

MACRONUTRIENT STATUS AND SPECIATION OF Cu, Fe, Zn AND Pb in soil CONTAINING PALM OIL MILL EFFLUENT

P. O. OVIASOGIE and A. E. AGHIMIEN

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ABSTRACT

The use and safe disposal of Palm Oil Mill Effluent (POME) will no doubt contribute to environmental sustainability. Hence, the macronutrient and forms (speciation) of Copper, Iron, Zinc and Lead status of soil containing POME were determined in this study. The concentrations were determined at 0-15cm and 15-30cm soil depths respectively and at 10m interval from the point of discharge of the POME. Soils at 100m away from the discharge point were regarded as normal or uncontaminated soils, while different extractants were used to determine the levels of Fe, Cu, Zn and Pb. The results showed enrichment of the soils in P, N, Ca, Mg, Na, K due to the application of the POME. Copper, Iron and Pb were predominant in the organic form, while Zinc was particularly present in the exchangeable form. There was an overall increase in the cation exchange capacity (CEC) of the soils especially at the area close to the source of the POME. Proper use and safe disposal of POME in the land environment will lead to improved soil fertility.

Key Words: macronutrient, speciation, Cation Exchange Capacity, soil fertility, sustainability.

INTRODUCTION

Palm Oil mill effluent (POME) contains substantial concentration of plant nutrients, and a number of investigations have shown that POME in various forms, when applied on land at controlled rates, improved palm growths and yields (Chan et al., 1981; Koh and P'ng, 1981; and Lim, 1986).

Raw POME has Biological Oxygen Demand (BOD) values averaging around 25,000 mg/l, making it about 100 times more polluting than domestic sewage (Carl et al., 1999). Subsequent to treatment, the POME can be applied onto land via the furrow, flat bed or other irrigation systems. While the macronutrient status of soils containing POME indicate significant levels and availability of nitrogen, phosphorus and potassium, determining the micronutrients (trace elements) will further promote environmental compliance and regulations as it affects the disposal of POME to the land environment.

Total analysis may give information concerning probable enrichment and/or contamination with micronutrients but generally and for most elements, it is the chemical form of the metal in the soil that determines its mobilization capacity and behaviour in the environment. The nature of this form or association has often been referred to as speciation (Gonzalez et al., 1993).

The relative impact of increased trace metal concentrations on soil - plant - animal systems is controlled by the dominant forms of the metal that are present. This has led to the increasing use of

partial dissolution techniques by researchers to identify the major reaction sites of metal that have undergone weathering and other chemical process. Despite the limitations that may be associated with the selectivity of some extractions, these extraction procedures are useful in examining the association of trace metals with the various reaction sites in soils (Barbarick et al., 1992).

The objectives of this study were to:

- (a) determine the physicochemical properties of soils treated with POME.
- (b) determine the concentrations of Cu, Fe, Pb, and Zn as they exist in organically bound, exchangeable water - soluble and plant available forms in the soil containing POME with depth.

MATERIALS AND METHODS

Soil Sampling:

The soils were sampled starting from the point of discharge of the POME (along the same transect from the mill). The mill is located at a village called Evboneka about 20km south of Benin City, Nigeria. Soil samples were taken at every 10m from the point source and at 0-15cm and 15-30cm soil depths, representing topsoil and sub-soils respectively. About 5 metric tonnes of effluent is discharged daily on the landmass of soil away from the palm oil mill production site. The soils were sampled during the dry season of the year and taken in four replicates at each point.

