Behavior of Metal Fractions with Depth in Soils of Children's Play Grounds within Owerri Metropolis, Imo State, Nigeria

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Abstract: *A total of 36 soil samples from 9 playgrounds were collected in dry and rainy seasons at 0-5 cm, 5-12 cm and 12-24 cm depths and then subjected to a six step sequential extraction procedure. Metal species of each in digests were analyzed by Perkin Elmer AAS, model A Analyst 400 and concentrations expressed in percent. Results showed metal fraction decreased with depth but most metals had fractions increasing after 12 cm. There were higher mean values of metal concentrations in the dry season compared to the rainy season. Values for residual fractions were highest for all metals in dry season while cobalt concentrations were lower in rainy season. Therefore there is slow leaching of metals which mineralize at increasing depth due to changing condition with depth.*

Keywords: *Fractionation, metal exposure, Spatial, vertical, Species.*

1. INTRODUCTION

Children of primary and nursing age bracket often engage in activities that make then ingest playground soil through their mouth [1, 2]. These pica activities have health implications due to presence of contaminants in the soil. Therefore, if polluted with toxic heavy metals, surface soil could become a major concern of health risks to the public[3, 5]. Researchers have linked child health to both type and cover of playgrounds and interesting literature exist on studies of children playgrounds in developing nations [4, 5]. However such studies are yet to be conducted in Nigeria. Children' s hands after playing contain elevated amount of metals and chromium (Cr) and arsenic (As) were largely adsorbed in children' s hands from playgrounds soils[6]. As a result of their toxicity, persistence and bioaccumulative behavior and above all their mode of action in children, heavy metals constitute a group of serious pollutants in our natural environment[7].

Hence, knowledge of spatial, vertical and seasonal variation in metal concentrations and species in playground soils could assist in controlling metal ingestion and accumulation in children. Here playtime is regulated according to these variations including nature of cover and other issues involved in playground construction.

Soils heavy metals have been known to vary with space, depth and time. Such variation could be useful for characterising pollutants contamination as well as modelling a wide range of environmental issues related to pollutant concentration. Heavy metal contaminations have received little attention and so metal variability with depth at playgrounds is almost non-existent.

Children are continuously being exposed to heavy metals by contact with surface soils of playgrounds and so variation of metal content at various depths could furnish useful information. This has been overlooked as most researches in the past on the heavy metals pollution in Nigeria have been concerned with the total heavy metal determinations [8, 9], while chemical fractionation of these soil metals have been rarely studied [10]. There has been no report on the depth variation of metals fractions in soils of children playgrounds.

The behavior of elements in the soil is a direct function of their chemical properties and this is currently being exploited to understand other metallic behaviors such as transport, reactivity in soil. In general biogeological behavior in different environmental matrix is better studied by speciation[11].

Surface soils may act as carriers and possible sources of metal pollution, since the mobility of these metals is such that they tend to stay in the upper layers except when leached without regard to type of soil. Moreover, these metals can be released by changes in climate or physicochemical properties of soils as well as rainfall. It is well known that natural soils contain significant concentration of iron [12, 13], at varying depths and space. Vertical and spatial variability of metals in most natural profiles gradually change from one horizon to the next. Urban soil profiles exhibit abrupt changes from one layer to another depending upon the constructional history of the soil. During construction topsoil may be scraped away and later filled thereby giving rise to distinct layers. This becomes even pronounced when the topsoil is from elsewhere. It has been observed that this lithologic change layer range from 6 to 35 cm in street side soil [14].

This research presents results on a study carried out to determine Mn, Co, Ni, Zn and Cu fractions of metals in soil through sequential extraction techniques with the aim of finding out the existence and trends of such special and vertical variation. This information could increase knowledge of present understanding of metals variation with depth and its contribution to ecotoxicology of these metals to in children's playgrounds

2. MATERIALS AND METHODS

2.1. Sample Location

Table1. *Coordinates of sampling location*

	Code	Name of school	DD	MM	SS	DD	MM	SS	ELEV
CSO		Central school I	05	29	00.4	007	01	48.8	73
HEO		Housing Estate Aladimma	05	29	50.7	007	02	44.6	70
IKS		Ikenegbu PS	05	29	27.0	007	02	23.2	74
MNO		Model P/S	05	28	56.4	006	59	59.4	77
TSO		Township P/S I	05	29	05.3	007	02	23.2	73
UPS		Urban P/S I	05	28	59.8	007	02	01.5	73
WSP		Waterside P/S	05	28	52.8	007	01	44.9	70
WBP		World Bank P/S	05	29	09.3	007	00	19.9	82
SCP		Shell Camp P/S	05	29	58.0	007	01	37.0	73

