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THE PHYSICO-CHEMISTRY AND HEAVY METALS (MN, CR, CD & PB) ACCUMULATION IN THREE REFUSE DUMP SITES IN RIVERS STATE, NIGERIA

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ABSTRACT: *The accumulation of four heavy metals (Mn, Cr, Cd & Pb) in Carica papaya and physico-chemical parameters of soil from three refuse dump sites in Rivers State, was examined. The study sites were located in three Local Government Areas of Rivers State namely Ikwerre (station1), Oyigbo (station2) and Eleme (station3). The leaf, root, fruit of Carica papaya and soil samples, were collected from the three stations in tandem with standard method. Samples were collected for six months, at intervals of six weeks. Atomic Absorption Spectrophometer (AAS) was used to analyse metals (Mn, Cr, Cd, and Pb) concentration (mg/kg). The soil samples were further analysed to obtain the physico-chemical parameters (pH, Electrical conductivity (µs/cm), NO_4^{-2}(mg/kg), and PO_3(mg/kg). The result showed that the metals concentration was descending as follows Mn>Pb>Cr>Cd in the leaf, root and fruit respectively across the sampled stations. The accumulations of metals in the sampled soils were higher than the temporal control in this study. The metals showed a strong and positive correlation with physico-chemical parameters in the three stations at $p<0.05$. The leaf, root and fruit of Carica papaya in the study sites, showed efficient accumulation of heavy metals and should not be consumed on a long term.*

KEYWORDS: Heavy Metals, Carica Papaya, Physico-Chemical, Accumulation, Dump Site

INTRODUCTION

Dump sites are traditional borrow pits or lands acquired by government for waste disposal. Dump sites are known to welcome all categories of wastes. Dump site is a crude method of waste disposal without sorting and recycling. (Abdus salam 2009).

Dump sites results in the pollution of nearby streams and rivers via runoffs and leachates (Frazer-Williams *et.al.*, 2011), pollution of ground water by leachate (Alloway and Ayres, 1997) and deterioration of surrounding air quality Frazer-Williams (2015). In unpolluted natural environments, heavy metals in the soil occur at low concentrations. However, at high concentrations as in the case of dump sites, they result in public health impacts. Hence, they release undesirable products into the environment. Heavy metals and soil characterization studies therefore provides an insight into speciation and bioavailability of heavy metals which are necessary for environmental studies.

Also, dump site is basically an open land, which is characterized by incineration, uncontrolled and indiscriminately dumping of waste, scavenging by people who seeks to recover reusable materials plastic, bottles and metals scraps. This is the cheapest and simplest form of waste management system of municipal disposing (Barret and Lawlor, 1995).

Frazer-Williams et. al., 2011 reported that at Granville Brook dump site, illegal gardening practices occur at the dump site and early studies have shown higher concentrations of Nickel, Cobalt, Zinc and Lead in both soil samples and vegetables at the sites.

MATERIALS AND METHODS

Study Area

This research was carried out in three refused dump sites in three Local Government Areas of Rivers State, namely; Ikwerre (station1), Oyigbo (sttation2) and Eleme (station3). The choice of these Local Government Areas was based on their proximity to Port Harcourt metropolis and the socio-economic activities going on in the studied area.

The study areas were characterized with metal scrap, plastic, can, domestic waste, electronic waste. Etc.

Sample Collection and Transportation

Soil samples were collected from the three sampling stations at intervals of six weeks for six months. Sample collection was duplicated for each sample collection. The samples were transported to the laboratory in a clean label bag for analysis.

Laboratory Analysis

Metals concentration in soil were analysed using Atomic Absorption Spectrophometer (AAS). The soil samples were further analysed using standard methods to obtain the physico-chemical parameters (pH, Electrical conductivity, Nitrate and Phosphate).

Statistical Analysis

The metals concentrations were statistically analysed using ANOVA. The correlation of metals and physico-chemical parameters was performed using JMP version10.

RESULT

In table 1, station1, Mn had the highest metal concentration with least square mean value of 77.60mg/kg followed by Pb, Cr and Cd.

In station 2, Mn had the highest concentration with least square mean value of 65.92mg/kg followed by Pb, Cr and Cd. In station 3, Mn had the highest concentration, with least square mean value of 75.91mg/kg followed by Pb, Cr and Cd. There was no significant difference in metal concentration across the stations at $p>0.05$.

