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Assessing Trends in Speciation of First-Row Transition Metals in Children's Playgrounds in Owerri, Nigeria

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Abstract

Chemical species of metals significantly affect their toxicity, yet the trends of these metal species in soils remain underexplored. This study investigated the trends and variability of metal species in soils from playgrounds across Owerri, Nigeria. A total of 81 composite soil samples were collected from nine playgrounds during the dry and rainy seasons to capture spatial-seasonal variability. Samples were analyzed using standard methods in triplicates, followed by sequential extraction. Metal concentrations were determined using the A. Analyst 400 Perkin Elmer AAS, and the data was evaluated using chemometric models. Results showed that metal species followed the decreasing order: Residual > water soluble > exchangeable > organic bound > carbonate bound > Fe–Mn oxides bound. Total extractable Zn, Mn, Cu, Ni, and Co concentrations were higher in the dry season but remained below WHO standards. Correlation analysis indicated weakly positive Mn-Ni and Co-Ni associations, while Mn-Cu exhibited a strong negative correlation across all playgrounds. Metal stability decreased in the order: of Ni > Mn > Cu > Co > Zn, suggesting variable mobility and environmental risks. Findings revealed notable seasonal and spatial variability in metal species, with potential implications for children's health due to prolonged exposure in playgrounds. The study underscores the need for regular monitoring and risk assessment of metal species in playground soils to safeguard public health.

Keywords: Contamination, extraction, speciation, spatio-seasonal, soil, toxicity, variability

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INTRODUCTION

According to Ure (1990), the term "speciation" is used for a wide variety of analyses, ranging from the determination of well-defined "species", e.g., oxidation states of elements or organometallic compounds, to forms of elements that are operationally defined about the extraction procedure adopted and which could be quoted as "bioavailable" and "mobile" forms of an element. Heavy metals refer to a hazardous (Adekunle et al., 2003 [1, 2]; Alloway and Ayres, 2000) group of metals and metalloids with a specific gravity that is at least 5 times that of water [3]. They are often toxic even at low concentrations, bioaccumulative, and non-biodegradable [4, 5].

The first International Conference on Trace Element Speciation in Biomedical, Nutritional, and Environmental Sciences [6] described IUPAC's definition as narrow. The conference suggested a more encompassing definition to include solid samples and found merit in the use of functionally and operationally defined species. Therefore, speciation may be defined in two ways:

(1) as the process of identifying and quantifying the different, defined species, forms, or phases present in a sample of material;
(2) as the description of the amounts and kinds of species, forms or phases present in the sample material.

In both definitions, the species, forms, or phases are defined (a) functionally, (b) operationally, or (c) as specific chemical compounds or oxidation states. IUPAC recently proposed a useful clarification and the definition given above is being abandoned in favor of the term speciation analysis while the term speciation is reserved for the concept of description of the distribution of species [7].

Generally, there exist three types of speciation based on functionally defined, operational, or specific chemical characteristics, for instance, oxidation states.

Functionally defined species are exemplified by the plant-available species in which the "function" is plant availability while operationally defined speciation is the physical or chemical fractionation procedure applied to the sample which defines the fraction isolated for measurement. For example, selective sequential extraction procedures are used to isolate metals associated with the "water/acid soluble", "exchangeable", "reducible", "oxidizable", and "residual" fractions in soil. The reducible, oxidizable, and residual fractions, for example, are often equated with the metals associated, bound, or adsorbed in the iron/manganese oxyhydroxide, organic matter/sulfide, and silicate phases, respectively. This is often a convenient concept, but it must be emphasized that these associations are nominal and can be misleading. Therefore, it is prudent to regard the isolated fractions as defined by the operational procedure. Physical procedures, such as the division of a solid sample into particle-size fractions or the isolation of a soil solution by filtration, centrifugation, or dialysis are also examples of operational speciation. Also, the distinction between soluble and insoluble species in aquatic systems can be considered as operational speciation as it is based on an arbitrary definition of "soluble" as the ability to pass a 0.45 μm filter [8].

Speciation in which the precise chemical form of an element is measured is the most difficult to achieve because analytical methodology of great selectivity, and sensitivity is required. Some success has been achieved in this narrowly defined type of speciation of elements in waters. For instance, using chromatographic and electrochemical methods and by the judicious choice of absorbent or reagent [9], separated chromium into its oxidation states. Mohammad et al., (1990) [10] employed chromatographic and electrochemical methods in the speciation of antimony according to its oxidation states. For solid samples, including soil sediments and biological materials, this type of speciation is seldom possible, and reference must be made to functionally or operationally defined speciation. Direct, usually non-destructive, methods may be able to identify the species but are generally unable to quantify it without resorting to associated separation techniques [11].

According to Tessier et al. (1979) [12], metal speciation is therefore the qualitative identification and the quantitative determination, of the individual chemical species (or forms) of the metal in a sample. These species are extracted by use of different extracting reagents and can be summed up to give a value close to or more than that usually called total heavy metal concentration. All environmental matrixes can be subjected to heavy metal speciation analysis.

The process of determining the actual form or phase of an element present within a given sample is referred to as speciation [3, 13–14]. The distribution, mobility, and bioavailability or bioaccessibility of heavy metals depend on their chemical and physical associations. However, a model recently developed by Rooney et al. (2006) [15], proposed that bioavailability could be predicted as a function of soil properties, such as texture, pH, organic matter (OC), and cation exchange capacity (CEC). In this thesis, the term speciation may be defined as the process of identification and quantification of different defined species, forms, or phases present in a soil sample. Interest in speciation procedures is predicted to expand as a wider spectrum of the scientific community recognizes that assessments of health hazards, toxicity, and bioavailability must be based on levels of specific chemical forms, rather than total element levels [3, 14].

Speciation analysis has been used to determine the toxicity of metals, the biogeochemistry of metals, the functionality of bio-metallic species, the potential environmental risks, the bioavailability, bioaccumulation, biosimulation, and attenuation of [16]. Heavy metals have been used in monitoring pollution in the environment. Chemical and biological indicators are of interest since they provide information on the concentration and accumulation of heavy metals in the environment. A range of metals found in the dust are harmful both to man and his environment. Pollutants can attack specific sites or organs of the body and disease can develop because of such exposure to metals [17]. Although there have been a considerable number of studies on the concentration of heavy metals in street dust, the vast majority have been carried out in developed countries with long histories of industrialization [18].

The molecular speciation of trace metals in soils could be considered as derived from thermodynamic and kinetics considerations [19]. However, of importance here is to distinguish chemical species according to their distributions among soil components, such as organic matter or hydrous oxides. The concentration of heavy metals in the soil environment is a function of pH, properties of metals, redox conditions, soil chemistry, organic matter content, clay content, cation exchange capacity, and other soil properties [20–21]. Therefore, the speciation of metals in soil depends on the soil properties. The distribution of trace metals among soil components is important for assessing the soil's ability to supply micronutrients or contain toxic quantities of metals, and for determining amelioration procedures for soils at risk of causing trace metal contamination. Metal cations may be soluble, readily exchangeable, complexed with organic matter, or hydrous oxides, substituted in stoichiometric compounds, or occluded in mineral structures [22–24].

Major chemical factors that affect the retention of specific chemical forms of trace metal (e.g., effects of pH and ionic strength of soil solution (I) on "specific adsorption") have been well studied [25–26]. Since there exist several components in soil, the distribution of a trace metal among them will also depend on the type and relative quantities of the soil components; how they change with pH, and the extent of saturation of adsorption sites on soil adsorbents.

Though literature reveals that sequential extractions vary widely, the method adopted here is the modified Tessier et al., 1979 [12, 27]. Studies of metals in children's playgrounds are scarce and the few are based on total metal extractions with popular digesting reagents like nitric, sulphuric, hydrochloric acids, or a combination of these acids [28].

Studies reveal that metals on children's playgrounds have been reported but speciation analyses are scarce despite being accepted as the most reliable method for estimating toxicity, ecotoxicity, and other health-related parameters associated with heavy metals. The significance of this work lies in the fact that metal speciation analysis will enable a proper understanding of such concepts as mobility, active concentrations, and bioavailability which are central to the toxicity of metals. Though speciation analysis has been reported elsewhere, special analysis of first-row transition metals in soils of children's playgrounds has not yet been reported. Probably the first of its kind, this research will lay the groundwork on which similar works could be based.

