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Total extractible concentration of Manganese, Cobalt, Nickel, Copper and Zinc in Soils of Children's playground within Owerri metropolis, Imo State, Nigeria

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Abstract

Surface soil samples from 9 public school playgrounds across Owerri metropolis were investigated for concentration of single extraction with nitric acid and total extractible metals as sum of species using various extractants. For both total metal determination and sequential extraction procedure, metal concentrations were quantified with A ANALYST 400 Perkin Elmer AAS. Results revealed that total extractible Zn (172.67 ± 65.07 mg/kg) > Mn (99.14 ± 53.58 mg/kg) > Cu (60.18 ± 25.88 mg/kg) > Ni (55.13 ± 15.61 mg/kg), and Co (9.61 ± 3.88 mg/kg) showed higher concentrations in dry season but were much lower than WHO standards and values reported elsewhere. Although percent metal recoveries for rainy season were abnormally high, the mean recovery values ranged from 95 – 188%, indicating good analysis. All playgrounds studied in the three years showed positive correlation with at least one other metal with Pearson's correlation coefficient ranging from 0.019 to 1 and then strongly negative for a few metals suggesting that all playgrounds had metals from a common source. Two groups of metal – metal correlations were observed ie one group showing strongly negative and all others were weakly positive.

Keywords: Pollution, Public School, Threshold, Maximum, Heavy Metals, Survey.

Introduction

Humans through their survival activities tend to release large quantities of heavy metals into the environment[1,2] including children playgrounds. When released these metals are distributed amongst all environmental segments in a manner that ends up affecting man and his environment in a negative way. Children are exposed to these contaminants at playgrounds and so attempts to improve playground conditions could be a sure way to reduce childhood environmentally related illnesses[3].

Speciation analysis have been gain the interest of researchers when studying toxicity of metals, their biogeochemistry, functionality of metallic species, risks of metals, bioavailability, bioaccumulation, biodimunition and attenuation of metals in the environment or in organisms[4]. Hence heavy metals have become useful biomarkers in monitoring pollution since they provide information on the concentration and accumulation in the environment. A range of metals found in the dust are harmful both to man and his environment. Pollutants are able to attack specific sites and or organs of humans thereby causing disease conditions due to such exposure[5]. Although there exists considerable number of studies on heavy metals concentration in dust the developing countries have no fair share of knowledge and so information on this subject is found mostly in developed countries whose industrialization dates back in centuries[6].

The nervous and digestive system of children usually becomes affected by metal and organic substance uptake since these systems are at developmental stages. To crown it all, children explore their world around by hand to mouth[7, 8]. Hence there are numerous exposure routes to heavy metals including absorption, food, ingestion of contaminated soil and inhaling of contaminated air[7]. Infant and children are particularly susceptible to neuro-toxicological damage from metal exposure throughout their ongoing intellectual development. The following factors aggravate metal toxicity particularly in children: varieties of heavy metals induce apoptosis[8], carcinogenic transition metals like Cd, Cr, and Ni promote apoptosis along with DNA base modification[9], special vulnerability of children and developing feotus[10], effects depend upon dose and timing of exposure, effect is exacerbated by adverse environmental and social conditions (e.g poverty, poor diet), exposure through unique route, transplacental and breast milk.

Effects of long-term and low- level exposure in children are a cause for concern[11]. Children of Yusho and Yu-cheng patients presented: reduce growth, low birth weight, hyper pigmentation, gingival hyperplasia, eye oedema, dentition at birth and skull calcification[11]. Children living around historic nonferrous smelters in France presented: stomach irritation, blood vessel damages and reduced nerve functions. Detailed toxicological symptoms of some heavy metals have been listed[12].

In the human body, the metallic toxicants attack the proteins notably the enzymes and their toxic effects are cumulative and cause slow poisoning of the system over a period of time[13,14]. Heavy metals have been implicated in the upsurge of liver and kidney diseases, and is believed to be responsible for a high proportion of mortality caused by kidney and liver morbidity[3,16], pains in bones[17], mutagenic, carcinogenic and teratogenic effects[3,18-20], neurological disorders, especially in the foetus and in children which can lead to behavioral changes and impaired performance in IQ tests[21,22].

