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Impact of Crude Oil on Physicochemical Properties and Trace Metals of Soil before and after Planting of Two Pepper species (*Capsicum annum* L and *C. frutescens* L)

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ABSTRACT: Crude oil pollution is one of the commonest environmental pollution plaguing the Niger Delta in Nigeria due to transportation, accidental discharge and spillage. This study aimed to ascertain the changes in physicochemical properties and heavy metals level of crude oil polluted soil propagated using randomized block design and measured by standard methods. The physicochemical properties of the soil before and after the end of the experiment were 0.89% (MC), 0.30% (N). 96.25ppm (P), 1.33meq/mg (K) and 1.62% (OC) as compared to 0.16% (MC), 0.27% (N), 6.00 ppm (P), 0.72 meq/mg (K) and 1.84% (OC) in control. The soil was maintained its alkaline status of 6.00 – 6.50. There was an increase in Cu, Fe and Mn in HI from 3.33 to 3.44 and 3.42 ppm, 108.99 to 138.67 and 139.05 ppm, and 147.21 to 169.97 and 170.23 ppm respectively. However, there was an increase in Zn and Pb content of HI from 94.44 to 73.93 and 74.02 ppm, and 42.10 to 27.80 and 25.45 ppm respectively of the *C. annum* and *C. frutescens.* In conclusion, crude oil affects soil properties irrespective of season by precipitating a hydrophobic layer thus creating a competitive interaction between heavy metals and essential nutrients.

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Oil pollution in the environment has been a major source of concern to the people living in the crude oil-rich-areas (Ohanmu and Bako, 2017) and the greatest effects of human advancement in technology. Pollution is itself defined as the persistent appearance of radioactive elements, toxic compounds, salts, chemicals, or disease causing agents, which have an adverse effect on the environment. Thus affecting the quality of human life, productivity in plant yield, survivals of animals and microbial populace. The contamination of the environment (mainly terrestrial and aquatic) by crude oil is referred to as crude oil pollution and it is estimated that 80% of crude oil pollution is as a result of spillage (Odu, 1997). Crude oil is the major source of energy in world and accounts for most of the pollution in Nigeria. In Nigeria, crude oil plays a pivotal role in the mainstay Nigerian economy in revenue generation and development of the country. Transportation of crude oil sometimes pollute the environment by accidental oil spills and operational discharge resulting to the loss of very large quantities of crude oil into land and sea bodies (Ohanmu *et al.,* 2014). Essien and John (2010) reported the frequent spillage on agricultural soils, and the consequent fouling effect on all forms of life by render the soil (especially the biologically active surface layer) toxic and unproductive. This reduces the soil's fertility such that most of the essential nutrients are no longer available for plant and crop utilization (Abii and Nwosu, 2009).

One of the biggest concerns associated with crude oil pollution in the environment is the risk to farmland, fisheries, and potable drinking water contamination (Ohanmu *et al.,* 2017). The soil physical properties such as pore spaces might be clogged thereby reducing soil aeration, infiltration of water into the soil and increased bulk density of the soil. These soil properties are involved in soil-plant-water relationship are degradable and include texture, infiltration, hydraulic conductivity, moisture content, pH and density, which affect root and leaf development and plant growth and yield (Michael, 1978; CIGR, 1999; Michael and Ojha, 2006). Oil spillage also affects crop yield and farm income, and by extension, the social and economic livelihoods of farming communities. Spilled crude-oil which is denser than water, reduces and restricts permeability: organic hydrocarbons which fill the soil pores expel water and air, thus depriving the plant roots the much needed water and air (Brian, 1977).

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Other effect range from disruption of plant water relations, direct impact to plant metabolism, for instance, nutrient uptake, toxicity to living cells for example the liquid component of the protoplasm, reduced oxygen exchange between the atmosphere and the soil affecting root function to reduction in biomass (Bako *et al.* (2008); Ohanmu *et al.* (2017)). Cutler *et al.* (1991) concluded in their experiment that there are three distinct factors related to phytotoxicity of oils namely: the properties of the oils, the quality applied and the environmental condition. An extensive research has been carried out on the effects of crude oil spill on various plant crops such as pawpaw, maize, lycopersicum and capsicum (Odugwu and Onianwa, 1987; Amadi *et al.,* 1996: Daniel-Kalio and Braide, 2004: Anoliefo and Nwosu, 1994; Daniel-Kalio and Pepple, 2006; Ohanmu *et al,* 2014). However, none has explicitly compared the changes in the soil properties in two seasons which this research aimed to bridge. Therefore, this research aimed to investigate the impact of crude oil on the soil physical properties and trace metal present before and after planting in two season.

