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Soil Quality Modeling of a Highly Acidic Eutric-tropofluvent Soil

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ABSTRACT

This research aims at developing several regression models establishing the relationship between pH and other selected soil physiochemical properties, to predict the values of these selected properties in the polluted soils. The study took place at Umuagwo-Ohaji garri processing centre in three sampling pedons; A, B and C using the technique of stratified random sampling for sample collections of soil and monthly collection of the CME between May 2007 to September 2009. The three morphological land unit representing the pedons were linked with a transect before sampling. Pedon A is the background or the control unit, pedon B or the discharge point is the Cassava Mill Effluent (CME) receiving unit and pedon C is the down stream, 500 m away from pedon B. The study examined the CME and soil properties of the collected samples at 5 layers of 0-15, 15-30, 30-70, 70-100 and 100-150 cm, respectively and was determined using standard methods. The result showed high values of soil physiochemical properties (mainly the heavy metals) at pedon B and the value gradually declined down stream of pedon B and lowest was recorded in pedon A. Along the depth profile, virtually all the values of the soil properties increased with depth except %porosity which declined with depth. This suggests intense chemical illuviation within the pedons. The investigated soil properties were used to develop regression model between pH and other properties. PH relationship with heavy metals in pedons A and B showed positive linear relationships with their coefficient of linearity (R2) ranging between 0.70-0.92 while other soil physiochemical properties obeyed polynomial relationships at reasonably high coefficient of fitness. Polynomial models fitted the pH relationships virtually in all the selected physiochemical properties of pedon C. with the models; the values of the soil physiochemical properties in this circumstance could be assessed.

Key words: Regression models, cassava mill effluent, soil pollution, soil physiochemical properties, heavy metals

INTRODUCTION

In Nigeria, Cassava (*Manihot esculent)* can be processed into different kinds of food such as fufu, garri, tapioca etc. (Oti, 2002). Garri production is most practiced in Nigeria and it is carried out at varying scales; in a small, medium and large scales. Most garri processing plants in Nigeria produce between 7-10 million tones of garri annually (FAO, 2004). Processing of garri requires large volume of water which in addition to some other solid substances forms part of the waste. This waste contains measurable quantity of heavy metals in a low acidic range (Claude and Denis, 1990). Apart from constituting foul smell and unattractive sight, the Cassava Mill Effluent

(CME) can also upset the ecological balance of the receiving bodies (Idu and Omoruyi, 2003). Arimoro *et al.* (2008) raveled total extinction of benthic macro invertebrate specie and aboundance of oligocheats and dipterans in a marine ecosystem by CME due to its high acidic medium. Also in marine environment, low acidic value of the effluent lowers the pH value of the stream leading to difficulty in fish breeding (Zualiya and Muzondo 1993). Low pH value of the CME also influences number of edaphic factors such as clay, organic matter, cation exchange capacity and some other soil phsiochemical properties such as heavy metals (Alloway, 1995; Nabulo *et al.*, 2008; Okafor and Opuene, 2007).

Several prediction studies of the physiochemical properties of heavily polluted soils with respect to pH have been carried out. Onweremadu and Eshett (2007) predicted the boron distribution and other soil properties with respect to pH in a heavily crude oil polluted sandy Paleudult soil. Similar study was also carried out by Chukwuma *et al.* (2010) in order to study zinc availability in a soil polluted by crude oil. Both sets of researchers separately observed that soils high in clay or organic matter had higher adsorptive capacities and higher bonding energies for boron and zinc respectively than sandy soils low in organic matter. But Onweremadu and Eshett (2007) had good linear prediction of boron with pH, surface area of clay, clay content and organic carbon surface area of clay, clay content and organic carbon, respectively.

Giving the apparent influence of pH on the physiochemical properties, developing the modeling in respect to the soil properties in such a low acidic CME polluted medium will create an enabling condition to predict the soil property values for assessment of their pollution potential and remediation. Therefore this study models the physiochemical properties of the CME receiving soil of Ohaji cassava processing center and its environs.