2.1.1. Sample Collection and Sample Pretreatment

Soil samples were collected from pre-designated five points along a " W" shape 2 x 2 meters drawn on with particular reference to potential sources of metals within each playground. The soil samples were obtained with a hand auger from topsoil only (to a maximum depth of 25cm), that is the *A*-horizon, also avoiding the surface contaminants. The control (background) samples are topsoil obtained form a location remote from the metropolis at the outskirts of Owerri and far removed from the influence of industrial activities, transportation and heavy construction[15].

2.2. Chemicals and Reagents

In the preparation of reagents, chemicals of high grade purity and distilled water were used. All glass wares were thoroughly washed with detergent solution followed by tap water and then distilled water was used for the rinsing. Throughout the course of this work, distilled water was used. Nitric acid (HNO_3) (suprapur), HCl (suprapur), sodium sulphate and potassium hydrogen carbonate were purchased from Merck (Fin lab. Owerri), while distilled water was used for heavy metals analyses; standard metal solutions for atomic absorption spectrophotometer were purchased from Fluka (Buchs, Switzerland). Appropriate calibration curves prepared in the same acid matrix with standard metal solutions for atomic absorption spectrophotometry were used for quantification.

2.3. Speciation Procedure

Nine playgrounds soils samples were subjected to a six step sequential extraction modified from Horsfall and Spiff,[17] to carry out speciation of metals in the soil as follows. Water Soluble Fractions (F1): 1g of the air dried soil sample (2mm sieve) were mixed with 10ml of de-ionized water with continuous agitation for 1 hour.

Exchangeable Phase (F2): The residue in (i) above is shaken at room temperature with 16ml of 1M $Mg(NO_3)_2$ at pH 7.0 for 1 hour. Oxidized Phase (bound to organic matter) (F3): Residue form (ii)

above +10 ml of 8.8 M H_2O_2 + 6 ml of 0.02 M HNO_3 was shaken for 5 + 1 hrs at 98°C. 10 ml of 3.5M CH_3COONH_4 was added as an extracting agent, the resulting mixture was then centrifuged. Acid Soluble Base (bound to carbonates) (F4): 25 ml of 0.05 M Na_2EDTA was added to the residue in (iii) above ad shaken for 6 hrs and centrifuged. Reducible Phase (bound to Fe– Mn oxides) (F5): Residue from (iv) above + 17.5 ml N H_2O + N HCl 0.1M + 17.5 ml CH_3COONH_4 3.5 M, shaken for 1 hr, centrifuged. Residential Phase (bound to silicates and deferential materials) (F6): Residue from (v) above was digested by using HCl – HNO_3/HF (0.35:12 w/v solid solutions) in acid digestion, Teflon cup. It was then dry ashed for 2 hrs and evaporated, filtered and diluted to 50 ml with double-distilled de-ionized water. After each successive extraction, the sample was centrifuged at 3000 rpm for 15 minutes. The supernatants was then removed with pipette and filtered with Whatman No. 42 filter paper. The residue in each case was washed with de-ionize water, and made up to 50ml mark. The extracts were subjected to A Analyst 400 Perkin Elmer Absorption spectrophotometer.

3. RESULTS AND DISCUSSION

Table1. *Some descriptive statistics of metal fractions, F (%) with depth (cm) in the dry and rainy season*

