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Effects of altering palm oil and cassava mill effluents pH before dumping on dumpsite soils physico-chemical parameters and selected enzyme activities

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Abstract

The effects of altering the pH of palm oil mill effluents (POME) and cassava mill effluents (CME) on dumpsite soil's physico-chemical parameters and selected enzyme activities was investigated after nine months of effluent dumping. Results indicated that the pH of these dumpsites changed from alkaline (pH7-10) to acid ($\text{pH}4.5 \pm 0.03 - 6.9 \pm 0.08$). The POME dumpsite soil samples had significantly higher temperatures and percentage moisture contents ($P < 0.05$) than the control sites. Calcium and aluminum ions concentrations were significantly high ($P < 0.05$). Total organic carbon (TOC), total nitrogen (N), acid phosphates, dehydrogenises and lipase enzyme activities were also higher ($P < 0.05$) in the dumpsites than in the control. In the altered CME dumpsites, EA, CEC, acid phosphates enzyme activity, ammonium and aluminum ions were significantly higher ($P < 0.05$) than in control sites while dehydrogenises and alkaline phosphates enzymes activities were significantly lower ($P < 0.05$). The altering of POME and CME pH using calcium hydroxide seem a viable step towards remedying pollution problems posed by these effluents. This also implies that, such POME and CME pH alterations before dumping will assist in rejuvenating these effluents dumpsites soils for agricultural purposes.

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Introduction

The palm oil and cassava mill industries are major agro-based ones in Nigeria especially in the South-Eastern part where palm oil and cassava flours are consumed daily. The palm oil when processed provides major sources of domestic cooking oil in this part of Nigeria although it may be put to other industrial uses as in soap making. During processing of the ripe fruit to extract the cooking oil, a lot of wastewater, palm oil mill effluent (POME) is generated (Nwaugo *et al.*, 2008). POME belongs to agricultural waste and can cause pollution if not properly handled. Much of the POME results from water used in processing the raw fruits (Okwute and Isu, 2007a; Abdul *et al.*, 2003) Palm oil mill effluents if untreated contains high amount of fatty acids, proteins, carbohydrates and other plant materials (Ngan *et al.*, 1996, Bek-Nelson *et al.*, 1999). Ma, (1999) reported that POME alters the environmental parameters causing changes in water and soil qualities – including BOD, C/N ratio and COD. These parameters affect soil microbial flora which in turn affects soil health (Aries *et al.*, 2005). Raw POME consisting of complex vegetative matter is a thick, brownish, colloidal slurry of water, oil and solids including about 2% suspended solids originate mainly from cellulose debris that is, plam mesocarp (Bek-Nelson, 1999). When POME is discharged the pH is generally acidic but gradually increases to alkaline as biodegradation takes place (Hemmings, 1997). The observed changes in soil pH affected plant nutrient availability (Skylberg, 1993) and growth (Okwute and Isu, 2007).

Similarly, the processing of cassava (*Mannihot estulata cratz*) has consistently generated so much waste from cassava mills which are usually discharged on land or water indiscriminately. This discharge has been reported to affect the biota especially in the southern part of Nigeria where most of the mills are located (Olorunfemi *et al.*, 2008). The cassava tuber consists about 15% peel and 85% flesh for use as human food. The peel is invariably removed and only the flesh is utilized.

Maduagwu and Okoro (1980) reported the presence of hydrocyanic acid toxic, to humans and animals in cassava peel and flesh. This is the reason why cassava tuber usually has to pass through several detoxification processes before it is safe for human and animal consumption (Onwueme and Sinha, 1991). Compounds that are generally toxic to living organisms will also at toxic concentrations prevent germination of seeds (Olorunfemi *et al.*, 2008). After milling the cassava tubers, the resultant pulp is stacked in sacks and pressed using hydraulic press to remove the watery content (cassava mill effluents: CME). Cassava mill effluents inhabits cyanide inform of linamarin and lotaustralin. It has been reported that CME increased C/N ratio (Ogboghodo *et al.*, 2001), and soil cyanide concentrations (Chinyere, 2001; 2003) at dumpsites. Cyanogenic glycosides have also been associated with off-odours inherent around dumpsites and increased soil alkalinity of these dumpsites (Dumestre *et al.*, 1977) due to ammonia release. The increased soil alkalinity led to reduction in plant growth (Ogboghodo *et al.*, 2006) and probably explains in part the high level of plant withering seen at dumpsites. Some of the methods advocated for the disposal of POME and CME included channelization into ditches, leadfills, direct discharge into streams and rivers, sludge treatment and discharge into open land spaces (Igwe and Onyegbado, 2007; Chinyere, 2003; Hemmings, 1977). However, the management that is based mainly on biological treatment of anaerobic and aerobic systems is quite inefficient to treat POME and CME which unfortunately leads to environmental polluting issues. This is because the high BOD loading and low pH of these effluents together with colloidal nature of the suspended solids renders treatment by conventional methods difficult (Ahmed *et al.*, 2005). Since most of the pollution problems associated with these effluents are linked to their acid pH, we decided to alter their pH to alkaline before dumping for nine months. Then evaluate the physicochemical parameters and plant nutrients of these dumpsites soils in order to determine changes that took place due to the altering of these effluents pH.