MATERIALS AND METHODS

Description of study area: The study was carried out at central garri processing center at Umuagwo, in Ohaji Egbema Local Government of Imo state, South- Eastern Nigeria between the months of May 2007 and September 2009. The area lies within the latitude 50 12'N to 50 48'N and at the temperature range of between 250-300 C (GPS 1998). The people of the area experience high rainfall of about 2000-2500 mm. Umuagwo is located in the sandy benin formation and therefore the geology of the region is characterized by quarternary, alluvium, meander belt, wooded back swamps as well as fresh water swamps (Orajaka, 1975) The soil of the area is classified as Eutric Tropofluvent FDALR (1985). Whereas the vegetation is that of a rain forest and the soil supports arable crop production. That explained why the major socio-economic activity of the area is cassava cultivation and processing. The garri processing centre which has been in operation for over ten years, takes up in commercial quantity. Processing ranging from cassava grinding to fermentation and frying are the major steps of the center. Liquid and some solid waste such as fibers form the processing centre are channeled to the nearby farmland and ordinary land that has been left fallow for years.

Soil sampling techniques and analytical methods: The entire study area was divided into three morphological units or pedons; namely the background (BA) or control, the waste receiving area or Point of Discharge (PD) and Down Stream (DS) of the discharged waste or the waste drainage channel. The three morphological units represent pedon A, poedon B and pedon C, respectively. A transect was drawn to link the three units. Given the high mobility of most substances constituting the cassava mill effluent in the soil, soil sampling was extended up to

100 cm in depth. Along the transect, three pedons were dug at the inter-pedon distance of 500 m. At each pedon, soil samples were collected form different soil layers corresponding to 0-15, 15-30, 30-70 and 70-100 cm in depth with a sterilized soil auger which was rinsed with a lot of distilled water and dry cleaned after every sampling to avoid contamination. The layers were designated as L1, L2, L3 and L4, respectively. The samples collected from each unit and layer were done in three replicates at the interval of 20 m, making a total sample of 36 soil samples for this study. The soil samples were subjected to various laboratory analysis using the following analytical methods after processes of air-drying, crushing and sieving using 2 mm sieve; Hydrometer method as conducted by Gee and Or (2002) and was used to analyzed for the particle size distribution, the SOLAAR UNICAM 969 Atomic Absorption Spectrometer (AAS) was used to analyze all the metals (Barabara *et al.,* 2002; Pardo, 2000). Core method of Grossman and Reinsch (2002) was used for the analysis of bulk density. Moisture content was determined using the gravimetric method as carried out by Obi (1990). Organic carbon was determined directly by furnace combustion at 3790 C.

Model approach: The models used for this study are the linear regression models of the least square method. Regression model was favored due to its reliability even in the face of limited data and ease of calibration and application. The model was developed based on the following conditions;

- That the flow of the CME down the soil horizon assumed one-dimensional flow
- That the concentration of the effluent on each horizon is homogenous
- That the samples collected at various sampling points be the representative of the study area
- The models were calibrated with the average concentration of heavy metals and other physiochemical soil properties obtained from the analysis

The linear regression or the predicted model was presented after Nwagozie (1998) as:

$$y = a_0 + a_1 x \quad (1)$$

where, a_0 and a_1 are the regression coefficients. Y and X are the dependent and dependent variables, respectively.

Method of least squares was used to estimate a_0 and a_1 in other to form the line of best fit to the data. For each data point there is always a difference between observed value of y, y_{obs} and the predicted value y_{pre}. The difference measures the error(e_i)or the residue and is denoted as:

$$y_{obs} - y_{pre} = e_i \quad (2)$$

To measure the goodness of fit for a given data, e_1+e_2+e_3........e_n must be minimum. This is mathematically represented as:

$$S = \sum_{i=1}^{n} e_i^2 = \text{minimum} \quad (3)$$

Substituting Eq. 2 into 3, it transforms to:

$$S = \sum_{i=1}^{n} \left(y_{obs} - y_{pre}\right)_i^2 = \text{minimum} \tag{4}$$

Substituting the y_{pre} as in Eq. 1 into 4, it becomes:

$$S = \sum_{i=1}^{n} \left(y_{obs} - a_0 + a_1 x\right)^2 = \text{minimum} \tag{5}$$

To solve for a_0 and a_1 partial derivative was made of equation 5 with respect to a_1 and a_0 to get:

$$\frac{\partial S}{\partial a_0} = \sum 2\left(y_{obs} - a_0 - a_1 x_1\right)(-1) = 0 \tag{6}$$

$$\frac{\partial S}{\partial a_1} = \sum 2\left(y_{obs} - a_0 - a_1 x_1\right)(-1) = 0 \tag{7}$$

