Risk associated with heavy metals in children playground soils of Owerri metropolis, Imo State, Nigeria

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ABSTRACT

Despite recording the worst heavy metal disaster involving children, there is still scarcity of information on risk assessment of playground soils in Nigeria. In this study, thirty-six soil samples at 0-5 cm depth were collected from nine playgrounds in Owerri metropolis during the dry and rainy seasons. Five heavy metals were fractionated into six chemical fractions using a modified sequential extraction scheme and mean concentrations quantified by AAnalyst 400 Perkin Elmer AAS. Predictive risk models were used to obtain information about the risk of metals contamination to children using these playgrounds for longer periods. These reveal that there were no significant differences in the mean values of bioconcentration factors of all five metals in the various playgrounds for the two years of data. Even though risk values for both dry and rainy season followed the same trend, it was observed that the Zinc showed highest bioconcentration factors (1.6), average daily dose (230.08 mg/kg/day) and risk (5095593 mg/kg/6 years). Overall, playgrounds UPS, TSO and SCP had the highest mean risk values, respectively. Though with no clear trend, mobility factors showed a weak and positive correlation with risk. Children in playgrounds of public schools within Owerri metropolis could, therefore, be at risk of Mn, Cu and Zn toxicity problems as projected risk values were high for all studied playgrounds. This assessment could help identifying playgrounds with urgent need for heavy metals reduction goals, consequently contributing to preserving children’s health.

Keywords: Bioconcentration, Metal fractions, Predictive, Models, Risk
1. INTRODUCTION

According to European Environment Agency (2003) there is a need to recognize and assess risks to children from environmental hazards. Children are at most risk from environmental hazards due to a number of factors (Maiko et al., 2014; De-Miguel et al., 2007; WHO, 2003). Children have been identified to be worse affected in many of the world notable cases of heavy metals poisoning (Verla et al., 2014; Horsfall, 2011; Zahir et al., 2005; Schwartz, 1994). Accumulations of heavy metals in the environment have led to hazards on humans (Horsfall, 2012; Adekunle et al., 2003). Urbanization and industrialization are encouraging factors to the ever increasing chances of child exposure to heavy metals. Therefore, there is an urgent need to assess risks to children arising from their playgrounds. As a result of a number of factors, including genetics, host state such as immune system, immaturity and exposure pathways (WHO, 2003) children are more at risk from environmental hazards. According to America Academy of Pediatric Committee on Environmental Health (2003), children are on vulnerability to metal toxicity. This is dependent on many factors including the fact that children’s nervous and digestive system are still developing (Bearer, 1995); children ingest more dust than adults and they have large surface to volume ratio (Popoola et al., 2012; De-Mingeul et al., 2007).

Most research focused on the concentrations of the heavy metals on environment, except for a few that have investigated metal concentrations in playgrounds (Popoola et al., 2012; Aliyu et al., 2009; Wong et al., 2007; Wong and Mak, 1997, Li et al., 2001). A few studies have reported risk assessment with respect to heavy metals due to consumption of fruits (Orisakwe et al., 2012). However, Harley (1995) reported risk assessment of heavy metals in contaminated soils. Studies based on heavy metals risk on children playground are scarce (De-Miguel et al., 2007) while the few available are limited to the metal lead (Aliyu et al., 2009). A risk-based exposure of children to trace metals in playgrounds in urban Madrid was conducted by De Miguel et al., 2006.

Results reveal that ingestion of soil particles was the highest contributor to the overall figure of risk followed by dermal adsorption. Inhalation of re-suspended particles through the mouth and nose was almost negligible when compared to the other exposure pathways. However reports of risk studies on intake of water with significant amounts of metals, particularly arsenic, might result in varying cancers, thus numerous researches were conducted on human health risk assessment relating to metals (Li et al., 2001; Ljung, 1999; De-Miguel, 2006). Risk assessment refers to determination of hazard, exposure, and finally risks values (Biney et al., 1994). It is a predictive model that gives an overall idea of the possibility of harm arising in the future due to some pollutant in the environment. Simple and complicated mathematical models for heavy metals risk assessment have been developed and used (Verla et al., 2012).