Materials and Methods

Experimental design: A total of eight(8) effluents dumping sites were established within the University environment and effluents pH altered and dumped on six(6) sites weekly for nine months (February-October).

Fifty litres of altered pH palm oil mill effluent (POME) dumped weekly on site 1 were of pH7, sites 2 = pH8 and site 3 = pH10. However, site 4 was also dumped fifty (50) litres of unaltered-pH POME weekly for nine months. Similarly cassava mill effluents (CME) of pH7 were dumped on site 5, pH8 = site 6 and pH10 = site 7 while CME of unaltered-pH was dumped on site 8. Calcium hydroxide Ca (OH)₂ was used for altering of effluents pH. The dumping sites were of same size (10m²) and similar topography. At the expiration of nine (9) months, soil samples were collected from each site thus; dumping point and five(5) metres from dumping point along effluents flow routes. The depths of soil samples collection using metal auger were 0-30cm. Collected soil samples were thoroughly mixed and their temperatures and pH determined at the site of collection. Soil samples collected were packed separately, in marked cellophane bags tightly tied to avoid contamination and stored in refrigerators 4-6°C before analysis. Soil samples were sieved (4mm) and sub samples for the determination of physicochemical parameters were air-dried and sieved (2mm) before analysis.

Soil sample analysis: Physicochemical properties, some selected soil enzymes activities and plant inorganic nutrients in the soil samples were determined thus; soil temperature was determined insitu at the site of collection with mercury-in-glass thermometer, while the soil pH was determined ex-situ as described by Bates (1954). The soil percentage moisture was measured using the method of APHA, (1998). Total organic carbon was determined by the method of Osuji and Adeniyani (2005) as described by Akubugwo *et al.*, (2007), while the analysis of soil cation exchange capacities, exchangeable acidities,

nitrites, phosphates and sulphates were done as described by Dewis and Freitas (1970). Soil sample nitrogen was determined using Udoh and Ogunwale (1986) method and soil ammonium ion measured as described by Vogel 1962. Finkel'stein (1940) method based on the reaction of cyanide ion (C≡N) with alkaline picrate producing a light-blue coloration which absorbs at 490nm was employed in determining the soil samples cyanide concentrations.

Soil Enzyme Activities: The soil samples acid and alkaline phosphatases activities were determined as described by Tabatabai and Bremner (1969) while Cassida *et al.* (1964) method modified by Li *et al.* (2005) was used to measure soil dehydrogenase activity. Soil urease and lipase activities were determined by the methods of Kandeler and Gerber (1988) and Macedo *et al.* (1997) respectively. Atomic absorption spectrophotometry (AAS) was used for the determination of sodium, potassium, calcium, magnesium and aluminium ions of the soil samples as described by AOAC (2005).

Data Analysis: Statistical analysis was done using analysis of variance (ANOVA) and differences between means compared using Duncan's multiple range test.

Results

Physicochemical Properties

The results of the physicochemical properties of the altered – pH POME dumpsites soils and altered –pH CME dumpsites soils are shown in table 1 and table IV respectively. For the altered –pH POME dumpsite soil samples, pH and EA values were not significantly different ($P > 0.05$) from values obtained for control soil samples. However the altered –pH POME dumpsites soil showed significantly higher ($P < 0.05$) temperatures ($32.5 \pm 0.01 - 33.1 \pm 0.03^\circ\text{C}$) compared to control soil samples. Similarly the dumpsites soils percentage moisture, total organic carbon (TOC), percentage nitrogen (N), C/N ratios, cation exchange capacities and ammonium ion were significantly higher ($P < 0.05$) than values obtained for the control

soil samples. We observed that the unaltered- pH POME dumpsite (site 4) soil sample ammonium ion

content was significantly lower ($P < 0.05$) than those of altered- pH dumpsite soil samples.

Table 1. Physicochemical Parameters of Altered-pH Palm Oil Mill Effluent (POME) Dumpsites Soils Samples.

