



### Full Length Research Paper

## Copper Availability in Relation to Selected Soil Properties in a Crude-oil-polluted Eutric Tropofluent, Part I

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### Abstract

The study focused on Cu availability in relation to selected soil properties in a crude-oil-polluted Eutric Tropofluent in Egbema, Southeastern Nigeria. The study had 3 treatments: UP (unpolluted soil), PwoV (polluted without vegetation) and PwV (polluted with vegetation) with 5 replicates each which was arranged in a randomized complete block design (RCBD). Guided by transect sampling technique, soil sampling was carried out in June 2008. Soil samples were collected from the three different land units as stated above 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 (ANOVA) and correlation analysis. Results showed highly significant variation ( $p=0.01$ ) in bulk density, porosity, silt:clay ratio, pH, effective cation exchange capacity (ECEC), percent base saturation, total N, organic matter, available P, Ca:Mg ratio and Cu. Clay indicated marked differences in Cu due to crude-oil spillage. Though there were differences in Cu availability due to pH, Organic matter and ECEC it was note like that of clay as the trend was same in the three land units. It was strongly recommended that reclamation activities be undertaken in such soils in a bid to ameliorate the situation.

**Keywords:** Tropical soils, crude-oil spillage, Cu availability, soil properties.

### Introduction

Soil is a complex heterogeneous medium comprising mineral and organic solids, aqueous and gaseous components (Singer and Munns, 1999). Soils suffer from pollution (Onweremadu, 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: example; pipeline vandalism among others. Crude oil spillage on soils causes lots of adverse effects which hinder soil productivity. Among these effects are: increased bulk density, reduced porosity leading to insufficient aeration, thus poor oxygen availability (Rowell, 1977), soil coagulation resulting in moisture impermeability, reduced availability of soil phosphorus and nitrogen, temporal attenuation of soil microbes, introduction of non-organic, carcinogenic and growth inhibiting chemicals into arable soils (Okpokwasili and Odokuna, 1990), root stress, leaf chlorosis and retardation of plant growth (Udo and Fayemi, 1975).

In addition, the availability or otherwise of heavy metals/micronutrients such as Cu is equally affected. Onweremadu *et al.* (2007) reported significant levels of heavy metals in soils that were contaminated with automobile waste oil. Copper 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 (Brady and Weil, 1999). It has however been observed that if Cu exceeds certain limits in soils it becomes toxic to biota (Alvarez-Benedi and Munoz-Carpena, 2005). In the Netherlands, the critical limit of Cu in soils has been put at 190 mg kg<sup>-1</sup> (Netherlands Ministry of Housing, Physical Planning and Environment, 1991). A number of edaphic factors have been indicated to affect Cu availability in soils. These include: pH, organic matter, effective cation exchange capacity and clay (Alloway, 1995). Therefore, this investigation aimed at studying Cu availability in relation to selected soil properties in a crude-oil-polluted Eutric Tropofluent, in Egbema, Imo State, Southeastern Nigeria.

### Materials and Methods

The study was located at Ugwugba, Obiagbu in Ohaji-Egbema Area of Imo State, South-eastern Nigeria where crude oil spillage occurred due to pipeline vandalism. Egbema is situated at the northern apex area of the lower Niger Delta, between latitudes 5° 21' and 5° 41' N, and longitudes 6° 37' and 6° 49' E. Geomorphologically, Egbema is located at the flood plain of recent alluviation and major river and valley all in the Deltaic Plain deposits. The geology is characterized by the following: quarternary,

alluvium, meander belt, wooded back swamps to 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 daily relative humidity of 64 to 75%, evaporation of above 1450 mm per year and a relief of 0-61 m above Sea level. In terms of hydrology, Egbema features Rivers, Streams, Lakes and many Creeks. Major soils of the area have been classified as Eutric Tropofluent (Federal Department of Agricultural Land Resources, 1985). Vegetation of the study site was mainly grassy. It also 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 the major socio-economic activities of area.