Table 1: Mean and standard deviation of metals concentration in the sampled stations

PARAMETER	Mn	Cr	Cd	Pb
STATION 1	77.60±27.00	24.07±29.41	0.50±0.37	18.47±8.35
STATION2	65.92±32.16	13.74±12.54	0.38±0.22	21.71±5.91
STATION 3	75.91±51.59	8.19±3.96	5.83±10.93	15.68±8.12

Physico-Chemical Parameters of Soil Samples for the Months of January, March, April and June 2018 across the three Sampled Stations

- In station 1, pH ranges from 6.6 to 7.3, Electrical conductivity ranges from 85 to 254(µs/cm), Nitrate range from 0.5 to 11.7mg/kg, Phosphate ranges from 0.4 to 0.8mg/kg
- In station 2, pH ranges from 6.8 to 7.4, Electrical conductivity ranges from 55-200(µs/cm), Nitrate ranges from 0.4 to 3.0mg/kg, Phosphate ranges from 0.4 to 2.7mg/kg.
- In station 3, pH ranges from 6.3 to 7.3, Electrical conductivity ranges from 95 to 200(µs/cm), Nitrate ranges from 0.5 to 4.2 and Phosphate ranges from 0.4 to 1.9, as shown in table 2.

Table2: Physico-Chemical Parameters of Sampled Stations Soils

PARAMETERS	pH	E'Cond (µs/cm)	NO_4^{-2} (mg/kg)	PO_3^- (mg/kg)
Station 1	6.9±45	167±89	4±40	2±3
Station 2	6.99±0.36	111.25±25	2.08±2.26	1.06±1.09
Station 3	6.84±0.49	160.75±70.38	2.05±1.49	1.02±0.68

Correlation of Heavy Metals with Physico-Chemical Parameters

The correlation coefficient of metals and physic-chemical parameters of sampled soil are shown in the tables 3, 4 and 5 below. Figure 1, 2 and 3 also showed the correlation matrix of the metals with physico-chemical parameters.

Table 3: Correlation Coefficient for Station 1

Variable	by Variable	Correlation	Count	SignifPrb
pH	Mn	0.8502	32	<.0001*
pH	Cr	0.5703	32	0.0007*
pH	Cad	0.3302	32	0.0649
pH	Pb	0.8120	32	<.0001*
		.		.
Con	Mn	0.5638	32	0.0008*
Con	Cr	0.7203	32	<.0001*
Con	Cad	0.3888	32	0.0279*
Con	Pb	0.7287	32	<.0001*
		.		.
Con	pH	0.8871	32	<.0001*
Nitrate	Mn	0.2921	32	0.1047
Nitrate	Cr	0.4887	32	0.0045*
Nitrate	Cad	0.2685	32	0.1374
Nitrate	Pb	0.5803	32	0.0005*
		.		.
Nitrate	pH	0.6219	32	0.0001*
Nitrate	Con	0.8404	32	<.0001*
P	Mn	0.2806	32	0.1197
P	Cr	0.4388	32	0.0120*
P	Cad	0.2552	32	0.1587
P	Pb	0.6161	32	0.0002*
		.		.
P	pH	0.5654	32	0.0007*
P	Con	0.7434	32	<.0001*
P	Nitrate	0.9687	32	<.0001*

Table 4: Correlation Coefficient for Station 2

Variable	by Variable	Correlation	Count	SignifProb
pH	Mn	0.8033	32	<.0001*
pH	Cr	0.5663	32	0.0007*
pH	Cad	0.2975	32	0.0983
pH	Pb	0.9011	32	<.0001*
		.		.
Con	Mn	0.7069	32	<.0001*
Con	Cr	0.7536	32	<.0001*
Con	Cad	0.4715	32	0.0064*
Con	Pb	0.8281	32	<.0001*
		.		.
Con	pH	0.8290	32	<.0001*
Nitrate	Mn	0.6258	32	0.0001*
Nitrate	Cr	0.4205	32	0.0166*
Nitrate	Cad	0.4133	32	0.0187*
Nitrate	Pb	0.6735	32	<.0001*
		.		.
Nitrate	pH	0.7553	32	<.0001*
Nitrate	Con	0.7043	32	<.0001*
P	Mn	0.5050	32	0.0032*
P	Cr	0.4349	32	0.0129*
P	Cad	0.4384	32	0.0121*
P	Pb	0.5952	32	0.0003*
		.		.
P	pH	0.6948	32	<.0001*
P	Con	0.7370	32	<.0001*
P	Nitrate	0.9706	32	<.0001*

