

## Zinc availability in relation to selected soil properties in a crude oil polluted eutric tropofluent

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**ABSTRACT:** The study investigated zinc availability in relation to selected soil properties in a crude-oil-polluted Eutric Tropofluent in Egbema, Southeastern Nigeria. For this purpose, three treatments have been applied: unpolluted soil, polluted without vegetation and polluted with vegetation with five replicates arranged in a randomized complete block design. Guided by transect sampling technique, soil sampling was carried out in June 2008. Soil samples were collected from the three different land units using soil auger at a depth of 0-20 cm. Standard laboratory procedures were adopted in analysing the soils. Soil generated data were subjected to analysis of variance and correlation analysis. Results showed highly significant variation ( $p = 0.01$ ) in bulk density, porosity, silt: clay ratio, pH, effective cation exchange capacity, percent base saturation, total nitrogen, organic matter, available phosphorus, calcium: magnesium ratio and zinc. It was found that zinc was higher in crude oil polluted soils than in non-polluted soil and it was below critical limits. Zinc availability in relation to selected soil properties in the crude oil polluted soils indicated that clay and organic matter did not affect zinc availability, while pH and effective cation exchange capacity did. A study on zinc dynamics in crude-oil-polluted soils will certainly provide further information on the management of crude-oil-polluted soils since it is one of the key micronutrient for crop productivity.

**Keywords:** Eutric tropofluent; Soil properties; Spillage; Tropical soils; Zinc availability

### INTRODUCTION

Soil is the aggregate of decaying organic matter (OM); living organisms and weathered mineral materials (Bellamy, 2007). Soils suffer from pollution (Onweremadu and Duruigbo, 2007) such as crude oil spillage. Crude oil which is abundantly located in the Niger-Delta region of Nigeria is spilled on soils due to several factors such as pipeline destruction (Nwilo and Badejo, 2001). Crude oil spillage on soils causes lots of adverse effects which hinder soil productivity (Udo and Fayemi, 1975; Rowell, 1977; Okpokwasili and Odokuna, 1990; Ladousse and Tramier, 1991).

In addition, the availability or otherwise of heavy metals and micronutrients such as zinc (Zn) is equally affected. Onweremadu and Duruigbo (2007) reported significant levels of heavy metals in soils that were contaminated with automobile waste oil. Zinc though a heavy metal is also micronutrient (Alvarez-Benedi and Munoz-Carpena, 2005). As a micronutrient, it has been indicated to be beneficial to both plants and

animals (Alloway, 1995). It has however been observed that if Zn exceeds certain limits in soils it becomes toxic to biota (Alvarez-Benedi and Munoz-Carpena, 2005; Ogundiran and Afolabi, 2008). In the Netherlands, the critical limits of Zn in soils has been defined at 720 mg/kg (NMHPPE, 1991).

A number of edaphic factors, including pH, organic matter, effective cation exchange capacity and clay have been indicated to affect Zn availability in soils (Alloway, 1995; Okafor and Opuene, 2007; Nabulo *et al.*, 2008). Zinc tends to be less available in soils with high pH. In a study conducted on the effect of pH on the adsorption of zinc (Shuman, 1975), it was revealed that low pH reduced zinc adsorption more for the sandy soils than for those high in colloidal-size materials. Also, Shuman (1975) and Lorenz *et al.* (2000) separately observed that soils high in clay or organic matter had higher adsorptive capacities and higher bonding energies for zinc than sandy soils low in organic matter. Furthermore, zinc can interrupt the activities in soils, as it negatively influences the activity of microorganisms and earthworms (Suthar

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and Sing, 2008). This process affects the breakdown of organic matter. Smolders *et al.* (2004) reported the negative effect of zinc toxicity on soil microbial processes, as it hinders the activities of microorganisms. In view of these observed effects of selected soil physicochemical properties on zinc availability, a study on zinc availability in crude-oil polluted soils would help in providing valuable information in reclaiming such soils. Therefore, this investigation aimed at studying Zn availability in relation to selected soil properties in a crude oil polluted Eutric Tropofluent, in Egbema, Imo State, Nigeria.

## MATERIALS AND METHODS

### Study area

The study was located at Ugwugba, Obiagbu in Ohaji-Egbema area of Imo State, southeastern Nigeria where crude oil spillage occurred for about two months. Egbema is situated at the northern apex area of the lower Niger Delta, between latitudes 5° 21' to 5° 41' N and longitudes 6° 37' to 6° 49' E. Geomorphologically, Egbema is located at the flood plain of recent illuvial formation. The geology of the studied region is characterized by quarternary, alluvium, meander belt, wooded back swamps as well as fresh water swamps and Sombreiro-Warri Deltaic Plains with large deposit of petroleum and natural gas and oil deep-test wells (Orajaka, 1975). The annual mean temperature is between 26.5 and 27.5 °C, mean annual rainfall greater than 2500 mm, mean daily relative humidity of 64 to 75 %, evaporation of above 1450 mm/y. Major soils of the area have been classified as Eutric Tropofluent (FDALR, 1985). Vegetation of the study site comprised some disturbed secondary forest, riparian forest and raffia, oil palm/food crop, mosaic commercial plantation, long cycle fallow areas and open field cultivation. Apart from crude oil exploration and exploitation, arable crop production is a major socio-economic activity of the area.