Equation 6 and 7 can be rearranged to get the following pair of equation:

$$na_0 + a_1 \sum x_i = \sum y_i \tag{8}$$

$$a_0 \sum x_i + a_1 \sum x_i^2 = \sum x_i y_i \tag{9}$$

Equation 8 and 9 can be solved simultaneously to get a_0 and a_1 as:

$$a_1 = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{n\sum x_i^2 - \left(\sum x_i\right)^2} \tag{10}$$

Substituting Eq. 10 into 8 and solving for a_0 results to:

$$a_0 = \frac{\sum y_i - a_1 \sum x_i}{n} \tag{11}$$

The quadratic regression model which is given as:

$$y = a_0 + a_1 x + a_2 x^2 \tag{12}$$

will also be used to predict the values of the selected physiochemical properties of the soil.
The least square estimates of a0, 1 and a2 were carried out in the same way as that of linear regression model. In the same manner, the error was estimated by determining the difference between the observed and the predicted value and this is expressed as:

$$S=\sum\left(y-a_0-a_1x-a_2x^2\right)^2 \quad (13)$$

The partial differential of Eq. 13 with respect to a_0, a_1 and a_2 yielded the following equations:

$$\sum y=a_0n+a_1\sum x+a_2\sum x^2 \quad (14)$$

$$\sum xy=a_0\sum x+a_1\sum x^2+a_2\sum x^3 \quad (15)$$

$$\sum x^2y=a_0\sum x^2+a_1\sum x^3+a_2\sum x^4 \quad (16)$$

Other least square polynomial models were also adopted for the predictions.

RESULTS AND DISCUSSION

Table 1 shows the physiochemical properties of the cassava mill effluent . The pH value of the effluent placed the effluent on the acidic range. All other values were within the range of a typical cassava mill effluent as observed by Oviasogie and Ndiokwere (2008) presented in Table 2 are the physiochemical values of the CME polluted soil with respect to the sampling pedons and layers.

Results from Table 2 showed that the values of the soil physiochemical properties such as Cn, Na, Cu, Zn, Cd, Pb, Ph, %s and, %silt, %clay CEC, OC, MC and BD increased with depth whereas %PO (percentage porosity) showed decline in value down the depth profile in pedons A and C. This trend of distribution is true for the soil properties in pedon B, where appreciable amount of CME was received, except Cd and %PO which showed a reverse trend. The reason is not necessarily the Cd content of the CME but mainly due to the release of Cd from the soil occasioned by the low acidic medium of the effluent at the top layer of the pedon. Another reason could be high adsorption capacity of Cd to soils predominant with clay at the top layers where the impact of the CME is pronounced. For %PO, the starchy constituent of the CME has binding energy which binds the soil aggregates together reducing its pore sizes and consequently the soil porosity. This was evident on the apparent pool and swampy state of the study area. There were glaring pH variations at different pedons. Similar observations was made by Prusty *et al.* (2009) on their study on the carbon, nitrogen, phosphorus and sulfur distribution at five different horizons of the study area.

Table 1: Physiochemical properties of Cassava Mill Wastewater(CMW) effluent

Parameters	Values(mg L^{-1})
Cn	54.2
Na	146.2
Cu	2.5
Zn	4.1
Cd	1.98
Ph	4.1
Pb	8.31
Conduct (µs)	1550

