

Chemical Partitioning of Cadmium, Copper, Nickel, Lead, Zinc, Chromium and Manganese in Dumpsite Soils of Okene Metropolis North-Central Nigeria

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Abstract

Selected heavy metals Cd, Cu, Ni, Pb, Zn, Cr, and Mn were studied in dumpsite soil samples collected from nine dumpsites and a control site at Okene metropolis, Kogi state, north-central Nigeria. Geochemical differentiation into different chemical fractions, using Ma and Rao six-step sequential chemical extraction procedure, was carried out to assess the potential mobility and bioavailability of the heavy metals in the dumpsite soil the wet and dry season using atomic absorption spectrophotometry. The non-residual fraction was found to be the most abundant pools for all the metals across the seasons (wet and dry) and significant amounts of the metals were mostly found in the bioavailable fractions across the sites in the seasons. Thus, these metals would readily be bioavailable to the environment. Overall, Cd and Zn were the most bioavailable metals with Cr and Mn been the least. The generally high values of bioavailability coupled with significantly high levels of association of the metals with the non-residual fraction, indicate that the metals pose environmental risk and hazard Tendencies of health risk for human and livestock due to the spread of the metal pollution from waste dumpsites to agricultural areas is high. Bioaccumulation of cadmium could cause liver, brain and intestinal disorders, irreversible damage to nervous system and brain, protoplasmic poisoning.

Keywords: Bioavailability; Trace Metals; Dumpsites; Soil; Toxicity

Introduction

Pollution is a worldwide problem and its potential in influencing the health of human population is great (Khan and Ghouri, 2011). The impact of pollution on overcrowded cities as a result of industrial effluents and automobile discharge has reached a disturbing magnitude and is arousing public awareness [1]. An excessive level of pollution has caused a lot of damage to human and animal health, also to plants including the tropical rain forests as well as the wider environment [2]. Pollution and subsequent contamination of the environment by toxic heavy metals are of great concern due to their sources, widespread distribution and multiple effects in the ecosystem. Studies have shown that soils of refuse dumpsite contain different kinds and concentrations of heavy metals [3]. In recent times, it has been reported that these elements accumulate and persist in soils at an environmentally hazardous levels [2].

Heavy metals in the soils of Otofure waste dumpsite environment near Benin City, Edo State in Southern Nigeria, were analysed in order to ascertain the level of heavy metal contamination of one of the several sites receiving municipal solid wastes daily using Atomic Absorption Spectrophotometer (Bulk Scientific210 VGP) and they noticed that there was a significant Zn enrichment and enrichment with Ni and V at the topsoil; and Extreme enrichment with Cr, Cd, and lead of the soil at the dumpsite. Also, the soil Contamination factor (CF) indicated a moderate contamination of iron (Fe), manganese (Mn) and copper (Cu), Very High contamination of zinc (Zn), chromium (Cr), cadmium (Cd), lead (Pb), nickel (Ni) and vanadium (V). Pollution Load Index (PLI) showed that Otofure dumpsite is heavily polluted (PLI > 1) by heavy metals in general [4].

Trace metals were analyzed in leachate sample obtained at different locations (Obosi public dumpsite, groundwater and agricultural soil farmland 45.6 km from Onitsha dumpsite) and it was discovered that very high concentrations of Mg (14.20-20.23 ppm), Hg (0.002-2.29 ppm), Pb (0.09-0.65 ppm), Cd (0.001-0.53 ppm), but Al and As were not detected in most of the samples [5].

The concentrations of metals in both soil and vegetables were determined using atomic absorption spectrophotometer (AAS) at Kuru Jantar dumpsites and results obtained showed that the farm was polluted with the metals (Cd, Cr, Cu, Mn, Fe, Pb, Zn, Ni) because the contamination pollution ranged from very slight to very severe. The overall order of the metals at the dumpsite was Fe > Mn > Zn > Cu > Cr > Ni > Pb > Cd while the order of the metal concentrations at the farm was Fe > Mn > Zn > Ni > Cd > Pb. In general, the metal concentrations were below the recommended limit of USEPA and FEPA standards for agricultural soils and vegetables except for Cd in vegetables. The concentrations were however higher in the farm than in the control. Thus, the farm was polluted with heavy metals from the dumpsite soils [6].