The scope of the research was limited to six species of each of the five transition metals from composite soils from nine public schools' playgrounds. Within Owerri, Imo state, Nigeria. Schools have soils from similar basement rocks and soil characteristics may not introduce a significant bias.

Secondly, the schools are under the same anthropogenic influences, and it is believed that the physical properties of soils will have the same effects on the trends of metal species.

Public schools are government-owned and thus belong to nobody in Nigeria. This made it easy to access and predesignate sampling points and to obtain assistance and cooperation from the principals of the various schools.

This research results could be useful to policymakers when making such policies that could reduce pollutant loading and enrichment in school playgrounds. Since children's skin is tender and many organs are still developing, metal species could easily be absorbed on the skin or inhaled through the mouth and nose during play, and this can constitute some level of danger.

MATERIALS AND METHODS

Site Description

Owerri Municipal is one of the three local government areas (LGAs) that make up Owerri City, the capital of Imo state of Nigeria set in the heart of Igboland. It has been fully described elsewhere [29].

Sampling of Soil

Nine different sampling sites were taken from playgrounds along major roads connecting Owerri municipality in Imo state as follows: Surface soil or dust samples at 0–5 cm depth were collected in June (rainy season) and January (dry season), of 2012. At each sampling site, a W-shaped line was drawn on a 2 × 2 m surface along which samples were collected from five points into previously treated polythene containers using a perforated container to allow water to drain. The samples were sundried for two days, then oven-dried at 50°C for 12 days; and grind in acid-washed porcelain mortar with a pestle.

The soil samples were pooled together and treated to coning and quartering to obtain a small laboratory sample. The samples were sieved through a 200 μm sieve to normalize variations in grain size distributions. The samples were stored in polythene containers with caps for further analysis.

Sequential Extraction Procedure

The extraction was carried out on three sub-samples in each step as follows:

- *Water Soluble Fractions (F_1):* 1g of the air-dried soil sample (2 mm sieve) was mixed with 10 ml of de-ionized water with continuous agitation for 1 hour, centrifuged and the supernatant decanted and made up to 50 ml with de-ionized water before analysis.
- *Exchangeable Phase (F_2):* The residue in (i) above is shaken at room temperature with 16 ml of 1M $Mg(NO_3)_2$ at pH 7.0 for 1 hour, centrifuged and supernatant decanted and made up to 50 ml with double distilled de-ionized water.
- *Oxidized Phase (bound to organic matter) (F_3):* Residue form (ii) above +10 ml of 8.8M 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 and supernatant made up to 50 ml with distilled water before analysis.
- *Acid Soluble Base (bound to carbonates) (F_4):* 25 ml of 0.05M Na_2EDTA was added to the residue in (iii) above and shaken for 6 hrs and centrifuged. The supernatant was decanted and made up to 50 ml with distilled water before analysis.
- *Reducible Phase (bound to Fe–Mn oxides) (F_5):* 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, the supernatant decanted and made up to 50 ml with distilled water before analysis.
- *Residential Phase (bound to silicates and deferential materials) (F_6):* 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 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 were then removed with a pipette and filtered with Whatman No. 42 filter paper. The residue in each case was washed with de-ionized water.

Determination of Heavy Metal in Soil Samples

The total heavy metal concentration in the soil samples was determined using the ANALYST 400 Perkin Elmer absorption spectrophotometer. Quantification was carried out using appropriate calibration curves prepared in the same acid matrix with standard metal solutions for the atomic absorption spectrophotometer.

Reagents and Chemicals

Nitric acid (HNO_3) (suprapur), HCl (suprapur), sodium sulfate, and potassium hydrogen carbonate were purchased from Merck (Fin lab. Owerri), while double distilled deionized water was used for heavy metals analyses; standard metal solutions for atomic absorption spectrophotometer were purchased from Fluka (Buchs, Switzerland).

Statistical Analysis

Mean and coefficient of variation (CV%) were used to determine the variation in heavy metal contents amongst schools within Owerri. Variability was ranked as follows: little variation (CV% < 20), moderate variation (CV% = 20–50), and high variation (CV% > 50) according to Mbah and Anikwe (2011). Analysis of variance (one-way ANOVA) was used to compare the mean metal concentrations among the sites. Statistical significance was described at 0.05 and 0.01 probability. The statistical analysis was performed using SPSS software, version 15 (Tables 1–2).

RESULTS AND DISCUSSION

Table 1. Descriptive statistics of metals fractions in playground soils for 2012.

Metals and Fractions		Mean		Min.		Max.		SD		CV	
		Dry Season	Rainy Season	Dry Season	Rainy Season	Dry Season	Rainy Season	Dry Season	Rainy Season	Dry Season	Rainy Season
Mn	F1	11.67	4.78	4.00	.00	20.00	11.00	5.43	11.00	46.5	230
	F2	7.400	15.78	3.00	.00	13.00	55.00	3.27	55.00	42.2	349
	F3	10.44	13.67	3.00	.00	31.00	34.00	8.73	34.00	83.62	258.2
	F4	20.11	14.33	5.00	.00	32.00	38.00	9.01	38.00	44.80	265.2
	F5	24.67	17.22	14.00	.00	42.00	33.00	8.11	33.00	32.87	191.6
	F6	26.22	33.11	12.00	16.00	57.00	48.00	15.01	48.00	57.25	145.0
Co	F1	9.89	2.44	1.00	.00	23.00	19.00	6.85	6.22	69.26	255.0
	F2	14.10	7.00	3.00	.00	34.00	24.00	11.28	9.04	80.0	129.1
	F3	10.56	12.22	5.00	.00	17.00	58.00	4.85	19.56	45.92	160.1
	F4	22.22	14.67	7.00	.00	32.00	38.00	9.31	15.14	41.90	103.2
	F5	25.56	11.78	11.00	.00	46.00	35.00	11.92	12.44	46.64	105.6
	F6	21.89	51.11	13.00	3.00	42.00	100.00	8.74	32.81	39.93	64.19
Ni	F1	20.44	11.33	2.00	1.00	53.00	25.00	20.56	8.85	100.59	78.11
	F2	9.50	7.89	1.00	2.00	16.00	14.00	5.46	4.53	57.47	57.41
	F3	11.33	10.67	3.00	3.00	39.00	24.00	12.02	6.38	107.68	59.79
	F4	13.56	12.44	2.00	6.00	39.00	16.00	13.17	3.36	97.12	27.01
	F5	20.33	13.89	6.00	.00	39.00	32.00	9.94	12.45	48.89	89.63
	F6	19.56	44.33	7.00	8.00	50.00	67.00	16.16	21.00	82.62	47.37
Cu	F1	14.11	6.44	5.00	1.00	37.00	18.00	9.64	5.151	68.32	79.97
	F2	12.50	21.44	4.00	2.00	37.00	41.00	10.31	11.58	82.48	54.01
	F3	11.56	25.33	6.00	5.00	27.00	146.00	7.33	45.63	63.41	180.1

	F4	21.89	7.78	9.00	2.00	31.00	16.00	8.15	4.32	37.23	55.53
	F5	20.44	17.00	3.00	2.00	49.00	59.00	13.28	16.69	64.97	98.18
	F6	13.67	30.78	1.00	3.00	26.00	58.00	7.97	17.96	58.30	58.25
Zn	F1	13.56	13.89	4.00	3.00	39.00	56.00	11.55	16.74	85.18	120.52
	F2	9.10	15.33	3.00	1.00	15.00	44.00	3.07	13.91	33.74	90.74
	F3	14.78	15.00	5.00	4.00	39.00	49.00	10.62	15.66	71.85	104.4
	F4	13.56	12.22	5.00	1.00	27.00	44.00	8.35	12.90	61.58	105.56
	F5	22.11	16.22	10.00	5.00	34.00	39.00	6.53	11.54	29.53	71.14
	F6	30.22	29.00	17.00	4.00	60.00	48.00	13.89	14.82	45.96	51.10

Table 2. Descriptive statistics of metals fractions in playground soils for 2013.