		Dry season														
	Metals	Mn			Co			Ni			Cu			Zn		
Fraction	Depth	0-5	5-12	12-24	0-5	5-12	12-24	0-5	5-12	12-24	0-5	5-12	12-24	0-5	5-12	12-24
FI	Mean	4.22	5.33	4	7.44	3.89	8.11	12.22	9.67	11.44	11.13	11.56	11.22	8.11	10.78	9
	Max.	13	11	11	35	18	40	39	26	46	29	43	28	25	27	27
	Min.	0	1	0	7	1	0	2	0	0	3	0	3	1	0	1
F2	Mean	12.89	8.56	8.44	8.78	6	3.11	9.67	12.22	8.44	17.11	12.78	18.33	23.44	18	22.78
	Max.	28	28	23	31	17	19	26	34	20	34	24	37	42	33	44
	Min.	1	0	0	2	0	0	0	1	0	5	4	6	9	1	7
F3	Mean	12.11	12.11	15.33	12.11	8.78	12	11.33	16.33	12.89	9.22	13.44	8.78	11.56	11.11	12.44
	Max.	31	28	37	44	36	49	32	32	34	19	25	19	24	16	26
	Min.	1	1	0	1	0	0	3	4	0	3	6	0	4	5	3
F4	Mean	13	13.11	14.56	19.78	13.56	12.67	10.33	10.89	8.22	10.67	10.89	12.22	14	16.33	13.33
	Max.	30	28	25	56	42	45	19	17	20	23	17	25	31	36	27
	Min.	2	3	0	0	0	0	2	4	0	4	4	4	3	4	3
F5	Mean	18.44	11.11	18.56	16.67	23.33	14.44	9.67	14.67	12.67	12.22	15.11	12.33	13	17.44	12.56
	Max.	35	26	32	30	3	28	28	45	37	21	31	26	32	40	37
	Min.	1	0	0	38.56	2	0	2	0	0	3	3	0	3	3	4
F6	Mean	39.33	49.78	39.44	68	44.44	49.67	46.67	36.89	46.33	40.11	36.56	37.11	31.33	26.33	29.89
	Max.	70	76	98	12	79	88	62	16	87	52	64	48	44	38	43
	Min.	20	19	13		9	10	29	12	16	25	20	22	11	14	11
		Rainy season														
		Mn			Co			Ni			Co			Zn		
	Depth	0-5	5-12	12-24	0-5	5-12	12-24	0-5	5-12	12-24	0-5	5-12	12-24	0-5	5-12	12-24
FI	Mean	8.89	9.78	9.11	11.3	15.33	10.44	13.89	13.44	14.33	10	9.78	11.22	13.33	13.22	13.33
	Max.	12	15	14	14	32	21	29	52	50	18	20	22	24	27	27
	Min.	4	2	5	8	7	1	3	0	2	7	5	5	4	4	4
F2	Mean	10.78	10.89	9.56	15.89	15.33	8.11	12.78	15.1	12.11	13.67	19.78	15.56	8.78	9.67	11.11
	Max.	19	21	20	26	32	17	33	52	31	43	51	40	12	13	24
	Min.	6	2	0	6	7	0	1	0	3	0	0	4	3	4	5
F3	Mean	10.89	10.67	15.33	15.33	15.78	13	8.78	8.11	10.33	11.67	8.11	10.78	18.44	17.56	17.56
	Max.	18	25	46	42	30	19	28	23	30	23	23	18	36	38	39
	Min.	3	3	5	8	7	2	3	0	3	4	0	5	5	3	6
F4	Mean	17.33	17	16.33	14	7	17.22	11.78	11.67	11.89	14.22	14.7	13.67	9.22	12.11	13
	Max.	31	36	29	26	31	26	36	44	32	24	24	26	18	25	27
	Min.	5	4	7	5	0	9	2	0	3	7	5	6	2	4	4
F5	Mean	25.56	24.89	23.67	24	23.33	21.89	19.89	19.44	26.67	19.11	21.22	20.44	21.11	18.60	19.33
	Max.	40	42	36	38	40	43	28	37	65	34	33	33	34	32	34
	Min.	14	0	8	7	11	10	6	6	8	13	13	14	10	8	10
F6	Mean	25.33	26.78	25.78	19.44	20.22	20.56	32.78	33.33	24.67	31.33	26.33	24.67	29.11	28.78	25.67
	Max.	58	63	49	35	47	30	68	67	42	49	51	42	58	69	47
	Min.	12	16	13	12	0	14	10	10	11	8	5	11	8	9	10