Table 2: Some physiochemical properties of the studied soil for various pedons

Depth (cm)	Cn	Na	Cu	Zn	Cd	Pb	pH	%Sand	%Silt	%Clay	CEC	OC	MC	%PO	BD
PEDON A (Background or control unit)															
0-15	2.7	17.5	3.2	5.1	1.4	0.6	6.5	48	29	29	80	40	121	46	1.11
15-30	2.9	17.8	3.4	5.2	1.4	0.55	6.8	35	26	26	150	31	136	38	1.25
30-70	2.9	18.5	3.4	5.7	1.7	0.59	6.7	30	25	25	163	28	157	39	1.20
70-100	2.9	18.6	3.7	5.2	1.6	0.6	6.9	25	24	24	196	15	178	32	1.47
100-150	3	19.2	4.2	6.1	1.9	0.81	7.8	21	20	20	219	10	189	30	1.59
PEDON B (Discharged piont)															
0-15	21.8	35.1	1.9	15.5	3.45	0.39	3.88	16	17	41	114	15	195	12	2.13
15-30	29.1	37.1	2.3	11.7	2.92	0.4	4.99	19	20	48	117	36	189	15	2.04
30-70	29.9	39.3	2.9	10.7	2.49	0.45	5.11	20	24	51	126	21	173	17	1.73
70-100	30.1	40.1	3.7	10.3	2.49	0.47	5.89	18	21	57	161	28	168	20	2.11
100-150	31.1	41.8	3.9	11.3	2.11	0.51	5.87	22	22	60	174	30	150	23	1.34
PEDON C (Down stream)															
0-15	11.34	11.7	2.11	10.9	0.47	4.91	20	20	41	90	43	189	189	21	1.9
15-30	15.1	15.1	2.31	11.39	0.71	6.03	18	19	40	100	51	178	178	18	1.9
30-70	17.01	15.37	2.57	8.73	0.93	6.49	18	18	45	140	33	170	170	18	2.0
70-100	14.43	15.78	2.54	8.32	0.91	6.86	18	22	46	175	21	170	170	12	2.01
100-150	18.43	16.43	3.24	9.12	0.99	6.98	15	15	52	185	16	168	168	10	2.3

Key; CEC: Cation exchange capacity, OC: Organic carbon, MC: Moisture content, PO: Porosity, BD: Bulk density

pH values were lowest in pedon B (discharged point DP) but highest in pedon A (Background or control unit). This established the fact that the lowest values of pH observed at pedon B was due to the discharge of the effluent on the units. The pH values in the pedon B (discharged point DP) appeared to be lower than the pH value of the CME. This observation was credited to the fact that the activities of micro-organisms responsible for increase in soil ecosystem pH, organic matter and nitrogen were rendered inactive by cassava mill effluent. Similar observation was glaring in the work of Ogboghodo *et al*. (2001). From the data, the soil pH seems to have overriding influence with respect to the level of abundance of many other selected heavy metals and soil properties. Heavy metal values at pedons A where the concentration of CME is low were the lowest while the most heavy metal concentrations at pedon B except lead (pb) were highest in value, followed by those in pedon C. However, heavy metal distribution in all the pedons was represented in this order pedon B> pedon C>pedon A. This trend of distribution is attributed to high concentration presence of CME and its low pH values in pedon A which was equally observed by Ogboghodo *et al*. (2001) and soil natural attenuation of the effluent for the reduction of heavy metal values observed in Pedon C. Reduction of heavy metals towards pedon C also indicates pronounced alluviation-illuviation processes. Earlier, Onweremadu and Eshett (2007) reported the depletion of boron, aluminum and iron and identified alluviation, illuviation and leaching of the heavily oil-polluted Arenic Paleudult soil of the study area. The seemingly low pb values observed in pedon B is attributed to the pb mitigating ability of CEM effluent due to abundant complexes of the cassava effluent with pb occasioned by low pH. The physiochemical characterization of wastewater polluted farm land by Onweremadu (2008) is also similar to this observation. The excessively high values of Cd recorded at pedon B (discharge piont DP) where appreciable amount of CME was received is not necessarily the Cd content of the CME but mainly due to the release of Cd from the soil occasioned by the low acidic medium of the effluent.

Low pH of the CME effluent equally has an influence on the other physiochemical properties of the soil. From Table 2, CEC increased with increase in pH. In Pedon B lowest value of CEC was recorded probably, due to its low acidic medium. This implies that the increased pH of CME polluted soil affected the CEC of the soil, as effective CEC increases with increased pH. This is similar to the observation of Singer and Munns (1999) where an increase in soil pH due to crude oil pollution resulted to a corresponding increase in its Cation Exchange Capacity(CEC). Also in pedon B low concentration of organic matter is noticed, suggesting the possibility of the soil-organic matter-producing micro-organisms being affected by low pH as equally observed by Oviasogie and Ndiokwere (2008) and Bolan and Duraisamy (2003).