Metals and Fractions		**Mean**		**Min.**		**Max.**		**SD**		**CV**	
		Dry Season	**Rainy Season**	**Dry Season**	**Rainy Season**	**Dry Season**	**Rainy Season**	**Dry Season**	**Rainy Season**	**Dry Season**	**Rainy Season**
Mn	F1	23.56	10.88	12.00	.00	49.00	65.00	11.54	20.80	48.98	191.18
	F2	12.67	11.78	8.00	1.00	20.00	27.00	4.36	10.01	34.41	84.47
	F3	6.44	11.56	4.00	1.00	10.00	31.00	2.00	10.93	31.06	94.55
	F4	18.33	12.44	3.00	2.00	37.00	30.00	11.89	10.16	64.89	81.67
	F5	19.56	15.78	8.00	1.00	28.00	33.00	7.00	11.14	35.78	70.60
	F6	21.11	39.33	6.00	20.00	32.00	70.00	8.94	15.67	42.35	39.84
Co	F1	19.67	11.33	11.00	.00	32.00	40.00	6.61	15.67	33.60	138.31
	F2	19.00	8.44	11.00	2.00	29.00	31.00	6.08	10.43	32.00	123.58
	F3	8.67	12.11	3.00	2.00	22.00	44.00	5.61	13.00	64.71	107.35
	F4	16.33	25.56	3.00	.00	27.00	65.00	8.02	25.09	49.11	98.16
	F5	18.22	16.56	9.00	5.00	30.00	36.00	6.08	10.65	33.37	64.31
	F6	21.00	32.11	13.00	3.00	28.00	68.00	5.38	22.48	25.62	70.04
Ni	F1	27.00	19.00	8.00	2.00	63.00	65.00	15.16	20.76	56.15	109.26
	F2	8.78	11.88	5.00	2.00	17.00	41.00	3.93	12.96	44.76	109.10
	F3	8.44	13.44	2.00	3.00	20.00	32.00	5.65	9.87	66.94	73.44
	F4	9.56	15.67	5.00	2.00	15.00	64.00	3.32	18.92	34.72	120.79
	F5	23.67	8.11	5.00	2.00	33.00	23.00	9.49	6.94	40.09	85.57
	F6	22.00	39.33	10.00	3.00	43.00	65.00	11.20	20.88	50.91	53.09
Cu	F1	25.22	19.67	6.00	6.00	55.00	55.00	14.27	9.64	56.58	49.00
	F2	14.78	19.67	5.00	5.00	27.00	27.00	6.10	10.30	41.27	52.36
	F3	9.56	11.67	5.00	5.00	16.00	16.00	4.03	7.33	42.15	62.81
	F4	13.56	9.33	3.00	3.00	36.00	36.00	12.23	8.15	90.19	87.35
	F5	15.89	11.44	4.00	4.00	37.00	37.00	10.96	13.27	68.97	116.00
	F6	22.56	27.67	7.00	7.00	52.00	52.00	15.96	7.97	70.74	28.80
Zn	F1	24.22	11.78	19.00	19.00	35.00	35.00	5.49	11.54	22.67	97.22
	F2	12.78	24.33	5.00	5.00	24.00	24.00	6.70	3.07	52.43	12.62
	F3	9.78	14.89	6.00	6.00	16.00	16.00	3.11	10.62	31.80	71.32
	F4	13.11	18.67	7.00	7.00	28.00	28.00	8.62	8.35	65.75	44.72
	F5	20.11	16.56	3.00	3.00	33.00	33.00	10.26	6.53	51.02	39.43
	F6	20.78	28.56	8.00	8.00	28.00	28.00	5.71	13.89	27.48	48.63

At the playground HEO metal species (Figure 1) in dry season were high for Ni and Zn. Mn, Co, and Cu showed low metal species. The order of prominence of the six fractions was $F_6 > F_5 > F_4 > F_3 > F_2 > F_1$ for dry season. It could be observed that the water-soluble cobalt was the least species at HEO. Metals at HEO generally showed poor speciation.

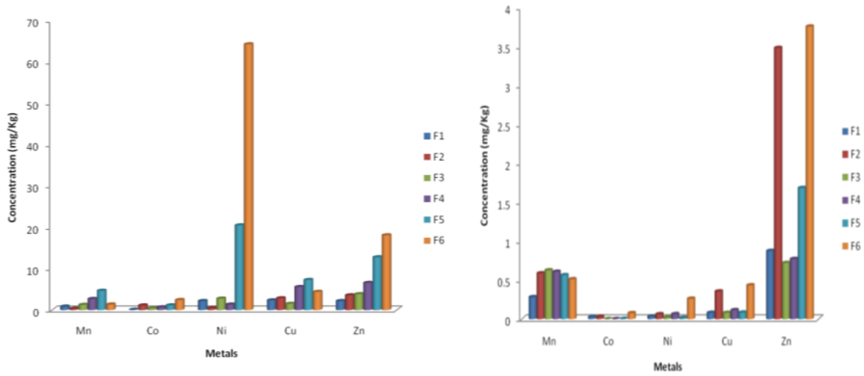

Figure 1. Heavy metals species at playground HEO in the rainy season of 2012.

In rainy season Zn and Mn had significant metal species than Ni and Cu. Cobalt species were lowest and when compared to Zn species they were insignificant. The residual fraction was the highest in both seasons while the water-soluble fraction and organic bound fraction were low.

The order of prominence of fractions follows the trend; $F_6 > F_2 > F_5 > F_1 > F_4 > F_3$ for rainy season.

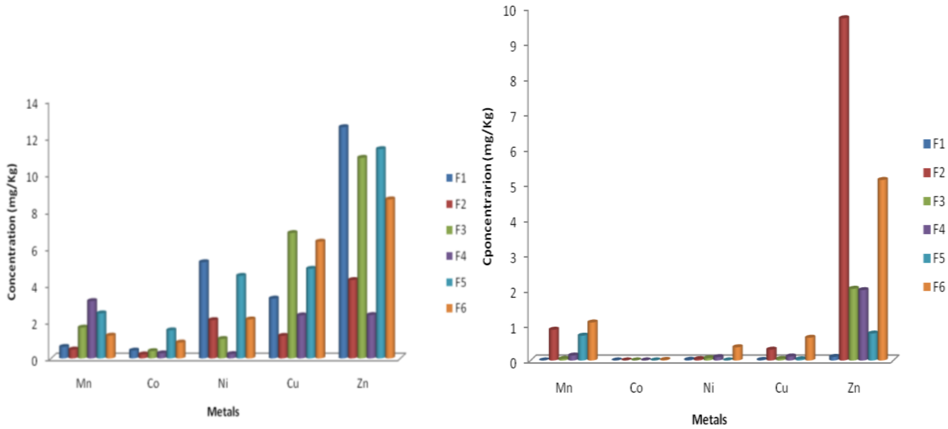

Figure 2. Heavy metals species at playground MNO of 2012.

In the dry season Zinc, Copper, Manganese, and Nickel had more significant metal species than Co. F_4 species of cobalt was the lowest compared to all metal species. The Fe-Mn species was the highest in dry seasons so too were H_2O soluble fractions and organically bound fractions were low during dry periods. The order of prominence of the six fractions follows the trend: $F_6 > F_2 > F_5 > F_1 > F_4 > F_3$ for the rainy season. Zn species were generally prominent except for F_4 which showed the same value as F_4 for Cu (Figure 2).

In the rainy season Co, Ni, and Cu had virtually no significant metal species though F_6 of Ni and Cu was comparable to F_5 of Zn. All species of cobalt were lowest compared to all metal species. The $F_{6,}$ $F_{5,}$ and F_2 species were the only significant species of Mn in dry seasons. The water-soluble fraction was low in the dry season, and this however was expected because Zn dissolution may require other ions which are normally not found. The order of prominence of the six fractions follows the trend: $F_2 > F_6 > F_3 > F_4 > F_5 > F_1$ in the rainy season. The Zn species were generally prominent except for F_1 which showed a higher value than Co species.