Table 5: Correlation Coefficient for Station 3

Variable	by Variable	Correlation	Count	SignifProb
pH	Mn	0.7730	32	<.0001*
pH	Cr	0.6081	32	0.0002*
pH	Cad	0.4315	32	0.0137*
pH	Pb	0.7624	32	<.0001*
		.		.
Con	Mn	0.8152	32	<.0001*
Con	Cr	0.5350	32	0.0016*
Con	Cad	0.4182	32	0.0172*
Con	Pb	0.7559	32	<.0001*
		.		.
Con	pH	0.9250	32	<.0001*
Nitrate	Mn	0.4971	32	0.0038*
Nitrate	Cr	0.2913	32	0.1057
Nitrate	Cad	0.2013	32	0.2693
Nitrate	Pb	0.4377	32	0.0122*
		.		.
Nitrate	pH	0.7650	32	<.0001*
Nitrate	Con	0.6208	32	0.0002*
P	Mn	0.5229	32	0.0021*
P	Cr	0.3534	32	0.0472*
P	Cad	0.3431	32	0.0545
P	Pb	0.5422	32	0.0013*
		.		.
P	pH	0.7976	32	<.0001*
P	Con	0.6756	32	<.0001*
P	Nitrate	0.9627	32	<.0001*

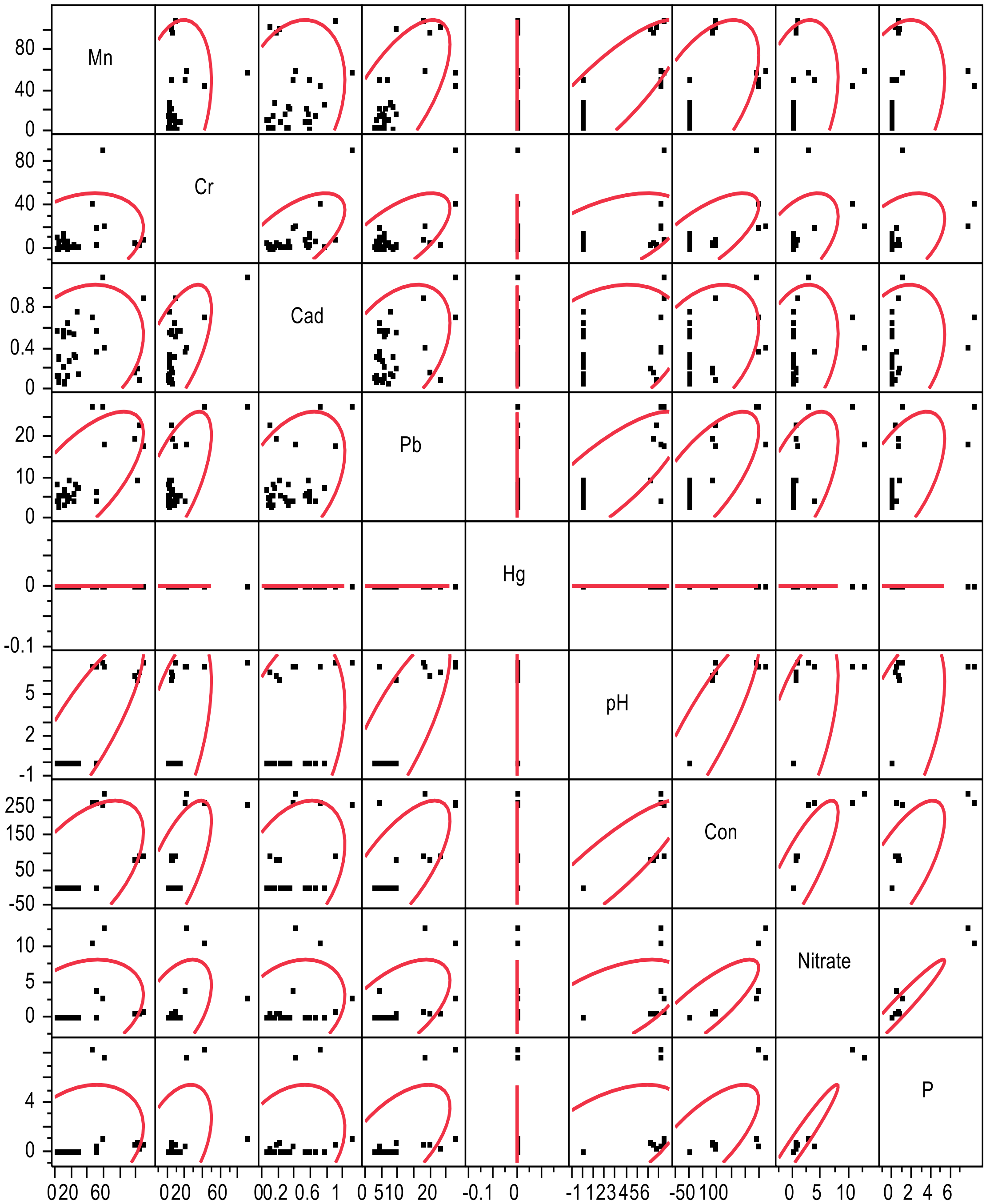

Fig.1: The Correlation Matrix of Physic-Chemical Parameters and Metals in Station 1