TABLE 1: MEAN LEVELS OF SELECTED PHYSICOCHEMICAL PROPERTIES OF SOILS CONTAINING POME

| S/N | Horizontal Distance(m) of Effluent discharged on Soil from discharge point | Depth(cm) | (%N) | (mg/Kg)P | (%C) | C/N Ratio | | C(molkg ⁻¹) | | | | | pH | (%Sand) | (%Silt) | (%Clay) |
|-----|--|-----------|------|----------|------|-----------|------|-------------------------|------|-------|------|-------|-----|---------|---------|---------|
| | | | | | | H | Na | K | Ca | Mg | ClC | | | | | |
| 1. | 10.0 | 0-15 | 0.46 | 31.2 | 3.9 | 8.47 | 0.20 | 0.19 | 1.91 | 8.24 | 5.36 | 18.81 | 6.1 | 92.0 | 5.9 | 2.0 |
| 2. | 10.0 | 15-30 | 0.28 | 20.4 | 2.8 | 10.60 | 0.30 | 0.19 | 1.82 | 6.32 | 1.84 | 10.56 | 6.0 | 87.8 | 9.4 | 3.0 |
| 3. | 20.0 | 0-15 | 0.40 | 36.9 | 3.8 | 9.50 | 0.30 | 0.17 | 2.28 | 9.26 | 3.76 | 15.89 | 6.0 | 90.0 | 7.9 | 2.0 |
| 4. | 20.0 | 15-30 | 0.27 | 24.7 | 1.5 | 5.50 | 0.20 | 0.09 | 2.00 | 4.40 | 1.92 | 9.18 | 6.7 | 84.5 | 11.6 | 3.5 |
| 5. | 30.0 | 0-15 | 0.33 | 30.3 | 3.5 | 10.60 | 0.30 | 0.18 | 2.05 | 6.72 | 3.28 | 13.1 | 6.8 | 90.8 | 6.4 | 3.0 |
| 6. | 30.0 | 15-30 | 0.21 | 19.8 | 1.5 | 7.10 | 0.20 | 0.17 | 1.41 | 2.64 | 1.20 | 6.26 | 6.5 | 85.2 | 10.2 | 4.6 |
| 7. | 40.0 | 0-15 | 0.34 | 28.0 | 4.7 | 13.80 | 0.30 | 0.17 | 2.73 | 4.88 | 3.20 | 9.26 | 4.9 | 90.2 | 7.8 | 2.0 |
| 8. | 40.0 | 15-30 | 0.32 | 11.9 | 2.2 | 6.90 | 0.20 | 0.14 | 1.50 | 3.12 | 2.24 | 7.35 | 5.5 | 84.2 | 12.8 | 3.0 |
| 9. | 50.0 | 0-15 | 0.14 | 20.2 | 4.5 | 32.10 | 0.27 | 0.20 | 1.41 | 11.76 | 7.36 | 24.32 | 5.0 | 90.5 | 5.5 | 4.0 |
| 10. | 50.0 | 15-30 | 0.12 | 15.5 | 3.6 | 30.00 | 0.21 | 0.17 | 0.96 | 6.28 | 1.84 | 7.13 | 5.4 | 84.8 | 10.7 | 4.5 |
| 11. | 60.0 | 0-15 | 0.07 | 18.3 | 2.3 | 32.90 | 0.18 | 0.26 | 0.55 | 1.12 | 0.64 | 3.16 | 5.3 | 81.7 | 12.8 | 5.5 |
| 12. | 60.0 | 15-30 | 0.03 | 10.8 | 0.7 | 23.00 | 0.14 | 0.14 | 0.68 | 1.04 | 0.50 | 3.39 | 5.6 | 77.7 | 15.4 | 6.9 |
| 13. | 70.0 | 0-15 | 0.09 | 25.7 | 2.0 | 22.00 | 0.19 | 0.20 | 0.72 | 2.36 | 1.04 | 4.62 | 5.5 | 77.8 | 13.2 | 9.0 |
| 14. | 70.0 | 15-30 | 0.02 | 20.6 | 0.9 | 45.00 | 0.16 | 0.15 | 0.64 | 1.12 | 0.4 | 2.52 | 5.7 | 73.9 | 15.6 | 10.5 |
| 15. | 80.0 | 0-15 | 0.08 | 19.5 | 2.1 | 26.25 | 0.18 | 0.19 | 0.69 | 2.66 | 1.21 | 4.93 | 5.8 | 84.6 | 10.9 | 4.5 |
| 16. | 80.0 | 15-30 | 0.06 | 12.6 | 0.7 | 11.60 | 0.13 | 0.11 | 0.42 | 1.12 | 0.61 | 3.39 | 6.0 | 80.5 | 15.8 | 3.7 |
| 17. | 90.0 | 0-15 | 0.08 | 15.2 | 2.2 | 27.50 | 0.19 | 0.19 | 1.33 | 2.05 | 1.07 | 2.83 | 5.9 | 90.9 | 6.3 | 2.8 |
| 18. | 90.0 | 15-30 | 0.05 | 7.7 | 0.8 | 27.00 | 0.16 | 0.10 | 0.75 | 1.32 | 0.69 | 3.02 | 5.8 | 82.5 | 14.6 | 2.9 |
| 19. | 100.0 | 0-15 | 0.07 | 15.9 | 2.0 | 28.50 | 0.18 | 0.20 | 1.28 | 2.61 | 1.21 | 5.18 | 6.0 | 84.9 | 11.4 | 3.7 |
| 20. | 100.0 | 15-30 | 0.06 | 8.4 | 0.7 | 13.30 | 0.15 | 0.15 | 0.66 | 1.11 | 0.74 | 3.1 | 6.2 | 83.6 | 13.3 | 4.1 |