Parameter		Site				
		1 pH(7)	2 pH(8)	3 pH(10)	4 (unaltered pH)	Control
Temperature (°c)	X _A	32.8 ^a ± 0.02	33 ^a .0 ± 0.01	32.7 ^a ± 0.15	28.6 ^{ab} ± 0.23	28.3 ^b ± 0.12
	X _B	32.5 ^a ± 0.01	33 ^a .1 ± 0.01	32.0 ^a ± 0.08	29.6 ^{ab} ± 0.09	
pH	X _A	5.9 ^a ± 0.03	5.8 ^a ± 0.01	6.9 ^a ± 0.08	3.4 ^b ± 0.03	6.0 ^a ± 0.11
	X _B	5.7 ^a ± 0.08	6.0 ^a ± 0.03	6.8 ^a ± 0.01	3.8 ^b ± 0.04	
Moisture (%)	X _A	16.32 ^a ± 0.19	16.18 ^a ± 0.11	16.30 ^a ± 0.08	18.34 ^a ± 0.19	10.41 ^b ± 0.03
	X _B	16.30 ^a ± 0.01	16.0 ^a ± 0.06	16.1 ^a ± 0.03	18.30 ^a ± 0.15	
TOC (mgg ⁻¹ soil)	X _A	45.32 ^a ± 0.11	45.61 ^a ± 0.81	45.33 ^a ± 0.71	46.28 ^a ± 0.41	21.91 ^b ± 0.73
	X _B	42.13 ^a ± 0.12	41.11 ^a ± 0.06	43.39 ^a ± 0.16	45.31 ^a ± 0.13	
Nitrogen (%)	X _A	4.18 ^a ± 0.63	4.02 ^a ± 0.05	4.63 ^a ± 0.19	4.71 ^a ± 0.35	3.08 ^b ± 0.15
	X _B	4.10 ^a ± 0.08	4.18 ^a ± 0.19	4.33 ^a ± 0.41	4.72 ^a ± 0.52	
C/N Ratio	X _A	10.84 ^a	11.35 ^a	9.79 ^a	9.83 ^a	7.11 ^b
	X _B	10.27 ^a	9.84 ^a	10.02 ^a	9.60 ^a	
CEC (meq100g ⁻¹ soil)	X _A	19.89 ^b ± 0.16	20.32 ^b ± 0.64	18.41 ^b ± 0.14	28.61 ^a ± 0.43	19.13 ^b ± 0.31
	X _B	19.13 ^b ± 0.09	19.72 ^b ± 0.85	18.15 ^b ± 0.25	23.42 ^a ± 0.31	
EA (MKg ⁻¹)	X _A	1.04 ^a ± 0.01	1.11 ^a ± 0.09	1.09 ^a ± 0.03	2.15 ^b ± 0.71	1.15 ^a ± 0.46
	X _B	1.00 ^a ± 0.14	1.14 ^a ± 0.08	1.23 ^a ± 0.05	1.98 ^b ± 0.03	
Ammonium ion (NH ₃ -N) (ppm)	X _A	6.50 ^a ± 0.13	6.51 ^a ± 0.51	6.45 ^a ± 0.33	4.16 ^b ± 0.61	5.53 ^{ab} ± 0.18
	X _B	5.97 ^b ± 0.08	6.45 ^a ± 0.09	6.49 ^a ± 0.15	4.11 ^b ± 0.09	

X_A = Effluent discharge point

X_B = 5.0 metres from X_A along effluent flow route

Values are mean of triplicate analysis ± SD

Values in the same row having the same superscript letters are not significantly different ($P > 0.05$)

However, the temperatures of the altered-pH CME dumpsite soil samples did not vary from those of controls ($P > 0.05$) except for site 7 (pH10) and unaltered -pH CME dumpsite (site 8) which showed significantly lower temperatures (25.8±0.40 - 26.1 ± 0.21). Also the altered-pH CME dumpsites soils percentage moisture, C/N ratio, CEC, EA, TOC and ammonium ions were significantly higher ($P < 0.05$) than values obtained for control soil samples while only site 7(pH10) and site 8(unaltered -pH) had significantly higher pH values ($P < 0.05$). Of the cations concentrations determined, aluminium, calcium and potassium ions were significantly higher ($P < 0.05$) in both altered-pH POME and CME

dumpsite soils samples compared to control soil samples. (Tables III and VI).

The dumpsite soil magnesium and sodium ions concentrations were similar to those of control soil samples ($P > 0.05$) for both effluents. However from both altered -pH POME and altered-pH CME dumpsites soils samples, were obtained significantly higher ($P < 0.05$) phosphate, sulphate and nitrate ions concentrations compared to the control soil samples (Tables III and VI).

In table II, the altered-pH POME dumpsites soils selected enzymes activities are shown while those of altered-pH CME dumpsites soils are in table V.

While the altered-pH POME dumpsites soils acid phosphatase, Lipase, urease and dehydrogenase enzymes activities were significantly higher ($P < 0.05$) than in control soil samples, alkaline phosphatase enzyme activity was lower ($P < 0.05$) in the effluent dumpsite soils. However, in the altered-pH CME dumpsites soils, acid phosphatase and urease enzyme activities were significantly higher ($P < 0.05$) than in

control soil samples while alkaline phosphatase, dehydrogenase and lipase enzymes showed lower activities ($P < 0.05$) in the altered-pH CME dumpsite soils. The altered-pH CME dumpsites soils gave soil cyanide ion concentration of $0.16 \pm 0.02 - 0.29 \pm 0.06 \mu\text{gg}^{-1}\text{soil}$. In all the parameters determined, the unaltered-pH effluents dumpsites soils samples gave variable results as shown in tables I – VI.

Table 2. Enzymatic Activities Evaluated in the Altered-pH Palm Oil Mill Effluent (POME) Dumpsites Soils Samples.