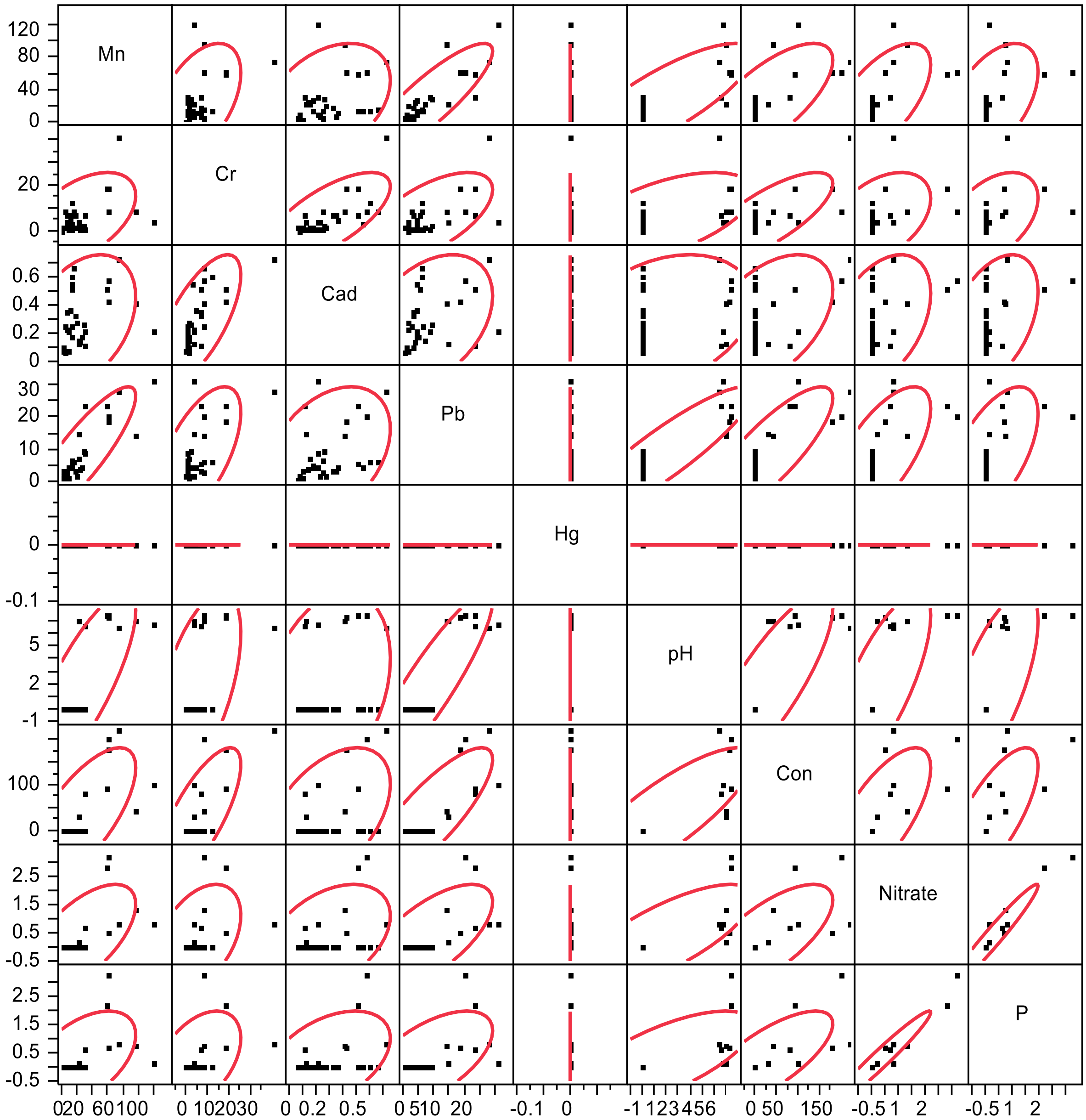

Fig. 2: The Correlation Matrix of Physic-Chemical Parameters and Metals for Station 2