Materials and Methods

Study area: The area of study, Owerri metropolis, lies between latitude 5.48^o North and longitude 7.03^o Imo State, southeast Nigeria. This falls within the humid tropics and lies within one of the three local government areas (LGAs) that make up Owerri city, the capital of Imo state of Nigeria usually referred to as the eastern heartland. The predominant parent material underlying Imo State from which most of the soils are formed are the coastal plain sands popularly known as “Acid Sands” [23]. Soils of the study site have been classified as Typic Paleudult/Dystric Nitosol for Owerri and Orlu towns; and Plinthic Tropudult/Plinthic Acrisol for Okigwe town[24]. They are acidic, have low cation exchange capacity, low base saturation, and low fertility status, usually suffering from multiple nutrient deficiencies[25]. Soil fertility is maintained by fallow, whose length is fast reducing due to high demographic pressure[26]. Farming is a major economic activity even in urban areas where patches of subsistence farms are found.

This area is under heavy traffic all year round since it is home to the biggest and modern market and the seat of state government. Even though there are no industries, connecting roads to neighboring states pass through the metropolis thereby increasing traffic volume.

Solid mineral deposits abound all over the metropolis council area such as phosphate, limestone, kaolin, galena, stones and granites, silica sand[26]. The council is also blessed with agricultural products like cassava, yam, maize, livestock, fruits examples - oranges, pineapple, banana, pawpaw which provide the raw materials for the agro-based industries[27].

There exist business and investment opportunities existing in the capital city of Owerri metropolis Council[23]. The climate of Imo State is typically humid tropics characterized by 9 months of rainfall (rainy season) and 3 months of dryness (dry seasion). Rainfall distribution is bimodal and averages about 2500 mm per annum, while the mean annual temperature ranges from 28 to 37[27].

Soil sample collection and treatment: Soil samples at 0-5 cm, 5-12 cm and 12-24 cm depths were collected in the months of June and September (rainy season), in January and March (dry season), of 2012, 2013 and in February (dry season) and August (rainy season) of 2014. Elbassam[28] reported that maximum contamination of heavy metals takes place in top layers of soil; hence the use of sub soil was accepted as most appropriate. At each sampling site, a “W” shaped line was drawn on a 2 x 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 for rainy season samples. These samples were sun/air dried for two days, and then oven dried at 50^{o}C for 2 days; ground in acid-washed porcelain mortar with pestle. The samples were sieved through a 2 mm sieve in order to normalize variations in grain size distributions. The samples were stored in polythene containers with caps for further analysis[6].

Determination of total heavy metal: The total heavy metal concentration in all 36 soil samples digests was determined for manganese, cobalt, nickel, copper and zinc were determined using A ANALYST Perkin Elmer 400 Atomic Absorption Spectrometer. Quantification was carried out using appropriate calibration curves prepared in the same acid matrix with standard metal solutions for atomic absorption spectrophotometer[25].

Chemical Speciation of Playground Soil Samples: The extraction was carried out with an initial mass of 1.0 g dried soil in polypropylene centrifuged tube of 50 ml capacity. The modified method[29] which fractionates the soil into six geochemical fractions was used. $Mg(NO_3)_2$ was used instead of $MgCl_2$ to avoid an increase in the solubility of heavy metals within the soil solution matrix.

Sequential Extraction procedure: 1 g of the air dried soil sample (2 mm sieve) were mixed with 10 ml of de-ionized water with continuous agitation for 1 hour. The residue was shaken at room temperature with 16 ml of 1M $Mg(NO_3)_2$ at pH 7.0 for 1 hour. Residue from 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 3.5 M CH_3COONH_4 was added as an extracting agent. 25 ml of 0.05M Na_2EDTA was added to the residue in (F3) above ad shaken for 6 hours and centrifuged. The residue from (F4) above + 17.5 ml H_2O_2 + HCl 0.1M + 17.5 ml CH_3COONH_4 3.5 M, shaken for 1 hour. Residue from (F5) 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 revolutions per minute (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[30].