Parameter		Site				
		1 pH(7)	2 pH(8)	3 pH(10)	4 (unaltered pH)	Control
Acid Phosphatase($\mu\text{mol-pNPg}^{-1}\text{soilh}^{-1}$)	X _A	19.61 ^c ± 0.03	28.13 ^a ± 0.15	27.43 ^a ± 0.31	39.13 ^b ± 0.15	
	X _B	19.13 ^c ± 0.06	26.92 ^a ± 0.16	27.11 ^a ± 0.82	29.11 ^a ± 0.52	18.33 ^c ± 0.54
Alkaline Phosphatase($\mu\text{mol-pNPg}^{-1}\text{soilh}^{-1}$)	X _A	3.48 ^b ± 0.02	3.49 ^b ± 0.03	3.51 ^b ± 0.12	2.82 ^b ± 0.19	
	X _B	3.49 ^b ± 0.01	3.18 ^b ± 0.04	3.49 ^b ± 0.18	3.00 ^b ± 0.16	6.71 ^a ± 0.06
Dehydrogenase ($\text{mgg}^{-1}\text{6h}^{-1}$)	X _A	39.28 ^d ± 6.13	31.92 ^a ± 0.88	33.19 ^a ± 0.76	25.19 ^b ± 0.85	
	X _B	39.17 ^d ± 8.21	33.66 ^a ± 0.71	35.14 ^a ± 0.82	28.16 ^c ± 0.83	28.43 ^c ± 3.14
Lipase ($\mu\text{MFFAg}^{-1}\text{soilh}^{-1}$)	X _A	10.43 ^a ± 0.15	9.80 ^a ± 0.78	10.10 ^a ± 0.67	8.63 ^b ± 0.91	
	X _B	11.13 ^a ± 0.92	10.63 ^a ± 6.41	9.89 ^a ± 0.19	9.22 ^a ± 0.63	1.83 ^c ± 0.41
Urease $\text{mgNH}_4^{+}\text{-Nkg}^{-1}\text{2h}^{-1}$)	X _A	37.31 ^a ± 6.11	35.19 ^c ± 0.72	38.67 ^b ± 0.15	28.32 ^c ± 0.19	
	X _B	35.15 ^a ± 3.13	35.00 ^a ± 0.63	33.36 ^b ± 0.42	29.14 ^c ± 0.48	22.15 ^d ± 0.51

X_A = Effluent discharge point

X_B = 5.0 metres from X_A along effluent flow route

Values are mean of triplicate analysis ± SD

Values in the same row having the same superscript letters are not significantly different ($P > 0.05$)

Discussion

Results obtained in this study suggest possible remedial effects by altering the pH of these effluents using calcium hydroxide. There were no significant changes ($P > 0.05$) in the pH of soil samples obtained from altered-pH POME dumpsites in relation to the control. In contrast site 4 which was dumped POME samples which pH was not altered showed significantly low pH ($P < 0.05$). This observation is an indication that some microbial/biochemical activities may have been induced by this effluent treatment.

Similar result on pH changes was also obtained from the altered-pH CME dumpsites.

However these altered –pH effluent dumpsites soils had higher temperatures than control soil samples. The higher change in pH and temperatures could be attributed to the high oxidative and reductive biochemical transformations taking place there. Nwaugo *et al.*, (2008) reported similar observations for deposited cassava effluents on soil temperature. However the high percentage moisture of these effluent dumpsites is attributed to their high

percentage water holding capacities (Akubugwo *et al.*, 2009; Okwute and Isu, 2007). The TOC and C:N ratio observed for the altered-pH CME and POME dumpsites soils reflects the contents of the effluents. CME is known to be high in organic carbon which could then reduce the C:N ratio of the impacted soil but increase the TOC.

This is due to the low protein but high carbohydrate contents of cassava hence the observed low C/N ratio. In contrast, though POME has high carbon content, the protein content being equally high increased the

C:N ratio. Shanhinroksar *et al.*, (2008) and Nattigpong and Alissara (2006) reported that soil impaction with organic matter resulted in decreased C/N ratio especially if the impacting material has low N content. The altered-pH POME dumpsite soil showed no changes in CEC and EA compared with the control soil samples. However the unaltered-pH POME dumpsite soil gave a significantly high ($P < 0.05$) CEC which is reflective of the low acid pH $3.4 \pm 0.3 - 3.8 \pm 0.04$. It is believed here that the low acid pH of this dumpsite soil (site 4) influenced the CEC obtained.

Table 3. Exchangeable Cations and Selected Anions of Altered-pH Palm Oil Mill Effluent (POME) Dumpsites Soils Samples.