### Experimental Design

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

### Soil Sampling

At the study site and guided by transect sapling technique; soil sampling was carried out in June 2010, about 2 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 (PwoV), polluted with vegetation (PwV) and unpolluted area (UP). Five samples were collected from each sampling point making it a total of 15 samples. Soil samples were thereafter air-dried, gently crushed and made to pass through 2 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 by the use of 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 saturations was obtained by calculations.

### Determination of Cu in Soils

Copper was determined in accordance with the procedure of Leschber *et al.* (1985). 1.000 g 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> conc. HNO<sub>3</sub> and evaporated to small volume. Then 5 cm<sup>3</sup> conc. HNO<sub>3</sub>, 5 cm<sup>3</sup> 70% HClO<sub>4</sub> and 10 cm<sup>3</sup> conc. HF were added and the whole heated to perchlorate fumes. After 30 minutes fuming, 10 cm<sup>3</sup> of HCl (1/1, v/v) was added and the mixture boiled for 10 minutes and then cooled and diluted to 100 cm<sup>3</sup> with distilled water. Copper concentrations in the supernatant were determined using Atomic Adsorption Spectrophotometer (S Series).

### Data Analysis

Generated soil data were subjected analysis of variance (ANOVA) and means were separated using least significance difference (LSD) at 5 per cent probability level. Copper 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

### Soil Physical Properties

Selected physical properties of the studied soils are shown in Table 1. Sand, silt and clay values for the UP (unpolluted soil) was 899, 83 and 21 g kg<sup>-1</sup> respectively, while for PwoV (polluted without vegetation) and PwV (polluted with vegetation) it was 857, 113, 30 and 927, 51, 22 g kg<sup>-1</sup> respectively. Silt:clay ratio (SCR) was 4.0, 3.8 and 2.8 for UP, PwoV and PwV 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 UP, PwoV and PwV respectively. Soil bulk density ranged between 1.25 (UP) and 1.36 g cm<sup>-3</sup> (PwoV). Sands and loam usually show bulk density variations of between 1.2 and 1.8 g cm<sup>-3</sup> (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 (UP), 48.7 (PwoV) and 49.8 % (PwV). Soil moisture values was 139, 210 and 167 g kg<sup>-1</sup> from UP, PwoV and PwV, 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 UP (6.48) was lower than that of PwoV (6.88) and that of PwV (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 (ECEC) for UP was 9.50 mg kg<sup>-1</sup>, lower than that of PwoV (25.39 mg kg<sup>-1</sup>) and PwV (14.31 mg kg<sup>-1</sup>). Soil available P was least in PwV (1.25 mg kg<sup>-1</sup>) and highest in UP (6.15 mg kg<sup>-1</sup>) followed by

PwoV (3.2 mg kg<sup>-1</sup>). This trend agrees with the findings of Amadi and Bari (1992). Total N and organic matter were least in UP (0.13 and 189.6 mg kg<sup>-1</sup> respectively) and highest in PwoV (0.17 and 320.6 mg kg<sup>-1</sup> respectively). Calcium Magnesium ratio (CMR) was highest in UP (4.52) and least in PwoV (0.18). Carbon: nitrogen ratio (CNR) was 8.46 for UP, 10.9 for PwoV and 10.5 for PwV. This is in line with the results of Amadi and Bari (1992) who reported higher values of CNR in crude-oil-polluted soils.

Figure 1a shows Cu concentrations in studied soils with distance away from pollution site, while Figure 1b shows mean values of Cu in each land unit. Copper had a mean value of 5.3 mg kg<sup>-1</sup> in UP, 36.1 mg kg<sup>-1</sup> (PwoV) and 69.8 mg kg<sup>-1</sup> (PwV). This indicated higher values in polluted soils. Figures 2(a-d), 3(a-d) and 4(a-d) show linear relationship between Cu and selected soil properties. Among the treatment means, Cu had a high significant difference at p=0.01.