Quality Control and Quality Assurance: Laboratory glass wares and plastics used had to be washed with high grade laboratory detergent, rinsed with deionized water then soaked overnight in 10% nitric acid before rinsing the second time with double deionized water.

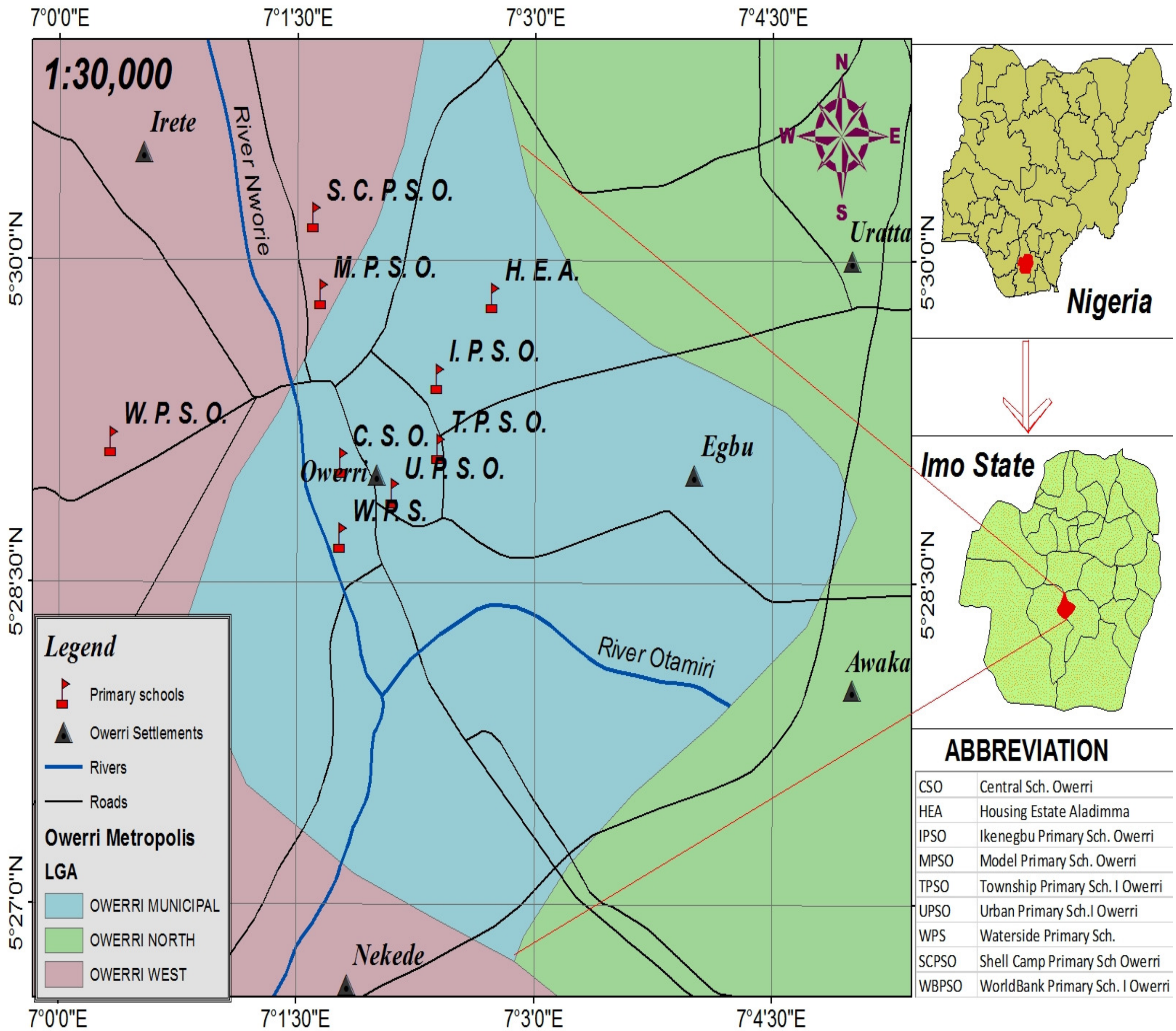

Figure-3.1
Map of study area showing sampling sites as red flags

Reagents: Analytical grade reagents and chemicals such as nitric acid (HNO_3) 6.5% v/v (suprapur),hydrochloric acid, HCl (suprapur), sodium sulphate (Na_2SO_4) and potassium hydrogen carbonate ($KHCO_4$) were purchased from Merck (Fin lab. Owerri). Working standard of metal for AAS were purchased from Fluka (Buchs, Switzerland) and prepared by diluting a concentrated stock solution of 1000 mg/dm^3 in 0.25 mol dm^3 of HNO_3.

Statistical Analysis: Data was analyzed using SPSS software, version 17 where appropriate. Descriptive statistics such as mean and standard deviation were calculated using coupled Microsoft Excel in which standard deviation (SDV) was calculated using Equation-1 while Coefficient of variation was calculated using Equation-2.

$$SDV = \sqrt{\sum \frac{(xi-\mu)^2}{n-1}} \quad (1)$$

$$CV = \frac{SDV}{xi} \times 100 \quad (2)$$

Variability ranking was characterized as little variation (CV % < 20), moderate variation (CV % 20 – 50) and high variation (CV % > 50) according[28].

Table-1
Standard values of various metals used to compare results in the this thesis

Metals	ULCMCB (mg/Kg)	[31,32] WHO, 2001; QTV (mg/Kg) Mostert, 2009		SRL(mg/Kg)[27],[31]	C_b (mg/Kg)
		DCC	CP		
Mn	0.88	1500	3000	25.00	556.59
Co	5.73	-	-	8.00	-
Ni	5.53	600	600	40.00	31.56
Cu	0.75	1000	2000	30.00	65.38