TABLE 2: Mean Concentrations of various forms of soil Cu in soil containing POME

| S/N | Horizontal Distance(m) of Effluent discharged on soil from discharge point | Depth (cm) | mg/kg | | | |
|-----|--|------------|---------|--------------|---------|-----------|
| | | | Soluble | Exchangeable | Organic | Available |
| 1. | 10.0 | 0-15 | 15.35 | 9.12 | 29.73 | 13.11 |
| 2. | 10.0 | 15-30 | 9.43 | 4.01 | 3.27 | 3.46 |
| 3. | 20.0 | 0-15 | 24.09 | 16.00 | 45.25 | 18.37 |
| 4. | 20.0 | 15-30 | 16.28 | 2.46 | 12.21 | 2.28 |
| 5. | 30.0 | 0-15 | 12.30 | 18.47 | 67.71 | 22.14 |
| 6. | 30.0 | 15-30 | 5.85 | 0.65 | 32.26 | 1.68 |
| 7. | 40.0 | 0-15 | 6.81 | 2.94 | 46.52 | 10.46 |
| 8. | 40.0 | 15-30 | 2.22 | 1.11 | 12.18 | 3.10 |
| 9. | 50.0 | 0-15 | 6.55 | 2.36 | 72.27 | 16.80 |
| 10. | 50.0 | 15-30 | 2.48 | 0.98 | 39.13 | 2.25 |
| 11. | 60.0 | 0-15 | ND | 4.26 | 27.70 | 4.66 |
| 12. | 60.0 | 15-30 | ND | 0.05 | 13.38 | 0.09 |
| 13. | 70.0 | 0-15 | ND | 8.14 | 15.96 | 4.57 |
| 14. | 70.0 | 15-30 | ND | 2.88 | 4.89 | 1.01 |
| 15. | 80.0 | 0-15 | ND | 3.13 | 7.42 | 1.50 |
| 16. | 80.0 | 15-30 | ND | 0.01 | 1.34 | ND |
| 17. | 90.0 | 0-15 | ND | 7.54 | 5.09 | 2.78 |
| 18. | 90.0 | 15-30 | ND | 1.29 | 0.55 | 0.34 |
| 19. | 100.0 | 0-15 | ND | 4.45 | 10.12 | 1.08 |
| 20. | 100.0 | 15-30 | ND | 0.18 | 2.10 | ND |

ND = Not Detected

SOIL PREPARATION AND CHEMICAL ANALYSES

In the laboratory, the soils were dried at ambient temperature (22-25°C), crushed in a porcelain mortar and sieved through a 2-mm (10 mesh) stainless sieve. Air dried <2-mm samples were stored in polyethylene bags for subsequent

analysis. The <2-mm fraction was used for the determination of selected soil properties: soil pH was determined using H₂O according to Folson et. al. (1981). The soil/solution ratio was 1:2. Soil organic carbon was determined by Walkley-Black rapid dichromate oxidation technique (Nelson and Sommers, 1982) with the use of correction factor 1.3 to account for the incomplete oxidation of

organic compound. Cation exchange capacity was estimated by summing the exchangeable cations (Cmolkg^{-1}) with the exchangeable H (Jackson, 1960).

Particle size analysis was achieved according to the method of Bouyoucos (1962).

Available phosphorus was determined by the Bray and Kurtz (1945) method, while N was analyzed using a micro-kjeldahl method (USDA, 1972)

TRACE METAL FRACTIONATION

Organic Metals

Metals associated with the soil organic fraction were extracted through solubilization of humic substances by placing 1.00g soil in a polyethylene centrifuge tube with 20ml of extracting solution ($0.10\text{MNa}_4\text{P}_2\text{O}_7$ and 0.10MNaOH ; $\text{pH} = 13$) and shaken for 16h (Kononova and Bel'chikova, 1960). The solutions

were filtered through whatman no. 42 filter paper and filtrates analyzed for metals using Pye Unicam model SP 192 Atomic Absorption Spectrophotometer. (AAS).