Five heavy metals (chromium, nickel, zinc, lead and copper) were analysed for their levels in soil at four different directions (east, west, north and south) by wet digestion spectrophotometrically and the mean heavy metals in soil were zinc (1133±897 mg/kg), nickel (26.3± 51.1 mg/kg), copper (110±90 mg/kg), lead (137± 64 mg/kg) and chromium (3.63±2.46 mg/kg). Concentration in sampling site were higher than soils from background with factors of 67 (zinc), 18 (copper), and 20 (lead). Index of geo-accumulation revealed soil to be moderately to strongly polluted with zinc, copper and lead. Inter-element correlation was in the range 0.90 – 0.99. Near-by farmlands are exposed to these heavy metals [7].

The concentration of heavy metals in soils and edible plant leaves grown in an abandoned dumpsite along Akachi road in Owerri municipality and their results were as follows Cr: 150-280 >Fe: 116.50-203 >Cu: 12.4-18.8 >Mn: 0-20 >Al: 0.08-0.16 >Zn: 0-1.4 mg/kg-1. Moreover, levels of metals in the edible plant leaves were in the order of: Zn>Fe>Cu>Al>Mn>Cr. Zn, in particular, was higher than FAO/WHO recommended limits. Still, the trends in Transfer Factor for the heavy metal in vegetable samples studied were in order: Zn>Al>Cu>Mn>Fe>Cr. Therefore, they concluded that abandoned solid waste dumpsites contained significant concentrations of heavy metals which are later absorbed and accumulated by plants growing it [8].

This chemical portioning of Cd, Cu, Ni, Pb, Zn, Mn, and Cr is vital in Okene metropolis because Like many cities in Nigeria, Okene faces problems of improper disposal, collection and handling of huge refuse near residential areas generated from industrial products, such as polythene bags, plastics from beverages, electronic materials, broken bottles and empty cartons, constitute hidden places for vector diseases. The situation is more serious and has become unbearable because the access to basic necessities, such as portable water and functional health facilities, is very poor. To worsen the matter, in Okene metropolis, there is a delayed and uncoordinated waste disposal system which makes many people vulnerable to the outbreak of diseases. Hence, have endangered the lives of both human and animals in Okene metropolis for ages. The presence of toxic heavy metals in the environment continues to generate a lot of concern to environmental scientists, government agencies and public health practitioners because of health implications of their presence. However, very little attention has been paid to its impact on the inhabitants. Thus, this research took into account chemical portioning of Cd, Cu, Ni, Pb, Zn, Mn, and Cr of the dumpsite soils of Idoji (ID), Okene (OK), Ikuehi (IK), Oboroke (OB), Uhwoze (UH), Nagazi(NA), Ozuri (OZ), Kabba Junction (KJ), Obehira (AC) dumpsites and Control (CTR) to ascertain if Cd, Cu, Ni, Pb, Zn, Mn, and Cr are present in the extractive fractions that could pose danger to the inhabitants of Okene metropolis.

Materials and Methods

Okene Metropolis is located at latitude 07° 33' N and longitude 06° 14'E and is presently one of the most important cities in Kogi State North Central Nigeria comprising of three local government areas namely Okene, Adavi and Okehi. It has a population of 722, 453 people (population census, 2006). It has total area of 339 Km². It has a tropical continental climate with dry season, lasting up to six months (October - March). Soils from nine dumpsites and a control site were collected from Okene metropolis during the dry and wet seasons of 2019 - 2021.

These dumpsites were Idoji (ID), Okene (OK), Ikuehi (IK), Oboroke (OB), Uhwoze (UH), Nagazi(NA), Ozuri (OZ), Kabba Junction (KJ), Obehira (AC) and Control (CTR). The area used for sampling in each dumpsite location was divided into four quadrants (Nuonamo et al., 2000). Soil samples were collected from each site with the aid of an auger stainless spoon at 0 – 15cm profile and composite samples were made in the laboratory for each season. A total of four (4) samples per month from each dumpsite were collected for a period of 24 months and placed in polythene bags and labeled.

All reagents and chemicals used during this research were of analar grades and double distilled water was used. Glass wares and polythene sample bottles were washed with liquid soap, rinsed with water and soaked in 10% HNO₃ for 24 hours, then cleaned thoroughly with double distilled water and dried. The results obtained were validated with certified soil reference materials (CSRM) SOIL-7 and NIST 1633b obtained from Gombe State University, Nigeria. Results reliability and repeatability were confirmed by the triplicates digestion throughout the study.

$$\% \text{ recovery for CSRM} = 1 - \frac{(\text{Literature values} - \text{results obtained by AAS})}{\text{Literature values}}$$