Zn	1.99	90.00	14000	90.00	141.99

DCC= Day Care Centers; CP= Children Park; ULCCB= Upper Limit Concentration of Metals in Children's Body; QTV= Queensland Threshold Value; WHO= World Health Organization 2001; SRL= Standard Regulatory Limit; C_b= Background Concentration of Metals in Soil.

Results and Discussion

Values of total extractable metals fractions (Table-2) for the three years were calculated by taking the sum of fractions for dry season for the three years, and then repeating same for the rainy season. These were used in assessing playground pollution and risk for children using these playgrounds.

Spatial variation of metal in playgrounds: Table-2 shows a summary of the concentrations of Mn, Ni, Co, Cu and Zn in playgrounds soils from Owerri metropolis. It is obvious that mean concentrations of Mn, increased systematically from HEO (13.56 ± 2.23 mg/Kg) to TSO (160.42 ± 46.95 mg/Kg) then a decrease to UPS (19.29 ± 14.67 mg/Kg). Mn amongst the nine playgrounds exhibits high standard deviations with a coefficient of variability categorized as high and was highest for dry season. The concentration of Co, ranged from SCP (5.31 ± 2.18 mg/Kg) to TSO (10.48 ± 6.46 mg/Kg) and a mean value slightly above background concentration. These were however the lowest concentrations of metals in the dry season with coefficient of variability of 40.27%.

The concentration of Ni across playgrounds ranged from MNO (21.86 ± 7.40 mg/Kg) to was WBP (73.82 ± 26.69 mg/Kg). Ni showed lowest variability in the dry season.

The highest concentration for Cu was detected at site SCP (124.43 ± 16.52mg/Kg) and the lowest at UPS and HEO (36.64 ± 24.72mg/Kg).

