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Evaluation of Crude Oil Contaminated Soil on the Mineral Nutrient Elements of Maize (*Zea mays* L.)

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Abstract: This study evaluated the effects of crude oil contaminated soil on the mineral nutrient elements of maize. The study was conducted in Asaba and Ozoro locations of Delta State during the 2003 and 2004 planting seasons. Open pollinated AMATZBR y maize variety was used for the study. The experiment was laid out in a split-plot design replicated four times. Five crude oil concentrations (0, 5.2, 10.4, 20.8 and 41.6 mL) applied (ring application) at five weeks after planting (5 WAP) constituted treatments. The study location formed the main plot and the oil levels, the sub-plots. Grains were harvested at 14 WAP, shelled and analysed for mineral nutrient contents. Soil chemical properties were also analysed. The results showed that while total carbon, organic carbon, C/N ratio, phosphorus, calcium, magnesium and pH were significantly higher ($p<0.05$) in soils amended with crude oil, crude oil application to soil significantly reduced ($p<0.05$) electrical conductivity, total nitrogen and nitrate nitrogen in both locations. The highest values of 23.49 and 16.67 were recorded for C/N ratio in soils with 41.6 mL of oil while the lowest values of 8.83 and 9.72 were obtained in soils without oil treatment in Asaba and Ozoro locations, respectively. Significant differences ($p = 0.05$) were observed in the nutrient contents of maize seeds grown in soils amended with crude oil when compared with those grown in the uncontaminated sub-plots. The present study has demonstrated that crude oil contamination can improve soil content of some nutrient elements including Mg^{2+}, K^{+}, P, Na^{+} and exhibit a highly significant effect of reducing the chemical composition of maize seeds.

Key words: Crude oil, soil contamination, nutrient elements, chemical composition, maize

INTRODUCTION

Maize (*Zea mays*) is an important food, fodder and industrial crop in the world (FAO, 2002). It is second to wheat in the world's cereal production (Rouanent, 1992). In Nigeria, maize is a major food and industrial crop grown both commercially and at subsistence level by most farmers (Miracle, 1966; Obi, 1991).

Nigeria, a major producer and exporter of crude petroleum oil, experiences crude oil pollution through accidental discharge, sabotage and other sources (Nwilo, 1998; Agbogidi and Nweke, 2005a; Agbogidi *et al.*, 2005a). Oil pollution has been reported to have harmful effects on agricultural lands and crops (Adams and Ellis, 1960; Atuanya, 1987; Anoliefo and Vwioko, 1994; Benka-Coker and Ekundayo, 1995; Ekundayo and Obukwe, 1997; Asuquo *et al.*, 2002; Agbogidi and Nweke, 2005b). There is however, dearth of information on the effects of crude oil impacted soil on the nutrient content of crop species especially cereals. The present study has been undertaken to evaluate the effects of crude oil contaminated soil on the mineral nutrient elements of maize, a principal food crop grown by most farmers in Delta State, Nigeria.

MATERIALS AND METHODS

Study locations: The study was carried out in the Research farm of the Delta State University, Asaba Campus and the Delta State College of Agriculture, Research farm, Ozoro. Asaba lies in latitude: 06° 14 ¹N, longitude: 06° 49¹ E, temperature: 28±6°C, rainfall 1505-1849 mm, relative humidity: 69-80% and monthly sunshine: 4.8 h. The soil type is acidic and it is located in the rainfall agro-ecological environment (Asaba Meteorological Station, 2003). Delta State College of Agriculture Research Farm, Ozoro lies between latitude 6° 13¹ E and longitude: 5° 33¹ N and it is under the rainforest ecological zone of Delta State. Ozoro experiences double peak periods of rainfall between June/July and September/October respectively. The annual rainfall is 1800 mm while that of the temperature is

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31°C and relative humidity 76-90% (College of Agriculture Meteorological Station, Ozoro, 2003). The experiment took place between April and September 2003 and 2004 cropping seasons.