Table 3 shows variability in some physicochemical properties of studied soils. Bulk density, porosity, silt:clay ratio, pH, ECEC, percent base saturation, total N, organic matter, available P and CMR showed high significant difference at p=0.01. In contrast, clay indicated significant difference at p=0.05 among treatment means, while CNR did not show any significance difference at p=0.05. Table 4 shows correlation matrix among physicochemical properties of the three sampling positions.

**Table 1:** Some physical properties of studied soils.

Sample Unit	Sand (g kg <sup>-1</sup> )	Silt	Clay	SCR	TC (g cm <sup>-3</sup> )	lb (%)	F (g kg <sup>-1</sup> )	MC
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

lb = Bulk density; F= Porosity; SCR= Silt:Clay MC= Moisture content; UP=Unpolluted soil; PwoV= Polluted without Vegetation; PwV= Polluted with Vegetation.

**Table 2.** Some chemical properties of studies soils.

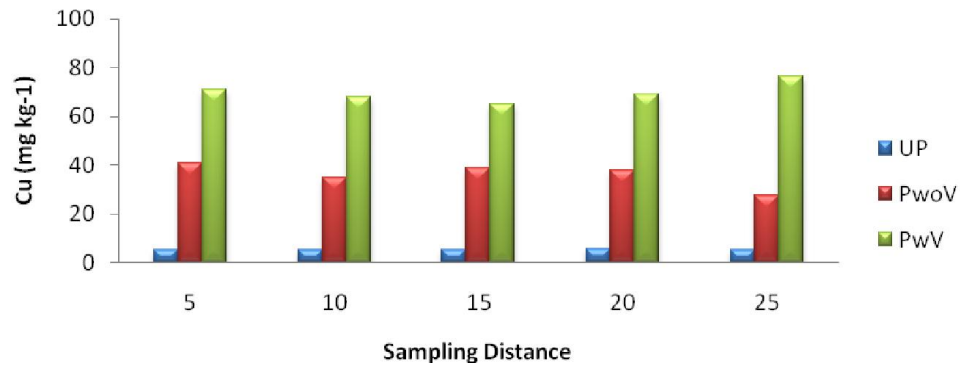
Sample Unit	pH	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	ECEC (mg kg <sup>-1</sup> )	Av. P	TN	OM	BS (%)	C:N Ratio	C:M Ratio
UP	6.48	0.59	0.92	1.40	6.10	9.50	6.15	0.13	18.96	94.8	8.46	4.52
PwoV	6.88	0.81	1.17	19.52	3.53	25.39	3.20	0.17	32.07	98.5	10.9	0.18
PwV	6.75	0.62	1.20	9.62	2.42	14.31	1.25	0.15	27.24	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.

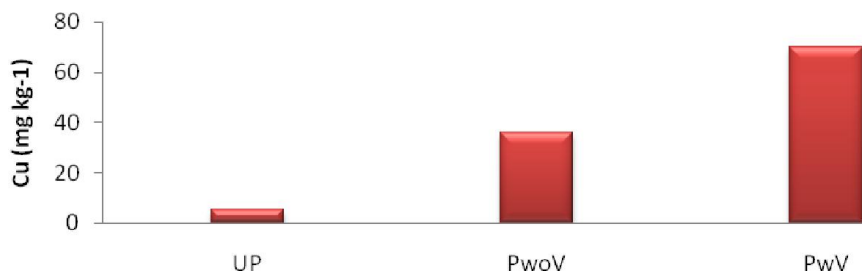
**Table 3.** Variability in some physico-chemical properties of studied soils.

Sample Unit	Clay (g kg <sup>-1</sup> )	lb (g cm <sup>-3</sup> )	F (%)	SCR	pH	ECEC (mg kg <sup>-1</sup> )	%BS	TN	OM (mg kg <sup>-1</sup> )	Av.P	C:N Ratio	C:M Ratio
UP	21	1.25	47.17	4.0	6.48	9.5	94.84	1.3	18.95	6.15	8.6	4.52
PwoV	30	1.36	51.32	3.9	6.84	25.41	98.50	1.7	32.06	3.20	11.0	0.18
PwV	22	1.33	50.1	2.34	6.75	14.32	96.84	1.5	27.24	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**	2.29**	0.26**	2.21 <sup>NS</sup>	0.57**

lb =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.