The concentrations of Zn ranged from MNO to UPS (83.60 ± 55.27 mg/Kg) to SCP (301.85 ± 44.36 mg/Kg). In the dry season metal concentrations followed the order: Mn> Co> Cu>Zn>Ni while variability was in the order: Zn>Mn>Cu> Ni>Co.

In the rainy season the concentrations of Mn, Ni, Co, Cu and Zn in playgrounds soils from Owerri metropolis were obviously lower than mean concentrations in the dry season. Mn, Ni, Co, Cu and Zn all showed mean values lower than background values. Metal concentrations followed the order: Zn> Cu> Ni>Mn>Co with variability categorized as high for Zn, Cu, Ni, Co except Mn that showed medium variability.

Percent recovery: Values of percent recovery for the present study are shown on Table 3 alongside the mean total heavy metal and mean sum of metals species that were used in the calculation.

Comparison with literature data also revealed that our data for metals in playground soils of Owerri municipality are much lower than those presented in Czech Republic and Italy, indicating that soils of children playgrounds within the municipality are not contaminated by heavy metals [32]

Comparing heavy metals concentrations with The occurrence and concentration of heavy metals in playgrounds of nine public schools located within the Owerri Municipal area in comparison with World Health Organization (WHO) threshold values / Queensland threshold values (QTV) and background values (BkV)[33], for metals in children playgrounds and other standard found in literature were equally compared with data from the present study.

However metals concentrations at all playgrounds were dwarfed by Queensland threshold values.

Schools, CSO and TSO had elevated metal concentrations when compared to background values. The two schools are located within commercial centers and surrounded by petrol stations and heavy traffic.

Table-2
Mean concentrations of total extractable metals in the playground soils for three years

Playground	Total extractible metals in dry season					Total extractible metals in rainy season				
	Mn	Co	Ni	Cu	Zn	Mn	Co	Ni	Cu	Zn
HEO	13.56 ± 2.23	7.04 ± 1.59	71.97± 44.20	36.64± 24.72	106.40± 110.58	9.32± 10.54	1.4± 1.81	6.23± 9.91	12.89± 11.03	106.40± 110.58
MNO	19.29± 14.67	5.99± 1.99	21.86± 7.40	46.87± 27.22	83.60± 55.27	11.31± 14.36	1.24± 2.03	9.14± 14.68	12.16± 9.03	83.60± 55.27
SCP	70.58± 87.98	5.31± 2.18	60.07± 7.46	124.43± 16.52	301.85± 44.36	23.75± 38.48	3.97± 6.55	31.53± 52.85	47.13± 67.56	301.86± 44.35
CSO	98.51± 57.24	8.34± 3.49	52.03± 18.66	60.33± 9.12	129.75± 41.70	10.38± 15.69	9.08± 14.22	7.53± 11.78	12.14± 18.21	129.75± 41.70
TSO	160.42± 46.95	10.48± 6.46	61.02± 15.68	50.39± 52.59	172.88± 53.69	11.1± 15.69	4.98± 6.54	20.81± 34.92	22.20± 7.39	172.88± 53.69
WSP	132.89± 65.55	9.11± 1.22	55.72± 22.67	50.62± 41.25	225.21± 18.98	9.50± 13.77	5.04± 7.59	11.45± 15.65	14.98± 2.34	225.21± 18.98
WBP	125.43± 106.16	8.45± 7.80	73.82± 26.69	37.04± 27.11	175.06± 45.31	15.55± 13.52	3.47± 4.48	25.67± 37.11	7.36± 6.80	175.06± 45.31
IKS	13.56 ± 2.23	7.04 ± 1.59	71.97± 44.20	36.64± 24.72	106.40± 110.58	8.79± 6.78	4.69± 6.42	19.83± 24.18	69.06± 35.86	188.33± 5.15
UPS	19.29± 14.67	5.99± 1.99	23.88± 7.30	46.87± 27.22	83.60± 55.27	11.70± 13.24	4.43± 5.17	21.51± 6.14	75.29± 45.44	170.93± 50.97
Mean	99.14	9.61	55.103	60.183	172.67	12.379	4.25	17.079	30.359	76.743
Min	19.29	5.31	21.86	37.05	83.61	8.79	1.24	6.23	7.36	20.47
Max	162.23	16	73.82	124.43	301.86	8.79	9.08	31.53	75.29	345.17
SDV	53.58	3.88	15.61	25.877	65.066	4.705	2.307	8.856	26.45	103.64
CV	54.05	40.27	28.41	43	37.67	37.96	54.35	51.81	87.12	135.05