Experimental materials and design: NPK fertilizer (20-10-10) was obtained from the Delta State Agricultural Procurement Agency (DAPA), Ibusa, Delta State. It was applied prior to planting based on the analytical information of the soil nutrient status. The crude oil used (with specific gravity of 0.8334 g cm^{-3} and AP1 gravity of 34.2897) was obtained from the Nigerian National Petroleum Corporation (NNPC), Warri. The maize AMATZBR y (open-pollinated) was sourced from the International Institute of Tropical Agriculture (IITA), Ibadan, Oyo State.

The experimental design was a split-plot arrangement replicated four times. Location of study formed the main plots while the crude oil levels were allotted the sub-plots. A sub-plot (2.8125 m^2) contained 24 stands of maize. Planting was done in 2003 and 2004 cropping seasons in both locations. Between row spacing was 75 cm and within row was 25 cm. Five crude oil levels (0, 5.2, 10.4, 20.8 and 41.6 mL) were applied to soil (ring applicable) at five Weeks after Planting (WAP). Ears were harvested at 14 WAP and mechanically shelled.

Proximate analysis of the maize seeds was carried out at the Nigerian Institute for Oil Palm Research (NIFOR) near Benin, Edo State. The samples were dried, weighed and a known amount ashed and then wet digested using nitric acid. The digests were later analysed for trace mineral contents by flame atomic absorption spectrophotometer using the standard addition method (AOAC, 1990). The effects of crude oil on soil chemical properties in both Asaba and Ozoro locations were also assessed in NIFOR using composite soil samples collected from 0-20 cm depth prior to treatment application and at harvest (14 WAP). Soil pH was determined in distilled water using a soil: liquid ratio, available phosphorus was measured in soil extracts by the ascorbic acid method (Bray and Kurtz, 1945). Total nitrogen was determined by the Regular Macro-Kjeldahl digestion technique (Jackson, 1964; Pearson, 1976). Nitrate nitrogen was determined by the phenoldisulphonic acid method (Esu, 1999), organic carbon was measured by the wet oxidation method (Walkley and Black, 1934) and converted to organic matter by multiplying the values by a factor of 1.724 following the procedure of Allison (1965). C/N ratio was calculated by dividing carbon values by those of total nitrogen.

Exchangeable calcium and magnesium were determined on atomic absorption spectrophotometer using penchloric acid while sodium and potassium were determined on flame photometer (Udo and Ogunwale, 1986). Ammonium acetate extracts of soil samples were used in these exchangeable bases determination. Determination of exchangeable acidity (H^+ and Al^{3+} was by KCl extraction method (McLean, 1965). Total Exchangeable Bases (TEB), was calculated by adding the values of all the exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+). Total Exchangeable Acidity (TEA) was calculated as the sum of exchangeable H^+ and Al^{3+} ions. Effective Cation Exchangeable Capacity (ECEC) was calculated by adding the values of the TEB and TEA. The Base Saturation (BS) was calculated by dividing the values of TEB by the ECEC and multiplying by 100. Data collected were subjected to analysis of variance and significant means were separated with the Duncan's multiple range test using SAS (1996).

RESULTS

The results of the effects of different crude oil levels on some chemical soil properties at Asaba and Ozoro locations are indicated in Table 1. Available P in the soil significantly increased ($p<0.05$) with an increase in oil level up till 20.8 mL of oil in the two locations and then decreased at 41.6 mL of crude oil treatment. The pH of the

Table 1: Effect of different crude oil levels on some chemical soil properties at Asaba and Ozoro locations

Crude oil level in soil (mL)	pH	EC (μg cm^{-1})	Total C (%)	Organic carbon (%)	Total N (%)	No_3 (%)	P (ppm)	C/N
Asaba location								
0	5.60c	142.5a	0.53c	0.91d	0.060b	4.88a	30.00d	8.83d
5.2	5.75c	88.6c	0.58bc	1.00c	0.058b	4.16b	35.45c	10.00d
10.4	5.71c	84.5cd	0.72b	1.24ab	0.050b	3.12c	41.04b	14.40b
20.8	5.79b	82.4cd	0.96a	1.66a	0.044c	3.00d	46.21a	21.82ab
41.6	6.00a	76.8d	1.01a	1.74a	0.043c	2.92d	40.56b	23.49a
Ozoro location								
0	4.80d	153.9a	0.70b	1.21d	0.072a	5.04a	34.31a	9.72d
5.2	4.90d	113.1ab	0.74b	1.28c	0.070a	4.56a	38.64b	10.57c
10.4	5.00d	102.4b	0.81ab	1.40b	0.065b	4.08b	45.82a	12.46c
20.8	5.10d	96.9b	0.98a	1.69a	0.063b	3.36c	49.00a	15.56b
41.6	5.25d	91.2bc	1.00a	1.72a	0.060b	3.25d	43.48ab	16.67b