Bioconcentration factor (BCF) is one simple model that is useful as a measure of the extent of pollutant accumulation by an organism above the environmental concentration of the pollutant (Horsfall and Spiff, 2013). Bioconcentration factor is mathematically expressed as

\[ BCF = \frac{[C]_{org}}{[C]_{en}} \] ………… (1)

\([C]_{org}\) is concentration of pollutant in the organism; \([C]_{en}\) is concentration in the environment. BCF relates to accumulation of a pollutant in an organism due to direct uptake from the

-50-
environment. In this study, a direct uptake is considered to be the metal ingested by children due to pica activities. Most children in Nigeria are likely to perform pica activities during play there by ingesting fine soil particles with high concentrations of toxic metals. Surface soil has been used for metal toxicity assessments following Elbassam (1977) and Mohr (1979) reports that maximum contamination of heavy metals takes place in top layers of soil.

One complicated risk assessment model is an average daily dose (ADD). It was used to assess exposure to metal-contaminated dust by ingestion in terms of non cancer toxic (chronic) risk of circuit board recycling workers and the general public including children living in Guniyu (Wang and Wu, 2007). Risk was calculated based on equations detailed in USEPA’s Exposure Factors Handbook (Rodriguez-Proteau, 2005). Average daily dose (ADD) was determined by the following equation:

\[
ADD_{\text{ingestion}} = \frac{C_w \times IR \times ABS \times EF \times ED}{BW \times AT} \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ (2)
\]

*Cw* is the mean heavy metal concentration (mg/kg) in dust, while conservative estimates of dust ingestion rates, *IR*, were chosen for children (200 mg/day) (Rodriguez-Proteau et al., 2005) and average body weight (BW), of 15 kg for children (USEPA, 2004). In this study, exposure frequency, (EF) 350 days/year; exposure duration, (ED) 6 years; while average time, (AT) 2190 days according to Bi et al., (2007) and Lansdown, (1986). Since many metals are usually taken in same dust at same time metal absorptivity (ABS), was assumed to be unity (U.S. EPA 1997).

Assessment of metal contents in soils and the risks due to exposures are important in environmental management decisions and overall protection of human health (Biasioli et al. 2007; De Miguel et al. 2007; Mielke et al. 2010). Risk is a mathematical concept, which refers to the likelihood of undesirable effects resulting from exposure to a pollutant. By definition, risk is the probability that a hazard will cause an adverse effect under specific exposure conditions. However, risk has been defined for the purpose of this paper as in equation (3).

\[
Risk = Hazard \times Exposure \ time \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ (3)
\]

Hazard is defined as the capability of a substance to cause an adverse effect (Chambers et al. 2002). Conversely, safety may be defined as the practical certainty that adverse effects will not occur when the substance is used in the manner and quantity proposed for its use (Horsfall and Spiff, 2012). As exposure increases so does the probability of harm, whereas a reduction in exposure reduces the risk.

Mobility describes the relative ease of movement of a metal in soil. Since metals exist in varying forms in the soils researchers have shown that some fractions are more mobile than others. Mobility is directly related to bioavailability (Horsfall and Spiff, 2005). Bioavailability is the extent to which a contaminant in a source is free for uptake by an organism. Children will not be exposed unless they come in close proximity to the media containing the contaminant. While other exposure routes like absorption, imbibing and inhalation of the contaminated soil exists, ingestion is considered a major route (Orisakwe et al., 2012; Otchere, 2003).

Hence the need for identifying and quantifying heavy metals and their contamination status cannot be overemphasized. Further risk quantification is of uttermost important for children’s playground since these metals accumulate overtime and the awareness regarding playgrounds safety is still low. The study presents bio-concentration factors-BCF, average daily
dose-ADD and risk estimates as useful tools for evaluating heavy metals risk on children’s playground. Equally other information for a better understanding of the complex dynamics of the heavy metals risk amongst the playgrounds has been discussed.

2. MATERIALS AND METHODS

2.1. Study area

Owerri metropolis lies within latitude 5.48° North and longitude 7.03°, Imo State, southeast Nigeria. It is one of the three local government areas of Owerri city, the capital of Imo state of Nigeria set in the heart of the Igbo land. Its population is about 215,038 as of 2006 census. The climate is typically humid tropics with 9 months of rainfall (rainy season) and 3 months of dryness (dry season) (Ijeoma and Arunsi, 1990). Rainfall distribution is bimodal and averages about 2,500 mm per annum, while the mean annual temperature ranges from 28 to 37 °C (Onweremadu et al., 2011). The predominant parent material is the coastal plain sands known as “Acid Sands” (Orajaka, 1975). Most of the metropolis has a flat topography and elevation of 159 m.

Table 1. Co-ordinates of the sampled schools playgrounds in Owerri metropolis.