Values reported as mean ± nSDV for n=3

Table-3
Total heavy metals, sum of metal species and percent recovery values of metals

Metals	Mean total heavy metal concentration (mg/kg)		Mean sum of metal species (mg/kg)		Seasonal recovery (%)		Mean recovery (%)
	Dry Season	Rainy season	Dry Season	Rainy Season	Dry season	Rainy season	
Mn	77.90	14.17	99.14	12.38	78.58	144.58	111.58
Co	7.51	12.67	9.61	4.25	78.14	298.11	188.13
Ni	42.95	30.37	55.10	17.08	78.00	177.81	127.91
Cu	59.36	27.88	60.18	30.36	98.64	91.83	95.24
Zn	149.67	98.54	172.67	76.74	86.70	128.40	107.55

Percent recovery is usually regarded as a fundamental parameter for method validation[33]. Since it was not originally included in the research design, recovery values were calculated in accordance with the concept of the GLP guidelines for analytical method validation. The term used for percent recovery there is accuracy. Accuracy should be reported as percent recovery by the assay of known added amount of analyte in the sample or as the difference between the mean and the accepted true value together with the confidence intervals. There was no spiking and therefore recovery here is majorly method specific in which the use of a large number of data, and modern instrument with internal standard all made it possible for percent recovery to be calculated relative to the method of interest[34].

Smaller percent recovery means larger bias is affecting the method and therefore; lowers the trueness. For this study, percent recovery values where generally high, ranging between 78-98.4 and 91-298.11 for dry season and rainy season respectively. It is not a high recovery but rather a recovery near 100 % (e.g. 80-110 %) that gives confidence[35]. Fortunately here all mean values of percent recovery were above 95. Some important issues of recoveries near 100% is that it is an indication of an almost complete mass balance of the recovery standard. Basically percent recovery was interpreted that there was consistency in the analysis in terms of (1) complete extraction, (2) minimal losses, and (3) the analytical system. However Manganese in the soil is different, the solubility of each of the metals relative to Mn may be significantly different from the concentration of the metal in the Mn oxide particles. There are substantial gaps in knowledge of Mn in the bulk soil due to difficulties in studying the typically small, low abundance, low-crystallinity Mn oxides[36]. And so neither total heavy metals extraction nor speciation analysis may account for all the metals in the soil. This could be reasons for variations in percent recovery. Manganese oxides may act as scavengers of trace metals[37], therefore other metals recovery values are influenced by the presence of Mn.

Comparison of metals in playground soils with literature values: Comparison of metals in playground soils studied in this work with literature values was done to obtain information on both the level of pollution and methods of analysis used. Five researchers were relevant to the present studies and have reported metal contents of children playgrounds[38,39]. Some results found in are literature are tabulated in table 4 alongside results from this work.

Table-4
Comparison of playground soil metals studied with literature values elsewhere

Metal	Queensland[30]	Madrid Miguel[38]		HongKong, 2002[39]	HongKong 2005 Nusery school Lam et al.,[39]	Beijing 2005 Chen et al.,[11]	This study: Owerri 2015	
Na	8.71	6.9	5.7	-	-	-	-	
K	2231	2436	1944	-	-	-	-	
Mg	2264.74	3449	3374	-	-	-	-	
Ca	2161.26	27077	-	-	-	-	-	
Cd	0.71	0.19	0.14	7	3.3	8.52	-	
Mn	125.92	285	249	518	218.5	-	46.04	*55.79
Co	3.20	3.6	3.2	-	-	-	10.09	*6.93
Ni	8.71	6.9	5.7	-	-	22.2	36.91	*36.09
Cu	14.54	20	14	143	246	71.2	43.58	*45.24
Zn	58.58	78	50	188.3	2267	87.6	124.11	*124.60
Pb	9.76	38	22	77.3	152.7	66.2	-	-

*Values determined from speciation

About eighty percent (80%) of these studies focus on Pb, Cd, Cu and Zn, with almost all emphasizing on Pb and Cd. Amongst the few studies found in Nigeria only one of them considered Pb on children's playgrounds[40].