(a) Values of Cu in each Sampling Point



(b) Mean Values of Cu in Studied Soils

Figure 1 (a-b): Concentrations of Cu in Studied Soils

Table 4: Correlation Matrix among physiochemical properties on the three sampling positions.

		Clay (g kg <sup>-1</sup> )	ℓb (g cm <sup>-3</sup> )	F (%)	SCR -	pH -	ECEC (mg kg <sup>-1</sup> )(%)	%BS (%)	TN (mg kg <sup>-1</sup> )(g kg <sup>-1</sup> )	OM (g kg <sup>-1</sup> )(mg kg <sup>-1</sup> )	Av.P (mg kg <sup>-1</sup> )
Clay	UP	1.0**									
	PwoV	1.0**									
	PwV	1.0**									
ℓb	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**	1.00**						
	PwV	0.64 <sup>NS</sup>	1.00**	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>
	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>
	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>
	Clay	lb	F	SCR	pH	ECEC	%BS	TN	OM	Av.P

lb =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.

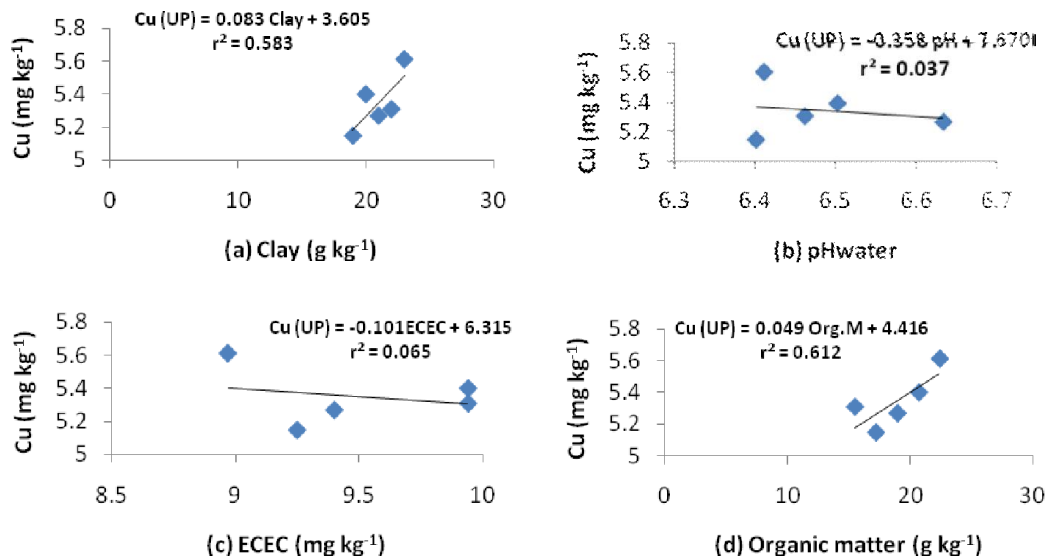


Figure 2 (a-d): The relationship between Cu and Clay, pH, ECEC and Org. M respectively in Unpolluted Soil