Parameter		Site				
		1 pH(7)	2 pH(8)	3 pH(10)	4 (unaltered pH)	Control
Nitrate (NO ₃ ⁻ N)(mgKg ⁻¹)	X _A	14.05 ^a ± 0.04	14.3 ^a ± 0.06	13.98 ^a ± 0.08	6.32 ^b ± 0.81	8.30 ^b ± 0.02
	X _B	13.96 ^a ± 0.09	14.11 ^a ± 0.07	14.00 ^a ± 0.12	7.10 ^b ± 0.72	
Phosphate ion (mgKg ⁻¹)	X _A	13.68 ^a ± 0.91	13.59 ^a ± 0.85	12.96 ^a ± 0.15	10.69 ^b ± 0.18	3.92 ^c ± 0.05
	X _B	13.10 ^a ± 0.81	13.35 ^a ± 0.66	13.01 ^a ± 0.28	11.62 ^b ± 0.15	
Sulphate ion (mgKg ⁻¹)	X _A	156.48 ^a ± 0.43	158.96 ^a ± 0.15	141.13 ^a ± 0.92	98.23 ^b ± 0.63	106.14 ^b ±
	X _B	150.19 ^a ± 0.19	141.12 ^a ± 0.61	139.82 ^a ± 0.71	110.33 ^b ± 0.62	1.01
Aluminium ion(Al ³⁺)(mgKg ⁻¹)	X _A	2.83 ^a	3.01 ^a	2.95 ^a	3.48 ^b	0.68 ^c
	X _B	2.88 ^a	3.14 ^a	3.23 ^a	3.96 ^b	
Calcium ion (mg100g ⁻¹)	X _A	13.18 ^a	12.89 ^a	13.43 ^a	12.22 ^a	4.10 ^b
	X _B	11.11 ^c	12.68 ^a	12.10 ^a	12.35 ^a	
Potassium ion (mg100g ⁻¹)	X _A	14.81 ^a ± 0.03	14.83 ^a ± 0.11	13.93 ^a ± 0.43	12.69 ^a ± 0.10	6.51 ^b ± 0.01
	X _B	14.70 ^a ± 0.92	14.82 ^a ± 0.59	14.01 ^a ± 0.33	12.67 ^a ± 0.17	
Sodium ion (mg100g ⁻¹)	X _A	31.01 ^a ± 0.19	30.66 ^a ± 0.15	30.52 ^a ± 0.93	31.12 ^a ± 0.46	30.11 ^a ±
	X _B	32.00 ^a ± 0.15	31.15 ^a ± 0.68	31.39 ^a ± 0.41	32.17 ^a ± 0.15	0.43
Magnesium ion (mg100g ⁻¹)	X _A	8.72 ^a ± 0.80	9.00 ^a ± 0.11	8.98 ^a ± 0.31	8.93 ^a ± 0.08	7.18 ^a ± 0.63
	X _B	7.99 ^a ± 0.63	8.93 ^a ± 0.19	8.91 ^a ± 0.71	8.91 ^a ± 0.19	

X_A = Effluent discharge point

X_B = 5.0 metres from X_A along effluent flow route

Values are mean of triplicate analysis ± SD

Values in the same row having the same superscript letters are not significantly different ($P > 0.05$)

Similarly results on CEC was also obtained for altered -pH CME dumpsites soil site 5(pH7). The biodegradation of the organic wastes of the effluents (POME and CME) in the soil led to increased ammonium ion concentrations observed in these

altered pH effluent dumpsites soils and this is discouraged by the low pH (acid) of the POME (site 4) unaltered-pH effluents. Also nitrification was high in both the altered-pH POME and altered-pH CME dumpsites soil as attested by the soil nitrate levels.

The soil nitrate concentrations decreased with increasing distance (5m) from point of effluent

impaction. This observation therefore implicates these effluents on the high soil nitrate levels.

Table 4. Physicochemical Parameters of Altered-pH Cassava Mill Effluent (CME) Dumpsites Soils Samples.