Means in the same column with same letter(s) are not significantly different (p = 0.05), using DMRT

Table 2: Effects of different crude oil levels on soil TEB, TEA, ECEC and BS at Asaba and Ozoro locations

Crude oil levels (mL)	Exchangeable ions Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	H^{+}	Al^{3+}	TEB	TEA	ECE	BS (%)
	c mol kg^{-1}									
Asaba location										
0	1.31b	0.16d	0.25b	0.17c	0.45d	0.08a	1.89c	0.53bc	2.42c	78.10b
5.2	1.34b	0.18d	0.10c	0.15c	0.57b	0.07a	1.77c	0.64b	2. 41c	73.44c
10.4	1.65a	0.40c	0.31a	0.14c	0.50c	0.06a	2.50a	0.56bc	3.06b	81.70b
20.8	1.74a	0.56ab	0.44a	0.13d	0.45d	0.04b	2.87c	0.49c	3.36b	85.42a
41.6	1.76a	0.64a	0.38a	0.11d	0.42d	0.02c	2.89a	0.44d	3.33b	86.79a
Ozoro location										
0	1.35b	0.48b	0.21c	0.26a	0.80a	0.09a	2.30b	0.89a	3.19b	71.10c
5.2	1.42b	0.56ab	0.19c	0.24ab	0.84a	0.05b	2.41b	0.89a	3.30b	73.03bc
10.4	1.66a	0.64a	0.16c	0.21b	0.83a	0.05b	2.67a	0.88a	3.55a	75.21b
20.8	1.78a	0.72a	0.15c	0.19bc	0.81a	0.04c	2.84a	0.85b	3.69a	76.68b
41.6	1.80a	0.80a	0.14c	0.17c	0.72a	0.03c	2.91a	0.75ab	3.66a	79.51ab

Means in the same column with same letter(s) are not significantly different (p = 0.05), using DMRT. TEB = Total Exchangeable Bases, TEA = Total Exchangeable Acidity, ECEC = Effective Cation Exchange Capacity and BS = Base Saturation

Table 3: Chemical composition of maize seeds as affected by crude oil levels in soil

Proximate composition of maize (%)	Oil level (mL) 0	5.2	10.4	20.8	41.6
Crude protein	2.60a	2.57a	2.54b	2.51b	2.24c
Fat	2.18a	2.16ab	2.10b	2.08b	2.01c
Ash	0.59a	0.57a	0.54b	0.50c	0.42d
Moisture	8.98a	8.96a	8.90b	8.81c	8.63d
Carbohydrate	85.63a	85.60ab	85.43b	84.03c	83.12d

Means in the same row with the same letter(s) are not significantly different (p = 0.05), using DMRT

Table 4: Nutrient content (% dry matter) of maize seeds as affected by different crude oil levels in Asaba and Ozoro

Crude oil levels (mL)	Nutrient content Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	P (%)	N (%)
	mol kg^{-1}					
Asaba location						
0	0.14a	0.66d	1.63c	1.01d	0.18d	0.63d
5.2	0.12b	0.68d	1.68c	1.23d	0.20d	0.65c
10.4	0.10c	0.72c	1.72c	1.45c	0.24c	0.68c
20.8	0.09c	0.76b	1.76b	1.58b	0.28b	0.72b
41.6	0.08d	0.79b	1.79b	2.00a	0.31b	0.77b
Ozoro location						
0	0.16a	0.71c	1.70c	1.24d	1.21d	0.73b
5.2	0.15a	0.74b	1.72c	1.39d	1.25c	0.76b
10.4	0.12b	0.76b	1.75b	1.48c	1.30b	0.82b
20.8	0.11c	0.82b	1.81b	1.68b	1.34a	0.88a
41.1	0.10c	0.86a	1.86a	1.94a	1.41a	0.91a