The most comprehensive study was that of Mostert[32] followed by that of De Minguel et al.[38]. The present study is perhaps the third in terms of number of metals studied. They used different analytical techniques ICP (inductively coupled plasma) which enabled a wider range of metals to be analyzed unlike the present study. Though different instruments have been used, the units of concentrations of metals determined gave some level of confidence for comparison. Toxicity of metals may be the most common reason for choice of analysis of these metals[41, 42].

In this study, it can be clearly seen that Na, K, Mg and Ca could be considered insignificant when compared with studies at Queensland playground, by Mostert[30]. Though Mn showed highest concentration of 55.79 mg/kg, it was still lower than Mn values for the rest of the studies.

The lowest value of cobalt compared well with values with all the researchers tabulated. Nickel value was more than one half of all other studies. Certainly this study showed higher values of nickel compared to other studies. Values of 246 mg/Kg of Copper per kg of soil for Nursery School playground at Hongkong have been reported[38] and this was about five times the value in this study. However this study is in agreement with most studies reported here. The concentrations of zinc for all studies here showed significant variation. The value of zinc (124.60 mg/kg) was third to value reported by Cheng et al.[43]. Zinc was perhaps the highest metal for playgrounds studied. All other Zinc values had a comparable range of 50 mg/Kg to 188.3 mg/Kg as per literature values. Many researchers have suggested that zinc sources are common in urban setting and therefore account for elevated levels in playgrounds.

The general trend for most published results (Table-4) is a decrease with time. This is because of the awareness of heavy metal effect on children being fought through mitigation processes such as change of playground cover and some other measures.

There was however no results for comparison with other metals within Nigeria as only Pb and Cd metals have been studied in playgrounds, but unfortunately these two metals were not studied in the present work.

Correlation matrices of mean total extractible metals within playgrounds: In order to identity playgrounds with common metal input and metal stability Pearson correlation was carried out for metal concentrations within playground. Mn correlated strongly with almost all metals in all playgrounds. Strong association reflects stability of metals in soil playgrounds[44] and common source of metal input into the playground[45, 46].

Table-4 shows the correlation grouping according to metal – metal being either strongly positive or negative. Amongst the sites investigated it could be observed that Mn showed a weakly positive association with cobalt in some five playgrounds. Though Mn showed strong associations with all metals, a negative association (> -0.6) with Cu at (p > 0.5) was observed at all playgrounds. This could be due to the fact that Mn was a product of natural processes occurring in playgrounds.

Mn-Zn had no clear trend except that HEO, MNO, SCO, TSO and IKS playgrounds showed weak positive correlations. Through not in playground soils many researchers have reported significant strong and positive associations for Co-Ni[45]. There was a weak positive association for Co-Ni observed in all playgrounds studied. Co – Cu showed strong positive associations at HEO, SCP, SCO, WSP, WBP and UPS while Co-Zn had a strong positive correlation at HEO, SCP, SCO, WBP and UPS. It was observed that Ni-Zn had strongly positive associations at NNO, TSO, and IKS.

In terms of metal stability in soil, groups with larger member of playgrounds reflected stability of the metals. Therefore the decreasing order of metal stability was observed to be Nn>Ni>Cu>Co>Zn

The stability of Mn was reported aggred with other researches who proposed that Mn originated from natural geochemical processes while low stability of Zn was possibly a product of human activity[49].