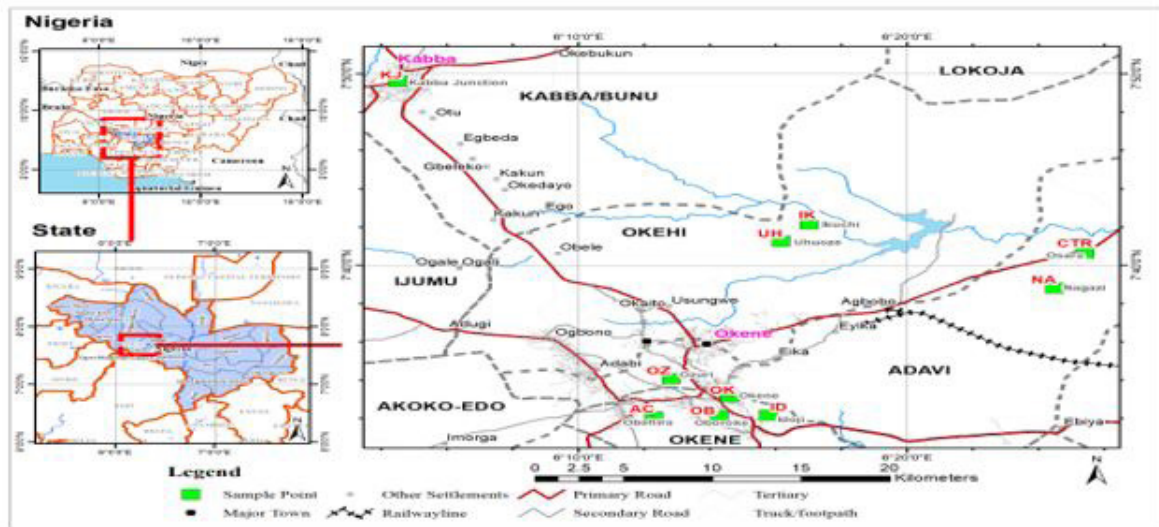


Figure 1: Map showing Okene metropolis and sampling points



Figure 2: One of the Dumpsite at Okene L.G.A. Dumping at the site is unrestricted

Sequential Extraction of Metals in dumpsite Soils

[9] fractionates soil samples into six geochemical fractions using sequential extraction method. However, in this studies $Mg(NO_3)_2$ was used instead of $MgCl_2$ to avoid an increase in the solubility of heavy metals within the soil solution matrix. The extraction was carried out on three sub-samples in each step as follows:

Water Soluble Fractions:

1g of the air dried soil sample (2mm sieve) were mixed with 10ml of de-ionized water with continuous agitation for 1 hour, centrifuged and the supernatant decanted and made up to 50ml with de-ionized water prior to analysis.

Exchangeable Phase:

The residue in (i) above is shaken at room temperature with 16ml of 1M $\text{Mg}(\text{NO}_3)_2$ at pH 7.0 for 1 hour, centrifuged and supernatant decanted and made up to 50ml with double distilled de-ionized water.

Oxidized Phase (bound to organic matter):

Residue from (ii) above +10ml of 8.8M H_2O_2 + 6ml of 0.02M HNO_3 was shaken for 5 + 1 hrs at 98°C. 10ml of 3.5M $\text{CH}_3\text{COONH}_4$ was added as an extracting agent, the resulting mixture was then centrifuged and supernatant made up to 50ml with distilled water prior to analysis.

Acid Soluble Base (bound to carbonates):

25ml 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 50ml with distilled water prior to analysis.

Reducible Phase (bound to Fe–Mn oxides):

Residue from (iv) above + 17.5ml $\text{NH}_2\text{OH}\cdot\text{HCl}$ 0.1M + 17.5ml $\text{CH}_3\text{COONH}_4$ 3.5M, shaken for 1 hr, centrifuged, the supernatant decanted and made up to 50ml with distilled water prior to analysis.

Residual Phase (bound to silicates and differential materials):

Residue from (v) above was digested by using $\text{HCl} - \text{HNO}_3/\text{HF}$ (0.35:12 w/v solid solution) in acid digestion, Teflon cup. It was then dry, ashed for 2 hrs and evaporated, filtered and diluted to 50ml with double-distilled de-ionized water. After each successive extraction, the sample was centrifuged at 3000rpm for 15 minutes. The supernatant was then removed with pipette and filtered with Whatman No. 42 filter paper. The residue in each case was washed with de-ionized water followed by vigorous handshaking and then 15 minutes centrifugation before the extraction.

