSION

The results of this study have indicated that oil spillage reduced soil pH, increased % TN, % TOC, Pb and Fe concentrations in contaminated area compared to control. However, decrease in available phosphorous was noticed in contaminated area. Considering the two locations, Kashe had higher values of EC, % TN and available phosphorous, while Nzarke had higher % TOC, % OM, CEC, THC and Pb. The concentration of Pb increased by 2-2.5 and 2-3 times than control for Kashe and Nzarke respectively. Strong negative correlation was found among pH, EC, % TOC, % OM, % TN, Pb, Fe and THC at $P<0.01$ and strong positive correlation between EC and (TN and Fe) at $P > 0.05$ and also % TOC positively correlated with % OM, % TN, Pb, Fe and THC at $P<0.01$. This research confirms the increase danger of the heavy metals by the time from crude oil spillage especially when released near farm lands. Thus, this study recommended preventing the occurrence of oil spillages as the best mean to achieve a sustainable environment development. So the petroleum companies and the government should be continually monitoring, evaluating, and managing the environment of the oilfield.

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