Exchangeable Metals

Exchangeable metals were extracted by placing 2.00g of soils in a polyethylene centrifuge tube and extracted with 25ml of $0.1\text{M NH}_4\text{OAc}$ ($\text{pH} = 7.0$) (Thomas, 1982). The suspension was shaken for 30min, filtered through whatman no. 42 filter paper, and analyzed for metals using AAS.

Soluble Metals

Water-soluble metals were extracted with a solution of $0.01\text{M Ca}(\text{NO}_3)_2$ that was chosen to stimulate the ionic strength of the soil solution of non saline soil (Schofield and Taylor, 1955). Solution/soil ratios of 1:1 was used and shaken for 16h, filtered through whatman no. 42 filter paper and the filtrate analyzed for metal using AAS

Available Metals

Metals in the plant available forms in the soil were extracted using $0.025\text{MH}_2\text{SO}_4$ and 0.05MHCl ('double acid'). Six (6)g of soil was placed in a polyethylene tube and 60ml of the extractant added. This was shaken for 1 hour, filtered through whatman no. 42 filter paper, and the filtrates analyzed for metal using AAS.

Simple linear regression analysis of the different forms of heavy metals on selected physico-chemical properties of the soils (CEC, N, P) was performed in order to assess the influence of

these factors on the soluble, organic, exchangeable and available heavy metals.

RESULTS AND DISCUSSION

Macronutrient Availability:

The concentrations of nitrogen (N) and phosphorus (P) and the cation exchange capacity (CEC) of the soil increased at points close to discharge of the effluent (60-10m) Table 1.

P had a maximum concentration of 36.9mg/kg at 20m away from the discharge point and 0-15cm soil depth. Soils at 100m away from the effluent source had comparatively lower quantity of P (15.9mg/kg) at 0-15cm soil depth. These soils may be regarded as having low amounts of the POME. The high level of 36.9mg/kg P is expected since raw POME contains between 108 and 267 mg/l P (Ma and Ong, 1985). The high level of carbon especially at the topsoil depth enhances P availability. This is due to the increased concentration of organic matter via the conversion of the POME'S free fatty acids, sugars, amino acids into organic acids, ketones, acetate, CO_2 , H_2 , through two groups (acidogenic and acetogenic) of fermentative anaerobic bacteria (Bitton, 1994).

Nitrogen

Total nitrogen in the POME discharged area equally showed increasing amount of nitrogen with closeness to the source of effluent. The topsoil depth had higher concentrations than the subsoil depths (Table 1). The value obtained at 10m from the discharge point at 0-15cm soil depth, was 0.46% while only 0.07% was obtained at 60m away from effluent source at the same soil depth. The greater concentration of mineral-N observed at points close to the POME source might be due to nutrient accumulation by immobilization over several years of POME applied on the landmass. POME sludge cake have been showed to contain 1.8 – 3.7% N (Teoh and Chew, 1983), while raw POME may contain 0.19% N (Lim, 1986). The greater availability of N in the organic substrate (0-15cm) depth than in the mineral soil substrate (15-30cm) soil depth is presumably due to the POME quality and a more favourable microbial environment (Ocio, 1991). The C/N ratio was lower in the organic layer and near the effluent source than in the mineral soil far away (50m to 100m) from the effluent source. This further suggests increased microbial decomposition activities at points close to the effluent source

Cation Exchange Capacity (CEC)