Determination of trace metals

The samples were digested with aqua-regia and analyzed for Cd, Cu, Ni, Pb, Zn, Mn and Cr using AA320N atomic absorption spectrophotometer which uses acetylene-air flame. SPSS statistical software model 2016 was used for the analysis of results obtained.

Results and Discussions

The percentage recoveries of Cd, Cu, Ni, Pb, Zn, Cr, and Mn using two soil reference materials SIOL-7 and NIST 1633b obtained from Gombe State University were presented in Table 1. The results of the percentage recoveries of Cd, Cu, Ni, Pb, Zn, Cr, and Mn in the SIOL-7 were 92.30 ± 0.014 , 91.82 ± 0.005 , 100.00 ± 0.001 , 95.00 ± 0.015 , 100.00 ± 0.003 , 93.33 ± 0.012 and $98.73\% \pm 0.010$ while 95.15 ± 0.123 , 95.84 ± 0.016 , 87.91 ± 0.002 , 92.53 ± 0.017 , 100.00 ± 0.002 , 97.38 ± 0.014 and $99.47\% \pm 0.003$ was recorded for Cd, Cu, Ni, Pb, Zn, Cr, and Mn in NIST 1633b respectively. Percentages > 85 % is good indication of a precise instrument [10-11].

Metals	Literature values SIOL-7	Literature values NIST 1633b	Results obtained by AAS (SOIL-7)	Results obtained by AAS NIST 1633b	Percentage recovery for SIOL-7	Percentage Recovery for NIST 1633b
Cd	1.3	0.784	1.200	0.746	92.30± 0.041	95.15± 0.123
Cu	11	112.8	10.100	108.113	91.82± 0.005	95.84± 0.016
Ni	ND	120.6	ND	106.200	100± 0.001	87.91± 0.002
Pb	60	68.2	5.700	53.106	95.00± 0.014	92.53± 0.017
Zn	ND	ND	ND	ND	100± 0.003	100± 0.002
Cr	60	198.2	56.000	193.000	93.33± 0.012	97.38± 0.014
Mn	631	131.80	623.000	131.100	98.73±0.010	99.47± 0.003

Table 1: Comparative mean percentage recoveries of metals for SOIL-7 and NIST 1633b

Cadmium (Cd) fractionation in dumpsite soils

Cd was found high in the residual fractions at most of the dumpsite studied though appreciable amount was present in the oxidizable organic matter bound and carbon bound fractions as shown in figure 1 and 2. This indicates the effectiveness of organic matter as a scavenger of Cd in the dumpsite soils. Similar studies on chemical fractionation of soil shows that Cd is mainly bound to oxidizable phase occurring as organic complexes metal species. This is attributed to Cd having high affinity for humic substances which are a fraction of natural organic matter chemically active in complexing such metal. Generally, residual fraction during both seasons forms major component of the fractions. In the wet season, high mobility factors were obtained at OB (66.0%), UH (62.0%), OZ (57.0%), AC (41.0%) and KJ (34%) while in the dry season, high mobility factors were obtained at OZ (67.0%), NA (61.0%), AC (60.0%), ID (52.0%) and OK (45.0%).as presented in table 2 and 3 respectively. This result indicates high Cd bioavailability and mobility, thus these dumpsites would be contaminated by Cd to a relatively large extent. This result is similar to that of [19] where cadmium was largely found in the residual fraction.

A trend of mobility in the dry season is given as: CTR<KJ<UH<OB<OK<ID<IK<AC<NA<OZ and CTR<ID<OK<NA<KJ<UH<AC<OZ<IK<OB.