### Experimental design

Three different land units: Unpolluted area (0.5 km away from spillage site), polluted without vegetation and polluted area with vegetation served as treatments. Five samples in a transect intervals of 5 m (A, B C, D and E) per land unit were used as replicates which was arranged in a randomised complete block design.

### Soil sampling

At the study site and guided by transect sampling

technique, soil sampling was carried out in June 2008, about two months after the spillage occurred. Soil samples were collected at the plough layer (0-20 cm) at intervals of 5 m in each land unit i.e. polluted without vegetation, polluted with vegetation and unpolluted area. Five samples were collected from each sampling point making it a total of fifteen samples. Collected samples were thereafter air-dried, gently crushed and made to pass through two mm mesh sieve preparatory to laboratory analysis.

### Laboratory analysis

Laboratory analyses were conducted for particle size distribution by hydrometer method (Gee and Or, 2002), bulk density by core method (Grossman and Reinsch, 2002), moisture content by gravimetric method (Obi, 1990), soil pH using pH meter (Hendershot *et al.*, 1993), total carbon by wet digestion (Nelson and Sommers, 1982), available phosphorus according to the procedure of Olson and Sommers (1990), exchangeable bases by ammonium acetate leaching and exchangeable acidity by titration (McLean, 1982), total nitrogen by microkjeldahl digestion technique (Bremner, 1996). Base saturation was obtained by calculations (Exchangeable bases/Effective cation exchange capacity x 100).

### Determination of Zn in soils

Zinc was determined in accordance with the procedure of Leschber *et al.* (1985). One gram dry soil finely ground, was moistened with distilled water and heated in a 100 cm<sup>3</sup> Teflon beaker with 10 cm<sup>3</sup> concentration HNO<sub>3</sub> and evaporated to small volume. Then, 5 cm<sup>3</sup> concentration HNO<sub>3</sub>, 5 cm<sup>3</sup> 70 % HClO<sub>4</sub> and 10 cm<sup>3</sup> concentration HF were added and the whole heated to perchlorate fumes. After 30 min fuming, 10 cm<sup>3</sup> of HCl (1/1, v/v) was added and the mixture boiled for 10 min and then cooled and diluted to 100 cm<sup>3</sup> with distilled water. Zinc concentrations in the supernatant was determined using atomic adsorption spectrophotometer (S Series).

### Data analysis

Generated soil data were subjected to analysis of variance (ANOVA) and means were separated using least significance difference (LSD) at 5 % probability level. Zinc was correlated and regressed against selected soil properties and their simple coefficient of determinants were obtained. These were carried out



with the aid of GenStat statistical software 8<sup>th</sup>. Edition (Buysse *et al.*, 2005).

## RESULTS AND DISCUSSION

### Soil physical properties

Selected physical properties of the studied soils are shown in Table 1. Sand, silt and clay values for the unpolluted soil was 899, 83 and 21 g/kg, respectively, while for polluted without vegetation and polluted with vegetation it was 857, 113, 30 and 927, 51, 22 g/kg, respectively. Silt:clay ratio (SCR) was 4.0, 3.8 and 2.8 for unpolluted, polluted without vegetation and polluted with vegetation, respectively. It was obvious that the soils were characteristically sandy (Onweremadu, 2007). This was further evidenced by the textural class of the soils which was sandy, loamy and sandy for unpolluted, polluted without vegetation and polluted with vegetation, respectively. Soil bulk density ranged between 1.25 (unpolluted) and 1.36 g/cm (polluted without vegetation). Sands and loam usually show bulk density variations of between 1.2 and 1.8 g/cm (Unger and Kasper, 1994). On total porosity, the usual range for soils is from 30-70 % (Landon, 1991). The total porosity for the soils were 52.1 (unpolluted), 48.7 (polluted without vegetation) and 49.8 % (polluted with vegetation). Soil moisture values was 139, 210 and 167 g/kg for unpolluted, polluted without vegetation and polluted with vegetation, respectively, indicating more moisture in polluted soils.

### Soil chemical properties

Results of selected soil chemical properties of studied soils are presented in Table 2. Soil pH<sub>water</sub> for unpolluted (6.48) was lower than that of polluted without vegetation (6.88) and that of polluted with vegetation (6.75). These results are consistent with that of Amadi *et al.* (1993), but varied from that of Isirimah *et al.* (1989). Soil effective cation exchange capacity for unpolluted was 9.50 mg/kg, which was lower than that of polluted without vegetation (25.39 mg/kg) and polluted with vegetation (14.31 mg/kg). Soil available phosphorus (P) was least in polluted with vegetation (1.25 mg/kg) and the highest in unpolluted (6.15 mg/kg) followed by polluted without vegetation (3.20 mg/kg). This trend agrees with the findings of Amadi and Bari (1992). Total nitrogen (TN) and organic matter were least in unpolluted (0.13 and 189.6 mg/kg, respectively) and highest in polluted without vegetation (0.17 and 320.6 mg/kg, respectively). Calcium:Magnesium ratio was highest in unpolluted (4.52) and least in polluted without vegetation (0.18). Carbon:nitrogen ratio was 8.46 for unpolluted, 10.9 for polluted without vegetation and 10.5 for polluted with vegetation. This is in line with the results of Amadi and Bari (1992) who reported higher values of carbon:nitrogen ratio in crude-oil-polluted soils.