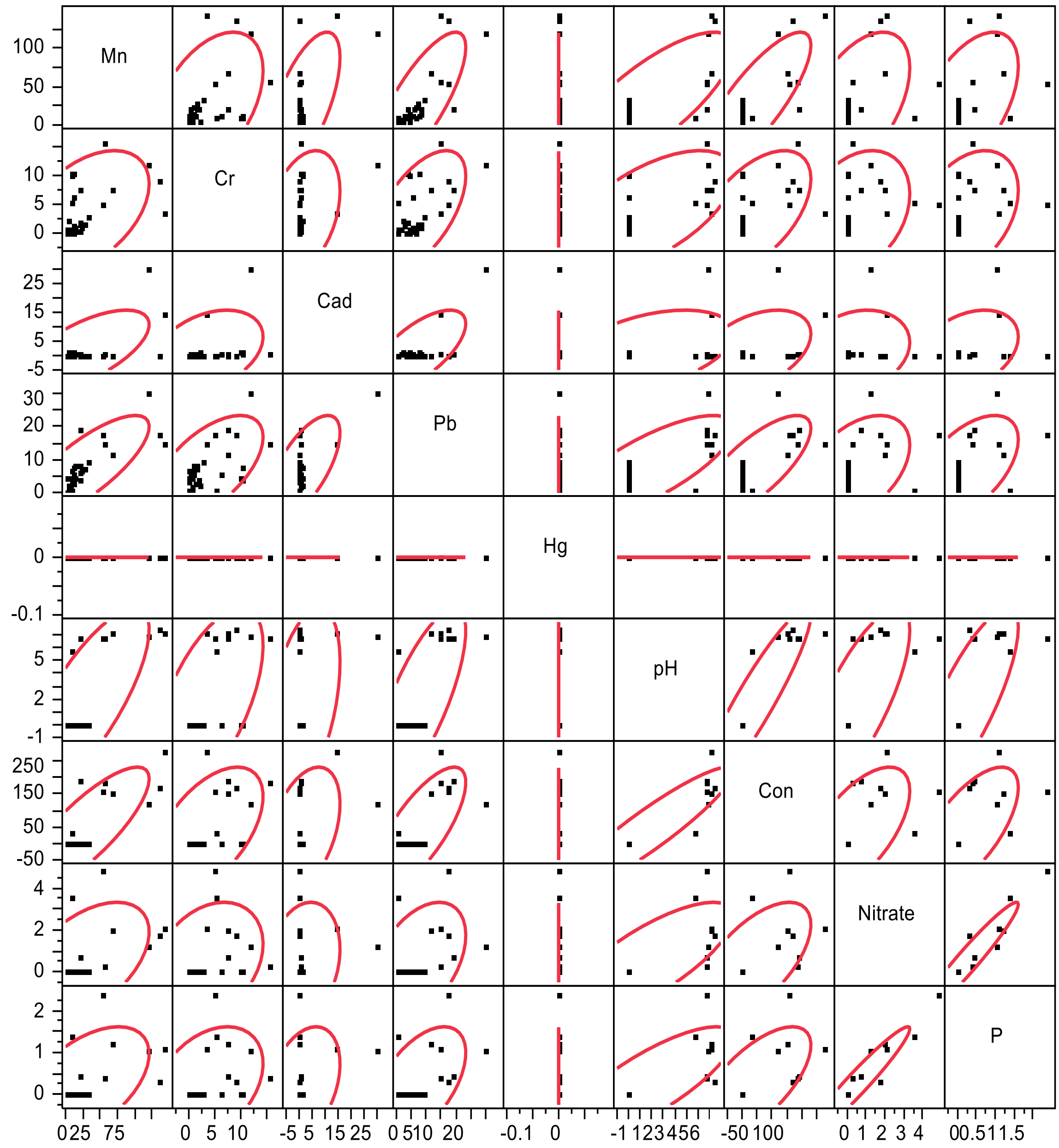

Fig. 3: The Correlation Matrix of Physic-Chemical Parameters and Metals for Station 3

DISCUSSION

The high amount of metals may be traced to the constituents of the sampled stations which include plastic can, tins, rubbers, metal scraps, electronic wastes, domestic waste and flash flood run-off deposited or concentrated in these dump sites. The accumulations of metals were higher in the soil of the three sampled stations than in the temporal control by (Obasi *et. al.*, 2012). Also, similar result of metals concentration ranging from 65-77mg/kg for Mn, 8-24mg/kg for Cr, 0.38-5.8mg/kg for Cd, 15.68-21.71mg/kg for Pb found in this study have been reported by (Karikpo *et. al.*, 2019).

The mean levels of Cr, in the sampled stations were lower than the permissible limit 750mg/kg by Visser (1993) and CCME(1994) for residential, domestic garden and agricultural activities. Metal-organic complex decrease metal mobility in soil and at low pH, thus the relative low mobility is as a result of low pH as reported by (Obasi *et al.*, 2012).

The mean concentrations of Cd, for the three sampled stations were below the permissible concentration of 3.0mg/kg for soil agricultural practice (USEPA 1986, MAFF. 1992). But Cd was more bio-available for plants absorption. This result was reported by Uba *et al*., (2008), Kuo *et al*., (1993), Gupta and Sinha (2006). The mean result was not affected by the variation in seasonal change.

Physico-Chemical Parameters of Soil

There was a variation in mean pH, across the sampled months. The dry season January and March had a slightly acidic pH and the rainy season April and June had alkaline pH. Similar alkaline results have been reported by (Gupta and Sinha 2006; Elaigwu *et al*., 2007; Sani *et. al*., 2012; Uba *et. al*., 2008). The soil pH, Conductivity, NO_4^{-2} and PO_3^- levels showed that the sampled stations are fertile and could support diverse plants growth. pH, affects the soil microbial activities, therefore, the pH may have effect on soil metal availability, uptake of metals by plants and microbial reactions.