Parameter		Site				
		5 pH(7)	6 pH(8)	7 pH(10)	8 (unaltered pH)	Control
Temperature (°c)	X _A	30.1 ^a ± 0.15	28.8 ^a ± 0.10	26.1 ^{bc} ± 0.21	25.8 ^c ± 0.40	28.3 ^a ± 0.12
	X _B	30.0 ^a ± 0.43	28.2 ^a ± 0.61	27.3 ^a ± 0.62	29.4 ^a ± 0.15	
pH	X _A	6.5 ^a ± 0.08	7.6 ^{ab} ± 0.16	8.1 ^b ± 0.02	8.9 ^b ± 0.41	6.0 ^a ± 0.11
	X _B	6.6 ^a ± 0.12	7.3 ^{ab} ± 0.15	7.5 ^{ab} ± 0.32	8.2 ^b ± 0.91	
Moisture (%)	X _A	18.24 ^a ± 0.03	18.89 ^a ± 0.30	18.10 ^a ± 0.09	19.71 ^a ± 0.38	16.41 ^b ± 0.03
	X _B	16.41 ^b ± 1.40	16.91 ^b ± 0.62	17.15 ^b ± 0.48	17.92 ^b ± 0.18	
TOC (mgg ⁻¹ soil)	X _A	46.43 ^a ± 0.12	47.11 ^a ± 0.62	47.30 ^a ± 1.02	47.43 ^a ± 0.82	21.91 ^b ± 0.73
	X _B	42.15 ^a ± 0.11	40.08 ^a ± 0.71	41.33 ^a ± 0.84	43.10 ^a ± 1.21	
Nitrogen (%)	X _A	2.40 ^a ± 0.31	2.38 ^a ± 0.15	2.37 ^a ± 0.67	2.11 ^a ± 0.10	3.01 ^a ± 0.41
	X _B	2.25 ^a ± 0.82	2.21 ^a ± 0.81	2.33 ^a ± 0.06	2.20 ^a ± 0.15	
C/N Ratio	X _A	19.35 ^a	19.79 ^a	19.95 ^a	22.47 ^a	7.23 ^b
	X _B	18.73 ^a	18.14 ^a	17.74 ^a	19.59 ^a	
CEC (meq100g ⁻¹ soil)	X _A	23.15 ^a ± 0.03	21.43 ^{ab} ± 0.41	21.95 ^{ab} ± 0.53	17.13 ^c ± 1.02	19.13 ^{bc} ± 0.31
	X _B	22.96 ^a ± 0.15	21.39 ^{ab} ± 0.62	22.51 ^{ab} ± 3.10	19.14 ^b ± 1.13	
EA (MKg ⁻¹)	X _A	2.31 ^a ± 0.01	2.06 ^a ± 0.15	2.10 ^a ± 0.08	1.03 ^b ± 0.15	1.15 ^b ± 0.46
	X _B	2.00 ^a ± 0.92	2.10 ^a ± 0.35	2.01 ^a ± 1.31	1.52 ^{ab} ± 0.76	
Ammonium ion (NH ₃ -N) (ppm)	X _A	7.24 ^a ± 0.18	7.20 ^a ± 0.32	7.24 ^a ± 1.10	7.92 ^a ± 0.09	22.15 ^b ± 0.51
	X _B	6.31 ^a ± 0.87	6.93 ^a ± 0.19	6.91 ^a ± 1.18	7.01 ^a ± 0.77	

X_A = Effluent discharge point

X_B = 5.0 metres from X_A along effluent flow route

Values are mean of triplicate analysis ± SD

Values in the same row having the same superscript letters are not significantly different (P>0.05)

High soil nitrate levels have been associated with increased aeration (Paul and Clark, 1989), increased activities of ammonia oxidizers in low alkaline pH soil (Okwute and Isu 2007a) and the concentration of ammonia (Lilifah *et al.*, 2007). Also the altered-pH effluent dumpsites soils gave significantly high (P<0.05) phosphate and sulphate ions. The observed increases in concentration of PO₄²⁻ and SO₄²⁻ in the impacted soils studied may be attributable in part to the cellulose debris of their effluents and enhanced organic matter decomposition (Williams, 1995). This is in contrast to lower phosphate and sulphate ions obtained from the unaltered-pH POME (site4) and unaltered pH CME (site 8) dumpsites soils.

Sulphur uptake in plants is in the form of inorganic sulphate (SO₄) and its availability depends on its mineralization or mobilization (Fitzgerald, 1976) from aromatic sulphate esters (R-O-SO₃). Therefore, its availability is dependent on the extracellular hydrolysis of these aromatic sulphate esters or intracellular oxidation of soluble organic matter absorbed by the micro-organism to yield energy and carbon skeletons for biosynthesis by which SO₄-S are released as a by-product (Dodgson *et al.*, 1982). The observed increases in soil SO₄²⁻ of the altered-pH effluent dumpsites attests to enhanced microbial activities which secrete the arylsulphatase enzymes in soils responsible for sulphate ester hydrolysis

(Kertesz and Mileau, 2004). Sulphate occurrence in different soil systems is often correlated with microbial biomass and rate of S immobilization (Vong *et al.*, 2003).

Soil pH and organic matter content and its type are some of the factors that affect soil sulphate concentrations (Acosta-Martinez and Tabatabai, 2000, Dala, 1981, Kertesz and Mirleau, 2004).

Table 5. Enzymatic Activities Evaluated in the Altered-pH Cassava Mill Effluent (CME) Dumpsites Soils Samples.

