Total and Available Copper and Zinc in Soils Affected by Palm Oil Mill Effluent in Oghareki, Oghara Kingdom, Delta State, Nigeria

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ABSTRACT: This study evaluates the physicochemical characteristics, total and available copper and zinc in soils affected by four palm oil mills effluent (POME) of Oghareki in Oghara Kingdom, Delta State, Nigeria using standard methods. The results showed generally increased pH, organic matter, electrical conductivity, available phosphorus, exchangeable bases and cation exchange capacity (CEC), compared to the non-POME-contaminated soils. Concentrations of the exchangeable bases increased in the order, Na < Mg < K <Ca, in both the POME- and non-POME-soils. Data of total copper and zinc also revealed higher amounts in the POME soils. Total copper in POME- and non-POME-soils gave means of 0.232 and 0.212 mmol/kg, and 0.237 and 0.219 mmol/kg in respect of zinc, respectively, with no significant difference (P<0.05). The increased amounts of the different soil physicochemical parameters recorded in the POME-affected soils may be accounted for by their enhancement with every discharge of the effluent on one hand**,** and perhaps, the greater level of biodegradation and mineralization of the constituent organic matter, on the other. The study lends support to the view that raw palm oil mill effluent (POME) could alter the physicochemical properties of the receiving environment.

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Palm oil is an important agricultural product world-wide. In Nigeria, palm oil constituted a major export commodity for many decades before agriculture was relegated to the back seat of economic importance following the discovery of crude petroleum in commercial quantity during late nineteen fifties. Nevertheless, the production of palm oil has continued in many communities across the southern parts of the country where the cultivation of the oil palm tree remains an active and flourishing business. Palm fruit processing which involves several unit operations is, therefore, carried out manually by means of locally constructed equipment and under conditions which lead to poor quality of products (Ohimain and Izah, 2014). The residual liquid left behind after extraction of the oil, referred to as palm oil mill effluent (POME), is discharged untreated into the surrounding environment. The effluent consists of a complex mixture containing about 95% water and 5% solid, oil and grease (Onyia *et al*., 2001; Singh *et al*., 2010; Wu *et al*., 2009). It has adverse effect on the environment, creating offensive odour and polluting water and soil into which it is discharged (Okwute and Isu, 2007).

Reports show that POME contains macronutrients, including phosphorus, nitrogen, potassium and magnesium and micronutrients, including zinc, copper, cadmium, manganese, chromium and iron (Madaki and Seng, 2013; Ubani, *et al*., 2017). The presence of these elements in soils treated with POME, therefore, may result in the alteration of their physicochemical properties. Nwoko and Ukiwe (2016), observed increased concentration in all parameters investigated in POME-contaminated soils, compared with control soil samples. The authors concluded that POME was capable of impacting on soils and could improve soil fertility and growth performance of crops under controlled application. Other reports also indicate that raw POME alters the physicochemical parameters of soils and water, but reduced impact on the environment was observed when treated before being discharged (Okwute and Isu, 2007; Eze, *et al*., 2013). Momoh (2019) and Maliki (2020) in more recent studies have indicated enhanced growth performance of *Amaranthushybridus* and tomato, respectively, in soils treated with palm oil wastes including POME. Increased yield and growth

performance have similarly been reported in respect of Napier grass and *Pennisetumpurpureum*, respectively, in soils treated with palm oil mill effluent (POME), attributing the effect to improved soil productivity (Haryani *et al.*, 2019; Osman, *et al.*, 2020). Investigations on the status of elements in soils are conducted either for agricultural purpose to reveal their potential to enhance crops production, or for their environmental pollution potential. Zinc and copper are important trace elements in both respects. In soils they are beneficial when they serve as micronutrient to plants, but may be a source of environmental hazard when they are present in underground water sources, especially above threshold limits. The amount of an element extractable with relatively mild reagents is used as an index of its availability, and various soil tests have been developed for the extraction of trace elements in soils. The use of a single reagent that will simultaneously extract elements in amounts similar to those extracted by reagents known to be effective for the extraction of the individual elements has gained interest over the years. In this regard, HOAc, dilute HCl EDTA and DTPA have, among several others, been found suitable for the simultaneous extraction of number of trace elements under different conditions (Ponnamperuma, *et al.*, 1981; Tyler and McBride, 1982).Agricultural activities are carried out around the palm oil mills of Oghareki in Oghara Kingdom, Ethiope West Local Government Area, Delta State, Nigeria. The literature and information obtained from the operators of the mills revealed the absence of previous studies of any scientific concern on the soils. It is important, therefore, that some knowledge of the effect of effluents from these mills on the soils of the surrounding environment be obtained. Therefore, this study evaluates the physicochemical characteristics and total and available copper and zinc in soils affected by four palm oil mills effluents of Oghareki in Oghara Kingdom, Delta State, Nigeria.