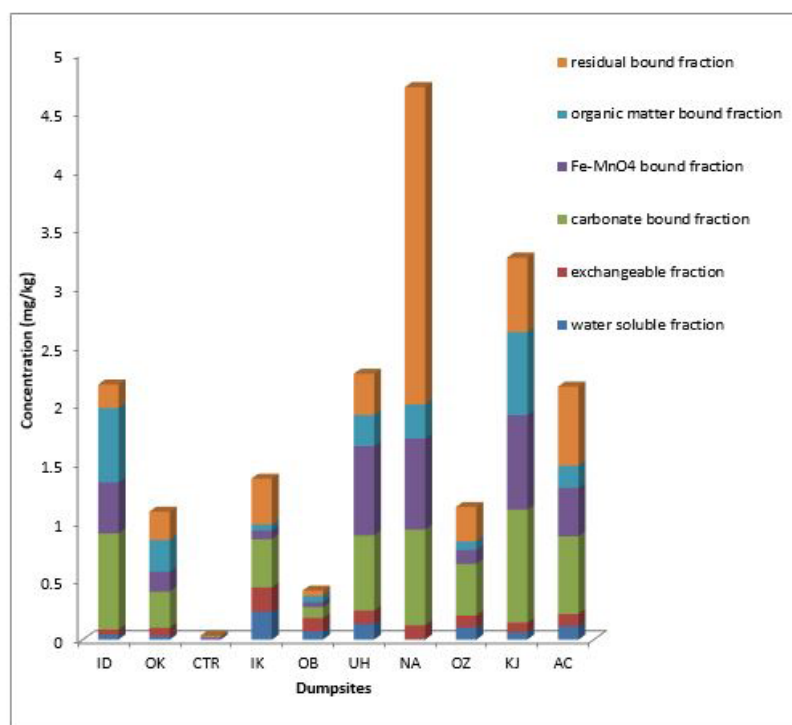


Figure 3: Cadmium concentrations in fractions of soil samples during wet season

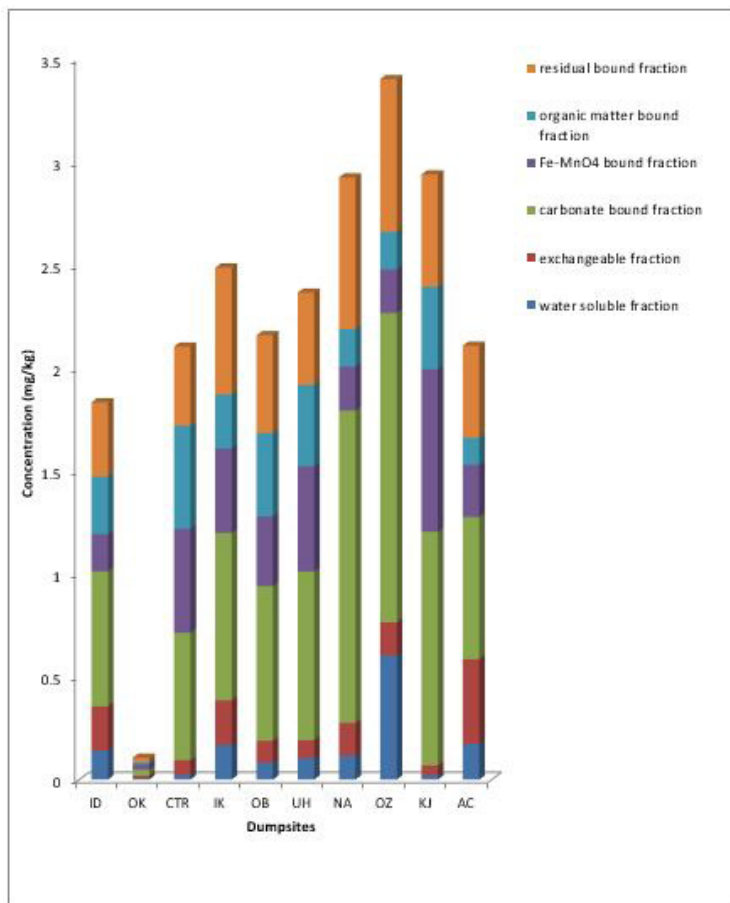


Figure 4: Cadmium concentrations in fractions of soil samples during dry season

Copper (Cu) fractionation in dumpsite soils

Cu was found relatively high in the residual fractions for ID, CTR, IK, KJ and AC (dry season) and OB, UH, NA, KJ, AC (wet season) across the dumpsites studied. Also appreciable amount was present in the oxidizable organic matter bound fractions as shown in figure 5 and 6. This shows the effectiveness of organic matter bound fractions as a scavenger of Cu in soil. A number of studies on chemical partitioning of Cu in soil have shown that it is mainly bounded to the oxidizable phase, occurring as organic complexed metal species. This is attributed to Cu having high affinity for humic substances which are a fraction of natural organic matter chemically active in complexing such metals. This further confirm the results of [12, 13, 14]. In the wet season high mobility values were obtained at OK (55.6%), ID (38.4%), NA (36.0 %) and IK (33.0%): while in the dry season high values were obtained at OK (45.0%) and IK, OB (41.0%) as presented in table 2 and 3 respectively. This result indicates high bioavailability and mobility, thus these dumpsites would be contaminated by Cu to a relatively large extent. Trend of mobility in the dumpsites during the rainy season is given as OK > ID > NA > IK > UH > OZ > CTR=AC >OB >KJ while in the dry season follows the order: OK > IK > KJ >OB> AC > OZ > UH >NA> ID>CTR >OB >KJ.