Fig. 1a shows Zn concentrations in studied soils with distance away from pollution site, while Fig. 1b shows mean values of Zn at each land unit. Zinc had a mean value of 9.828 mg/kg in unpolluted, 15.684 mg/kg

Table 1: Some physical properties of studied soils

| Sample | Sand   | Silt | Clay | SCR | TC | $\rho_b$ | F    | MC     |
|--------|--------|------|------|-----|----|----------|------|--------|
| Unit   | (g/kg) |      |      | -   |    | (g/cm)   | (%)  | (g/kg) |
| UP     | 899    | 83   | 21   | 4.0 | S  | 1.25     | 52.1 | 139    |
| PwoV   | 857    | 113  | 30   | 3.8 | L  | 1.36     | 48.7 | 210    |
| PwV    | 927    | 51   | 22   | 2.3 | S  | 1.33     | 49.8 | 167    |

$\rho_b$  = Bulk density; F= Porosity; SCR= Silt:clay ratio MC= Moisture content; UP=Unpolluted soil; PwoV= Polluted without vegetation; PwV= Polluted with vegetation.

Table 2: Some chemical properties of studies soils

| Sample | pH   | Na <sup>+</sup> | K <sup>+</sup> | Mg <sup>2+</sup> | Ca <sup>2+</sup> | ECEC  | Av. P | TN   | OM    | BS   | C:N   | C:M  |
|--------|------|-----------------|----------------|------------------|------------------|-------|-------|------|-------|------|-------|------|
| Unit   |      |                 |                |                  |                  |       |       |      |       | (%)  | Ratio |      |
| UP     | 6.48 | 0.59            | 0.92           | 1.40             | 6.10             | 9.50  | 6.15  | 0.13 | 189.6 | 94.8 | 8.46  | 4.52 |
| PwoV   | 6.88 | 0.81            | 1.17           | 19.52            | 3.53             | 25.39 | 3.20  | 0.17 | 320.7 | 98.5 | 10.9  | 0.18 |
| PwV    | 6.75 | 0.62            | 1.20           | 9.62             | 2.42             | 14.31 | 1.25  | 0.15 | 272.4 | 96.9 | 10.5  | 0.25 |

ECEC= Effective cation exchange capacity; % BS= Percent base saturation; TN= Total nitrogen; OM= Organic matter; Av.P= Available phosphorus; C:NR= Carbon:nitrogen ratio; C:MR= Calcium:magnesium ratio; UP= Unpolluted soil; PwoV= Polluted without vegetation; PwV= Polluted with vegetation.



(polluted without vegetation) and 21.828 mg/kg (polluted with vegetation). This indicated higher values in polluted soils. Figs. 2 a-d, 3 a-d and 4 a-d show linear relationship between Zn and selected soil properties. Among the treatment means, Zn had a high significant difference at  $p = 0.01$  (Table 5).

Table 4 shows variability in some physicochemical properties of studied soils. Bulk density, porosity, silt:clay ratio, pH, effective cation exchange capacity, percent base saturation, total N, organic matter, available P and calcium:magnesium ratio showed high

significant difference at  $p=0.01$ . In contrast, clay indicated significant difference at  $p=0.05$  among treatment means, while carbon:nitrogen did not show any significance difference at  $p=0.05$ . Table 3 shows correlation matrix among physicochemical properties of the three sampling positions.

#### Physical properties

Aggressive weather conditions of the area may have contributed to the nature of the soils' texture (Jungeruis and Levell, 1964). High precipitation in the area

Table 3: Correlation matrix among physiochemical properties on the three sampling positions