Down the soil profile, the pH values increased down the layer in all the pedons, implying that the pH range is highest at the deepest depth range of 100-150 cm as displayed on Table 2. The observed pH distribution pattern could explain why most heavy metal values increased with depth, further buttressing the abundance of heavy metals with increase in pH as studied by Igbozuruike *et al.* (2009). Values of other physiochemical properties of the soil also reacted to the pH variation down the soil profile. CEC values increases down the profile because of high pH value observed down the soil depth. Low concentration of the CEM effluent due to poor infiltration nature of the soil at the top layer, occasioned by the effluent is responsible for the high pH down the profile. Generally. The heavy metal distribution in and within the study area might impact adversely on the vegetations as Wang *et al.* (2003) observed adequate plant uptake of heavy metals in a soil contaminated study area in china.

Regression model: In this study, soil pH determined the fate of other physiochemical properties. In the light of this, regression analysis was carried out, establishing the relationship between pH and other soil properties of the pedoshere. Several models such as linear regression, polynomial, power function and exponential were used to test the data with the view of determining the model that best fit the data. In each case, pH was chosen as the independent variable (X) while other respective physiochemical property was taken as the dependent variable (Y). The choice of using pH as an independent variable was due to the easiness in determining its value in addition to being a function of other soil physiochemical properties. Confronting with similar problems in the same geology, other soil properties in the pedosphere can be evaluated by mere determining the pH value of the soil, saving financial resources and man hour. pH values, the predictor was regressed on individual bases with other physiochemical properties of the soil. Tables 3-5 represent the regression models in pedons A, B and C respectively, conducted on the predictability of other soil properties that correlate significantly with pH.

In Table 3 and 4, pH relationship with all the heavy metals were linear with their linear coefficients (R2) ranging from 0.9-0.6 and 0.9-0.8 for metals in pedons A and B, respectively. This is not totally in consonance with the study of Sanchez-Martin *et al.* (2007) as most of the heavy metals gave quadratic and exponential functions with pH in their oil-polluted Arenic Paleudult soil study. Difference in the pollution source and soil type could be responsible for the glaring variation. The work of Ghosh (2008) which compares the distribution rate of hydrocarbon constituents of different crude oil in different soil media equally substantiated the claim. With other physiochemical properties, pH also varied linearly with %sand, %silt, OC, PO and BD in pedon A, having their coefficients of linearity as follows; 0.57, 0.87, 0.70 and 0.79, respectively while pH relationship with %clay, CEC and MC, respectively showed quadratic regression model. Also, virtually all the other physiochemical properties of the soil in pedon B except %clay and OC showed

Table 3: Model Equations of pH with the selected soil properties in Pedon A

Name	Model equations	R^2
pH-Pb	Y = 0.2182x - 0.8982	0.9574
pH-Cd	Y = 0.3664x - 0.9668	0.8691
pH- Zn	Y = 0.6385x + 1.0225	0.8691
pH-Cu	Y = 0.7583x - 1.6846	0.9681
pH-Na	Y = 1.1565x + 10.302	0.7125
pH-Cn	Y = 0.2484x + 1.204	0.741
pH-%sand	Y = -15.968x + 142.62	0.5881
pH-%silt	Y = -6.087x + 67.043	0.8761
pH-%clay	$Y = -28.738x_2 + 429.33x - 1551.4$	0.5724
pH-CEC	$Y = -170.97x_2 + 2547.7x - 9251.5$	0.9341
pH-OC	Y = -20.415x + 166.48	0.7091
pH-MC	$Y = -67.788x_2 + 1021.6x - 3655.1$	0.784
pH-PO	Y = -10.277x + 108.32	0.668
pH-BD	Y = 0.353x - 1.1256	0.668

Table 4: Model Equations of pH with the selected soil properties in Pedon B

Name	Model equations	R^2
pH-Pb	y = 4.1653x + 7.0049	0.8388
pH-Cd	y = 5.6642x + 8.4288	0.9127
pH- Zn	y = -0.5767x + 5.6541	0.8667
pH-Cu	y = -2.2366x + 23.427	0.8069
pH-Na	y = 1.0035x - 2.2338	0.8782
pH-Cn	y = 0.053x + 0.1723	0.878
pH-%sand	$y = -2.4618x_2 + 26.393x - 48.474$	0.9265
pH-%silt	$y = 1.418x_2 - 9.0632x + 25.769$	0.9243
pH-%clay	$y = -2.4618x_2 + 26.393x - 48.474$	0.7265
pH-CEC	y = 8.9108x + 5.634	0.9618
pH-OC	$y = 26.434x_2 - 231.38x + 613.85$	0.9648
pH-MC	$y = -6.5816x_2 + 45.884x + 116.54$	0.8035
pH-PO	$y=23.54x_2+43.77x+98.43$	0.8583
pH-BD	y = -0.2075x + 2.9356	0.8657