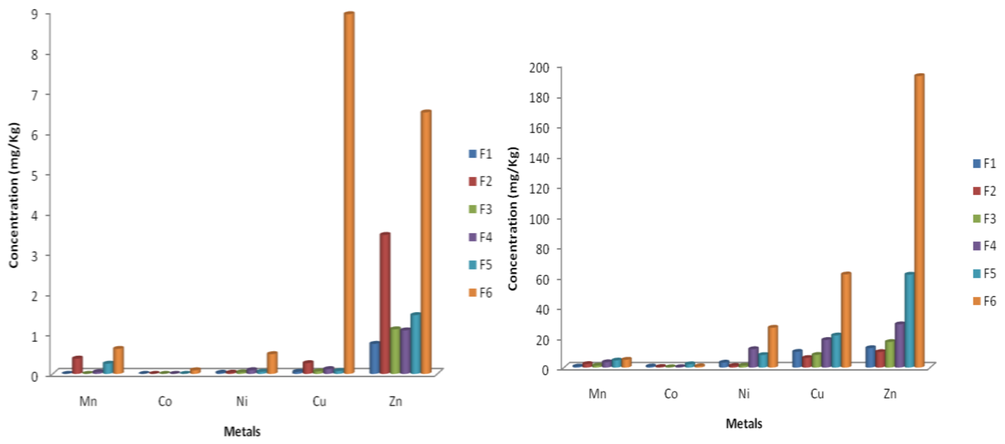

Figure 3. Heavy metals species at playground SCP in the dry season of 2012.

At playground SCP (Figure 3), metal species in the dry season were low for Co, Mn, and Ni whereas metals species were high for Zn and Cu. The residual fraction was highest for metals as follows: Zn > Cu > Ni. Mn, Co, and Ni species were still low. All species of Zn for both seasons were high. The overall order of decreasing metal species concentrations was $F_6 > F_5 > F_4 > F_3 > F_1 > F_2$ in dry season.

Figure 3 shows that metal species in the rainy season were lowest for Co, Ni Mn, and Cu except for F_6 of Cu. Residual species was highest amongst metals studied though it followed order as C_u > Zn > Mn > Ni > Co. Mn, Co, and Ni species were not comparable to Zn species. All species of Zn for both seasons were high. The overall order of decreasing metal species concentrations was $F_2 > F_6 > F_2 > F_5 > F_3 > F_1$ in the rainy season.

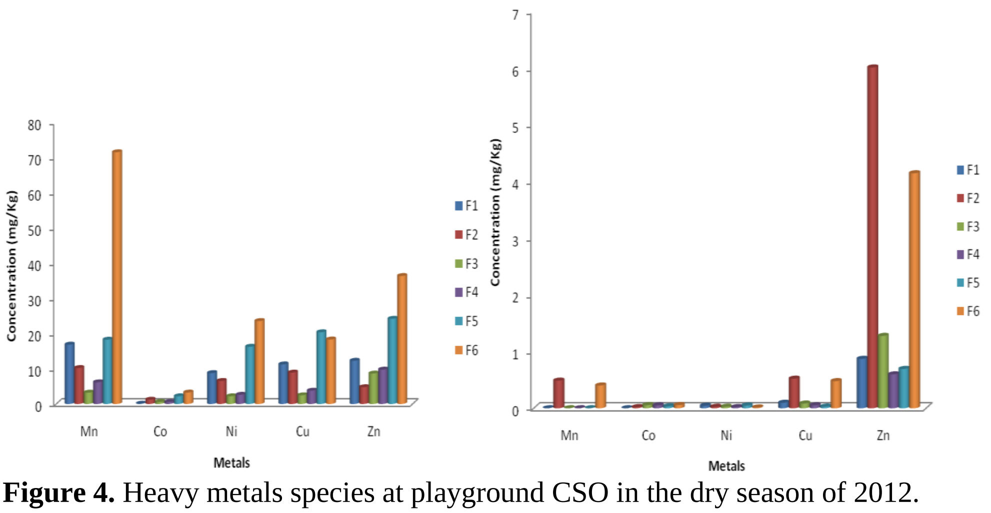

Figure 4. Heavy metals species at playground CSO in the dry season of 2012.

At playground CSO (Figure 4), metal species were high in the case of Mn, Zn, $C_{u,}$ and N_i whereas all species of Co were lowest. Residual fraction was the highest and water-soluble fraction was the least in dry season. Iron and Manganese bound species were recorded second after residual species dry season. The order of decreasing metal species was $F_6 > F_5 > F_1 > F_4 > F_3 > F_2$ in dry season and $F_2 > F_6 > F_3 > F_1 > F_5 >$ F4 in rainy season.

At playground CSO (Figure 4), metal species in the rainy season were high for only Zn. Though F_6 and F_5 fractions for Cu alongside Mn were significant in the rainy season they were only comparable to F_4 and F_5 of Zn. Ni and Co were virtually insignificant for all species. The order of decreasing metal species was $F_6 > F_5 > F_1 > F_4 > F_3 > F_2$ in dry season.

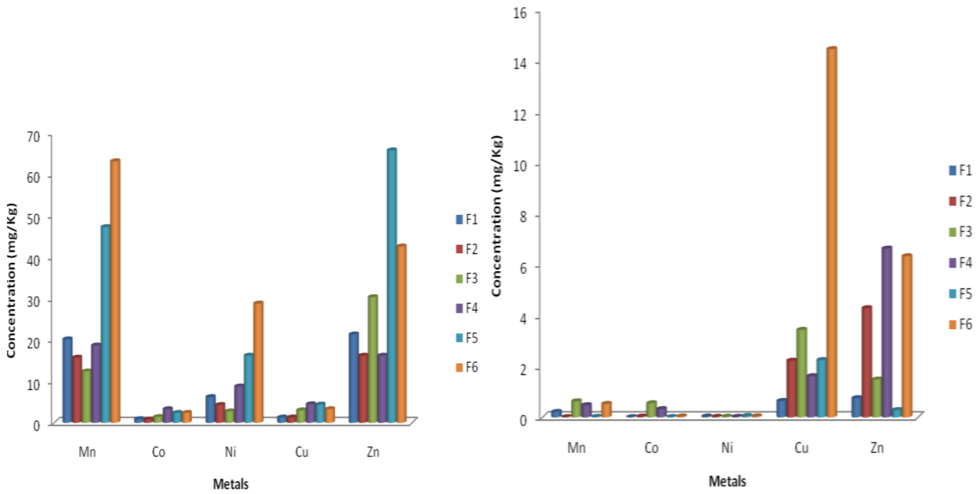

Figure 5. Heavy metals species at playground TSO in the dry season of 2012.

At playground TSO (Figure 5), metal species in the dry season were high for Mn, Ni, and Zn and lowest concentrations for Co and Cu. There was no doubt that the water-soluble fraction of Co was the lowest fraction for all metals in the rainy season. Fe-Mn oxide fraction for Zn had the highest concentration. The order of decreasing metal species was $F_5 > F_6 > F_3 > F_1 > F_4 > F_2$ in dry season. At playground TSO (Figure 5), metal species in the dry season were high for Mn, Ni, and Zn and lowest concentrations for Co and Cu. In the rainy season, all other metals had a much higher concentration than Co. F_5 had the highest concentration while the F_2 fraction showed the least value in the dry season for Mn, Co, and Ni while the F_5 fraction was the least in the dry season for the most prominent metal. The order of decreasing metal species was: $F_6 > F_4 > F_2 > F_3 > F_5 > F_1$ in the rainy season.