<table>
<thead>
<tr>
<th>S/N</th>
<th>CODE / Name of school</th>
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<th>Longitude</th>
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<tr>
<td></td>
<td></td>
<td>DD</td>
<td>MM</td>
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<tr>
<td>1</td>
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<td>IKS-Ikenegbu Primary school</td>
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<td>MNO-Model P/S New Owerri</td>
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<td>TSO-Township P/S I Owerri</td>
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<td>UPS-Urban P/S I Owerri</td>
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<td>9</td>
<td>SCP-Shell Camp P/S Owerri</td>
<td>05 29</td>
<td>58.0</td>
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</table>
2. 2. Sample collection and pretreatment

Out of 25 schools, nine playgrounds were selected randomly to reflect the entire playgrounds which were used in this study. Also Playgrounds were selected to reflect spatial variability and traffic/commercial influence associated with each zone, as well as differences in land used within an urban setting. Three different sampling sites were taken from each playgrounds. Surface soil or dust samples at 0-5 cm depth were collected in the months of June (rainy season) and in January (dry season), of 2012 and 2013. 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 clean polythene containers. Samples were sun/air dried for two days, and then oven dried at 50 °C for hours; ground in acid-washed porcelain mortar with pestle. The soil samples were pooled together, treated to coning and quartering to obtain a small laboratory sample. The samples were sieved through a 200 mm sieve size in order to normalize variations in grain size distributions. The samples were stored in polythene containers with caps for further analysis (Jaradat et al., 1999).

2. 3. Chemical speciation of soil samples

1.0 g dried soil in polypropylene centrifuged tube of 50 ml capacity was subjected to a modified method of Tessier (1979), according to Finzgar et al., (2007), by fractionating the soil into six geochemical fractions, was used. Mg(NO₃)₂ was used instead of MgCl₂ to avoid an increase in the solubility of heavy metals within the soil solution matrix. The extraction was carried out on triplicates. Water soluble fractions (F₁) were extracted with deionized water, followed by the Exchangeable phase (F₂) in which the residue in (i) was extracted using 1 M Mg(NO₃)₂ at pH 7.0 for 1 hour. Oxidized phase (bound to organic matter) (F₃) fraction was extracted from residue of (ii) in which 10 ml of 8.8 M H₂O₂ and 6 ml of 0.02 M HNO₃ were added and shaken for 5 plus 1 h, respectively at 98 °C. The extracting agent here was 10 ml of 3.5 M CH₃COONH₄. Acid Soluble Base (metals bound to carbonates) (F₄) was extracted with 25 ml of 0.05 M Na₂EDTA added to the residue in (iii). The Reducible Phase (bound to Fe–Mn oxides) (F₅) was extracted from Residue in (iv) above with N HCl 0.1 M + 17.5 ml of 3.5M CH₃COONH₄, Reducible Phase (metals bound to silicates and differential materials) (F₆), was extracted from (v) above using HCl – HNO₃/HF (0.35:12 w/v solid solutions) in acid digestion, Teflon cup. After each successive extraction, the sample was treated, as reported by Horsfall and Spiff, 1999, Wilson et al., 2006; Finzgar et al., 2007; Osakwe and Egharevba, 2008; and Osakwe, 2010.

2. 4. Quality control

All reagents and chemicals used in this work were of purest grade available. Nitric acid (HNO₃) (suprapur), HCl (suprapur), sodium sulfate and potassium hydrogen carbonate were purchased from Merck (Fin lab. Owerri), while double distilled water was used for heavy metals analyses; standard metal solutions for atomic absorption spectrophotometer were purchased from Fluka (Buchs, Switzerland through Spring Board Laboratories Ltd. Awka, Anambra State, Nigeria.

Mean, standard deviation, and range were calculated using coupled Microsoft Excel 2009 + Analyse-it® v2.2 (2010). Standard Deviation (SDV) was calculated and statistical significance was described at P>0.05.
3. RESULTS AND DISCUSSION

3.1. Bioconcentration factors (BCF)

Results of BCFs, shown in Figs. 1 and 2 were calculated using the upper limit of normal concentration of metals in children (ULNCC), 0.88, 5.73, 5.53, 0.75 and 1.99 mg/kg for Mn, Co, Ni, Cu, and Zn, respectively, (WHO 2006) and total heavy metals concentrations, as determined in this work. BCFs were observed to be generally low. Except for cobalt at WBP and SCP, all other metals had BCF bellow 1. In 2012, maximum BCF was recorded for cobalt (1.5) at SCP, copper showed lowest BCF ranging from HEO (0.01) to TSO (0.03). The order of decreasing BCFs for all nine playgrounds was:

SCP>MNO>WBP>IKS>HEO>UPS>CSO>WSP>TSO

when ranked metals in order of decreasing BCFs, for 2012, metals showed that Co>Ni>Mn>Zn>Cu. Fig. 1 shows that cobalt had the highest BCF for all nine playground whereas Zn and Mn compared well with each other and were both lowest at each playgrounds.