Parameter		Site				
		5 pH(7)	6 pH(8)	7 pH(10)	8 (unaltered pH)	Control
Acid Phosphatase ($\mu\text{mol-pNPg}^{-1}\text{soilh}^{-1}$)	X _A	29.41 ^a ± 0.69	29.11 ^a ± 8.13	28.89 ^a ± 0.32	13.21 ^b ± 0.41	18.33 ^c ± 0.57
	X _B	29.25 ^a ± 0.17	28.53 ^a ± 0.68	28.27 ^a ± 0.97	13.11 ^b ± 0.24	
Alkaline Phosphatase ($\mu\text{mol-pNPg}^{-1}\text{soilh}^{-1}$)	X _A	2.15 ^c ± 0.13	2.83 ^c ± 0.17	2.19 ^c ± 0.46	8.92 ^a ± 0.66	6.71 ^a ± 0.06
	X _B	4.28 ^b ± 0.71	3.69 ^b ± 0.13	3.08 ^b ± 0.44	8.72 ^a ± 1.13	
Dehydrogenase ($\text{mgg}^{-1}\text{6h}^{-1}$)	X _A	13.33 ^a ± 0.11	13.01 ^a ± 0.73	12.96 ^a ± 0.51	7.89 ^d ± 0.37	28.43 ^c ± 3.14
	X _B	16.49 ^b ± 0.15	17.01 ^b ± 1.10	16.92 ^b ± 0.39	8.88 ^d ± 1.15	
Lipase ($\mu\text{MFFAg}^{-1}\text{soilh}^{-1}$)	X _A	0.98 ^a ± 0.03	0.91 ^a ± 0.32	1.10 ^a ± 0.01	0.63 ^b ± 0.06	1.83 ^c ± 0.41
	X _B	1.31 ^{bc} ± 0.07	1.28 ^b ± 0.59	0.96 ^a ± 0.13	0.93 ^a ± 0.37	
Urease ($\text{mgNH}_4^{+}\text{-Nkg}^{-1}\text{2h}^{-1}$)	X _A	27.28 ^a ± 6.14	27.36 ^a ± 0.91	28.14 ^a ± 0.37	29.14 ^a ± 0.88	22.15 ^b ± 0.51
	X _B	23.01 ^b ± 0.11	24.28 ^b ± 0.69	24.20 ^b ± 0.98	27.77 ^a ± 1.07	

X_A = Effluent discharge point

X_B = 5.0 metres from X_A along effluent flow route

Values are mean of triplicate analysis ± SD

Values in the same row having the same superscript letters are not significantly different (P>0.05)

Observations in this study concerning exchangeable cations suggest that these effluents did not cause much variation on sodium and magnesium ions concentrations. However calcium and aluminium ions contents of the soil were significantly affected. This calcium ion changes in soil impacted with POME and CME are attributable to its presence in the plant tissues. Similar observations had been made by Nwaugo *et al.*(2008), Aderiye and Laleye, (2003) and Adewoye *et al.* (2005). In contrast, the observed increased Al³⁺ in the impacted soil is associated with pH changes of these sites. Aluminium hydroxides like the mineral gibbsite are known to be very insoluble at neutral or alkaline pH. As the soil pH decreases however, the excess of hydrogen ions can combine

with hydroxide ions to form water, yielding water and Al³⁺ in solution. This ionized Al³⁺ has been noted to become much more soluble as for other forms in soil (Birx, 2008). At low soil pH below pH6 availability of aluminium and manganese increases and may reach toxic level to plants (Birx, 2008). Excess Al³⁺ in the soil solution has been noted to interfere with growth and function as well as restricting plant uptake of Ca²⁺ and Mg²⁺. Acid soils also cause phosphate ions to form insoluble compounds with aluminium and iron, thereby inhibiting plant root growth (Rincom and Gonzalez, 1992). This could attest to observations made on Al³⁺ content of the unaltered pH POME dumpsite soils.

Table 6. Exchangeable Cations and Selected Anions of Altered-pH Cassava Mill Effluent (CME) Dumpsites Soils Samples.

Parameter		Site				
		5 pH(7)	6 pH(8)	7 pH(10)	8 (unaltered pH)	Control
Nitrate (NO ₃ -N)(mgKg ⁻¹)	X _A	15.13 ^a ± 4.01	14.61 ^a ± 1.03	13.92 ^a ± 0.73	10.33 ^b ± 0.63	8.30 ^c ± 0.43
	X _B	14.82 ^a ± 1.11	14.07 ^a ± 1.00	12.01 ^{ab} ± 0.67	11.27 ^b ± 0.71	
Phosphate ion (mgKg ⁻¹)	X _A	11.69 ^a ± 0.71	11.62 ^a ± 0.58	12.61 ^a ± 0.82	10.97 ^b ± 1.13	3.92 ^c ± 0.05
	X _B	11.23 ^a ± 0.94	11.53 ^a ± 0.43	12.72 ^a ± 6.43	10.98 ^b ± 3.16	
Sulphate ion (mgKg ⁻¹)	X _A	152.63 ^a ± 2.18	161.17 ^a ± 6.19	163.23 ^a ± 3.32	107.01 ^b ± 2.11	106.14 ^b ± 1.01
	X _B	160.15 ^a ± 7.12	159.33 ^a ± 1.17	102.10 ^b ± 3.15	103.81 ^b ± 2.92	
Aluminium ion(Al ³⁺)(mgKg ⁻¹)	X _A	2.40 ^a	2.68 ^a	2.41 ^a	0.39 ^c	0.68 ^b
	X _B	2.41 ^a	2.39 ^a	2.37 ^a	0.20 ^c	
Calcium ion (mg100g ⁻¹)	X _A	11.51 ^a	12.28 ^a	12.29 ^a	12.27 ^a	4.10 ^b
	X _B	10.91 ^d	12.30 ^{ad}	11.88 ^{ad}	13.01 ^a	
Potassium ion (mg100g ⁻¹)	X _A	11.79 ^a ± 0.32	11.87 ^a ± 0.61	12.16 ^a ± 0.74	13.92 ^a ± 4.10	6.51 ^b ± 0.25
	X _B	12.29 ^a ± 1.03	11.93 ^a ± 3.09	12.10 ^a ± 0.92	12.99 ^a ± 3.16	
Sodium ion (mg100g ⁻¹)	X _A	30.70 ^a ± 0.82	30.98 ^a ± 0.44	31.09 ^a ± 0.13	30.64 ^a ± 2.20	30.11 ^a ± 0.43
	X _B	30.68 ^a ± 0.15	30.73 ^a ± 0.19	31.32 ^a ± 6.40	30.31 ^a ± 0.45	
Magnesium ion (mg100g ⁻¹)	X _A	8.52 ^a ± 1.13	8.67 ^a ± 0.91	9.11 ^a ± 0.83	9.63 ^a ± 1.81	7.16 ^a ± 0.63
	X _B	9.18 ^a ± 1.02	8.23 ^a ± 0.71	9.63 ^a ± 2.14	8.97 ^a ± 1.66	
Cyanide ion (µgg ⁻¹ soil)		0.16 ± 0.02	0.18 ± 0.03	0.18 ± 0.01	0.19 ± 0.06	UND.