|          |      | Clay<br>(g/kg)      | $\ell b$<br>(g/cm)   | F<br>(%)            | SCR<br>-            | pH<br>-             | ECEC<br>(mg/kg)     | BS<br>(%)           | TN<br>(mg/kg)       | OM<br>(g/kg)        | Av.P<br>(mg/kg) |
|----------|------|---------------------|----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|-----------------|
| Clay     | UP   | 1.0                 |                      |                     |                     |                     |                     |                     |                     |                     |                 |
|          | PwoV | 1.0                 |                      |                     |                     |                     |                     |                     |                     |                     |                 |
|          | PwV  | 1.0                 |                      |                     |                     |                     |                     |                     |                     |                     |                 |
| $\ell b$ | UP   | 0.09 <sup>NS</sup>  | 1.00                 |                     |                     |                     |                     |                     |                     |                     |                 |
|          | PwoV | 0.016 <sup>NS</sup> | 1.00                 |                     |                     |                     |                     |                     |                     |                     |                 |
|          | PwV  | 0.61 <sup>NS</sup>  | 1.00                 |                     |                     |                     |                     |                     |                     |                     |                 |
| F        | UP   | 0.09 <sup>NS</sup>  | 1.00                 | 1.00                |                     |                     |                     |                     |                     |                     |                 |
|          | PwoV | 0.017 <sup>NS</sup> | 1.00                 | 1.00                |                     |                     |                     |                     |                     |                     |                 |
|          | PwV  | 0.64 <sup>NS</sup>  | 1.00                 | 1.00                |                     |                     |                     |                     |                     |                     |                 |
| SCR      | UP   | 0.98                | 0.09 <sup>NS</sup>   | 0.091 <sup>NS</sup> | 1.00                |                     |                     |                     |                     |                     |                 |
|          | PwoV | 0.96                | 0.074 <sup>NS</sup>  | 0.074 <sup>NS</sup> | 1.00                |                     |                     |                     |                     |                     |                 |
|          | PwV  | 0.67                | 0.78 <sup>NS</sup>   | 0.80                | 1.00                |                     |                     |                     |                     |                     |                 |
| pH       | UP   | 0.01 <sup>NS</sup>  | 0.065 <sup>NS</sup>  | 0.064 <sup>NS</sup> | 0.00 <sup>NS</sup>  | 1.00                |                     |                     |                     |                     |                 |
|          | PwoV | 0.234 <sup>NS</sup> | 0.01 <sup>NS</sup>   | 0.01 <sup>NS</sup>  | 0.256 <sup>NS</sup> | 1.00                |                     |                     |                     |                     |                 |
|          | PwV  | 0.87 <sup>NS</sup>  | 0.88                 | 0.90                | 0.861               | 1.00                |                     |                     |                     |                     |                 |
| ECEC     | UP   | 0.042 <sup>NS</sup> | 0.023 <sup>NS</sup>  | 0.021 <sup>NS</sup> | 0.005 <sup>NS</sup> | 0.069 <sup>NS</sup> | 1.00                |                     |                     |                     |                 |
|          | PwoV | 0.00 <sup>NS</sup>  | 0.29 <sup>NS</sup>   | 0.29 <sup>NS</sup>  | 0.00 <sup>NS</sup>  | 0.24 <sup>NS</sup>  | 1.00                |                     |                     |                     |                 |
|          | PwV  | 0.37 <sup>NS</sup>  | 0.094 <sup>NS</sup>  | 0.104 <sup>NS</sup> | 0.009 <sup>NS</sup> | 0.159 <sup>NS</sup> | 1.00                |                     |                     |                     |                 |
| %BS      | UP   | 0.11 <sup>NS</sup>  | 0.087 <sup>NS</sup>  | 0.09 <sup>NS</sup>  | 0.198 <sup>NS</sup> | 0.00 <sup>NS</sup>  | 0.63 <sup>NS</sup>  | 1.00                |                     |                     |                 |
|          | PwoV | 0.18 <sup>NS</sup>  | 0.42 <sup>NS</sup>   | 0.417 <sup>NS</sup> | 0.14 <sup>NS</sup>  | 0.00 <sup>NS</sup>  | 0.833               | 1.00                |                     |                     |                 |
|          | PwV  | 0.116 <sup>NS</sup> | 0.25 <sup>NS</sup>   | 0.234 <sup>NS</sup> | 0.008 <sup>NS</sup> | 0.171 <sup>NS</sup> | 0.52 <sup>NS</sup>  | 1.00                |                     |                     |                 |
| TN       | UP   | 0.09 <sup>NS</sup>  | 0.49 <sup>NS</sup>   | 0.49 <sup>NS</sup>  | 0.15 <sup>NS</sup>  | 0.003 <sup>NS</sup> | 0.00 <sup>NS</sup>  | 0.165 <sup>NS</sup> | 1.00                |                     |                 |
|          | PwoV | 0.21 <sup>NS</sup>  | 0.09 <sup>NS</sup>   | 0.088 <sup>NS</sup> | 0.144 <sup>NS</sup> | 0.25 <sup>NS</sup>  | 0.72*               | 0.42 <sup>NS</sup>  | 1.00                |                     |                 |
|          | PwV  | 0.21 <sup>NS</sup>  | 0.46 <sup>NS</sup>   | 0.45 <sup>NS</sup>  | 0.073 <sup>NS</sup> | 0.29 <sup>NS</sup>  | 0.22 <sup>NS</sup>  | 0.82                | 1.00                |                     |                 |
| OM       | UP   | 0.09 <sup>NS</sup>  | 0.0646 <sup>NS</sup> | 0.65 <sup>NS</sup>  | 0.047 <sup>NS</sup> | 0.00 <sup>NS</sup>  | 0.276 <sup>NS</sup> | 0.49 <sup>NS</sup>  | 0.042 <sup>NS</sup> | 1.00                |                 |
|          | PwoV | 0.14 <sup>NS</sup>  | 0.55 <sup>NS</sup>   | 0.55 <sup>NS</sup>  | 0.065 <sup>NS</sup> | 0.055 <sup>NS</sup> | 0.097 <sup>NS</sup> | 0.83                | 0.68                | 1.00                |                 |
|          | PwV  | 0.003 <sup>NS</sup> | 0.017 <sup>NS</sup>  | 0.015 <sup>NS</sup> | 0.071 <sup>NS</sup> | 0.007 <sup>NS</sup> | 0.005 <sup>NS</sup> | 0.278 <sup>NS</sup> | 0.51 <sup>NS</sup>  | 1.00                |                 |
| Av.P     | UP   | 0.01 <sup>NS</sup>  | 0.005 <sup>NS</sup>  | 0.004 <sup>NS</sup> | 0.017 <sup>NS</sup> | 0.00 <sup>NS</sup>  | 0.011 <sup>NS</sup> | 0.023 <sup>NS</sup> | 0.034 <sup>NS</sup> | 0.004 <sup>NS</sup> | 1.00            |
|          | PwoV | 0.76                | 0.11 <sup>NS</sup>   | 0.11 <sup>NS</sup>  | 0.631 <sup>NS</sup> | 0.356 <sup>NS</sup> | 0.288 <sup>NS</sup> | 0.397 <sup>NS</sup> | 0.144 <sup>NS</sup> | 0.33 <sup>NS</sup>  | 1.00            |
|          | PwV  | 0.09 <sup>NS</sup>  | 0.378 <sup>NS</sup>  | 0.36 <sup>NS</sup>  | 0.031 <sup>NS</sup> | 0.176 <sup>NS</sup> | 0.282 <sup>NS</sup> | 0.79                | 0.96                | 0.58 <sup>NS</sup>  | 1.00            |
|          |      | Clay                | $\ell b$             | F                   | SCR                 | pH                  | ECEC                | % BS                | TN                  | OM                  | Av.P            |