MATERIALS AND METHODS

*Study Area:*The Oghareki community in Oghara kingdom, Delta state, Nigeria, has a number of palm oil mills located in it that are still in operation. Some of the mills which have existed for several decades were inherited by the present operators from their parents. They are mainly smallholder practitioners in the business who lack the financial capacity that will enable them acquire the necessary machinery and other equipment to upgrade their operations and add value to their products.

*Sample Collection and Treatment:*Six samples of soils were collected during the dry season from the land around each of four local palm oil mills in Oghareki community of Oghara kingdom which have been receiving effluents that are discharged untreated after the oil has been removed at a stage during the extraction process. Surface soils were collected at a depth of 0 - 20cm along the opposite edges of the shallow drainage channels that carry away the effluent from the point of discharge, and within 30m from this point at intervals of about 5cm from each other after the loose top soil had been removed. Samples were similarly collected from adjacent land not less than 10m away from the channels and which ordinarily, did not receive any effluent. These samples served as control. Following sampling, the samples were air-dried in the open laboratory air for seven days, crushed and sieved using a 2mm mesh size sieve. In order to obtain the final sample for laboratory analysis, the six different samples from each of the mills were bulked, thoroughly mixed and kept in appropriately labeled polypropylene bags pending analyses. Further sample pre-treatment involved only the sieving of the 2mm grains to pass through a 0.5mm sieve for the determination of organic matter.

*Sample Analysis:*The pH of the 2mm sieved soil samples was determined in a 1:1 (m/v) soil-water suspension using a pH meter (SEARCHTECH PHS-3C), while soil conductivity was measured with a conductivity meter (DDS-307). Available phosphorus was extracted by following the Bray 5 NO.1 procedure as described by Udo, *et al.,* (2009) and determined using a UV-Visible spectrophotometer (752N). Exchangeable bases (Na^+, K^+, Ca^{2+}, and Mg^{2+}) were extracted with a neutral solution of NH4OAc and determined by atomic absorption spectrophotometry (AAS), while exchangeable acidity (Al^{3+} and H^+) was estimated by titration with 0.1 mol. dm^{-3} NaOH solution after extraction with 1mol. dm^{-3} KCl solution. Cation exchange capacity (CEC), on the other hand, was determined by summation of the exchangeable bases and exchangeable acidity, while soil particle size distribution was determined by the hydrometer method of Day as described by Osaigbovo and Orhue (2011) using sodium hexametaphosphate as dispersing agent. The wet oxidation method of Walkley and Black described by Osaigbovo and Orhue (2011) was used for the determination of organic matter and atomic absorption spectrophotometry was used for the determination of total and dilute HCl- and EDTA-extractable zinc and copper in the aqueous suspensions of the soils.