MATERIALS AND METHODS

Site: Edo State is geographically located between longitude 6°04'E and 6°43'E and latitude 5°44'N and 7°34'N of the equator. The natural vegetation consists of rain forest in the Benin low-land and is of humid tropical climate with an average annual rainfall of about 2500 mm (NDDC, 2006). The experimental site was Ahmadu Bello University, Zaria located between longitude 7°38'N and latitude 11°11'E. Kaduna State is located in the Northern Guinea savannah vegetative zone of Nigeria (Ohanmu *et al.,* 2017).

Soil collection: The crude oil polluted soil used in this study was obtained from the dumpsite at Oredo Flow Station field of the Nigerian Petroleum Development Corporation (NPDC), Ologbo, Benin City on the 11th of November, 2011. The soils were collected from three different sampling sites in Ologbo. The plant used for the experiment was *Capsicum annum* L. and *C. frutescens* L.

Layout: There were three concentrations namely; the heavily impacted soil (HI) (50% unpolluted soil + 50% crude oil polluted soil), medium impacted soil ((MI) (75% unpolluted soil + 25% crude oil polluted soil) and control (C). This was by weighing the soils. The heavily impacted soil was obtained from the point of spillage; the medium impacted soil was obtained from the burrow pit and the control from a pristine distance of 500m. The composite soil samples were bulked correspondingly in the laboratory, air-dried and crushed to break the large soil aggregates to pass through a 2mm sieve according to Ekpo and Ebeagwu (2009). The experiment was monitored taking the dry and rainy season into consideration. Each polybag contained a total of 5kg of soil. There were six (6) treatments and three (3) replicates.

Analysis of soil samples: pH and nitrogen content was done using the method of watanabe and olsen, (1965), organic carbon (C) using the method of Black, (1965), Phosphorus (P) was determine using the Bray-1 method according to Watanabe and Olsen (1965) while heavy metals such as Mn, Cu, Zn, Fe and Pb were determined using atomic absorption spectrophotometric (AAS).

Statistical analysis: The data shown in the Tables were means ($\overline{X}$) and standard errors (S.E). The results were subjected to Analysis of variance (ANOVA) using SPSS version 20.0. Duncan multiple range test was used to separate their means.

RESULTS AND DISCUSSIONS

In this present study crude oil reduced the physicochemical properties of the soil. The soil was a well-drained sandy-loam, slightly acidic with high potassium, phosphorus and percentage organic carbon but low nitrogen content. Table 1 shows that the soil was within the optimal rate for crop growth (pH 6.50), high in potassium (1.33Cmol/kg), phosphorus (96.25) and low in nitrogen content (0.30%) and percentage organic carbon (1.62%). This implies that the observed negative effects were not due to the natural poor condition of the soil but can be attributed to crude oil pollution. The low nitrogen content of the soil is typical for this soil type. Nitrogen is easily leached by rain and as a result is very often deficient in sandy soil (Ekpo and Ebeagwu, 2009). There was no significant difference in the pH of the various crude oil polluted soils as compared with the control; the range was from 6.10 – 6.20 with the highest value of pH 6.50 for control. The pH fell within the optimum range for crop cultivation and the soil pH in the various crude oil polluted soil ranges from 6.00 – 6.20 with the highest pH of 6.50 for the control (Table 1) is agree with the previous work by Nasamu (2000). Nasamu reported pH range of 5.85 – 6.10 for soils treated with Corexit9527 and Goldcrew crude oils with the highest values of pH 6.35 for the control. Treatmment had no significant effect ($p \geq 0.05$) on soil physical properties. The soils were mainly sandy in nature. At the end of the experiment, the available phosphorus in the soil was significantly reduced irrespective of concentration in the control (6.00) and (6.05) respectively as compared to 96.25 of the initial control value. The moisture content was significantly reduced ($P<0.05$) with increased in crude oil concentration. There was also a significant reduction in all other parameters. However, the soil pH was not significantly different from the initial soil pH level. However, visual observation showed that pots treated with crude oil had reduced water infiltration and percolation in the soil. This resulted in water accumulating in small pools (Ohanmu *et al.,* 2017). During the dry season, the crude oil polluted soil gave a cemented waxy appearance which more or less repelled or resisted water/rewetting.

Table 1: The physicochemical properties of the two species of pepper from soil samples at the beginning and after the experiment

	C. annum						*C. frutescens*					
	Start of Experiment			**End of Experiment**			**Start of Experiment**			**End of Experiment**		
	C	**MI**	**HI**	**C**	**MI**	**HI**	**C**	**MI**	**HI**	**C**	**MI**	**HI**
pH0.01$CaCl_2$	6.50	6.20	6.10	6.40	6.20	6.10	6.50	6.20	6.10	6.35	6.20	6.00
MC (%)	0.89^{**}	0.07	0.13	0.16^{*}	0.04	0.08	0.89^{**}	0.07	0.13^{*}	0.16^{*}	0.04	0.07
N (%)	0.30^{ns}	0.31	0.33	0.27	0.35	0.20	0.30	0.31	0.33	0.27	0.35	0.19
P (ppm)	96.25^{**}	19.25	14.00	6.00	22.75^{*}	13.13	96.25^{**}	19.25	14.00	6.05	22.75^{*}	13.18
K (meq/mg)	1.33^{*}	0.33	0.27	0.72	0.34	0.25	1.33^{*}	0.33	0.27	0.68	0.35	0.24
OC (%)	1.62	1.81	1.84	1.58	1.90	1.62	1.62	1.81	1.84	1.56	1.83	1.68