Mean of triplicate determinations, Max: Maximum, Min: Minimum

Table 1 shows the mean, maximum and minimum concentrations of metals fractions at various depths for all five metals studied. Fractions of Mn at 5cm were higher than for dry season. This could be due to increased solubility in soil moisture during the rainy season. This trend was exhibited by all metals. Minimum values of metals F1 fractions were observed at 5cm were as F6 fractions had highest values in the dry season.
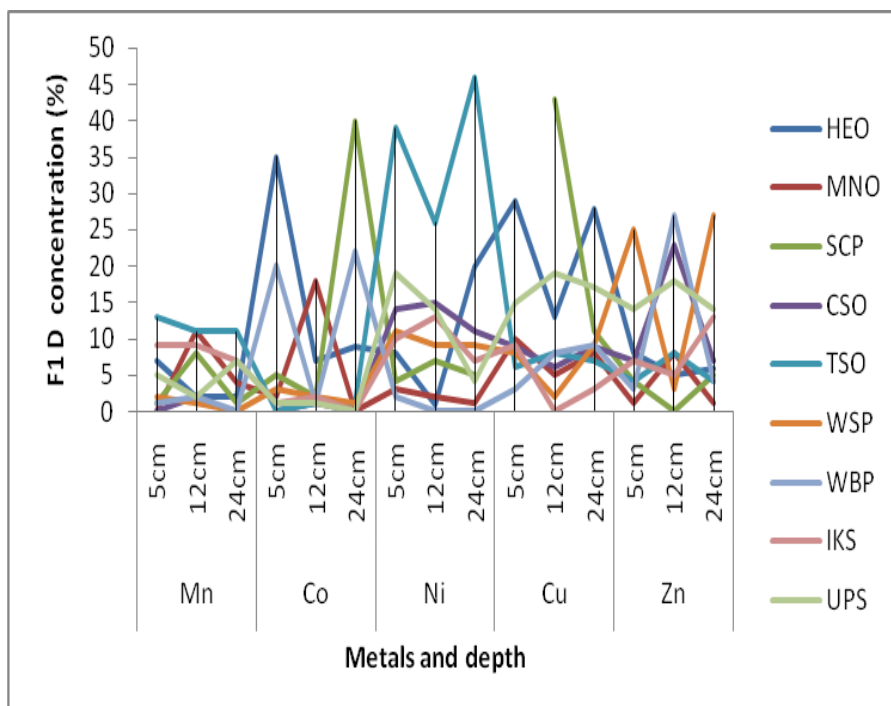
3.1. Water Soluble Fraction

The water soluble metal fractions were lowest for most playgrounds in dry season and in some cases not detectable (MNO and CSO) at 5cm in 2014. Also CSO, TSO for Co were undetectable. Cobalt had highest F1 fraction (35 % at HEO) at 5 cm. The mean percent F1 fraction for all metals range from 4.22 to 11.56% at 5 cm. It was observed that all five metals had F1 fractions that increase with depth.

Mn showed the generally low F1 fractions as can be seen on fig.1 where as Ni (46%) has the highest F_1 which occurred at 24cm. The F1 fractions for all playgrounds with depth showed the following order of increasing values Ni>Cu>Co>Zn>Nn. Metals exhibited highest values at 24 cm in the case of Co, Ni and Zn while Cu and Mn showed highest water soluble fractions at 12 cm and 5cm respectively. The water soluble fractions are perhaps most important in toxicity studies as they are readily absorbed and absorbed into children. It is therefore advantages that water soluble fractions were lowest for most 5 cm.

Due to possible leaching the soluble fraction for Co, Ni and Zn were low, while Cu and Mn showed highest water soluble fractions at 12 cm and 5 cm respectively. The water soluble fractions are perhaps most important in toxicity studies as they are readily absorbed into children' s body through the skin. Therefore it is advantageous that water soluble fractions were lowest at most of 5 cm samples. Due to possible leaching the soluble fractions for Co, Ni and Zn appeared highest at 24 cm. High values of soluble metal fractions for Cu, and Zn at surface soils have been reported[16]. Results obtained here are not significantly different from those reported in which Cu and Zn where higher in the residual fraction[17].

The trend of decreasing water soluble metal fraction in the rainy season was Ni > Co > Zn > Cu > Mn. Highest water soluble fraction in the rainy season was observed at 12 cm for Mn, Co, and Ni while Cu and Zn had highest values at 24 cm. For most water soluble fractions the change from increasing trend occur just above 12 cm. Ni was however the only metal detected at 12 cm. The average F1 fractions were lower in the dry season than in the rainy season.