RESULTS AND DISCUSSION

The results of the different soil physicochemical properties are presented in Table 1 from which it can be seen that the mean values of the parameters determined in this study were generally higher with regard to the POME-affected soils. Both of these soil

samples indicated acidic reactions. The POME-affected soils gave a mean pH value of about 4.5 and are less acidic compared to those of the adjacent non-POME-affected ones with a mean of about 3.9. Maliki *et al.*, (2020) reported similar increase in pH of POME- treated soils compared with that of untreated soils, and is in agreement with the findings of some of the other similar reports which indicated that raw POME, though acidic in reaction, gradually becomes alkaline with time as biodegradation by microbes sets in (Nta *et al.*, 2020; Osubor and Oikeh, 2013; Nwoko and Ukiwe, 2016). The result, however, is in contrast with the findings of Awotoye, *et al.*, (2011) and Chinyere, *et al.*, (2018), both of which showed that the non-POME affected soils were more alkaline than the POME affected soils. It is also important to note here that although plant growth and performance were not investigated in the present investigation, mention needs to be made of the performances of crops, particularly okra, which was cultivated almost exclusively in all the four sites sampled. The plants on portions of the land which received the effluent tended to show better performance than others that fell outside it. Nonetheless, pH is only one of the several factors which influence plant growth and the acidity level of the soils may not have been such that was capable of causing any negative observable effect.

Table 1: Physical and Chemical Properties of POME and Control Soils of Oghareki Community

	pH (H$_2$O)	EC (µS/cm)	Organic Carbon (%)	Matter (%)	Available Phosphorus (mg/dm^3)	Ea H$^+$	Al^{3+}	Exchangeable Bases Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	CEC	Soil Texture Sand (%)	Silt+ Clay (%)
POME affected soils														
Range	2.87-5.20	205.20-250.0	0.13-0.90	0.22-1.56	0.85-9.80	27.6-38.0	29.8-69.80	0.87-1.56	3.51-32.06	3.90-75.35	3.35-4.16	98.31-190.43	92.96-94.08	5.92-7.04
Mean	4.52	218.75	0.59	1.02	5.31	34.87	41.25	1.21	16.13	29.30	3.71	126.57	93.77	6.23
STD	1.11	20.97	0.35	0.61	3.87	4.87	19.16	0.28	13.40	33.82	0.36	43.56	0.54	0.54
NON POME affected soils														
Range	3.01-4.71	195.1-206.9	0.07-0.44	0.12-0.76	0.15-7.71	35.3-107.7	13.1-87.2	0.78-1.39	3.10-4.67	2.82-61.88	2.37-3.80	58.0-205.13	92.36-93.21	6.79-7.64
Mean	3.93	202.27	0.33	0.58	3.08	67.85	41.42	0.93	4.05	17.71	2.76	134.72	92.92	7.07
STD	0.81	5.45	0.17	0.31	3.48	34.71	31.93	0.30	0.67	29.44	0.69	60.87	0.39	0.39

EC: Electrical Conductivity.   Ea: Exchangeable Acidity   CEC: Cation Exchange Capacity

Electrical conductivity measurements gave mean values of 218.75 µS/cm in POME-contaminated soils and 202.27 µS/cm in non-POME soils. The result may be indicative of high concentrations of mobile matter, especially those of inorganic nature, in the soil solution. The conductivity values were higher, but non-significantly (P< 0.05) in the POME-contaminated soils than in the corresponding non-POME soils, which is in agreement with the findings of. Osunbor and Oikeh (2013), who reported similar increased conductivity of POME-treated soils, compared to non-POME affected soils. Nta, *et al.*, (2020) also reported highly significantly different values of electrical conductivities between POME- and non-POME soils of Abak Local Government area, AkwaIbom state, Nigeria. Mean values of available phosphorus were respectively, 5.31 and 3.08 mg/dm^3 in POME and non-POME soils, with no significant difference (P<0.05). Nta *et al.*, (2020) and Chinyere *et al.*, (2018) also reported higher P values for samples of palm oil effluent-receiving soils of South-south and South-east, Nigeria, respectively. However, Osubor and Oikeh (2013) recorded values of available P that showed a reversal of these results; with POME-contaminated soils recording lower available P. The authors remarked that this could have grave implications for soil P fertility in the soils concerned. Very low values of organic matter of mean 1.02 percent and 0.58 percent in the POME and non-POME affected soils, respectively, were recorded. This soil property is vital to plant growth and performance. Awotoye, *et al.*, (2011) reported similarly low values of organic matter which were also lower in non-POME soils, compared to those of POME-contaminated soils. Nmaduka, *et al.*, (2018) also showed that organic matter and organic carbon were higher in soil samples affected by POME. For POME-affected soils of Anyigba, Okwute and Isu (2007) reported a mean value of 3.39% and 2.31% for non-POME soils in respect of organic carbon. A similar report of organic matter content of some soils of Gombe state also revealed low values of this soil property (Mustapha *et al.*, 2011). It is believed that the critical threshold of organic carbon value is 2%, while the organic matter is about 3.4%, below which potentially serious decline in soil quality will occur (Loveland and Webb, 2003). In essence, therefore, the values of organic matter obtained in this study may be interpreted to mean that the productive capacity of the soils for agricultural purpose will be negatively affected as a result of poor soil chemical properties and impairment of soil nutrient cycling mechanism. This conclusion becomes valid when considered from the point of view of Fontan *et al.*, (2003), that low quality