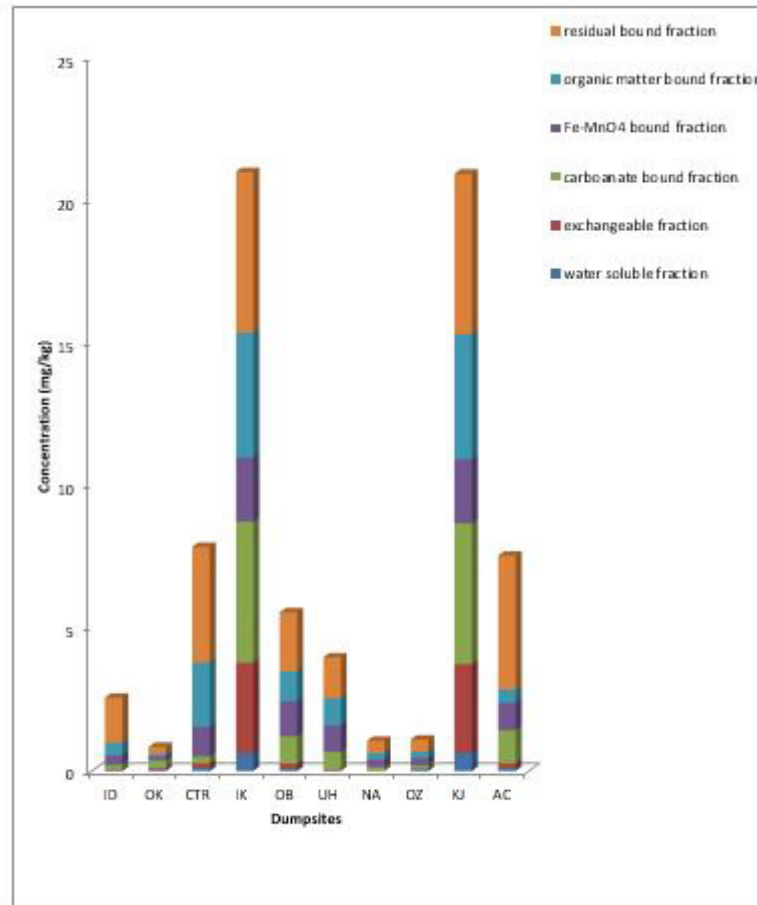


Figure 5: Copper concentrations in fractions of soil samples during dry season

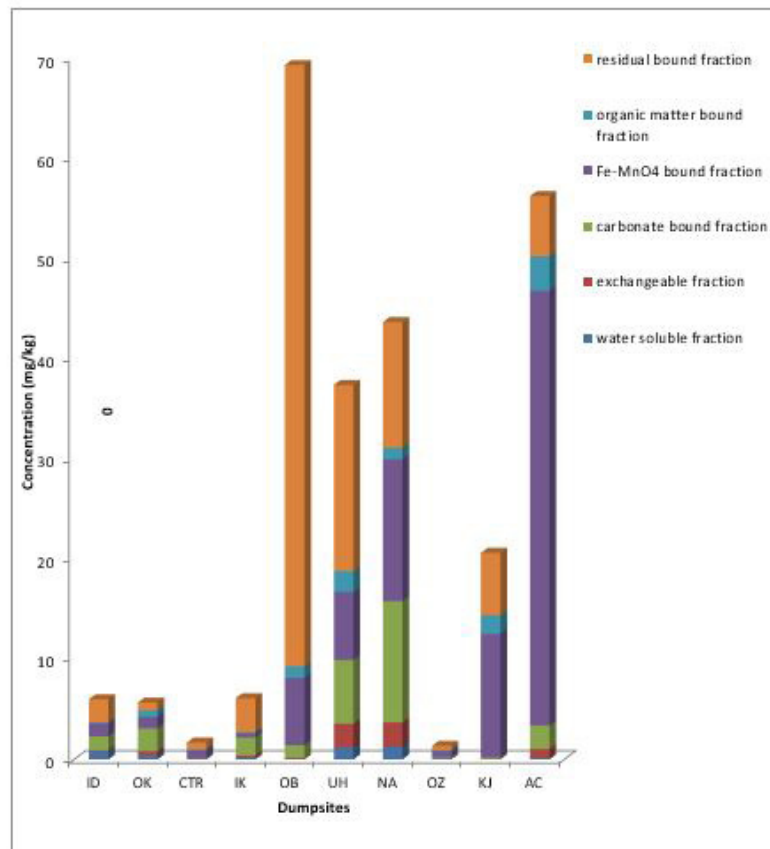


Figure 6: Copper concentrations in fractions of soil samples during wet season

Nickel (Ni) fractionation in dumpsite soils

Ni was found quite high in the exchangeable fractions across both wet and dry. Also for the dry season low amount Ni was found in the residual fractions as shown in figure 7. Whereas in the wet season amount relatively high than the dry season was found in the residual fractions across all dumpsites as shown in figure 8. The higher concentration of Ni in the exchangeable and appreciable amount in the residual fraction indicates that there is an increased rate of interaction with the biotic community of the soil. This is in agreement with the studies of [15, 16] where Ni dominated the exchangeable fractions. In the wet and dry season as shown in tables 2 and 3 very high mobility values were obtained with the exception of IK-dumpsites in the dry season. This result indicates high bioavailability and mobility, thus these dumpsites would be contaminated by Ni to a relatively extent. Trend of mobility in the dumpsites during the rainy season is given as $OK > OB > NA > KJ > IK > ID > AC > UH > OZ > CTR$ while in the dry season follows the order: $OK = UH > ID > AC > KJ > CTR > UH > NA > OZ > IK$