There was indeed a general increase in the

TABLE 3: Mean Concentrations of various forms of soil Fe in soil containing POME

| S/N | Horizontal Distance(m) of Effluent discharged on soil from discharge point | Depth (cm) | mg/kg | | | |
|-----|--|------------|---------|--------------|---------|-----------|
| | | | Soluble | Exchangeable | Organic | Available |
| 1. | 10.0 | 0-15 | 4.67 | 13.35 | 31.72 | 13.60 |
| 2. | 10.0 | 15-30 | 3.24 | 0.94 | 19.90 | 8.05 |
| 3. | 20.0 | 0-15 | 7.34 | 10.68 | 39.49 | 11.18 |
| 4. | 20.0 | 15-30 | 1.55 | 5.34 | 14.51 | 4.66 |
| 5. | 30.0 | 0-15 | 11.0 | 9.35 | 28.71 | 13.75 |
| 6. | 30.0 | 15-30 | 1.81 | 0.67 | 8.97 | 6.12 |
| 7. | 40.0 | 0-15 | 4.59 | 8.65 | 26.70 | 12.89 |
| 8. | 40.0 | 15-30 | 1.64 | 0.58 | 12.64 | 4.15 |
| 9. | 50.0 | 0-15 | 8.50 | 4.00 | 41.25 | 13.28 |
| 10. | 50.0 | 15-30 | 4.02 | 0.49 | 18.82 | 6.55 |
| 11. | 60.0 | 0-15 | 2.67 | 16.02 | 15.64 | 12.46 |
| 12. | 60.0 | 15-30 | 1.34 | 2.14 | 13.57 | 5.94 |
| 13. | 70.0 | 0-15 | 7.08 | 2.14 | 18.06 | 4.83 |
| 14. | 70.0 | 15-30 | 3.29 | 0.68 | 11.92 | 1.92 |
| 15. | 80.0 | 0-15 | 5.72 | 3.42 | 21.33 | 4.76 |
| 16. | 80.0 | 15-30 | 1.48 | 0.11 | 6.80 | 2.19 |
| 17. | 90.0 | 0-15 | 2.98 | 3.64 | 10.14 | 2.79 |
| 18. | 90.0 | 15-30 | 0.99 | 0.86 | 1.92 | 0.09 |
| 19. | 100.0 | 0-15 | 3.11 | 2.46 | 5.00 | 1.64 |
| 20. | 100.0 | 15-30 | 1.64 | 0.01 | 0.18 | 0.03 |

TABLE 4: Mean Concentrations of various forms of soil Zn in soil containing POME

| S/N | Horizontal Distance(m) of Effluent discharged on soil from discharge point | Depth (cm) | mg/kg | | | |
|-----|--|------------|---------|--------------|---------|-----------|
| | | | Soluble | Exchangeable | Organic | Available |
| 1. | 10.0 | 0-15 | 6.78 | 20.92 | 4.21 | 3.27 |
| 2. | 10.0 | 15-30 | 7.32 | 19.35 | 3.59 | 4.90 |
| 3. | 20.0 | 0-15 | 6.27 | 21.44 | 8.37 | 4.86 |
| 4. | 20.0 | 15-30 | 7.06 | 11.51 | 1.57 | 3.92 |
| 5. | 30.0 | 0-15 | 6.78 | 15.16 | 7.32 | 4.90 |
| 6. | 30.0 | 15-30 | 7.32 | 7.85 | 4.18 | 2.88 |
| 7. | 40.0 | 0-15 | 8.11 | 15.69 | 6.78 | 6.28 |
| 8. | 40.0 | 15-30 | 7.32 | 9.29 | 5.23 | 5.11 |
| 9. | 50.0 | 0-15 | 8.12 | 29.29 | 2.84 | 4.66 |
| 10. | 50.0 | 15-30 | 7.58 | 10.46 | 1.01 | 3.85 |
| 11. | 60.0 | 0-15 | 3.44 | 5.99 | 1.48 | 2.11 |
| 12. | 60.0 | 15-30 | 4.63 | 3.65 | 0.88 | 1.89 |
| 13. | 70.0 | 0-15 | 2.99 | 6.48 | ND | 1.99 |
| 14. | 70.0 | 15-30 | 3.56 | 4.92 | ND | 1.86 |
| 15. | 80.0 | 0-15 | 4.14 | 5.26 | ND | 0.92 |
| 16. | 80.0 | 15-30 | 2.92 | 3.94 | ND | 0.65 |
| 17. | 90.0 | 0-15 | 2.16 | 6.37 | ND | 0.10 |
| 18. | 90.0 | 15-30 | 2.62 | 5.24 | ND | 0.02 |
| 19. | 100.0 | 0-15 | 3.48 | 3.11 | ND | 0.86 |
| 20. | 100.0 | 15-30 | 4.66 | 1.04 | ND | 0.06 |

ND = Not Detected

amounts of Na, K, Ca, Mg, and H as the discharge point of the POME was approached. Table 1 shows that the highest concentration of exchangeable Ca (8.24 cmolKg^{-1}) was obtained at 10m from the source and at 0-15cm soil depth and having a CEC of $15.81 \text{ cmolKg}^{-1}$ at the same soil depth. The CEC was higher at 0 to 50m and reduced at 50 to 100m away from the source of POME.

The residual soil organic matter and the organic matrix from the POME is a polymeric weak acid exchanger with carboxylic (-COOH) ion contributing most to the CEC at $\text{pH} < 8$. Phenolic hydroxyl groups (Ar - OH) also contribute to the CEC at $\text{pH} > 7$, while other functional groups (alcoholic OH, Ketonic CO, etc.) contribute only a minor fraction (Stevenson, 1982).