**C = Control, MI = Medium Impacted Soil, HI = Heavily Impacted Soil, MC = Moisture Content, N = Nitrogen, P = Phosphorus, K = Potassium, OC = Organic Carbon, CA = C. annum in Control, MA = C. annum in Medium polluted soil, HA = C. annum in Heavily polluted soil, CF = C. frutescens in Control, MF = C. frutescens in Medium polluted soil, HF = C. frutescens in Heavily polluted soil.*

Table 2: Heavy metal of the two species of pepper from soil samples at the beginning and after the experiment

Heavy Metal Conc. (ppm)	*C. annum*						*C. frutescens*						**FEPA Critical Value (2002)**
	Start of Experiment			**End of Experiment**			**Start of Experiment**			**End of Experiment**			
	C	**MI**	**HI**	**C**	**MI**	**HI**	**C**	**MI**	**HI**	**C**	**MI**	**HI**	
Cu	0.17	1.59	3.33^{*}	1.68	2.25	3.44	0.17	1.59	3.33^{*}	1.64	2.30	3.42	**36.00**
Fe	47.61	55.93	108.99^{*}	79.50	80.18	138.67^{**}	47.61	55.93	108.99^{*}	79.53	80.00	139.05^{**}	**40.00**
Mn	67.06	118.25^{**}	147.21^{**}	19.73	69.66	169.97^{**}	67.06	118.25^{**}	147.21^{**}	69.27	19.43	170.23^{**}	**48.00**
Zn	12.25	19.23	94.44^{**}	14.10	26.23	73.93^{**}	12.25	19.23	94.44^{**}	14.54	27.11	74.02^{**}	**43.00**
Pb	2.19	15.18	42.10^{*}	2.19	10.17	27.80^{*}	2.19	15.18	42.10^{*}	1.15	9.87	25.45^{*}	**140.00**

**C = Control, MI = Medium Impacted Soil, HI = Heavily Impacted Soil, Cu = Copper, Fe = Iron, Mn = Manganese, Zn = Zinc, Pb = Lead, CA = C. annum in Control, MA = C. annum in Medium polluted soil, HA = C. annum in Heavily polluted soil, CF = C. frutescens in Control, MF = C. frutescens in Medium polluted soil, HF = C. frutescens in Heavily polluted soil*

There was buildup of heavy metal in the soils contaminated with crude oil. Soil contents of Fe, Zn, Cu, Mn and Pb were significantly ($P\leq0.05$) higher in soils contaminated with crude oil when compared with the control (Table 2). Table 3 shows the concentration of micronutrient at the end of the experiment in the various categories of crude oil polluted soils and control. There was an increase in the concentration of Cu, Fe and Zn; and decrease in Mn and Pb in all treatments as compared to the initial concentration (Table 3). Increased level of Zn^{2+} can decrease the amount of Ca^{2+} that is assimilated by plants (Larison *et al.,* 2000). A similar relationship exists between Cd^{2+} and phosphorus (John *et al.,* 1972). Asoquo *et al.* (2002) reported that heavy metals (Fe, Cu, Zn, Ni, Cd and V) absorption by okra and *Telfairia* increased with an increase in crude oil concentration similar to what was observed in this investigation. The analysis of heavy metals in the crude oil polluted soil show that Cu and Pb were below the critical values of 36ppm and 140ppm respectively (FEPA, 2002). In general, metals tend to accumulate in the clay fraction of the soil because clay-sized particles have a large number of ionic binding sites due to a higher amount of surface area (Ohanmu *et al.,* 2017). Similarly, metals could tightly bind to the organic matter of the soil, which was found to be high (6.30%). Thereby, resulting in the immobilization of heavy metals making them unavailable to plants (Odu, 1981), and probably responsible for the amount of heavy metal residue present in the soils. Heavy metal effect could be due to the competitive interactions between heavy metals and essential nutrients. The values in the treatment were significantly higher than the critical value set by FEPA (2002) for such elements and could inhibit the uptake of nutrients absorption by plant root (Table 2).

Conclusion: The findings of this study has revealed that crude oil pollution adversely affected soil properties during the rainy and dry season. The unavailability of mineral nutrients in soils following crude oil application is due to the fact that the crude oil forms a hydrophobic layer over the root, which limits the availability of absorption of water and nutrients in plant.

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