Conclusion

A significant amount of the heavy metals were found in non residual fraction in the soils studied. Soils in public schools playgrounds within Owerri metropolis are moderately contaminated. The mean concentrations of the heavy metals were generally within and below permissible limits recommended by WHO standards and Queensland standards for children's playgrounds. The heavy metals investigated could potentially pose toxicity problems to children who make use of these playgrounds over long periods. The findings of this study therefore suggest that there is a need for regulating the concentrations of heavy metals in soil playgrounds. One way recommended is that soils could be periodically monitored and results used to develop children playgrounds soil standards. Playgrounds by implications could be sighted at residential areas only rather than the current practice where the sighting of schools is strictly the choice of the proprietor or the government agency in charge.

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Table-5
Pearson's correlation matrix for total extractible metal within playgrounds

	Mn	Co	Ni	Cu	Zn		Mn	Co	Ni	Cu	Zn		Mn	Co	Ni	Cu	Zn
HEO						SCO						WBP					
Mn	1.000					Mn	1.000					Mn	1.000				
Co	0.290	1.000				Co	0.290	1.000				Co	0.290	1.000			
Ni	0.126	0.371	1.000			Ni	0.258	0.311	1.000			Ni	0.268	0.300	1.000		
Cu	-0.090	0.582	0.533	1.000		Cu	-0.740	0.582	0.594	1.000		Cu	-0.690	0.582	0.599	1.000	
Zn	0.221	0.719	0.037	0.063	1.0	Zn	0.228	0.719	0.038	0.568	1.0	Zn	0.027	0.719	0.037	0.587	1.000
MNO						TSO						IKS					
Mn	1.000					Mn	1.000					Mn	1.000				
Co	0.082	1.000				Co	0.066	1.000				Co	0.032	1.000			
Ni	0.436	0.277	1.000			Ni	0.436	0.344	1.000			Ni	0.661	0.332	1.000		
Cu	-0.671	0.038	0.525	1.000		Cu	-0.721	0.038	0.525	1.000		Cu	-0.654	0.238	0.589	1.000	
Zn	0.223	0.029	0.819	0.160	1.0	Zn	0.204	0.019	0.819	0.577	1.0	Zn	0.209	0.139	0.819	0.568	1.000
SCP						WSP						UPS					
Mn	1.000					Mn	1.000					Mn	1.000				
Co	0.290	1.000				Co	0.290	1.000				Co	0.290	1.000			
Ni	0.249	0.302	1.000			Ni	0.258	0.331	1.000			Ni	0.281	0.390	1.000		
Cu	-0.820	0.582	0.550	1.000		Cu	-0.610	0.482	0.498	1.000		Cu	-0.710	0.582	0.623	1.000	
Zn	0.019	0.719	0.037	0.430	1.0	Zn	0.078	0.719	0.037	0.553	1.0	Zn	0.086	0.719	0.037	0.479	1.000

Table-6
Groups of playgrounds according to Pearson's correlation coefficients

Metal-Metal	Mn-Co	Mn-Ni	Mn-Cu	Mn-Zn	Co-Ni	Co-Cu	Co-Zn	Ni-Cu	Ni-Zn
	HEO	HEO	HEO	HEO	HEO	HEO	HEO	HEO	_
	_	MNO	MNO	MNO	MNO	_	_	_	MNO
	SCP	SCP	SCP		SCP	SCP	SCP	SCP	_
	CSO	CSO	CSO	CSO	CSO	CSO	CSO		CSO
Playgrounds	_	TSO	TSO	TSO	TSO	_	_	TSO	TSO
	_	WSP	WSP	_	WSP	WSP	_	WSP	_
	WBP	WBP	WBP	_	WBP	WBP	WBP	WBP	_
	_	IKS	IKS	IKS	IKS	_	_		IKS
	UPS	UPS	UPS	_	UPS	UPS	UPS	UPS	
Summary of associations	Weakly positive	Weakly positive	Strongly negative	Weakly positive	Weakly positive	Weakly positive	Weakly positive	Weakly positive	Weakly positive

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