High CEC values were recorded between $\text{pH} 6.1$ and 6.8 . The carboxylate group is considered a strong field anion (Reichenberg, 1966) and mono- and dicarboxylic acids (including salicylic and phthalic acids, which are commonly used as models for exchange sites) show typical preference for alkaline earth ions with $\text{Ca} > \text{Mg}$ (Martell and Smith, 1979).

This is the inverse of the preference typically observed for soil organic matter and peat soils that are similar to weak field exchangers like smectite clays and Polysulphonate resins (Reichenberg, 1966).

It therefore appears that there is a competing reaction between the exchange sites of carboxylate and other anionic groups in the POME and the weak field exchangers in the soils containing POME and the alkaline earth metals (Ca and Mg). Also the percent organic carbon (matter) and CEC tend to regulate the soil pH. Overall soil pH ranged between $5.7 - 6.8$. It may be possible that the POME applied in the soil has a buffering capacity.

Cu

Copper had the highest concentration in the organic form with 67.71 mg/kg at 30m from the effluent source and 0-15cm soil depth (Table 2). The preference of Cu for organic matter is supported by the high stability constant of Cu complexes with organic matter (Irving and Williams, 1953). Other studies have shown that Cu is associated with the organic fraction of soil (Olade, 1987; Pardo et al, 1990). Cu in the available form from the regression analysis (Table 6) on N showed significant level of interaction ($P = 0.001$). Similarly the regression of available Cu on P was highly significant at $P = 0.001$. This effect may be attributed to the high microbial activity (decomposition) involved in the organic fraction thereby releasing and transforming Cu to the available form with subsequent release of N and P involved in the organic matrix (humus, amino acids). The work by Baker (1990) indicates

TABLE 5: Mean Concentrations of various forms of soil Pb in soil containing POME

| S/N | Horizontal Distance(m) of Effluent discharged on soil from discharge point | Depth (cm) | mg/kg | | | |
|-----|--|------------|---------|--------------|---------|-----------|
| | | | Soluble | Exchangeable | Organic | Available |
| 1. | 10.0 | 0-15 | 4.76 | 0.33 | 3.13 | 0.77 |
| 2. | 10.0 | 15-30 | 2.49 | 0.03 | 3.27 | 0.23 |
| 3. | 20.0 | 0-15 | 9.01 | 1.47 | 4.33 | 0.12 |
| 4. | 20.0 | 15-30 | 1.90 | 0.50 | 1.90 | 0.02 |
| 5. | 30.0 | 0-15 | 10.95 | 2.77 | 1.28 | 0.26 |
| 6. | 30.0 | 15-30 | 3.81 | 1.85 | 1.08 | 0.21 |
| 7. | 40.0 | 0-15 | 7.88 | 1.98 | 2.63 | 0.03 |
| 8. | 40.0 | 15-30 | 0.25 | 0.90 | 1.62 | 0.01 |
| 9. | 50.0 | 0-15 | 6.05 | 2.34 | 1.17 | 0.10 |
| 10. | 50.0 | 15-30 | 1.55 | 1.27 | 1.49 | 0.03 |
| 11. | 60.0 | 0-15 | 1.28 | 3.22 | 0.97 | 0.01 |
| 12. | 60.0 | 15-30 | 0.08 | 0.66 | 0.58 | 0.04 |
| 13. | 70.0 | 0-15 | 0.26 | 0.95 | 0.86 | ND |
| 14. | 70.0 | 15-30 | 0.02 | 1.92 | 0.60 | ND |
| 15. | 80.0 | 0-15 | 0.29 | 1.26 | 0.39 | ND |
| 16. | 80.0 | 15-30 | 0.02 | 0.76 | 0.08 | ND |
| 17. | 90.0 | 0-15 | 0.15 | 0.92 | ND | ND |
| 18. | 90.0 | 15-30 | 0.06 | 0.08 | ND | ND |
| 19. | 100.0 | 0-15 | ND | 0.91 | ND | ND |
| 20. | 100.0 | 15-30 | ND | 0.05 | ND | ND |

ND = Not Detected

Table 6: Regression Equation of Forms of Fe, Zn, Cu and Pb on N and P and their r^2 values.