The Electrical conductivity value showed that the soil is slightly clay and good for agricultural practice. This high value may be attributed to the metal scraps, which is one of the refuse dump site constituents. This also indicated that there were more soluble salts in the soil as reported by other researchers Karaca 2004; and Arias *et al.,* 2005). The value of NO_4^{-2} and PO_3^- in the soils of the sampled stations is an indication that the sampled stations will enhance growth of diverse plants, (Okalebo *et al*., 1993, Obute *et al*., 2010).

Correlation of Metals and Physico-Chemical Parameters.

Metals showed a positive correlation with physico-chemical parameters in the three sampled stations. pH and Conductivity were determinants in the metal availability in the soil of three sampled stations. The variation in the correlation coefficient is due to localize activities that influence metal deposit and distributions in the sampled stations. This study showed that Metals increases with pH and Conductivity. NO_4^{-2} and PO_3^- are not determinants on metal availability.

Cu and Pb concentration have been reported by Rusu *et. al*., (2000), to be a function of soil pH. Angelvicova and Fazekasova(2014) reported positive correlation between Cu, Pb and Zn in soil from mining sites in Slovakia. The positive and strong correlation of metals with pH and conductivity in this study could indicate the source of metals in the sampled stations and the affinity with the physico-chemistry of the soil.

CONCLUSION

The metals concentrations in the soil were below the USPEA permissible limit. It is important to examine soil activities in dump sites, to understand the dynamic of the soil. The pH and conductivity were directly proportional to heavy metals concentrations. Through metals accumulations in soil, humans are at risk of environmental contaminants which may be either through ingestion of edible plants or biomagnifications across the food chain. Therefore, soil assessment is important in order to monitor and control environmental pollutions.

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