Means in the same column with same letter (s) are not significantly different (p = 0.05), using DMRT

soils significantly ($p<0.05$) increased with increasing oil levels within the locations. The highest pH values of 6.00 (Asaba) and 5.25 (Ozoro) were recorded for the 41.6 mL of oil treatment. Contamination of soil with crude oil resulted in an increase in total carbon (Table 1). The organic carbon increased from initial value of 0.91 to 1.21% in the control to 1.74 and 1.72% in soils amended with 41.6 mL of oil in Asaba and Ozoro respectively. Total nitrogen and nitrate nitrogen in the soils were observed to significantly decrease ($p<0.05$) with an increase in crude oil concentration (Table 1). The C/N ratio in soil under control for Asaba and Ozoro locations were 8.83 and 9.72, respectively (Table 1). The highest C/N ratio of 23.49 and 16.67 at 41.6 mL were recorded for Asaba and Ozoro, respectively.

The exchangeable cation contents, Total Exchangeable Bases (TEB), Total Exchangeable Acidity (TEA), Effective Cation Exchange Capacity (ECEC) and Base Saturation (BS) of soils of the experimental sites (Asaba and Ozoro) are indicated in Table 2. Exchangeable H^{+} was significantly higher ($p\leq 0.05$) in soils amended with 5.2 mL crude oil and lower in soils that were treated with the highest volume (41.6 mL) of crude oil. Exchangeable Al^{3+} significantly decreased ($p\leq 0.05$) with increasing level of crude oil. Similarly, TEB, TEA and ECEC showed no consistent trend between treatments; however the base saturation significantly increased, with increasing amount of oil at $p\leq 0.05$.

The proximate/chemical composition of maize seeds as affected by crude oil levels in soil is presented in Table 3. The results showed that oil application to soil had a significant ($p = 0.05$) effect on the carbohydrate content of the maize seeds. When compared with the maize seeds from the uncontaminated soils, significant ($p<0.05$) reductions were observed in the carbohydrate, protein, fat and moisture contents of maize seeds exposed to crude oil treatment (Table 3). The mineral element composition of the maize seeds as influenced by five levels of oil in soil is indicated in Table 4. The results showed significantly ($p<0.05$) higher amounts of Mg^{2+}, K^{+}, Na^{+} and P in maize seeds subjected to crude oil amendment when compared with their counterparts not exposed to oil treatment. Significant reductions ($p<0.05$) were observed in Ca^{2+} values as the concentration of crude oil in soil increased (Table 4).

DISCUSSION

The observed increase in exchangeable Ca^{2+} and Mg^{2+} contents as a result of crude oil application is in line with the findings of Amadi *et al.* (1993) who noted increases in the cations of soils treated with crude oil. The high concentration of exchangeable Ca^{2+} and Mg^{2+} in soil can be attributed to rapid decay and mineralization of organic and mineral materials in the soils. These processes lead to the release of cations and trace elements (Nnaji *et al.*, 2005). All the values of the exchangeable Ca^{2+} still fall below critical limit (4 cmol kg^{-1}) for fertile soils (FAO, 1976). Thus, they are far below the optimum (10 cmol kg^{-1}) requirements for agricultural productivity (FAO, 1976). Exchangeable H^{+} was highest in soils amended with 5.2 mL crude oil and least in soils that were treated with the highest volume (41.6 mL) of crude oil. Exchangeable Al^{3+} decreased with increasing level of oil. These reductions may be due to the reduction of leaching as a result of hydrophobic action. Reduction in K^{+} and Na^{+} may be due to nutrient immobilization consequent on the formation of complexes in the soil after degradation and uptake. The observed increase in the phosphorus content of the crude oil contaminated soil may be due to the increase in soil pH resulting from amendment application. This finding supports earlier reports by Bielski and Ferguson (1983) who noted that increasing pH increases weathering and mineralization rate. This could have increased phosphorus availability and reduced its fixation (Isirimah *et al.*, 2003) up to a pH of about 5.5-6.0 thereafter, phosphorus availability started to decrease. Siddiqui and Adams (2002) had also recorded increased P with increasing concentrations of diesel hydrocarbons up to a stage and then it declined. This increase in soil pH may be attributed to the accumulation of exchangeable bases (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) in the oil contaminated soils. This finding is consistent with those of Benka-Coker and Ekundayo (1995) and Ekundayo and Obuekwe (1997). The values measured are not detrimental to crops as high agricultural productivity can be obtained in soils with pH up to 6.5 (FAO, 1976). All the values of available phosphorus fall within the range of 20-100 mg kg^{-1} of soil; indicating optimum levels for growth of crop plants (FEPA, 2002).