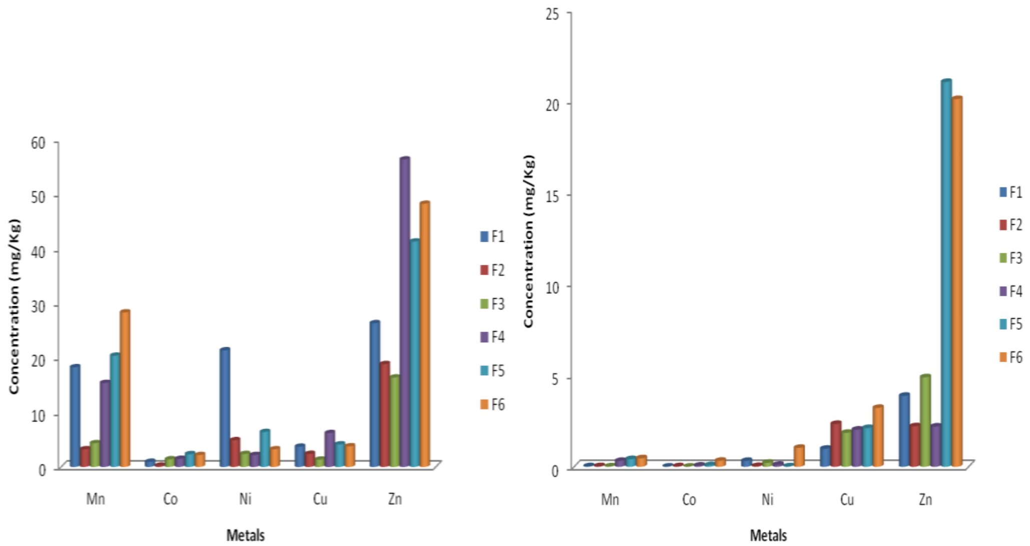

Figure 6. Heavy metals species at playground WSP in the dry season of 2012.

At playground WSP (Figure 6), metal species in the dry season had more concentrations of the metals than in the dry season. The carbonate bound fraction had the highest concentrations followed by the residual fraction in the dry season while the exchangeable fraction was the highest concentrations followed by residual too. The order of decreasing metal species was: $F_5 > F_6 > F_1 > F_3$

> F_5 > F_4 in rainy season.

At playground WSP (Figure 6), metal species in the rainy season had more concentrations than of the metals than in the dry season. The carbonate bound fraction had the highest concentrations followed by residual fraction in dry season while exchangeable fraction was the highest concentrations followed by residual too. Mn, Co and Ni showed insignificant metals species. The order of decreasing metal species was: $F_4 > F_6 > F_5 > F_1 > F_2 > F_3$ It was observed that F_6 was the highest fraction for all metals.

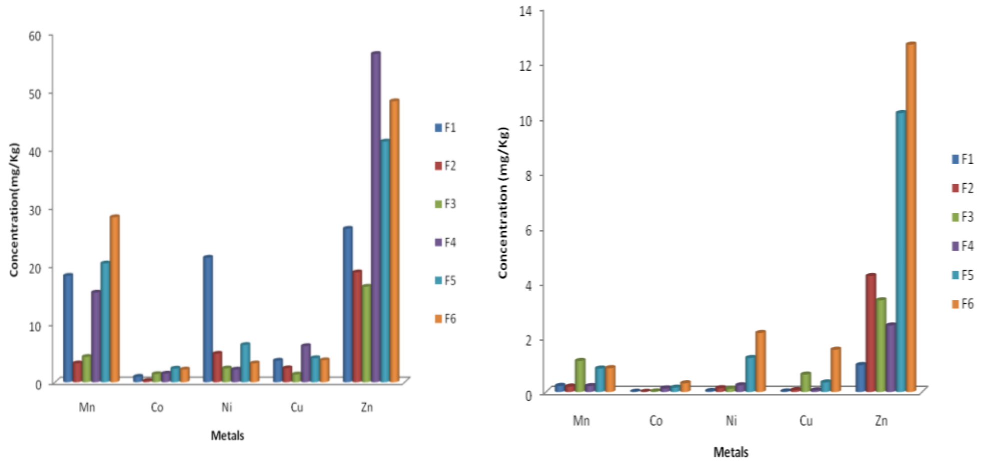

Figure 7. Heavy metals species at playground WBP in the dry season of 2012.

At the playground, WBP (Figure 7), the metal species for dry season Zn and Mn showed higher values compared to Co, Cu, and Ni. The carbonate bound fraction was most prominent among all the fractions of Zn. In the dry season, Zn had the highest metal species. The order of decreasing metal species was: $F_4 > F_6 > F_5 > F_1 > F_2 > F_3$ in dry season.

At playground WBP (Figure 7), the metal species for the rainy season showed that Mn, Ni, and Zn were higher than Co and Cu. Residual metals fraction was more prominent among all the fractions, but Zn had the highest metal residual species. The order of decreasing metal species was: $F_6 > F_5 > F_2 > F_3 > F_4 > F_1$ in rainy season. It could be seen that Co had all the species lowest compared to species of other metals.

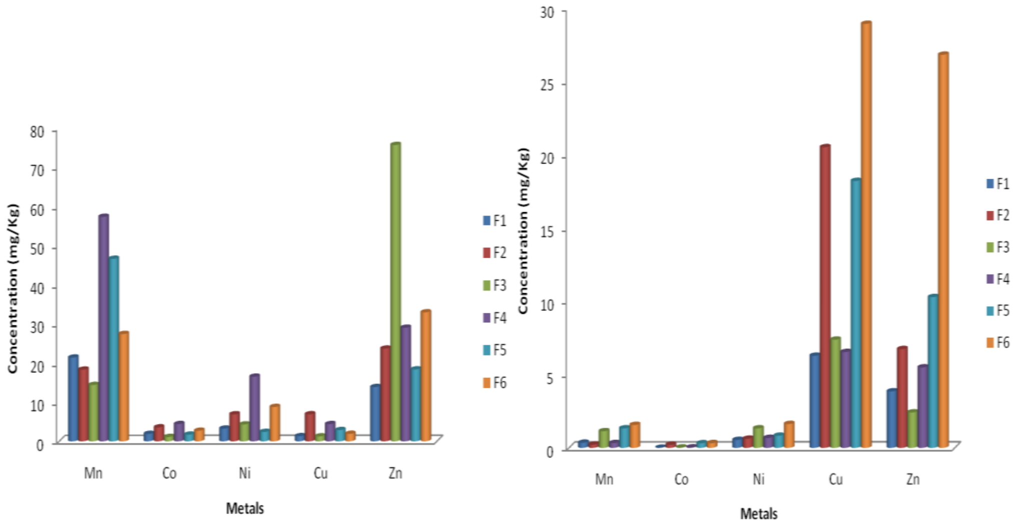

Figure 8. Heavy metals species at playground IKS in the dry season of 2012.

At playground IKS (Figure 8), the metal species were high for Mn and Zn with organically bound fractions leading in dry season. Co, Ni, and Cu had the lowest metal species. Reducible fraction was more pronounced both for Cu and Zn followed by exchangeable fraction. The order of decreasing metal species was $F_3 > F_4 > F_5 > F_6 > F_1 > F_2$ in dry season.

At playground IKS (Figure 8), the metal species were high for Cu and Zn showed high species, unlike Co, Ni, and Mn. The metals Cu and Zn had F_6 species with the highest concentration of species. Co and Ni metals had the lowest species.

Reducible fraction is more pronounced both for Cu and Zn followed by exchangeable fraction. The order of decreasing metal species was: $F_6 > F_2 > F_5 > F_3 > F_4 > F_1$ in rainy season.

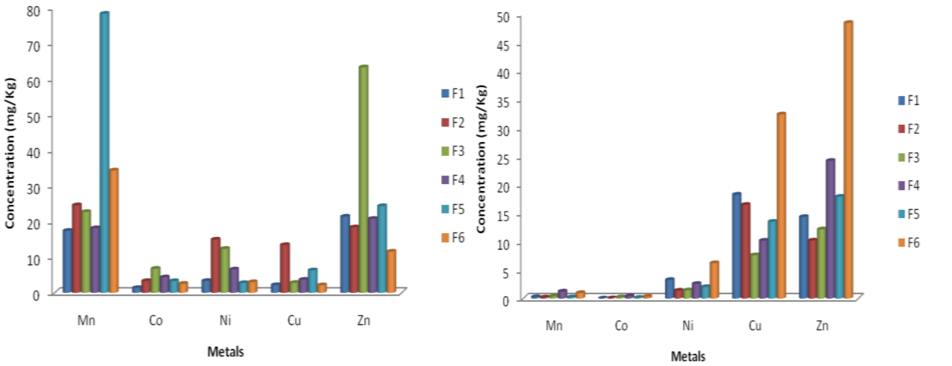

Figure 9. Heavy metals species at playground UPS in the dry season of 2012.