of organic matter limits the amount of energy available for soil microorganisms and in turn the rate of soil carbon mineralization.The results of particle size analysis showed that the soils of the sites sampled are characteristically sandy and may lack good water holding capacity. This was the finding of Noguera *et al*., (2003), who reported influences on water holding capacity, electrical conductivity and macro- and micro-nutrient content of different particle sizes of the soils investigated by these authors. Exchangeable bases of the soils were found to be lower than those reported to be low by Ahukaemere *et al*., (2016) in respect of soils of Egbema, Southeastern Nigeria and Mustapha, *et al.,* (2011) in Gombe, Northeastern Nigeria soils. The present investigation, however, showed that the non-POME affected soils were poorer in this soil property than was obtained for the POME-contaminated samples. In this regard, sodium and potassium, respectively, had mean values of 1.21 and 16.13 mmol/kg, in POME and 0.93 and 4.05 mmol/kg in the non-POME soils. Calcium and magnesium, on the other hand, had mean values of 29.30 and 3.71mmol/kg in POME soils, respectively, and 17.71 and 2.76 mmol/kg, respectively, in the non-POME-affected soils. While the increases recorded in the values of exchangeable bases in POME-affected soils is in agreement with the findings of some of the earlier investigations (Osunbor and Oikeh, 2013; Nmaduka, *et al.,* 2018; Maliki, *et al*., 2020), Ubani *et al*., (2017), however, reported comparatively lower values of these elements in POME-contaminated soils and decreased plant growth and performance with increase in effluent concentration. It was also observed in the present study that the concentrations of the bases increased in the order, Na < Mg < K <Ca, in both POME- and non-POME-contaminated soils. The higher values observed in the POME-contaminated soils may be related to the continued additions of the elements with every discharge of the raw effluent and perhaps the greater rate of mineralization of the organic matter which in itself lends support to the higher pH values recorded for these soils. Mean of values in respect of the cation exchange capacity (CEC) of the soil samples were 50.35 and 25.45 mmol/kg for the POME- and non- POME-contaminated soils, respectively. The result reported by Chinyere *et al*., (2018), however, showed that POME-affected soils had higher exchange acidity and CEC in the samples investigated. CEC of a given soil is important to the availability of, particularly, ionic species and according to Chukwuma *et al*., (2010) and Wu *et al*., (2009), increase in CEC could decrease the availability of certain trace metals, such as copper and zinc in soils due to increased nutrient sorption.Table 2 shows the values of total and available copper and zinc in the soils investigated. Mean total copper contents of the experimental soils were 0.232 and 0.212 mmol/kg in the POME-and non-POME-affected soils, respectively, and showing no significant (p<0.05) difference.

Table 2: Total and Available Copper and Zinc in POME and Control Soils of Oghareki Community.