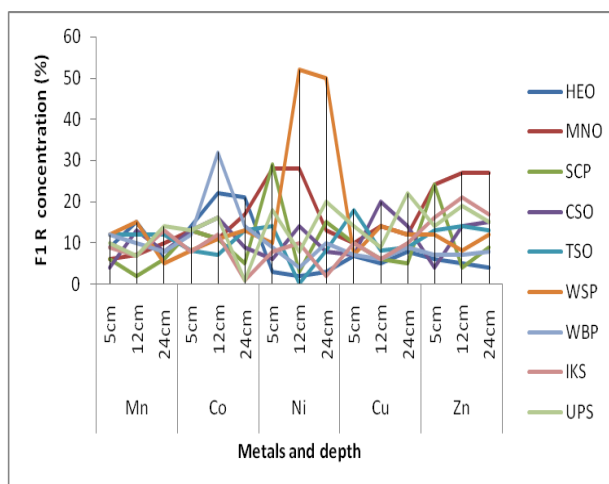**Figure1.** *Trends of water soluble metal fractions (F₁) and depth in the dry season*

Figure2. *Trends of water soluble metal fractions and depth in the rainy season*

3.2. Exchangeable Fraction

However the exchangeable fractions were highest for Zn and Cu at 24 cm, for Mn and Co at 5 cm while Ni exchangeable fraction was highest at 12cm. The mean values for F2 fractions show a range of 8.11 to 15.89%. Cobalt recorded more undetectable F2 fractions at 24 cm while Ni and Mn were equally undetected in F2 at 24cm. As expected the exchangeable fractions for most metals were generally low irrespectively of the depth. However there was a general decrease with depth with a greater portion occurring between 5 cm to 12 cm. Osakwe[19] reported generally low exchangeable metal fractions between 0-15 cm. Therefore this study is in agreement with works elsewhere.
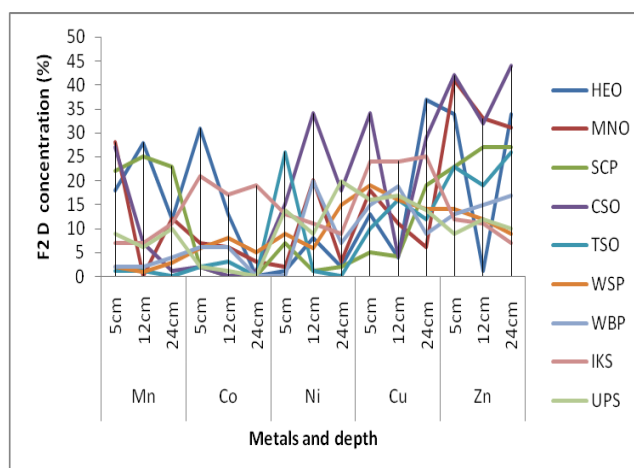
Figure3. *Trends of exchangeable fractions (F_2) and depth in the dry season*
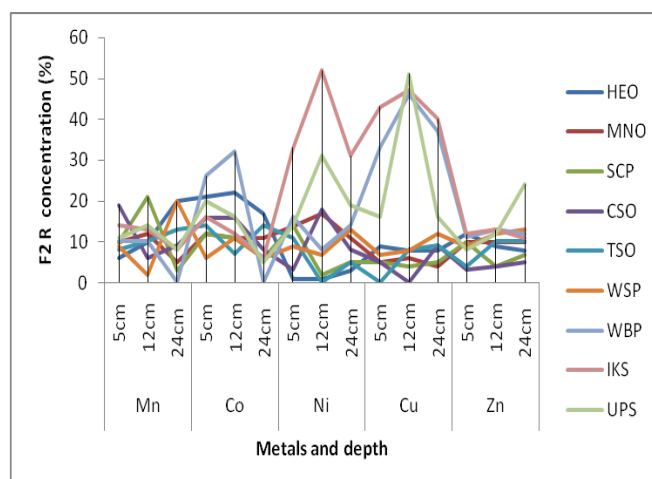
Figure4. *Trends of exchangeable fractions (F_2) and depth in the rainy season*

Values of exchangeable fractions recorded in rainy season (Table 2). This study shows a range of 01 to 52% except for Mn, Co, Ni and Cu that showed undetectable exchangeable fractions at varying depth. This range is similar to that reported by Iwegbue[20]. The order of decreasing values was Ni>Cu>Co>Zn>Mn. It was observed that Mn, Co, Ni and Cu showed highest values at 12cm in the rainy season (fig 4). Highest metal fraction F2 followed the trend of decreasing order Zn > Cu > Ni > Co > Mn.