In playground UPS (Figure 9), the metals Mn as well as Zn had high values in the dry season while species prominence amongst metals was: Mn> Zn > Ni > Cu > Co. F_5 species of Mn was highest followed by organic bound fraction for Zn in dry season. The order of decreasing metal species was $F_3 > F_4 > F_5 > F_6 > F_1 > F_2$ in dry season. In playground UPS (Figure 9), the metals Cu and Zn were high in the rainy season. For Zn, Cu, and Ni Mn and Co metals the residual fraction was highest in this order. Exchangeable fraction and organically bound fraction were the least in the dry season for Mn and Co respectively. Co and Mn were very insignificant in the rainy season for all metal species. The order of decreasing metal species was $F_6 > F_4 > F_5 > F_1 > F_2 > F_3$ in rainy season.

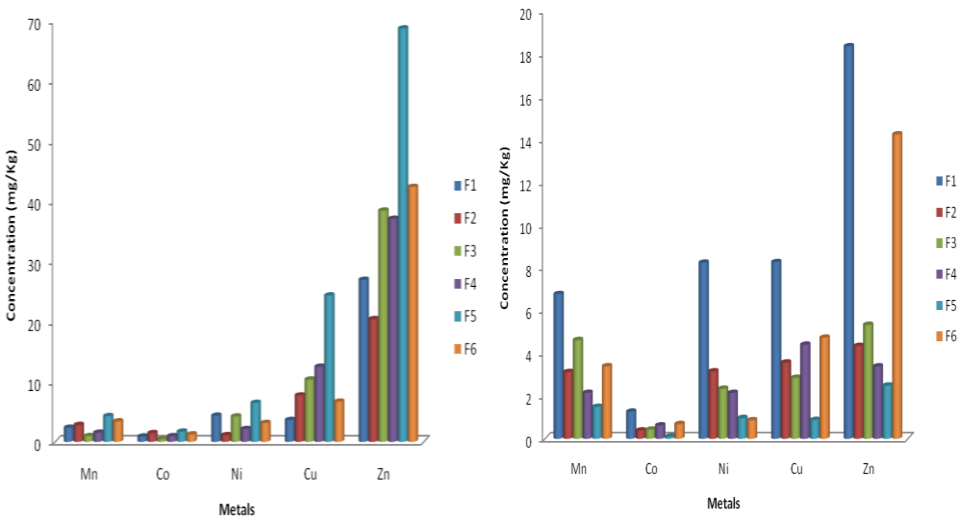

Figure 10. Heavy metals species at playgrounds HEO for the dry season in 2013.

In playground HEO (Figure 10), metal species in the dry season for Cu and Zn were high compared to Mn, Ni, and Co. Metal species for Co were low in dry season. Fe-Mn bound fraction and was highest in dry seasons. Co in other cases was the lowest metal species and its carbonate-bound fraction was the least in dry seasons. The order of decreasing metal species was $F_5 > F_6 > F_3 > F_4 > F_1 > F_2$ in dry season.

In the playground, HEO (Figure 10), metal species in the dry season for Cu and Zn were high compared to Mn, Ni, and Co. In the rainy season, the Co species were all low. Fe-Mn bound fraction and water-soluble fraction were high in dry. Co was the lowest metal species in both seasons. The order of decreasing metal species was $F_1 > F_6 > F_3 > F_2 > F_4 > F_5$ in rainy season.

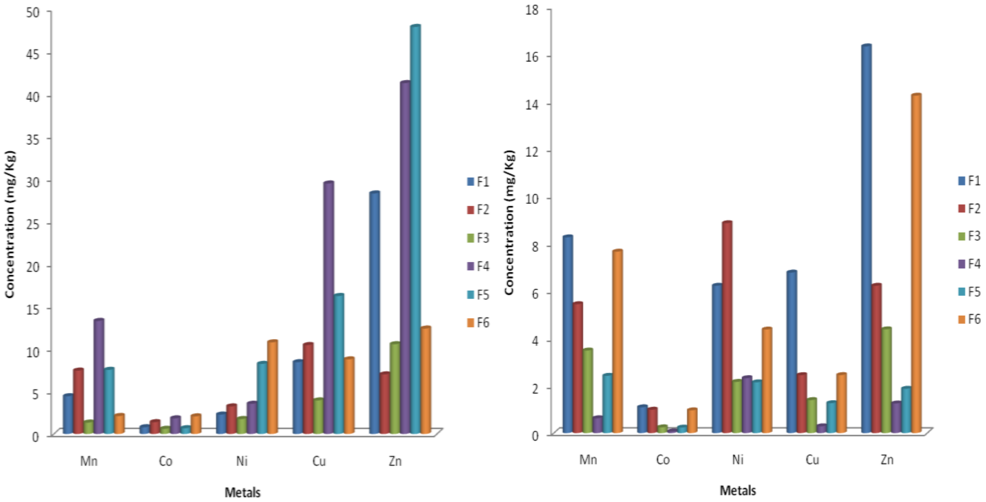

Figure 11. Heavy metals species at playground MNO for the dry season in 2013.

In playground, MNO (Figure 11), metal species were high for Zn and Cu while Mn and Ni were low in the dry season, and Co was much lower. Surprising residual metal species were less prominent for all metals while Fe-Mn bound fraction and water-soluble were high in dry. The order of decreasing metal species in the dry season at MNO was $F_5 > F_4 > F_1 > F_6 > F_3 > F_2$.

In playground MNO (Figure 11), metal species were high for Ni, Mn, Cu, and Zn while Co species were low in the dry season. All the other five metals were high whereas Co had the least species, being F_4 in the rainy season. Fe-Mn bound fraction and water-soluble were high in the rainy season. The order of decreasing metal species was: $F_1 > F_6 > F_2 > F_3 > F_4 > F_5$ in rainy season.

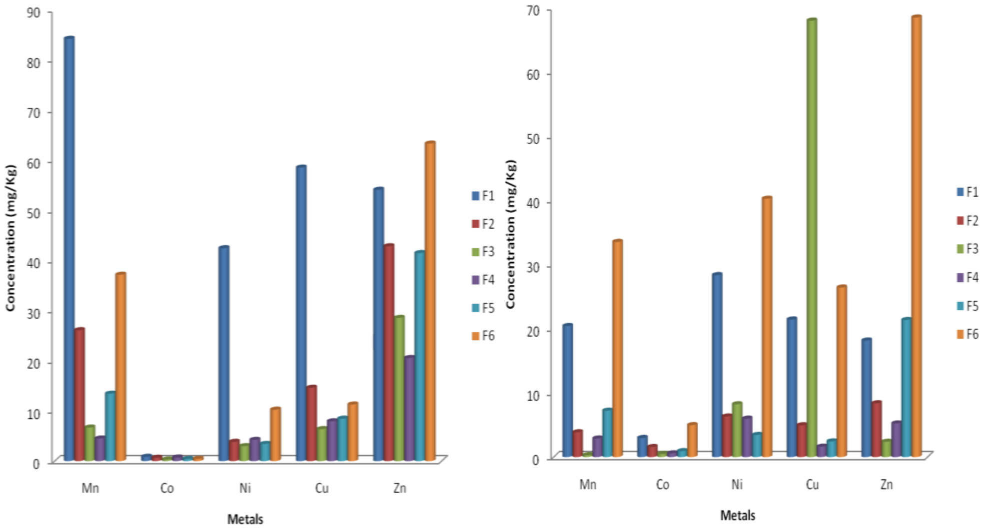

Figure 12. Heavy metals species at the playground in SCP for dry season in 2013.

In playground SCP (Figure 12), Co recorded the lowest metal species in the two seasons. Water soluble fraction was almost very prominent in all the fractions in the dry season. Water soluble fraction for Mn > Cu > Zn > Ni was highest while residual fractions for Zn and Mn were comparable. The order of decreasing metal species was $F_3 > F_4 > F_5 > F_6 > F_1 > F_2$ in dry season.

In playground SCP (Figure 12), Co recorded the lowest metal species in the rainy seasons. Water soluble fraction was almost very prominent in all the fractions in the rainy season. Water soluble fraction and residual fraction are the highest in the rainy season. The order of decreasing metal species was F_3, $F_6 > F_2 > F_5 > F_3 > F_4$ in the rainy season.