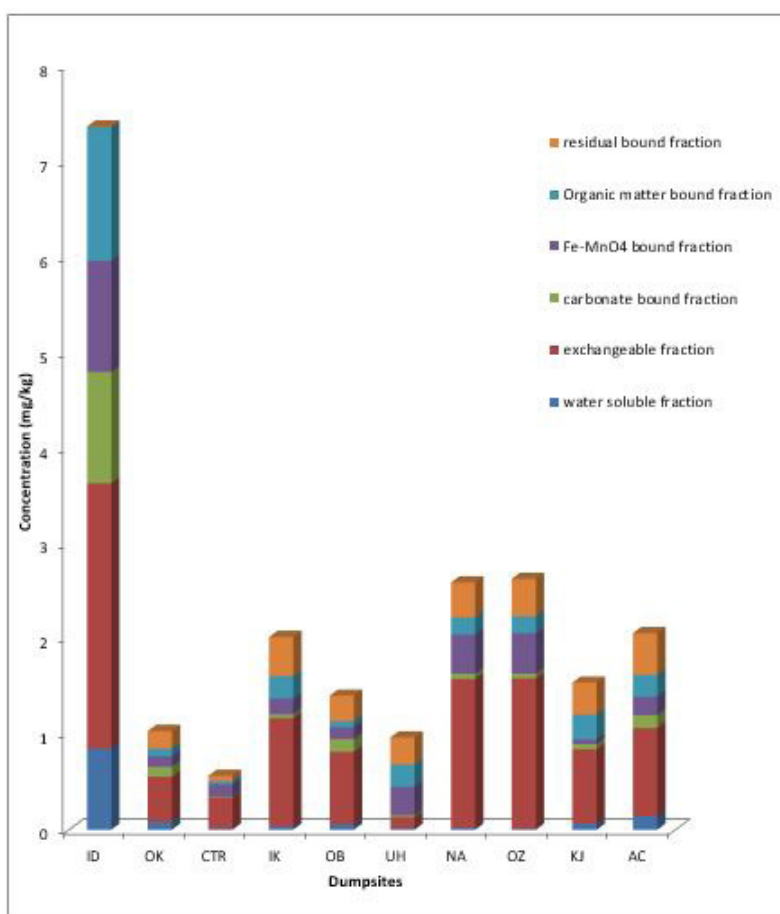


Figure 7: Nickel concentrations in fractions of soil samples during dry season

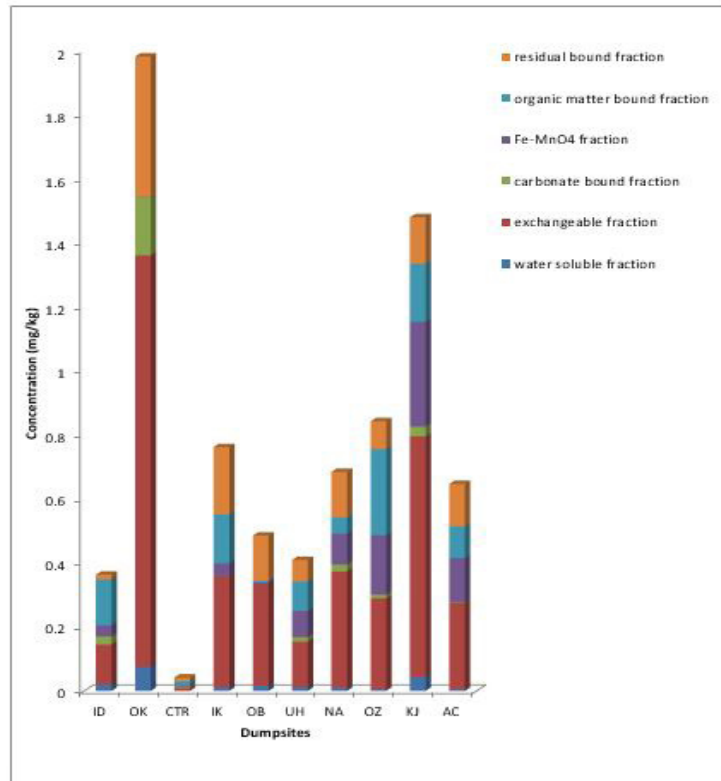


Figure 8: Nickel concentrations in fractions of soil samples during wet season

Lead (Pb) fractionation in dumpsite soils

Pb was found high in the residual fractions at most of the dumpsite studied though appreciable amount was present in the oxidizable organic matter bound and carbon bound fractions as shown in figure 9 and 10. This indicates the effectiveness of organic matter as a scavenger of Pb in the dumpsite soils. Similar studies on chemical fractionation of soil shows that Pb is mainly bound to oxidizable phase occurring as organic complexes metal species [17]. This