$\ell b$  =Bulk density; F=Porosity; SCR=Silt:clay ratio; ECEC=effective cation exchange capacity; %BS=Percent base saturation; TN=Total nitrogen; OM=Organic matter; Av.P=Available phosphorus; CNR=Carbon:nitrogen ratio; CMR=Calcium:magnesium ratio; UP=Unpolluted soil; PwoV=Polluted without vegetation; PwV=Polluted with vegetation; NS: Not significant



Table 4: Variability in some physicochemical properties of studied soils (N=15)

| Sample              | Clay   | $\ell/b$ | F     | SCR  | pH <sub>water</sub> | ECEC    | %BS   | TN   | OM      | Av.P | C:NR               | C:MR  |
|---------------------|--------|----------|-------|------|---------------------|---------|-------|------|---------|------|--------------------|-------|
| Unit                | (g/kg) | (g/cm)   | (%)   |      |                     | (mg/kg) |       |      | (mg/kg) |      |                    | Ratio |
| UP                  | 21     | 1.25     | 47.17 | 4.0  | 6.48                | 9.5     | 94.84 | 1.3  | 189.5   | 6.15 | 8.6                | 4.52  |
| PwoV                | 30     | 1.36     | 51.32 | 3.9  | 6.84                | 25.41   | 98.50 | 1.7  | 320.6   | 3.20 | 11.0               | 0.18  |
| PwV                 | 22     | 1.33     | 50.1  | 2.34 | 6.75                | 14.32   | 96.84 | 1.5  | 272.4   | 1.25 | 10.8               | 0.25  |
| LSD <sub>0.05</sub> | 6.16   | 0.035    | 1.28  | 0.94 | 0.09                | 0.76    | 0.47  | 0.25 | 22.9    | 0.26 | 2.21 <sup>NS</sup> | 0.57  |

$\ell/b$  = Bulk density; F=Porosity; SCR=Silt:clay ratio; ECEC=effective cation exchange capacity; %BS=Percent base saturation; TN=Total nitrogen; OM=Organic matter; Av.P=Available phosphorus; C:NR=Carbon:nitrogen ratio; C:MR=Calcium:magnesium ratio; UP=Unpolluted soil; PwoV=Polluted without vegetation; PwV=Polluted with vegetation; NS: Not significant

resulting in clay leaviness could have led to the sandiness of the soils (Unamba-Oparah *et al.*, 1987; Eshett *et al.*, 1990). This characteristic may lead to the low bulk density of the soils and therefore high porosity (Landon, 1991). Soils with such high porosity provide avenue for eutrophication of groundwater leading to its pollution. Also, at increased bulk density as was the case for crude-oil-polluted soils, there was reduced porosity and this attenuated porosity results in reduced aeration and oxygen availability. Thus, the activities of aerobes would therefore be affected leading to poor microbial functions in the pedosphere. Schwendinger (1968) noted that crude-oil contamination of soils leads to the formation of an anaerobic condition in the soil. Rowell (1977) reported that insufficient aeration results in the soil because of displacement of air from the spaces between soil particles by crude oil and thus makes it unsatisfactory for plant growth. Moisture content of polluted soils were higher than that of unpolluted soils. This could have resulted from the anaerobic conditions of polluted soils. Fresh crude oil shows a coagulatory effect on the soil, binding the soil particles into a water impermeable soil block, which seriously impairs water drainage and oxygen diffusion, and seeds sown in such soil failed to germinate (Atuanya, 1987).

#### Chemical properties

Soil reaction otherwise expressed as soil pH determines the fate of many soil pollutants (Brady and Weil, 1999). Ogaji *et al.* (2005) reported increase in soil pH with crude-oil pollution. This was similar to this study. The increased soil pH of crude oil polluted soils affected the soils' effective cation exchange capacity, as effective cation exchange capacity increased with increased pH (Singer and Munns, 1999). Available P has been noted to be limiting in crude oil polluted soils (Ladousse and Tramier, 1991; Amadi and Bari, 1992;

Table 5: Variability of Zn in studied soils

|                     | Zn (mg/kg) |
|---------------------|------------|
| UP                  | 98.8       |
| PwoV                | 156.8      |
| PwV                 | 211.9      |
| LSD <sub>0.05</sub> | 27.09      |