In 2013, the highest BCF was observed for cobalt (1.64) at SCP, while copper (0.01) was the lowest at the same playground. Playgrounds ranking in order of decreasing BCF in 2013 showed that SCP>HEO>WBP>MNO >IKS >UPS>CSO>WSP>TSO.

Metals showed the following decreasing order of BCF: Co>Ni>Zn>Mn >Cu and in 2013. As shown on Fig. 2, there were significant differences in BCF of TSO and other playgrounds, where Zn was observed to have the highest bio-concentration factor. Generally, there were no significant differences in BCFs of playgrounds between 2012 and 2013.

3.2. Average daily dose (ADD)

Average daily dose (mg/kg/day) indicates the intake of each metal by children using the playground. Values of ADD were calculated using sum of fractions as the metal concentrations in the soil samples. In the dry season 2012, mean ADD showed a range of Co (10.69 mg/kg/day) to Zn (186.58 mg/kg/day). Zinc showed generally high values of ADD across the seasons. This could be due to the fact that zinc metal is used in many commercial goods such as zinc roofs and other packaging materials from where zinc metal gradually fallout or rusted to add to soil. Even though manganese had low values of ADD, its mean (108.80 mg/kg/day) was second to that of Zn. The order of decreasing mean values of ADD for all five metals in the dry season of 2012 was: Zn>Mn>Ni>Cu>Co.
Fig. 1. Bar chart of bio-concentration factors of heavy metals in children of playgrounds (2012)

Fig. 2. Bar Chart of bio-concentration factors of heavy metals in children of playgrounds (2013)
Fig. 3. Bar Chart of average Daily Dose (mg/kg/year) for January, 2012

Fig. 4. Bar Chart of average Daily Dose (mg/kg/year) for June, 2012
**Fig. 5.** Bar chart of average Daily Dose (mg/kg/day) for January, 2012

**Fig. 6.** Bar chart of average Daily Dose (mg/kg/day) for June, 2013
In the rainy season 2012, lower values of mean ADD were observed. Mean ADD values ranged from Ni (0.62 mg/kg/day) to Zn (169.54 mg/kg/day). Cobalt equally had low values of ADD, where HEO, MNO, SCP, CSO, WSP and WBP had values lesser than unity. It was observed that mean ADD showed the following decreasing order: Zn>Cu>Ni>Mn>Co. Figure 1 and 2 show bar charts comparing ADD for metals and the playgrounds studied. Values of ADD for Co are lower than for all metals in both seasons in 2012. This could be due to the fact the cobalt does not find extensive commercial use as other metals. While UPS, IKS WSP and TSO had comparable ADD values, HEO and MNO had the lowest values. Fig. 2 shows that UPS, WBP, WSP and CSO were dominated by zinc, HEO, MNO, SCP, TSO and IKS were dominated by copper (Figures 3, 4).

In the dry season 2013, mean ADD showed a range of Co (7.21 mg/kg/day) to Zn (230.38 mg/kg/day). Zinc showed higher values of ADD for all playgrounds except for WBP where Mn (215.69 mg/kg/day) was higher than Zn (209.5 mg/kg/day). The order of decreasing mean ADD for all five metals in the dry season 2013 was: Zn>Mn>Cu>Ni>Co.

Mean ADD in the rainy season showed the following decreasing order: Zn> Ni >Mn, Cu >Co. Figures 5 and 6 show that comparing ADD, dry season values are lower than for all metals in both dry seasons in 2012 and 2013. Cobalt values are again the lowest for all metals and all playgrounds.

3. 3. Risk assessment

Table 2 shows risk values for children at all nine playgrounds during the dry season and rainy season 2012. In dry season 2012, the calculated mean risk of metals due to ingestion showed that Zn (158602) was the highest. The sequence of decreasing risk for all five metals was Zn>Mn >Ni >Cu>Co. Arranging playgrounds in decreasing risk order for dry season of 2012 was observed to be: UPS>IKS>SCP>WSP>TSO>WBP>MNO>HEO>CSO.

Risk values for dry 2012 were generally lower than for rainy season. Cobalt had an abnormally low risk of 22 mg/kg/6 years, a value considered an outlier. However, the range of mean risk values of metals for rainy season 2012 was Zn (116119 mg/kg/6 years) to Co (1321 mg/kg/6 years). The trend of decreasing mean risk values for the metals was Zn>Cu>Ni >Mn>Co. Except for Mn and Cu, the trend of mean risk value was significantly similar in both seasons in 2012. This may be due the fact that the mean heavy metal concentrations used to calculate risk were the major determining factor.