3.3. Organic Bound Fraction
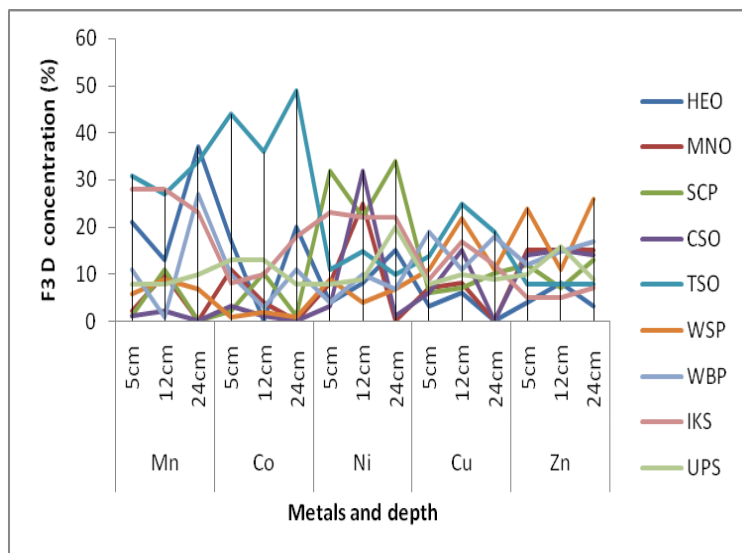
Figure5. *Trends of organic bound fractions and depth in the dry season*
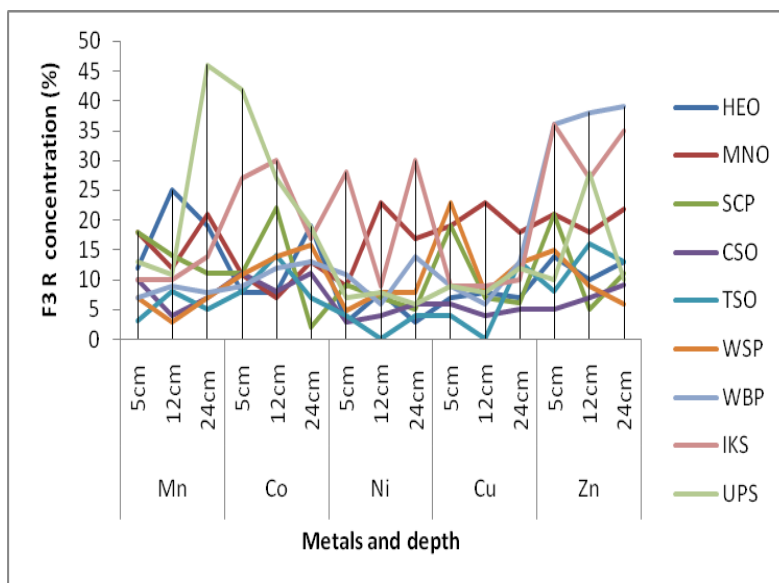
Figure6. *Trends of organic bound metal fractions and depth in the rainy season*

The mean concentrations were observed to range from 8.87 to 16.33%. The highest metal fraction occurred at TSO (49%). In the raining season the mean organically bound metal fractions ranged from 8.1 to 18.44%. The order of decreasing fraction was Co > Mn > Ni > Zn > Cu. The highest organically bound metal fraction was observed at 24 cm for Mn, Co, Ni and Zn while Cu exhibited highest F3 fraction at 12cm. Only playground TSO recorded undetected F3 fractions for Ni and Cu both at 12 cm.

### 3.4. Carbonate Bound Fraction

In the dry season Mn in the carbonate bound fractions were within the range 1 to 39% with the highest found at playground TSO. The acid bound fractions as this F4 is sometimes called would

imply that the metal fractions become soluble since the soil pH is likely acidic as depth increases. Therefore most playgrounds soil samples at 5 cm had detectable carbonate bound fractions. The order of decreasing F4 fraction was generally Co > Zn > Mn > Cu > Ni with their highest concentrations found at varying depths with Co and Ni at 5 cm, Cu and Ni at 24 cm and Zn at 12 cm. The mean values of F4fractions for dry season ranged from 8.22 to 19.78%.