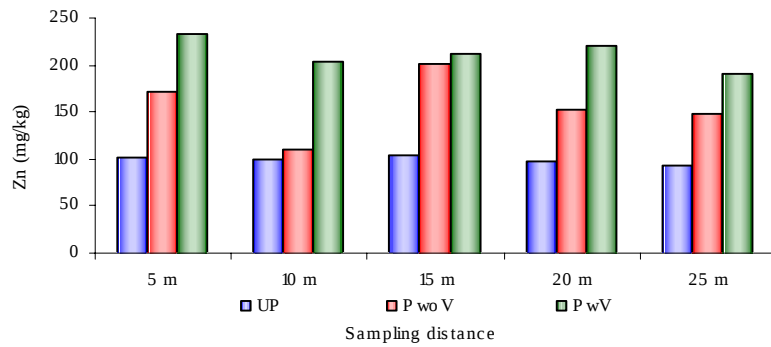
Amadi *et al.*, 1993). Higher values of organic matter in crude oil polluted soils have resulted from the increased hydrocarbon content (which caused high organic carbon content of polluted soils) of oil polluted soils and organic matter is a product of organic carbon.

Similar finding has been reported by Ogaji *et al.* (2005). Total N equally increased with crude oil pollution, implying higher total N values in polluted without vegetation and polluted with vegetation, respectively. It was noted in this study that organic matter positively correlated with total N. Unamba-Oparah (1982) found a positive relationship between organic matter and total N in soils. Therefore, the increased values of total N in oil polluted soils would have been contributed by organic matter. Carbon:nitrogen ratio was observed to have been widened by the presence of crude-oil in soils (Amadi and Bari, 1992). This was corroborated in this study. Landon (1991) reported that a decrease of Ca:Mg ratio to a level below 3 leads to the unavailability of  $Ca^{2+}$  and P. Calcium:magnesium ratio reduced with oil pollution and this equally affected  $Ca^{2+}$  and P availability in polluted soils (Table 2).

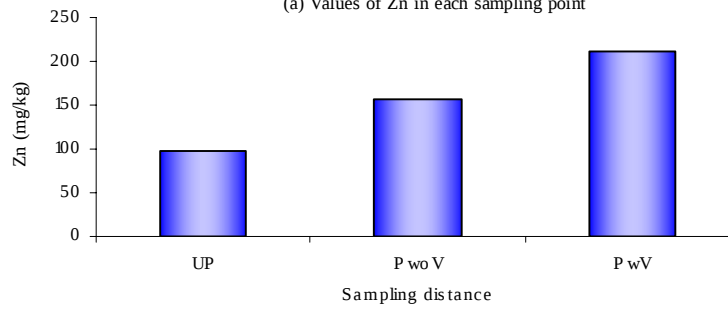
#### Zinc availability in relation to selected soil properties in studied soils

Total Zn content of soils is largely dependent on the composition of the parent rock materials (Kabata-Pendias and Pendias, 1992) other factors such as pH, organic matter content, temperature, high P levels, clay and other soil nutrients (Alloway, 1995) affect Zn availability in soils.