	Total ($\times 10^{-2}$ mmol/kg)		EDTA ($\times 10^{-2}$ mmol/kg)		HCl ($\times 10^{-2}$ mmol/kg)	
	Cu	**Zn**	**Cu**	**Zn**	**Cu**	**Zn**
POME affected soils						
Range	18.21-26.82	20.21-25.86	7.10-12.61	6.47-12.14	5.10-11.53	4.50-11.41
Mean	23.25	23.69	10.01	9.74	8.63	7.77
STD	4.17	2.42	2.36	2.43	2.69	2.82
NON POME affected soils						
Range	17.21-23.83	17.08-23.96	6.37-9.58	5.46-11.50	3.10-10.54	4.12-10.95
Mean	21.20	21.73	7.53	8.98	6.59	8.08
STD	3.08	3.14	1.42	2.57	3.28	3.36

With regard to total zinc content, on the other hand, a mean of 0.237 mmol/kg was obtained for the POME-soils while the non-POME soils produced a value of 0.219 mmol/kg with no significant (p<0.05) difference occurring between the two values. Total copper in soils of Lower Benue Valley was reported to be in the range of 2.72 to 49.8 mg/kg, while zinc gave total content of range 6.50 to 77.50 mg/kg (Sha'Ato *et al*., 2012). A range of 15 to 52 mg/kg total copper content was reported by Chude and Obigbesan, (1982), with a mean of 35.8 mg/kg for tree crop plantation in South-western Nigeria, while Kparmwang *et al*., (1998) reported a range of 15 to 65 mg/kg with a mean of 41mg/kg for soils of Nigeria savanna. These latter authors also reported a range of 25 to 265mg/kg with a mean of 89 mg/kg in respect of total zinc content in the same soils. For a similar investigation on soils of Benue valley, Sha'Ato *et al*., (2012), obtained total zinc content of range 6.50 to 77.50 mg/kg, with a mean of 9.0 mg/kg. The authors observed that zinc content increased with increase in clay content of the soils. The mean values obtained by these authors are generally much higher than those obtained in the present investigation which had their highest mean value, in

some cases, being lower than the lowest value of the respective ranges reported by the earlier authors. This may be traceable to a combination of the factors of low soil organic matter indicated earlier and to a much greater extent, the influence of the coarse-textured sandy nature of these soils (Noguera *et al*., 2003; Loveland and Webb, 2003). However, in spite of the low total content of these two important metals in the soils studied, the result revealed higher values in the POME-affected soils than was found for the non-POME soils, indicating a level of contribution from the effluent.The HCl- and EDTA-extractable copper in the POME-affected soils produced means of 0.086 and 0.102 mmol/kg, respectively. For the non-POME-affected soils on the other hand, means of 0.066 and 0.075mmol/kg, respectively, were obtained with no significant ($P<0.05$) difference between the results for the POME and non-POME-affected soils. Although the result is in agreement with that of an earlier report (Ako *et al*., 2002) with regard to the relative strengths of these two extractants, a much earlier investigation (Lombin, 1983a) had reported a range of 0.54 to 1.69 mg/kg with a mean of 1.03 mg/kg, and 0.49 to 1.60 mg/kg (mean 0.87mg/kg) for dilute HCl- and EDTA-extractable copper, respectively, in soils of Nigeria semi-arid savanna. This result showed that HCl was a more effective reagent for the extraction of copper, contrary to what the present investigation has proved in favour of EDTA for both POME- and non-POME soils. Moreover, Tyler and McBride (1982) had observed that HCl is less effective in the extraction of zinc, cadmium, copper and nickel from non-acid mineral and organic soils, attributing the effect to partially irreversible binding of the metals in organic matter. The contribution of Ojobor (2020) to the effectiveness of soil chemical extractants, however, showed that HCl was more efficient than EDTA for the extraction of zinc, while the reverse was the case for the extraction of copper. Furthermore, Alva (1992) had reported that EDTA extracts predominantly from the organic fraction of soils.The results of extractable zinc gave means of HCl- and EDTA-zinc to be 0.078 and 0.098 mmol/kg, respectively, for the POME soils. For the non-POME soils the study produced means of 0.081 and 0.090 mmol/kg, respectively. No significant ($P<0.05$) difference occurred between HCl-zinc in POME soils and in non-POME soils. Similarly, there was no significant ($P<0.05$) difference between EDTA-zinc content in the POME and non-POME soils. In respect of HCl-available zinc in unpolluted sois, Kparmwang *et al*., (1998) reported a range of 3.0 to 6.20 mg/kg, with a mean of 4.65 mg/kg and Mustapha *et al*., (2011) had a range of 0.13 to 0.37 mg/kg and a mean of 0.22 mg/kg. Again, attention is drawn to the fact that as found for total and extractable copper in this study, more zinc was extracted by EDTA