In the rainy season the range of carbonate bound fraction was 1 to 36% with highest at WBP for Mn whereas the mean values were from 7 to 17.33%. But the order of decreasing carbonate bound fraction for various metals was Ni > Mn > Cu > Zn > Co. All metals showed highest values of carbonate bound fractions at 12cm except Zn at 24cm. Playground TSO had Co and Ni carbonate bound fractions that were not detected.

3.5. Fe- Mn Bound Fraction

They were many undetected values of Fe-Mn bound fractions spread across HEO, MNO, SCP CSO TSO and WSP. However, the range was low compared to other operationally defined fractions.
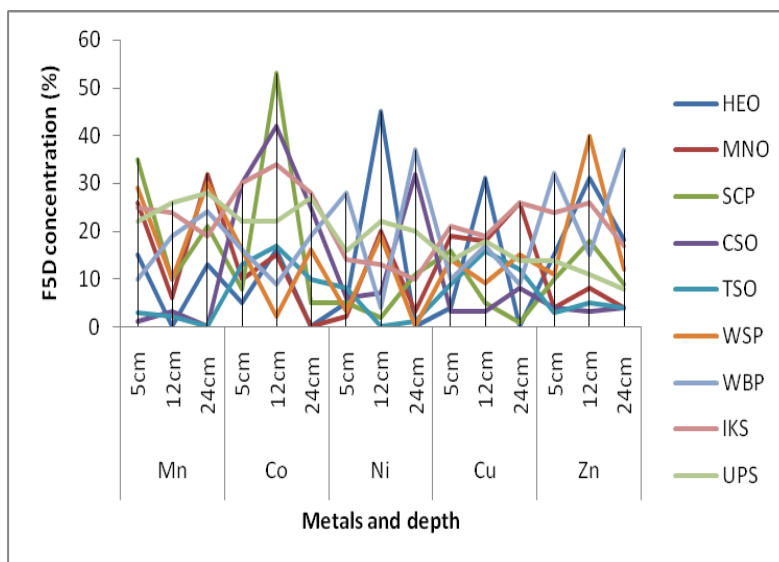
**Figure7.** *Trends of Fe-Mn bound fractions and depth in the dry season*
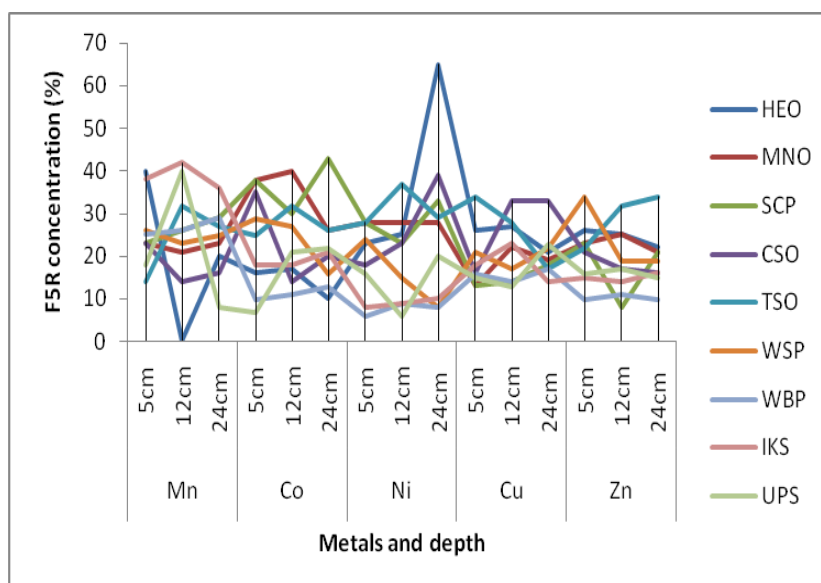
**Figure8.** *Trends of Fe-Mn bound metal fractions and depth in the rainy season*

The highest Fe-Mn bound fraction was recorded for HEO (45%) for the metal Ni. This is not strange as Ni has been reported to be associated with Fe-Mn oxides. The order of decreasing Fe-Mn bound metal fractions was Co > Ni > Zn > Mn > Cu. The mean Fe-Mn bound metal fractions for dry season ranged from 9.67 to 23.33%. The Fe-Mn bound metal fraction showed a higher range in the rainy

season (1 to 65%) than dry season. This differs from expected results however it is the total metal content that is expected to be higher in the dry season. The order of decreasing metal fraction was Ni > Co > Mn > Zn > Cu with all highest values recorded at 12cm except for Zn at 24 cm. The mean values ranged from 18.67 to 26.67%. However at 12 cm Mn and Co were undetected at HEO and MNO respectively.