(a) Values of Zn in each sampling point



(b) Mean values of Zn in studied soils

Fig. 1: Concentrations of Zn in studied soils

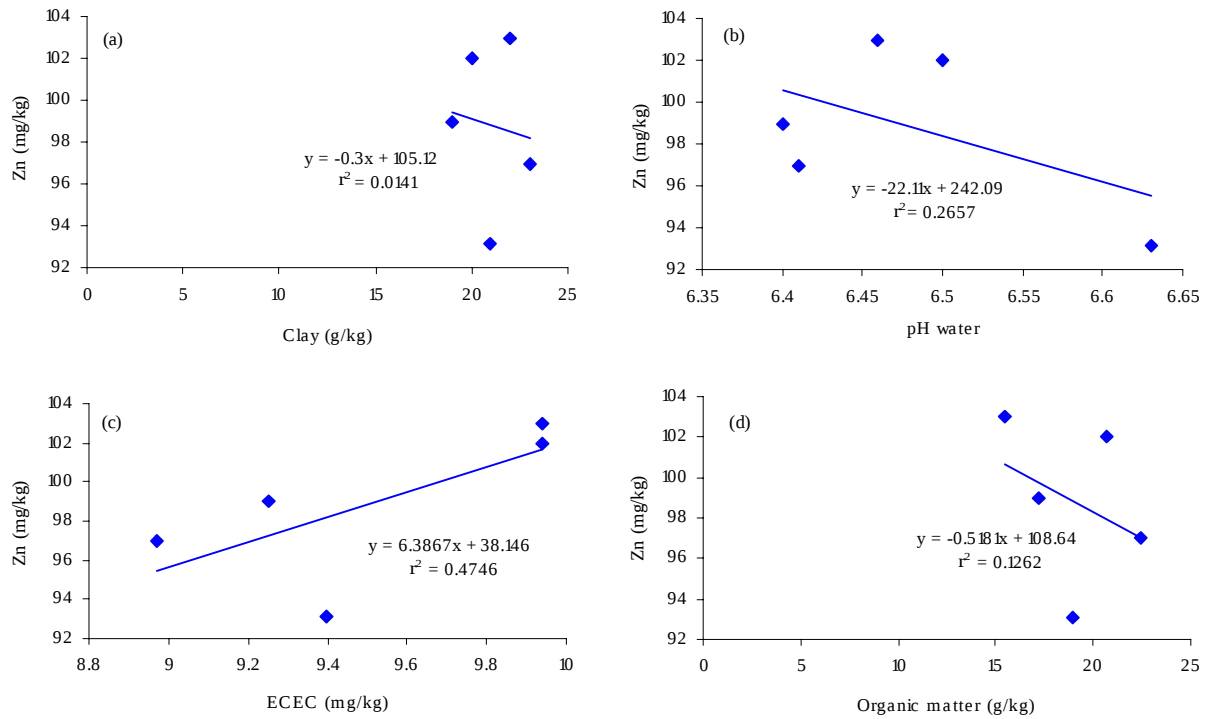


Fig. 2: The relationship between Zn and clay, pH, ECEC and organic matter, respectively in unpolluted soil (UP)



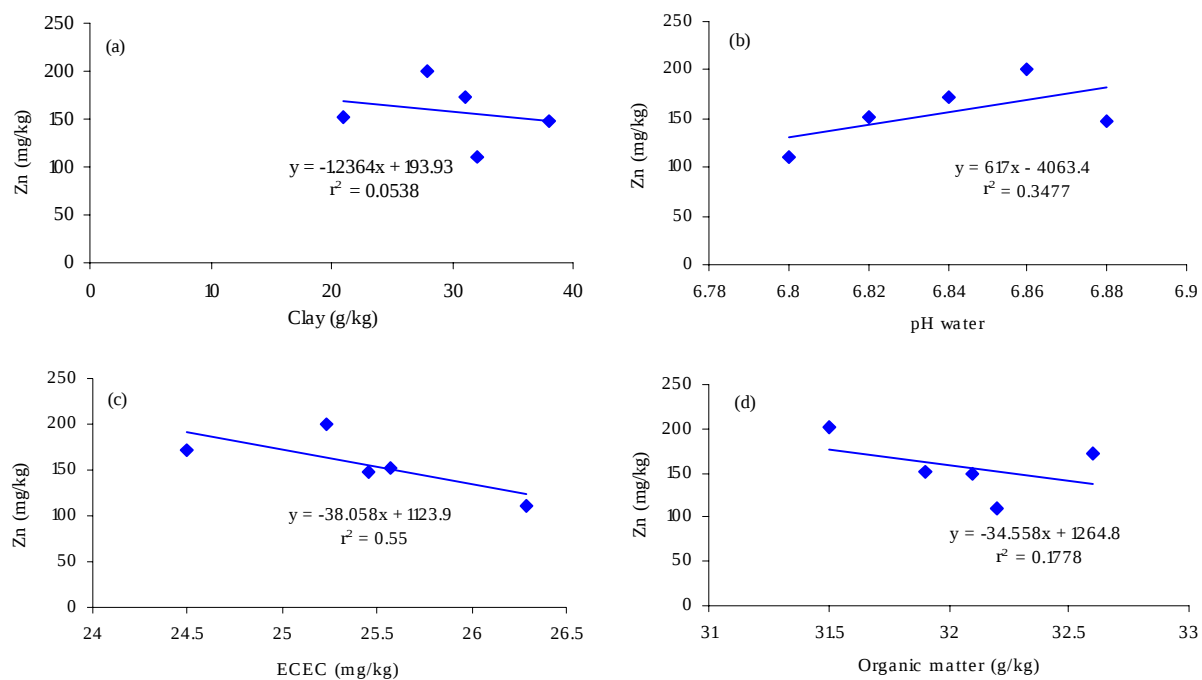


Fig. 3: The relationship between Zn and Clay, pH, ECEC and organic matter respectively in polluted soil without vegetation (PwoV)