than by dilute HCl and that the effluent may have impacted on the soil's micronutrient content. The reason adduced earlier for the superiority of EDTA over HCl in respect of copper may still be valid in considering the effect of this extractant on available soil zinc.Percent of total copper and zinc extractable by HCl and EDTA are presented in Table 3, to give a clearer indication of the relative effectiveness of these extracting reagents in the POME and non-POME-affected soils environment.

Table 3: Percent of total Cu and Zn extracted from POME and non-POME soils ofOghareki.

Cu		Zn		Cu/Zn	
HCl	EDTA	HCl	EDTA	HCl	EDTA
37.16	43.87	32.80	41.16	1.15	1.07
31.04	35.52	37.12	41.35	0.84	0.86

Without doubt, EDTA showed greater effectiveness than dilute HCl as soil Cu and Zn extracting reagent and it is also clear from the ratio of Cu/Zn that more copper was extracted from the POME soils by each of HCl and EDTA than from the non-POME soils. In the non-POME soils, on the other hand, each of the reagents extracted generally higher amounts of zinc than copper. In the analysis of soils of the savannah region of Nigeria, Lawal, *et al*., (2012) obtained HCl-Cu and HCl-Zn values of 1.73 and 4.49 mg/kg, respectively, in basement complex soils and 1.00 and 4.17mg/kg in sedimentary soils, respectively. Several other authors have reported values of available copper and zinc which also showed higher levels of zinc (Isika, 2019; Ahukaemere *et al.,* 2016; Oyinlola and Chude, 2010; Kparmwang *et al.,* 1998). Kingsley *et al*., (2019) also reported consistently higher HCl-Zn than HCl-Cu in virtually all the soil depths of the four different slopes investigated. This observation tends to suggest a probable negative effect on available copper in relation to zinc in these soils environment, or that zinc's mobility is enhanced more above that of copper in the presence of the extractants. In this regard of mobility of the elements in soils, Sha'Ato *et al*., (2012) reported greater mobility of zinc compared to copper, which is explained by the association of copper with organic matter, soil minerals, Fe and Mn oxides, which renders it less mobile (.Okwute and Isu, 2007). However, it is noteworthy that the effectiveness or efficiency of the extracting reagent is also subject to the formation constant of the metal-extractant complex which for Cu-EDTA and Zn-EDTA complexes, are 18.5 and 16.3, respectively (Bohn *et al*., 1985).

*Conclusion:*The results gave a general indication of higher values of the parameters determined in the POME- than in the non-POME-contaminated soils and that EDTA was a more effective extracting reagent for copper and zinc in both the POME- and non-POME-

affected soils. Furthermore, both extracting reagents generally extracted more copper from the POME- than from the non-POME-contaminated soils. However, with regard to zinc, it was observed that higher amounts of this element were extracted from the non-POME-contaminated soils, compared to copper.

REFERENCES

Ahukaemere, CM; Uzoho, BN; Irokwe, IF; Ndukwu, BN; Osujieke, DN (2016). Iron, Zinc,Copper and Manganese availability in four contrasting hydromorphic soils of Egbema, Southeastern Nigeria. ResearchGate. Pp. 27-34.

Ako, PAE; Ezenwa, MIS; Yisa, J (2002). Zinc and copper status of Orchardsoils derived from sedimentary rocks in Southern Guinea Savanna regionof Nigeria. Acad. *J. Sci. Eng.* 2 (1): 26-31.

Alva, AK (1992). Micronutrient status of Florida soils under citrus production. *Commun. Soil Sci. Plant Anal*. 23: 2493-2510.

Awotoye, OO; Dada, AC; Arowomo, GAO (2011). Impact of palm oilprocessing effluent discharged on the quality of receiving soil and river inSouth Western. *Nig. J. Appl. Sci. Res.* 7: 111-118.