| Metal on N and P | Regression Equation | |
|------------------|---------------------------|----------|
| Soluble/Fe | N $Y = 0.018 + N 0.100$ | 0.131ns |
| | P $Y = 1.987 + P 11.865$ | 0.474** |
| Organic Fe | N $Y = 0.003 + N 0.106$ | 0.120ns |
| | P $Y = 0.364 + P 12.260$ | 0.454** |
| Exchangeable Fe | N $Y = 0.014 + N 0.109$ | 0.123* |
| | P $Y = 1.070 + P 15.069$ | 0.424* |
| Available Fe | N $Y = 0.019 + N 0.047$ | 0.424* |
| | P $Y = 1.187 + P 11.910$ | 0.503*** |
| Soluble Zn | N $Y = 0.048 + N 0.0864$ | 0.517*** |
| | P $Y = 1.591 + P 11.149$ | 0.174ns |
| Organic Zn | N $Y = 0.043 + N 0.069$ | 0.760*** |
| | P $Y = 1.936 + P 15.086$ | 0.463** |
| Exchangeable Zn | N $Y = 0.012 + N 0.039$ | 0.490** |
| | P $Y = 0.672 + P 12.731$ | 0.414* |
| Available Zn | N $Y = 0.055 + N 0.021$ | 0.605*** |
| | P $Y = 2.440 + P 12.948$ | 0.371* |
| Soluble Cu | N $Y = 0.016 + N 0.088$ | 0.711*** |
| | P $Y = 0.896 + P 15.14$ | 0.636*** |
| Organic Cu | N $Y = 0.003 + N 0.105$ | 0.229* |
| | P $Y = 0.210 + P 14.960$ | 0.339ns |
| Exchangeable Cu | N $Y = 0.021 + N 0.108$ | 0.279** |
| | P $Y = 1.175 + P 14.389$ | 0.575*** |
| Available Cu | N $Y = 0.101 + N 0.098$ | 0.444** |
| | P $Y = 0.886 + P 14.820$ | 0.581*** |
| Soluble Pb | N $Y = 0.029 + N 0.097$ | 0.527*** |
| | P $Y = 1.783 + P 15.147$ | 0.594*** |
| Organic Pb | N $Y = 0.070 + N 0.071$ | 0.533*** |
| | P $Y = 3.600 + P 14.460$ | 0.435* |
| Exchangeable Pb | N $Y = 0.067 + N 0.165$ | 0.002ns |
| | P $Y = 3.178 + P 15.839$ | 0.131ns |
| Available Pb | N $Y = 0.515 + N 0.126$ | 0.443** |
| | P $Y = 22.182 + P 17.650$ | 0.256* |

*** = Highly significant at (P= 0.001)

** = Significant at (P= 0.001)

* = Significant at (P= 0.05)

ns = not Significant.

Fe

The highest concentration of Fe (48.06mg/kg) in the organic form occurred at 70m away from the effluent source at 0-15cm soil depths. Available Fe (Table 3) had a significant interaction with N ($P = 0.05$) and from the r^2 value of the regression on P there was a high interaction at $P = 0.001$. (Table 6). These observations may be due to the high organic fraction and the associated biosorption by microorganisms. These may lead to the release/transformation of Fe from the organic to the available form and enhance the availability of N and P. Furthermore Mandal and Holdar (1980) in their study found that applied P source decreased the organically bound Fe, Mn, Zn, and Cu in soil, while Haseman et al., (1950) reported that rapid fixation of P was caused by the reaction of phosphate with readily available Fe and Al, and their phosphates were the reaction products in the soil effluent system. Reactions of P with Fe and K ions in the soil solution resulted in slow precipitated reaction of Fe and K phosphates as $K[Fe(OH)_{1.33}]_3 [H_2PO_4]_6 \cdot H_2O$ and Fe-K-taranakite (Kim et al., 1983). The solubilities of Fe^{3+} and Fe^{2+} are much lower at higher pH than at low pH, (soluble Fe extractant pH = 7 and available Fe extractant pH < 5.5). Both $Fe(OH)_3$ and $Fe(OH)_2$ have low solubilities and can be precipitated at high pH. The seemingly higher levels of available Fe and low levels of soluble Fe (Table 3) may be due to the extractants used in the present study. However the different forms of Fe had higher concentration between the source of POME and midway (50m) from the sampling point compared with lower concentrations between 50m and 100m of the source of POME.