X_A = Effluent discharge point

X_B = 5.0 metres from X_A along effluent flow route

Values are mean of triplicate analysis ± SD

Values in the same row having the same superscript letters are not significantly different (P>0.05)

UND = Undetected.

Results from the soils enzymes activities analyzed showed some of the biochemical transformations taking place in the soils vividly. Dehydrogenase which is found in bacterial cell and its activity usually used as overall index of soil fertility had its highest activity in the altered-pH (site1,pH7) POME dumpsite soil. Also all the other altered-pH POME dumpsites had significantly high (P<05) dehydrogenase activities in relation to both the control and unaltered – pH dumpsite soils. This high dehydrogenase enzyme activity indicates enhanced biodegradation of POME by microorganisms. Ranamukharachchi and Doi, (2009) had correlated soils dehydrogenases enzymes activities with bacterial populations in soils.

The soils total dehydrogenase activity reflects the workings of a group of intracellular enzymes that are present in living soil microbes (Dick, 1997) and their assay offers a continuous measure of soil microbial activity as a result of the total redox sequence. This thus serves as an integrative measure of the soil quality. Dehydrogenase isoenzymes of a microbial species respond to different environmental impacts in different ways (Berchet *et al.*, 2000) but the formation of formazan is measured as a single variable (Sollod *et al.*, 1992). The low altered-pH CME dumpsite soil dehydrogenase activities are associated with the presence of CN⁻ in the cassava mill effluent.

Cyanide ion levels of up to $0.29 \pm 0.06 \mu\text{g}^{-1}$ was obtained. Cyanide is a metabolic poison and will inhibit oxidation/reduction processes in non-resistant micro-organisms thereby reducing their overall activities. The activities of urease were also significant in this study and correlated with TOC content of the dumpsites. Shanhinrokhsar *et al.* (2008) stated that high TOC stimulated urease activities while Cookson and Lepiece (1996) reported increased urease activities in N-content soils. The acid and alkaline phosphatases activities were related to the dumpsite soil pH. Acid phosphatases act best in acid environment while the alkaline phosphatases are most active in alkaline medium. However another factor that influence the secretion of acid phosphatase enzyme in soils is the availability of soluble phosphate ion. In soil ecosystems, these enzymes play critical roles in P-cycle (Speir and Ross, 1978) as evidence shows that they correlated to P-stress and plant growth. When there is signal indicating P-deficiency in the soil, acid phosphatases secretion from plants roots and micro-organisms are increased to enhance the solubilization of the phosphate thus influencing the ability of plants and microbes to cope with P-stressed conditions (Kai, *et al.*, 2002, Karthikenyan *et al.*, 2002; Mudge *et al.*, 2002). As earlier stated at acid pH, aluminium and iron ties up phosphate to form insoluble complexes thereby are causing P-stress conditions.

This explains the significantly high PO_4^{2-} of the altered-pH dumpsites soils yet high acid phosphatase activities. However normal altered-pH dumpsite soil acid phosphatae activity was observed for the site 1 (pH7 POME) – indicating that the P-stressed condition was relieved by this POME pH alteration.

The activities of the altered-pH effluent dumpsite soil lipase enzyme correlated with presence of substrate. POME contains unharvestedS acylglycerols which are substrates to these enzymes. However CME are devoid of these acylglycerols and in conjunction with the presence of CN^- in the effluent,

lipase activity was low in the altered-pH CME dumpsite soils.

In conclusion, this study revealed the various effects of altering POME and CME pH on dumpsite soil physicochemical parameters and selected soil enzymes activities. It showed that the altering of effluent pH (especially pH7) tended to alleviate most of the pollution problems posed by these effluents. It is therefore suggested that altering of the pH of these effluents using calcium hydroxide be part of the initial measures employed in countering POME and CME pollution problems.

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