Bohn, HL; McNeeal, BL; O'Connor, D (1985). Soil Chemistry. 2nd Ed. JohnWiley and Sons. New York.

Chinyere, GC; Nwaogugu, CJ; Atasie, OC (2018). Effect of palm oil milleffluent (POME) Dumping on soil physicochemical characteristics andselected plant nutrients in Uturu, Abia state. *Glob. Sci. J.* 6(1): 244-259.

Chude, VO; Obigbesan, GOO (1982). Copper and zinc status of tree cropPlantation soils in south-western Nigeria. *Niger. J. Soil Sci.* 3: 1-13.

Chukwuma, MC; Eshett, ET; Onweremadu, EU; Okon, MA (2010). Zincavailability in relation to selected properties in crude oil polluted eutrictropofluvent. *Inter. J. Envr. Sci. Tech.* 7: 261-270.

Eze, VC; Owunna, ND; Avoaja, DA (2013). Microbial and physicochemicalcharacteristics of soils receiving palm oil mill effluents in Umuahia, Abia State, Nigeria. *J. Natur. Sci.* 3:163-169.

Fontain, S; Mariotti, A; Abbadie, L (2003). The priming effect of organic matter:A question of microbial competition?.*Soi. Bio. Biochem.* 35(6): 837- 843.

Haryani, H; Norlindawata, AP; Aswanimiyuni, A; Azman, A; ZulEdham, W(2019). Effect of palm oil mill effluent on yield and nutritive values of Napiergrass. *Malays. J. Vet. Res.* 10 (2): 62-67.

Kingsley, J; Ayito, EO; Akpan-Idiok, AU; Effiom, OD (2019). Status anddistribution of soil available micronutrients along a hillslope at EkpriIbiamin Akamkpa Local Government Area of Cross River state, Nigeria. *Afri. J. Agric. Res.* 14(1): 40-45

Kparmwang, T; Esu, IE; Chude, VO (2008). Available and total forms ofCopper and zinc in balsaltic soils of the Nigerian Savanna.*Communic. Soil Sci. and PlnAnaly.* 29: 2235-2245.

Lawal, BA; Adeboye, MKA; Tsado, PA; Ezenwa, MIS; Bayode, O (2012).Extractable zinc and copper in hydromorphic soils developed on basementcomplex rocks and sedimentary rocks in Niger state, Nigeria. *Savanna.J. Agric.* 7(1): 130-136.

Lombin, G (1983). Evaluating the micronutrient fertility of Nigeria semi-aridsavanna soils I: Cu and Mn. *Soil Sci*. 135: 377-384

Loveland, P; Webb, J (2003). Is there a critical level of organic matter in theagricultural soils of temperate regions? A review. *Soil.Tillage. Res.* 70(1) 1-18.

Madaki, YS; Seng, L (2013). Palm oil mill effluent (POME) from Malaysia palmoil mills: Waste or Resource. *Intern. J. Sci. Environ. Technol.* 2(6): 1138-1155.

Maliki, M; Ikhuoria, EU; Omorogbe, SO; Ekebafe, MO (2020). Comparativestudy on nutrient availability and growth of tomato (*Lycopersiconesculestum*) seedligs in soils amended with palm oil mill effluents andrubber processing effluents. *Cogent Food and Agric.* 6(1).Published Online

Momoh, TB (2019). Effect of palm oil waste soil on growth and physicochemicalconstituents of Amaranthus*hybridus*. *Asian J. of Biolog. Sci.* 12 (4): 792-796.

Mustapha, S; Voucir, N; Umar, S; Abdulhamid, NA (2011). Status anddistribution of some available micronutrients in the HaplicUsterts of Akko Local

Government Area, Gombe State Nigeria. *Intern. J. Soil Sci.* 6(4): 267-274.

Noguera, P; Abad, M; Puchades, R; Maquira, A; Noguera, V; (2003). Influenceof particle size on physical and chemical properties of coconut coir dustas container medium. *Comm. Soi. Sci. Plan. Anal.* 34(2-4): 593-605.