Zn

Exchangeable Zn had the highest amount of 29.29mg/kg at mid - way from the source of the POME (Table 4). There was a significant regression between exchangeable Zn and N ($P = 0.001$) and a corresponding interaction between available Zn and P ($P=0.05$). A major portion of available Zn is associated with the solid phase in soil in the form of exchangeable Zn (Pasricha et al., 1987). This may perhaps account for the significant interaction ($P = 0.05$) between available and exchangeable Zn with P (Table 6). There was no statistically significant interaction between soluble Zn and P from the regression values of r^2 . Several workers have also observed no change in the concentration of soluble Zn in the soil with low to high rates of applied source of P (Brown et al., 1970; Stuckenholtz, 1966). Lonergan et al., (1979) suggested that one of

that the components of Cu pool rank in the following order with respect to their retention of Cu: Organic > Fe/Mn oxides >>> clay minerals.

Table 7 Mean concentration of the different forms of Cu, Zn, Fe, Pb, N, P, CEC, pH and the distance from the source of applied POME.

| | | Mean (mg/kg) | |
|----------------|-----------|--------------|---------|
| | | 0-50m | 50-100m |
| Soluble Copper | Cu | 10.136 | 0 |
| Organic | Cu | 36.053 | 8.588 |
| Exchangeable | Cu | 5.81 | 3.193 |
| Available | Cu | 9.365 | 1.603 |
| Soluble Iron | Fe | 4.836 | 3.03 |
| Organic | Fe | 24.271 | 16.456 |
| Exchangeable | Fe | 5.405 | 3.148 |
| Available | Fe | 9.423 | 3.665 |
| Soluble Zinc | Zn | 7.266 | 3.46 |
| Organic | Zn | 4.51 | 0.236 |
| Exchangeable | Zn | 16.096 | 4.6 |
| Available | Zn | 4.463 | 1.046 |
| Soluble Lead | Pb | 4.865 | 0.216 |
| Organic | Pb | 2.55 | 0.348 |
| Exchangeable | Pb | 1.344 | 1.073 |
| Available | Pb | 0.178 | 0.005 |
| Nitrogen | N% | 0.287 | 0.059 |
| Phosphorus | P (mg/kg) | 23.89 | 15.47 |
| CEC | cmol/kg | 1.809 | 3.435 |
| pH | | 5.89 | 5.78 |

the reasons for this observation is that P would enhance Zn adsorption by sesquioxides, especially in acid soils, and consequently the concentration of Zn in the soil solution would be decreased. The effect of the addition of POME on the concentration of organic Zn is less pronounced between 50 and 100m from the source of POME (Table 7) and organic Zn was not detected between 70 and 100m. The effect of organic matter addition such as POME on Zn is usually less than those for other micronutrients like Fe (Shuman, 1988). This is because Zn is not comparatively sensitive to redox changes in the soil. Furthermore, Sims and Patrick (1978) are of the opinion that there seem to be a competing reaction between the exchange sites in the soil and the chelating effect of organic ligands contained in the POME.

Pb

Lead generally had the lowest concentration of all four metals studied (Table 5). The highest concentration of Pb occurred in the organic form (4.47mg/kg) with a significant interaction with P ($P = 0.001$) at 50m away from the effluent source at the 0-15cm soil depth. In acid soils, Pb is mainly in cationic form with some organic complexation (Davies, 1990). The amount of lead in the fraction studied follow the order soluble > organic > exchangeable > available.

CONCLUSION

The macronutrient levels of the soils containing palm oil mill effluent (POME), especially in the

area close to the discharge point (0-50m) had statistically significant high concentration of P, N and exchangeable cations of Ca, K, Na and Mg. This suggests enrichment of soil with macronutrients due to POME and possible biological activities.

Cu and Fe generally had the highest concentrations in almost all the forms studied with Fe having the highest concentration in the available form at 0-15cm topsoil. Zn was particularly present in the exchangeable and soluble forms, while the highest concentration of Pb occurred in the soluble matrix. Despite the addition of POME to the soil, the concentration of metals reduced considerably beyond the 50m point. This general lack or reduction of metal movement with most of the metals having higher concentrations between 0 and 50m point of discharge of POME may be attributed to shifts to a more stable forms of these metals.

In all, the levels of Cu, Zn, and Fe in the plant-available form indicates soil enrichment with these micronutrients, while the macronutrient status suggests availability of N, P and enhanced CEC. The relatively high levels of Cu, Fe and Pb in the organic species suggests safe disposal of POME on land, while the high level Pb in the soluble form may imply the restricted disposal of POME into water bodies or aquatic environments due to the dissolution/solubility of Pb in aqueous systems.

There is no doubt that the proper use and safe disposal of POME in the land environment will eventually lead to improved soil fertility for greater productivity of both arable and tree crops.

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