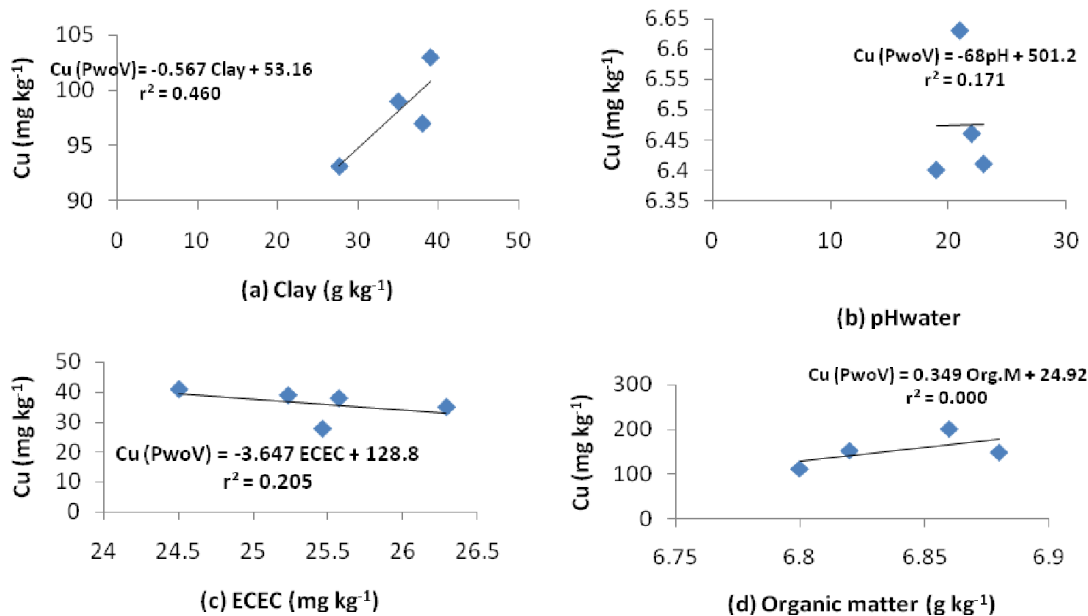
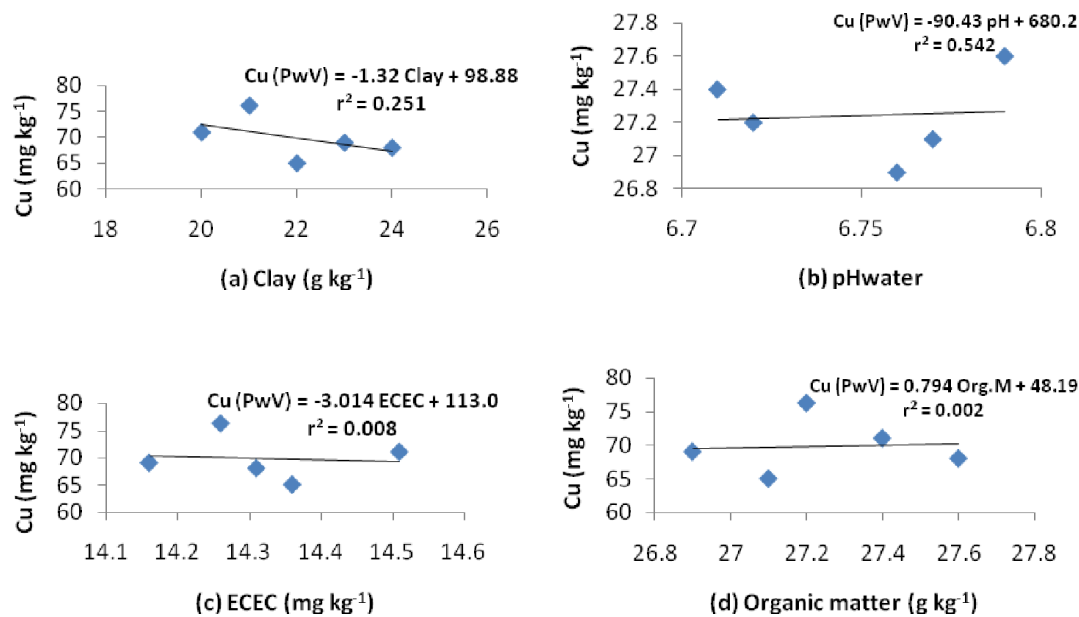


Figure 3 (a-d): The relationship between Cu and Clay, pH, ECEC and Org. M respectively in Polluted Soil without Vegetation



**Figure 4 (a-d):** The relationship between Cu and Clay, pH, ECEC and Org. M respectively in Polluted Soil with Vegetation.