The calculated risk using mean measured heavy metal concentrations in public schools playgrounds for the dust ingestion pathway for children in 2013 are presented in Table 3. Amongst the five metals the mean risk of Zn was highest for the two seasons in 2013. It was not surprising that Zn showed a consistently high value of risk indicating that the Zn was the most common metal in Owerri metropolis. Children with an average body weight of 15 kg, playing on the playground for six years, are likely going to be affected by serious zinc related toxicity problems. The mean risk for Mn (166243 mg/kg/6 years) was second only to that of Zn. In terms of playgrounds, the mean risk showed a range from HEO (95467 mg/kg/6 years) to SCP (275599 mg/kg/6 years). The trend of decreasing risk at playgrounds was observed as follows: SCP>TSO> UPS>CSO >WSP >IKS> WBP>MNO>HEO.

Risk values showed variations in seasons and between seasons. The mean risk values for playgrounds in dry season of 2012 ranged from MNO (54492 mg/kg/6 years) to SCP (275599 mg/kg/6 years). These values are lower compared to mean risk values for rainy season 2012.
which ranged from CSO (8509 mg/kg/6 years) to UPS (130001 mg/kg/6 years).

**Table 2.** Risk values (mg/kg) of selected heavy metals for 2012

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<th>Risk values (mg/kg) January 2012</th>
<th>Risk values (mg/kg) June 2012</th>
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<td></td>
<td>Mn</td>
<td>Co</td>
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The sequence of decreasing risk of metal toxicity due to ingestion in dry season of 2013 was Zn>Mn>Cu>Ni >Co.

In 2013, the mean risk values in the dry season ranged from CSO (8,509 mg/kg/6 years) to UPS (130,001 mg/kg/6 years). The range in the rainy season showed that lowest risk was at HEO (61,123 mg/kg/6 years) while the highest risk was to SCP (221,870 mg/kg/6 years).

There was a significant difference in mean risk values for both dry and rainy season. These are reflected in both, 2012 and 2013. Therefore, anthropogenic rather than geogenic sources are responsible for metals enrichment of playground within the metropolis.

**Table 3.** Calculated Risk values (mg/kg) of selected heavy metals for 2013.

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<tr>
<th></th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
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3.4. Risk against mobility factors

To further understand the nature of risk of heavy metals toxicity in children’s playgrounds, plots of risk against mobility factors were examined. Figures 7 to 11, show that there was no clear trend for these correlations in dry season of 2012. However Mn and Zn had weak but positive correlations with $R^2$ values of $-6.56$ and $-1.43$, respectively. By implication only 26% and 12% of the Mf was predictive of risk of these two metals. On the other hand, Co, Ni, and Cu had weak negative correlations. Ni showed the highest $R^2$ value for all metals in the dry season of 2012.

In rainy season of 2012 (Figures 12 to 16) plots of Mf against risk for all five metals were weak and positive even though Cu and Zn had low $R^2$ values. Figures 17 to 21 show the Mf against risk for dry season of 2013. While Mf of Mn showed no correlation with risk and $R^2$ value of $-2.36$, a weak negative correlation was obtained for Co. The Mfs of Ni, Cu and Zn correlated positively but weak with the metals’ risk. A trend was observed for the against risk for all metals in rainy season of 2013 (Figs. 22-26). All metals showed a weak positive correlation. $R^2$ values for Mn ($-23.2$), Co ($-15.8$) and Ni ($-29.0$) were higher than for other seasons while Cu (2.44) and Zn ($-5.44$), were low.
Figs. 7-11. Risk of metals against mobility factors in dry season of 2012.

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**Fig. 12-16.** Risk of metals against mobility factors in rainy season of 2012.
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**Fig. 17-21.** Risk of metals against mobility factors in dry season of 2013.

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4. CONCLUSION

Following the above discussion, some values of cumulative risk of the five metals over the six years period are alarming and so constitute major concern for all playgrounds within Owerri metropolis. Though limited to ingestion of the heavy metals in dust, the risk assessment models used in this work provide important basic tools for quantifying and identifying relative health risks of children, making use of studied playgrounds. Some inherent uncertainties include actual exposure duration, ingestion rate, and heavy metal concentrations in the dust resulting from its heterogeneous nature. It is therefore suggested that further studies should address these uncertainties.

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