Table 5: Model Equations of pH with the selected soil properties in Pedon C

Name	Model equations	R^2
pH-Pb	$Y = -0.8075x_2 + 12.259x - 29.367$	0.7097
pH-Cd	Y = 2.185x + 1.2512	0.9566
pH- Zn	Y = 0.9271e0.1604x	0.7029
pH-Cu	$Y = -0.9166x_2 + 9.6307x - 14.175$	0.6802
pH-Na	$Y = 0.0586x_2 - 0.2214x + 1.48$	0.6802
pH-Cn	$Y = -0.0445x_2 + 0.7667x - 2.2359$	0.9546
pH-%sand	Y = -1.7338x + 28.643	0.6591
pH-%silt	$Y = -0.4586x_2 + 4.4887x + 8.922$	0.1018
pH-%clay	$Y = 5.456x_2 - 60.364x + 205.85$	0.8857
pH-CEC	$Y = 29.903x_2 - 309.1x + 886.71$	0.9995
pH-OC	$Y = -19.353x_2 + 216.3x - 552.12$	0.9762
pH-MC	Y = -10.255x + 239.13	0.9708
pH-PO	$Y = 0.1745x_2 - 1.9333x + 7.1915$	0.7409
pH-BD	$Y=0.2487x_2-1.537x+3.458$	0.9630

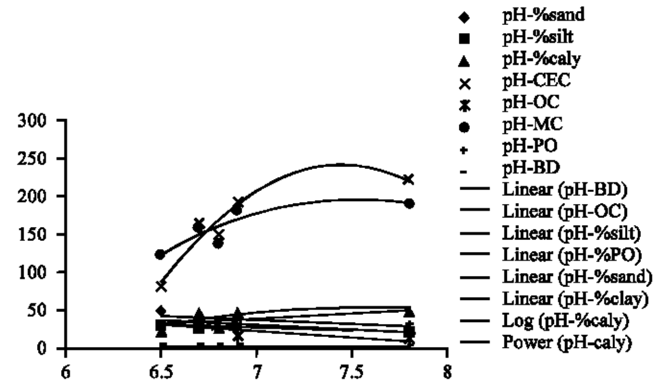

Fig. 1: Regression curves of pH with selected soil physiochemical proerties in pedon A

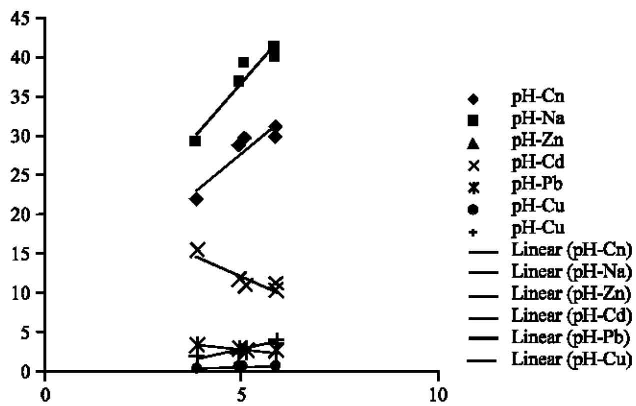

Fig. 2: Regression curves of pH in relation to the heavy metals in pedon B

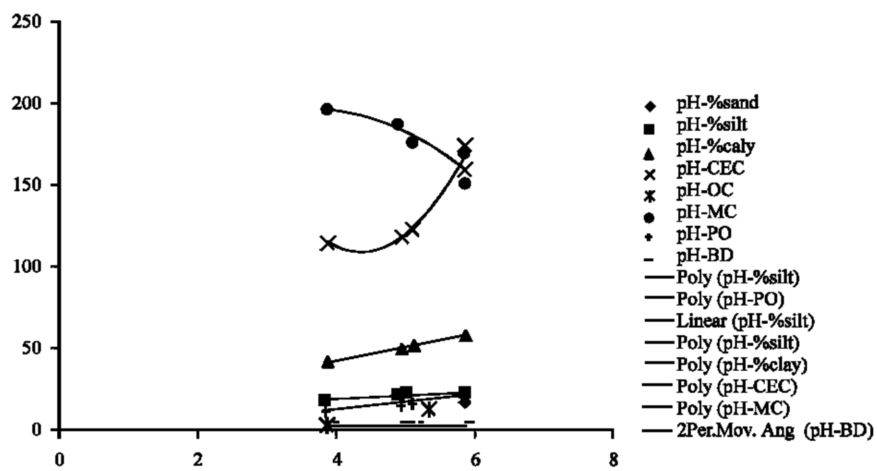

Fig. 3: The Regression curves of pH the sele physiochemical properties in pedon B