## Discussion

### Physical properties

Aggressive weather conditions of the area may have contributed to the nature of the soils' texture (Jungeruis and Levelt, 1964). High precipitation in the area resulting in clay lessivage could have led to the sandiness of the soils (Unamba-Oparah *et al.*, 1987 and Eshett *et al.*, 1990). This characteristic sandiness led to the low bulk density of the soils and therefore high porosity (Landon, 1991). Soils with such high porosity provides avenue for eutrophication of ground water leading to it's 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. Soil 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 impregnable 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' ECEC, as ECEC 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 and 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 PwoV and PwV 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 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<sup>2+</sup> and P. Calcium:Magnesium ratio reduced with oil pollution and this equally affected Ca<sup>2+</sup> and P availability in polluted soils (Table 2).

### Cu availability in relation to selected soil properties in a crude-oil polluted Eutric Tropofluent

Copper availability is influenced in a characteristic way by the soil environment. However, certain soil factors have general effects on the availability of Cu (Weil and Holah, 1989). Among known factors affecting Cu in soil; clay, pH, effective cation exchange

capacity and organic matter were considered. Figures 2 (a-d), 3 (a-d) and 4 (a-d) show the relationships between Cu and these selected soil properties, respectively..

In unpolluted soils, Cu availability increased with increasing clay content, this is due possibly to the high exchange capacity of clay minerals (Clemens *et al.*, 1990). In contrast, it decreased with increasing clay in polluted soils (Figures 3a and 4a, respectively). This implied that crude-oil pollution has affected Cu availability in relation to clay. Soil pH has been reported to determine the fate of many pollutants in soils (Brady and Weil, 1999). Thus, pH plays critical role in determining the availability of micronutrients such as Cu. In all the soils, there was decreasing Cu at increasing pH. Steepness was however more in polluted soils as PwoV and PwV had slope or pH coefficients of -68 and -90, respectively; while that of UP was -0.358. These indicate that there would be greater toxicity of Cu in polluted soils at decreasing pH value. Crude-oil pollution therefore has heightened the negative consequence of Cu in soils of the area.

Effective cation exchange capacity (ECEC) negatively affected Cu availability in the three different land units. Although, the relationship between Cu and ECEC was steeper in polluted than unpolluted, the trend was similar. This indicates that crude-oil pollution did not have marked influence on Cu availability in relation to ECEC.

Soil organic matter is known to have high exchange capacity when compared to clay minerals (Singer and Munns, 1999). This therefore would make it have remarkable effect on Cu availability. In unpolluted soil, it had positive relationship with Cu and a coefficient determinant of 0.612, thus accounting for over 60% variation in Cu. In polluted soils, it equally had a positive relationship with Cu, but with much lower  $r^2$  of 0.0001 and 0.002 for PwoV and PwV, respectively. Crude-oil pollution therefore affected Cu availability soils in relation to organic matter.

Among the four factors that were considered, all had similar gradient pattern except clay which differed in unpolluted and polluted soils respectively. Copper is capable of acting as electron carrier in the enzyme systems that bring about oxidation reduction reactions in plants (Sillanpaa, 1982). Such reactions are essential steps in photosynthesis, respiration and many other metabolic processes. Crude-oil pollution as was found in this study affects Cu availability in relation to soil properties, this therefore could explain one of the reasons why crops in oil-polluted soils normally suffer from chlorosis and eventual death.

## Conclusion

Crude-oil-pollution of an Eutric Tropofluent affected soil physicochemical properties. Worse still, it affected Cu availability in relation to selected soil properties. Clay indicated marked differences in Cu due to crude-oil spillage. Though there were differences in Cu availability due to pH, Organic matter and ECEC it was note like that of clay as the trend was same in the three land units. It was strongly recommended that reclamation activities be undertaken in such soils in a bid to ameliorate the situation.

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