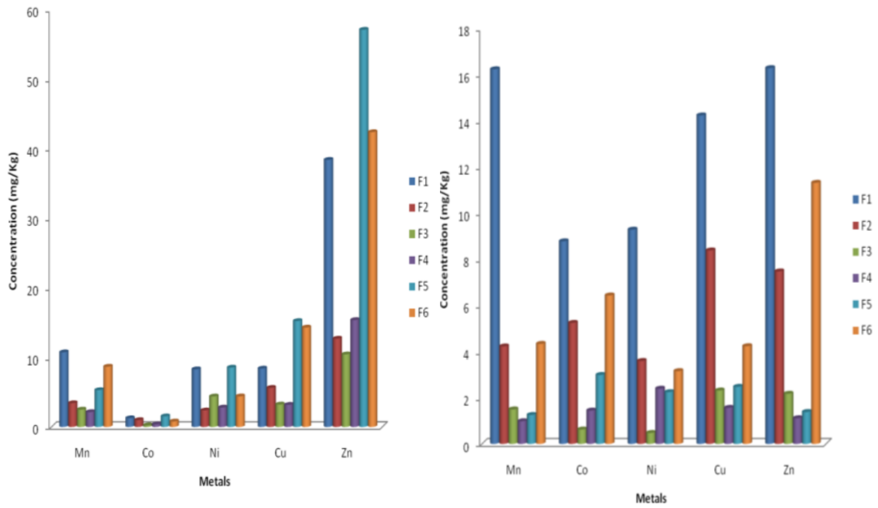

Figure 13. Heavy metals species at playground CSO for dry season in 2013.

In the playground, CSO (Figure 13) the metal Zn was in the sum of species concentration high in the dry season and exhibited higher species concentration than others. The Fe-Mn bound and water-soluble species for Zn were higher while Cu, Co, Ni, and Mn were low in the dry season. Order of decreasing metal species was $F_5 > F_6 > F_1 > F_4 > F_2 > F_3$ in dry season. Cobalt showed low metal species and was no doubt the metal with the lowest concentration of species organic-bound species.

In playground CSO (Figure 13) all metals exhibited significant speciation, but metal Zn was high in the rainy season, but Mn, Co, Ni, and Cu were equally high. Water-soluble species for all metals were prominent. The order of decreasing metal species was $F_1 > F_6 > F_2 > F_5 > F_3 > F_4$ in rainy season.

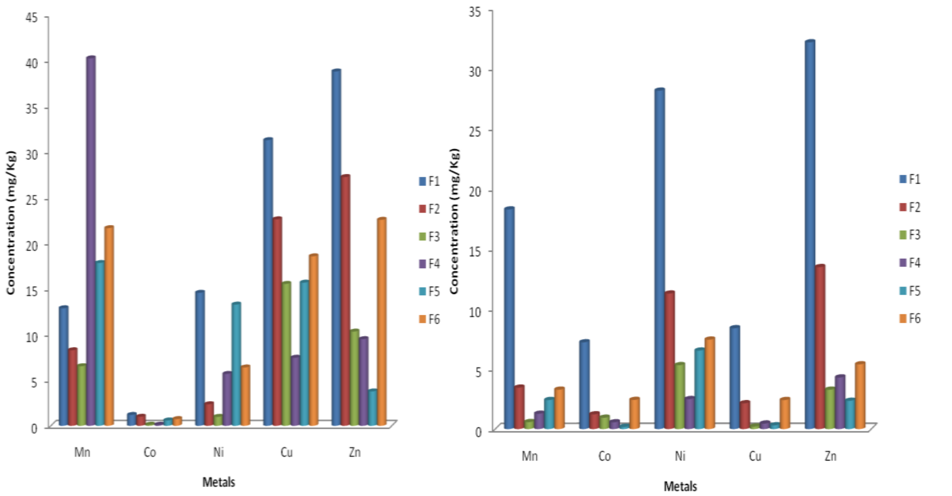

Figure 14. Heavy metals species at playground TSO for the dry season in 2013.

In playground TSO (Figure 14), the metals Mn, Ni, Cu, and Zn were high in the dry season, showing good speciation. The water-soluble species were prominent for all metals except Co. However, Mn showed abnormal speciation with carbonate fraction being the highest amongst all species. F_5 fractions as well as Organic fractions were least in dry periods. Order of decreasing metal species was $F_4 > F_1 > F_2 > F_6 > F_3 > F_5$ in dry season.

In the playground, TSO (Figure 14), the metals Co, Cu, and Mn were low whereas Zn and Ni were high in the rainy season. Though the water-soluble fraction for Zn was the highest of all species and was the most prominent species amongst all metals, Ni showed overall good speciation. F_5 fraction and Organic fractions were the least in the dry and rainy seasons respectively. The order of decreasing metal species was: $F_1 > F_2 > F_6 > F_5 > F_3 > F_4$ in rainy season.

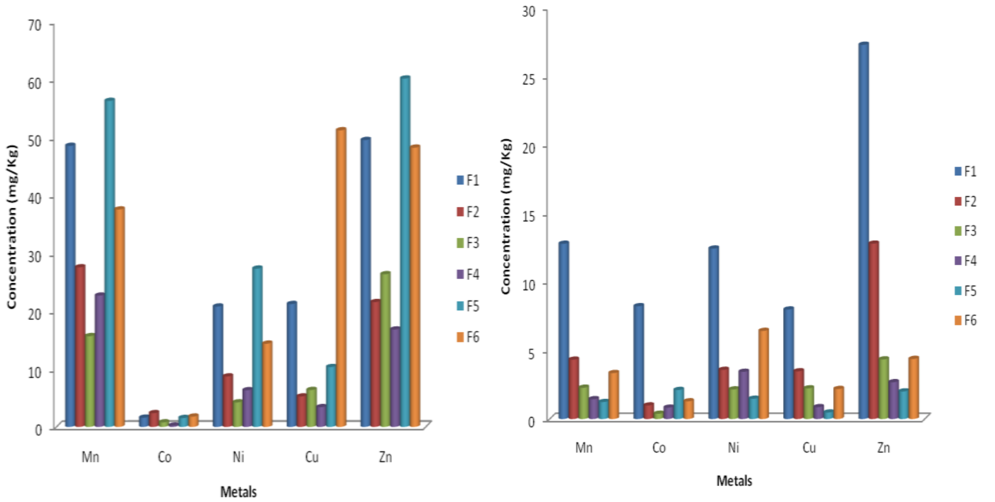

Figure 15. Heavy metals species at playground WSP for the dry season in 2013.

At playground WSP (Figure 15), the metal species for the dry season showed that Mn, Cu, Ni, and Zn were high and were well distributed amongst the six species showing decreasing order: Zinc >Manganese> Copper > Nickel > Cobalt. Fe- Mn bound fraction was more prominent among all the fractions in the dry season. The order of decreasing metal species was $F_5 > F_6 > F_1 > F_3 > F_2 > F_4$.

The metal species for the dry season at playground WSP revealed that Mn, Co, Cu, Ni, and Zn had significant concentrations. However, species concentrations were lower and F_5 was more prominent among all fractions. In the rainy season, Zn had the highest metal species, and the order of decreasing metal species was $F_1 > F_2 > F_6 > F_3 > F_4 > F_5$ in the rainy season.