quadratic relationship with high levels of relationship of between 0.73-0.97. There was what seemed to be a reverse trend in pedon C where the impacts of the CME were received in reduced

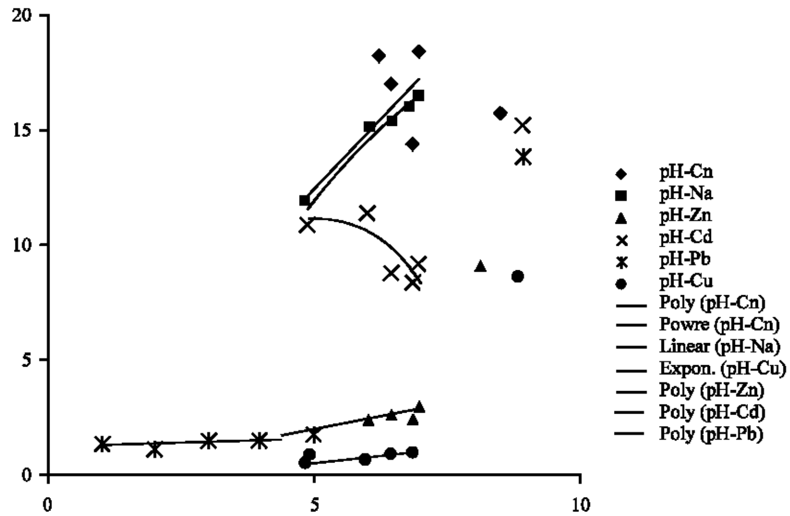

Fig. 4: The Regression curves of pH with the heavy metals in pedon C

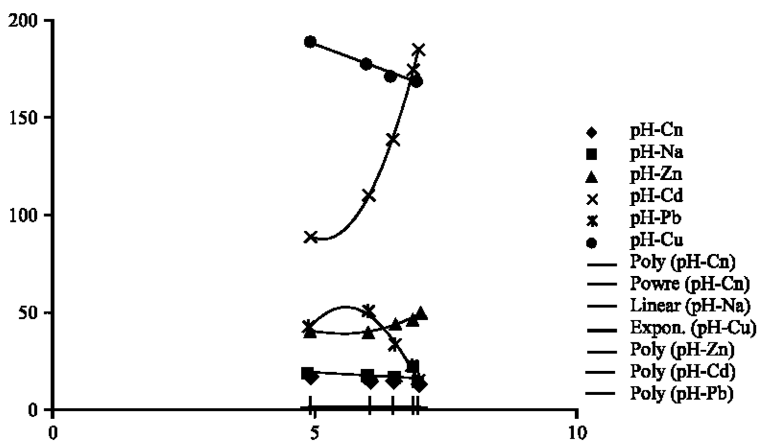

Fig. 5: The Regression curves of pH with the soil chemical properties at pedon C

concentrations. In this pedon, almost all the heavy metals except Cu and Na obeyed the quadratic regression model. Their strong quadratic relationships were evident on the high coefficient values (0.60-0.99). Various regression curves are represented in Fig.1-5.

Linear relationship of pH with heavy metals showed positive coefficient of linearity in pedons A and B, implying more heavy metal abundance as the acidic range of the soil increases. But the reverse is true for Cu and Na where the distribution these metals are more with low acidic medium.

CONCLUSION

Cassava mill effluent has enormous influence on the soil acidity which on the other hand a function of the distribution of many soil properties on the study site. The influence is high on the pedons which have appreciable amount of the effluent. Linear regression models fitted the ph relationships with heavy metals while polynomials also fitted ph with other physiochemical properties especially in background pedon and the pedon which directly received the effluent. All the heavy metals and other physiochemical properties of the soil gave the highest linear and polynomial prediction, respectively of soil ph in cassava-mill-effluent receiving pedon

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