3.6. Residual Fraction
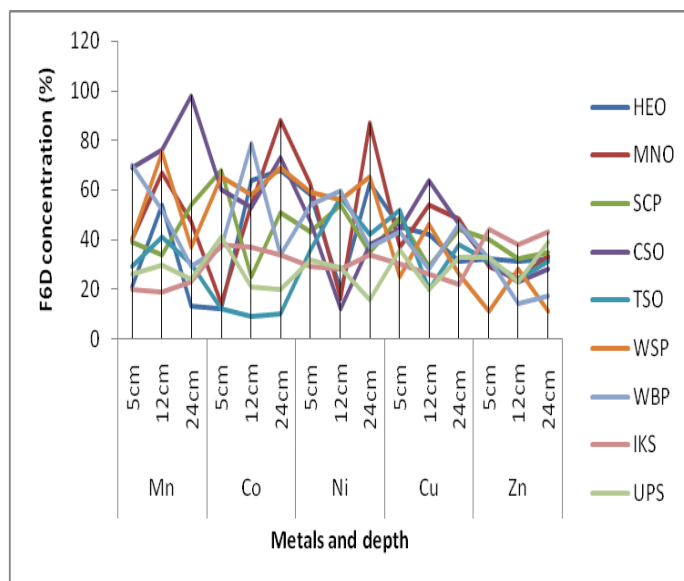
Figure9. *Trends of Residual metal fractions and depth in the dry season*
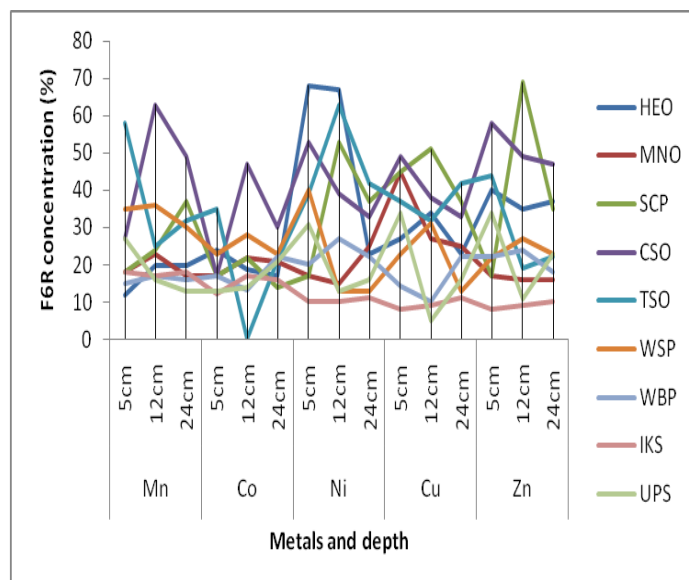
Figure10. *Trends of Residual metal fractions and depth in the rainy season*

The mean values were ranging from 26.33 to 49.78 and 20.22 to 33.33%. The residual fractions were most prominent for all metals and for all seasons. However, the dry season residual fractions were usually higher than those in the raining season. This may not pose any health risk because the residual fraction is usually much less available.

The residual fraction has been reported widely as the most abundant fraction [21, 22]. This fraction range was from 9 to 98%. Despite the wide range most fractions were above 20%, hence the importance of the residual fractions. The highest concentrations of these fractions were found at 12cm except for Zn at 5cm and so the order of decreasing fractional concentration was Mn > Co > Ni > Cu > Zn. The range of residual metal fraction (Table 2) in the rainy season was lower ranging from 05 to 67%. The order of decreasing residual metal fraction is Zn > Ni > Mn > Cu > Co. The highest values of these fractions were found in 12 cm except Ni that had both high values at 5 and 12cm.

4. CONCLUSION

Metal fractions varied widely with depth often showing significant difference at 12 cm. The results of vertical distribution showed that the heavy metal concentrations were generally higher at the top soil than the sub and bottom soils. This is expected since the top soil is the point of contact from anthropogenic activities. The residual fractions were dominant for most metals though metal fractions showed varying trends at various playgrounds. Dry season fractions were usually higher than same metal fraction in the rainy season.

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