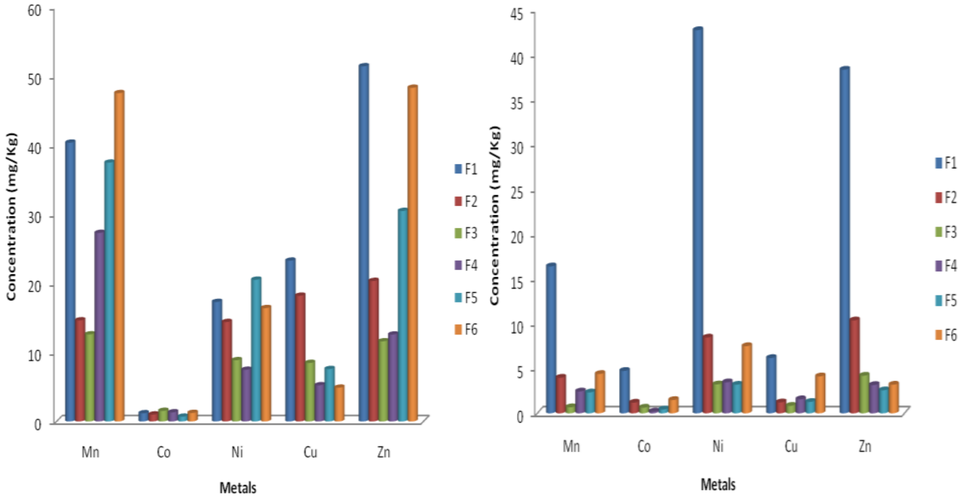

Figure 16. Heavy metals species at playground WBP for dry in 2013.

At playground WSP (Figure 16), metal species in the dry season had more concentrations of the metals than in the rainy season. Co had the lowest concentration among all the seasons and showed the lowest speciation. Zn had a water-soluble fraction as the highest concentration followed by the residual fraction in the dry season. The order of decreasing metal species was $F_1 > F_6 > F_5 > F_2 > F_4 > F_3$ in dry season.

At the playground, WSP (Figure 16), Zn and Ni metals species in the rainy season had more concentrations of the metals than in the rainy season. Co had the lowest concentration among all the seasons. Water soluble fraction had the highest concentrations followed by residual fraction in the rainy season. The order of decreasing metal species revealed that $F_1>F_2>F_6>F_3>F_4> F_5$ in rainy season.

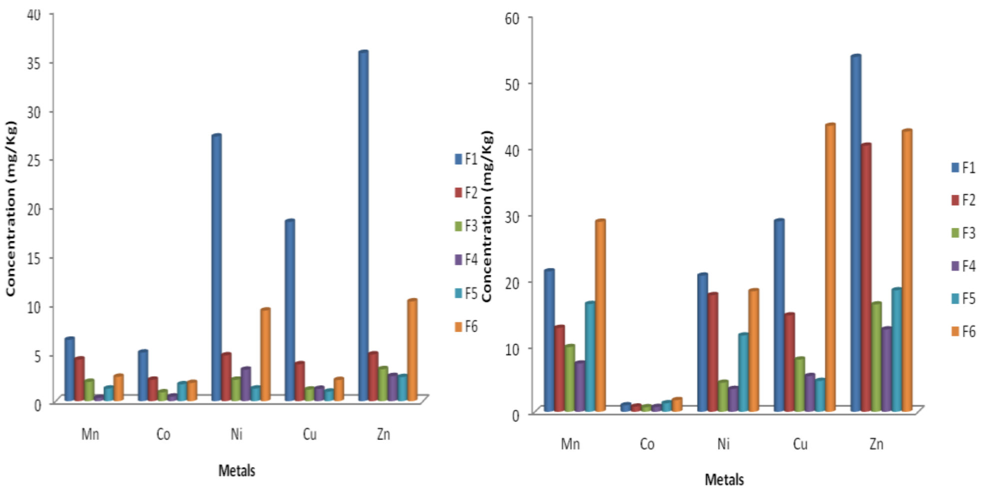

Figure 17. Heavy metals species at playground IKS for the dry season in 2013.

At playground IKS (Figure 17), the metal species had high concentrations of Mn, Ni, Cu, and Zn but were very insignificant for cobalt in the dry season. Zn showed prominent speciation and was highest in its water-soluble fraction. The order of decreasing metal species was $F_1 > F_6 > F_2 > F_5 > F_3$

> F_4 in dry season.

At playground IKS (Figure 17), the metal species had high concentrations for Mn, Ni, Cu, and Zn but very insignificant speciation for cobalt in the rainy season. The metal species were low while water-soluble fraction was the highest among the six species. The order of decreasing metal species was $F_1 > F_6 > F_2 > F_3 > F_4 > F_5$ in the rainy season.

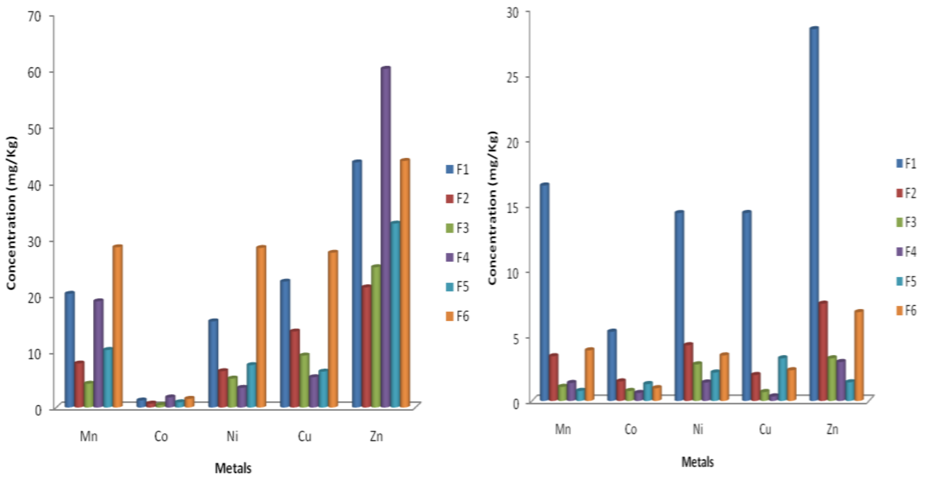

Figure 18. Heavy metals species at playground UPS for dry season in 2013.

At playground UPS (Figure 18), the metal species had high concentrations for all the metals except Co which was very insignificant in the dry season. The carbonate bound fraction was the highest while water-soluble fraction was recorded as the highest in the dry season. Zn showed prominent speciation with all species above 20 mg/kg much above all species of co put together. The order of decreasing metal species was $F_4 > F_6 > F_1 > F_5 > F_3 > F_2$ in dry season.

Water soluble species for all metals at playground UPS (Figure 18) were the highest. The metal species had high concentrations for all the metals except Co which was very insignificant in the rainy season. The highest species were water soluble in the rainy season with the order of decreasing metal species being $F_1>F_2>F_6>F_3>F_4>F_5$ in the rainy season.

VARIABILITY

In 2012 Mn (32.87–82.63%) showed medium to high variability in the dry season while a variability range of 145–349% was recorded for Mn in the rainy season. Mn was observed to be the metal with the highest variability with all metals showing higher variability in the rainy season than dry season. From Table 1, the order of variability was rainy: Mn > Co > Cu > Ni > Zn and dry season: Ni > Cu > Zn > Co > Mn.

In 2013 the trend in variability was slightly even though Mn was still the highest amongst all five metals in the rainy season. Metal variability followed the order Mn > Co > Ni > Cu > Zn and dry season: Cu > Co > Mn > Ni > Zn.

For most metals (Mn, Co, and Zn) F1 species showed the highest variability. In both years of study, the trend of variability for F1 was generally Mn > Co > Zn > Cu> Ni. Most F6 species showed low variability, and it was observed that metal variability decreased from F1 to F6 and was the general trend for both rainy and dry seasons.

CONCLUSIONS

In conclusion, there was no recurring trend though in many cases there were repeated sub-trends, such as F1 being the highest in many cases and Mn being the highest for most playgrounds. Speciation analysis has revealed that F1, F2, and F3 species for the five metals were usually higher. Since these species are the most mobile in soil, children using these playgrounds frequently could be at risk of metal toxicity. The trends and variations of six species from five metals determined in soils of nine public school playgrounds within the Owerri metropolis have been successfully reported here. The seasonal variations in trends were much similar for all metals with F1 fractions usually highest while F6 was lowest though in some cases (Zn and Cu) F4, F5, and F6 showed higher variations than F1, F2, and F3. In the dry season metal variability was generally in the decreasing order Mn > Co > Ni > Cu > Zn while in the rainy season Cu> Co >Mn > Ni> Zn. The influence of physicochemical factors on the behavior of metal species needs to be studied to improve the current understanding of trends of metal species in soil playgrounds.

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