Nmaduka, NJ; Njoku, UO; Agu, CV; Okonkwo, CC; Obidiegwu, CJ (2018). Impact of palm oil mill effluent (POME) contamination on soil enzymeactivities and physicochemical properties. *Res. J. of Environ.Toxic.* 12: 34-41.

Nta, SA; Udom, IJ; Udo, SO (2020). Investigation of palm oil mill effluent pollution impact on groundwater quality and agricultural soils. *Asian J. Environ. Ecol.* 12: 28-36.

Nwoko, CIA; Ukiwe, LN (2016). Physicochemical characteristics of Soils Treated with Palm Oil Mill Effluent in Three Localities in Imo State, Nigeria.*Pur. Appl. Sci.* 4 (1): 1-8.

Ohimain, EI; Izah, IS (2014). Possible Contributions of palm Oil Mill Effluentsto Greenhouse Gas Emissions in Nigeria. Briti. J. Appl. Sci. Tech. 4(13): 4705-4720.

Ojobor, SA. (2020). Micronutrient distribution in soils of Ethiope region of Delta state,Nigeria. *Niger. J. Soi. Sci.* 30(1):70-76.

Okwute, LO; Isu, NR (2007). The environmental impacts of palm oil mill effluent(POME) on some physico-chemical parameters and total aerobic bioload ofsoil at a dump site in Anyigba, Kogi State, Nigeria. *Afri. J. Agri. Res.* 2(12): 656-662.

Onyia, CO; Uyub, AM; Akunna, JC; Norulaini, NA; Omar, AKM (2001). Increasing the fertilizer value of palm oil mill sludge. Bioaugmentation in nitrification. *Wat. Sci. Tech.* 44 (10): 157- 162.

Osaigbovo, AU; Orhue, ER (2011). Effect of palm oil mill effluent on some soil chemical properties and growth of maize. *Nig. J. Agri. Food and Environ.* 7(3): 51-54.

Osman, NA; Ujang, FA; Roslan, AM (2020). The effect of palm oil mill effluent final discharge on the characteristics of *Pennisetum purpureum. Sci. Rep.* 10: No. 6613

Osubor, CC; Oike, EI (2013). Impact of Palm OIL Mill Effluent on soil physicochemical properties and some vegetable parameters of maize (Zea *mays L.*). *NISEB J.* 13(1&2):19-22

Oyinlola, EY; Chude, VO (2010). Status of available micronutrients of the basement complex rock-derived alfisols in Northern Nigeria savanna. *Trop. and Subtrop. Agroeco.* 12: 229-237.

Ponnamperuma, FN; Cayton, MT; Lantin, RS (1981). Dilute HCl as an extractant for available Zn, Cu and B in rice soils. *Pla.Soi. Sci.* 61: 297-310.

Sha'Ato, R; Ajayi, SO; Ojanuga, AG (2012). Total and extractable copper, iron, manganese and zinc in major agricultural soils in the Lower BenueValley, Central Nigeria and the concept of extractant efficiency. *Nig. J. Chem. Resear.* 17: 59-82.

Singh, RP; Ibrahim, MH; Norizan, E; Iliyana, MS (2010).Composting ofwaste from palm oil mill: A sustainable waste management practice. *Rev. Environ. Sci. Biotechnol.* 9: 331-344.

Tyler, LD; McBride, MB (1982). Mobility and extractability of Cd, Cu, Ni and Zn in organic and mineral soil columns. *Soi. Sci.* 134: 198-205.

Ubani, CS; Onwuneme, C; Okpanashi, VE; Osuji, AC; Nwadike, U (2017). Palm oil Mill effluent effect on soil fertility: A longitudinal assessment of Zea*mays* plant. EQA. *Environ. Quali.* 23: 43-53

Udo, EJ: Ibia, TO: Ogunwale, JA: Ano, AO; Esu, IE (2009). Manual of Soil, Plant and Water Analysis. Sibon Books Limited. Lagos.

Wu, TY; Mohammad, AW; Jahim, J; Amar, N (2009). A holistic approach to managing Palm oil mill effluents (POME): Biotechnological advances in sustainable reuse of POME. *Biotechnol. Advanc.* 27(1): 40-52.