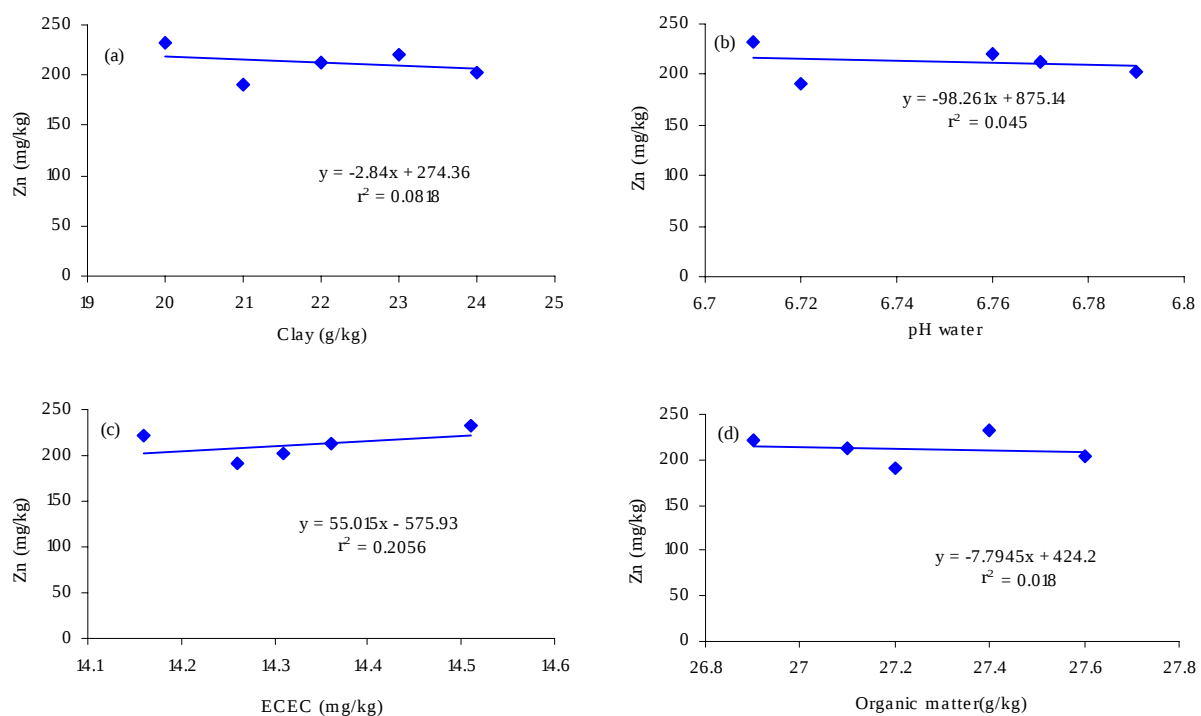


Fig. 4: The relationship between Zn and clay, pH, ECEC and organic matter respectively in polluted soil with vegetation



In this study, clay fraction of the soil texture that was not polluted with crude-oil showed negative correlation with Zn (Fig. 2a). Similarly, clay equally correlated with Zn in crude-oil-polluted this time with higher  $r^2$  values (Figs. 3a and 4a). Though there was clay increases in oil-polluted soils, it was however observed that at increasing clay content, Zn was decreasing. Higher values of Zn were obtained in crude-oil-polluted soils. Given the equations in Figs. 2a, 3a and 4a, respectively, if clay is put at zero (0), Zn would be highest in polluted with vegetation (274.3 mg/kg), followed by polluted without vegetation (193.9 mg/kg) and least in unpolluted (105.1 mg/kg). This portends that Zn availability in relation to clay was affected by crude oil pollution. This observed correlation between Zn and clay was corroborated by Kiekens (1986) which he reported was due to Zn adsorption by clayey fraction of the soil.

In the three studied soils (unpolluted, polluted without vegetation and polluted with vegetation), organic matter negatively correlated with Zn (Figs. 2d, 3d and 4d). This implied that at increasing organic matter, Zn was decreasing. Organic matter have been reported to form stable complexes with micronutrients such as Zn (Alloway, 1995). This complexation or chelation leads to its unavailability. Onweremadu (2008) reported that organic matter promoted fixation of heavy metals in soils contaminated with waste water in Owerri, Nigeria. Therefore, Zn availability was not affected in crude oil polluted soils in relation organic matter. The availability of Zn decreases at increasing pH values of the soil, due to the lower solubility of Zn minerals and increasing adsorption of Zn by negatively charged colloidal soil particles (Alloway, 1995). Zinc availability in unpolluted and polluted with vegetation increased with decreasing soil pH (Figs. 2b and 4b), however, in polluted without vegetation the relationship was different (Fig. 3b) as there was positive relationship. The effect of crude oil pollution on Zn availability in relation to pH could not be effectively ascertained because of the conflicting results in polluted without vegetation and polluted with vegetation. This notwithstanding, the presence of vegetation could have accounted for this variation. In unpolluted soils, Zn showed a positive correlation with effective cation exchange capacity. This implied that Zn tended to be more available at increasing soil effective cation exchange capacity (Fig. 2c). This was same for crude-oil-polluted soil with vegetation (Fig. 3c). It however

had a negative correlation with effective cation exchange capacity in polluted soil without vegetation. At neutral or normal soil pH values Zn is adsorbed reversibly by ion-exchange and irreversibly by lattice penetration of clay minerals (Tiller and Hodgson, 1962). It is evident that soil pH in polluted without vegetation presented better sorptive sites for Zn adsorption thus reducing its availability at increasing effective cation exchange capacity.

Alloway (1995) concluded that clay minerals, organic matter and pH are likely to be the most important factors affecting Zn adsorption by soils. This is consistent with the findings of this study, where only effective cation exchange capacity positively correlated with Zn in unpolluted soil. Shuman (1975) studied the effect of soil properties on Zn availability and found that soils high in clay or organic matter had higher adsorption capacity for Zn than sandy soils low in organic matter.

## CONCLUSION

It was found that crude oil pollution affected some soil properties. Zinc availability was affected by some soil properties in the crude oil polluted Eutric Tropofluvent. pH and effective cation exchange capacity affected Zn availability with crude-oil pollution. With increase in pH, Zn decreased in unpolluted and polluted with vegetation, but increased in polluted without vegetation. While on effective cation exchange capacity, Zn increased with increase in the value of effective cation exchange capacity in unpolluted and polluted without vegetation, but decreased in polluted with vegetation. However, clay and organic matter did not affect Zn availability with crude-oil pollution as Zn decreased with increased clay and organic matter content, respectively. This therefore necessitates the need for further study on Zn dynamics in crude oil polluted soils since it is an essential micronutrient for plant growth. Also, there is the need for quick reclamation of the soils in order to save fragile arable soils from degradation.

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