The observed increase in the total carbon content of the soil with increasing concentration of the crude oil may be attributed to the high content of carbon in the oil. This could have been converted to soil organic carbon. Similar findings have been reported (Ellis and Adams, 1961; Benka-Coker and Ekundayo, 1995). This observation also agrees with the findings of Ekundayo and Obuekwe (1997) who noted increases in organic carbon content of oil polluted soils in Southern Nigeria. It may also be related to the slow decomposition rate of the amendment by soil organisms since contamination of soil with crude oil might have resulted in poor soil aeration. The soil organic carbon contents are not above the 2.0% critical levels required for plant growth (FAO, 2002).

The decrease in total nitrogen and available nitrate with increase in oil levels may be due to temporal immobilization of this nutrient by microbes resulting, which might have increased in population. Jobson *et al.* (1974) had earlier reported that oil spills on land resulted in an imbalance in the carbon: nitrogen ratio which, if greater than 17:1 in soils resulted in net immobilization of nutrients by microbes leading to loss of soil fertility. Nutrient immobilization following oil pollution of soil has also been reported by De Jong (1980) for cereals. The resultant increase in the microbial population would demand initial nitrogen from the soil thereby decreasing the total nitrogen and available nitrate in the soil in the short term. The decrease with time may also be interpreted to be due to high uptake of nitrogen with increased plant growth since N is one of the most important nutrients taken up by plants in large amount. Total N content of soils was below (0.2%) the critical value required for optimum agricultural productions (FMANR, 1990). The observed change in electrical conductivity indicates that the application of crude oil affected the ionic stability of the soil, which could have contributed to the decreased conductivity with increasing oil levels. An increase in crude oil concentration increased the soils ionic strength thereby increasing nutrient available in the soils. The values of the total exchangeable bases, total exchangeable acidity and effective cation exchange capacity did not exceed the critical values suitable for optimum crop productions if other environmental factors are favourable (FAO, 1976; Holland *et al.*, 1989).

The observed increase in the amount of Ca^{2+}, K^{+}, P and Na^{+} content of soil due to application of the crude oil could have enhanced soil fertility (Mangel and Kirkby, 1987). Although this did not result in better crop or yield performance, it can be suggested that these nutrients could have been antagonized and made non-available by those toxic, non-essential nutrients (Epstein, 1972) thereby preventing their uptake by plants. Alternatively, the observed slight acidity level of soils could have been responsible for the poor utilization of the nutrients in the growth medium.

The observed reduction in the chemical composition of the maize seeds with increasing oil level in soil supports the observation of Jaja and Barber (1999) who reported that crude oil pollution reduced the carbohydrate content of rice. A significant reduction in the protein, fat and moisture contents of the maize seeds as observed in the present study could be attributed to one or a combination of the following factors; a disturbance in the soil-water relation of the maize plant, impairment of photosynthetic activities through cell injury and disruption in the cell membrane, distortion in the metabolic activities of the plant, heavy metal accumulation, chemical composition and or toxic nature of the crude oil or other stress imposing properties of the crude oil applied resulting in anatomical aberration. Previous findings by Gill *et al.* (1999) and Agbogidi *et al.* (2005b) showed that crude oil has a deleterious effect on plant growth.

The study has demonstrated that soil contamination with crude oil has a highly significant effect of reducing some mineral element composition of maize seeds and this could provide a basis for future work by plant breeders who are searching for means of boosting maize production in the oil producing areas of the Niger Delta region.

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