is attributed to Pb having high affinity for humic substances which are a fraction of natural organic matter chemically active in complexing such metal. Generally, residual fraction during both seasons forms major component of the fractions. In the wet season, high mobility factors were obtained at OZ (29.0%), and IK (26.0%) while in the dry season, high mobility factors were obtained at OK (35.0%), ID (30.0%), NA (28.0%) and KJ (27.0%) as presented in tables 2 and 3 respectively. This result indicates high Pb bioavailability and mobility, thus these dumpsites would be contaminated by Pb to a relatively extent.

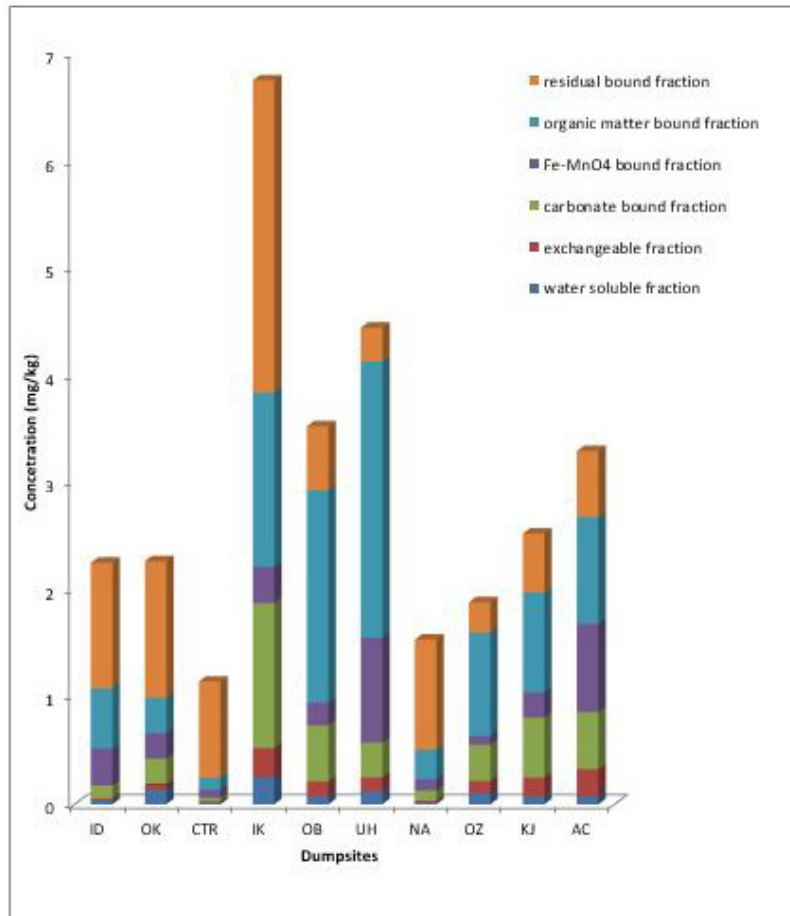


Figure 9: Lead concentrations in fractions of soil samples during wet season

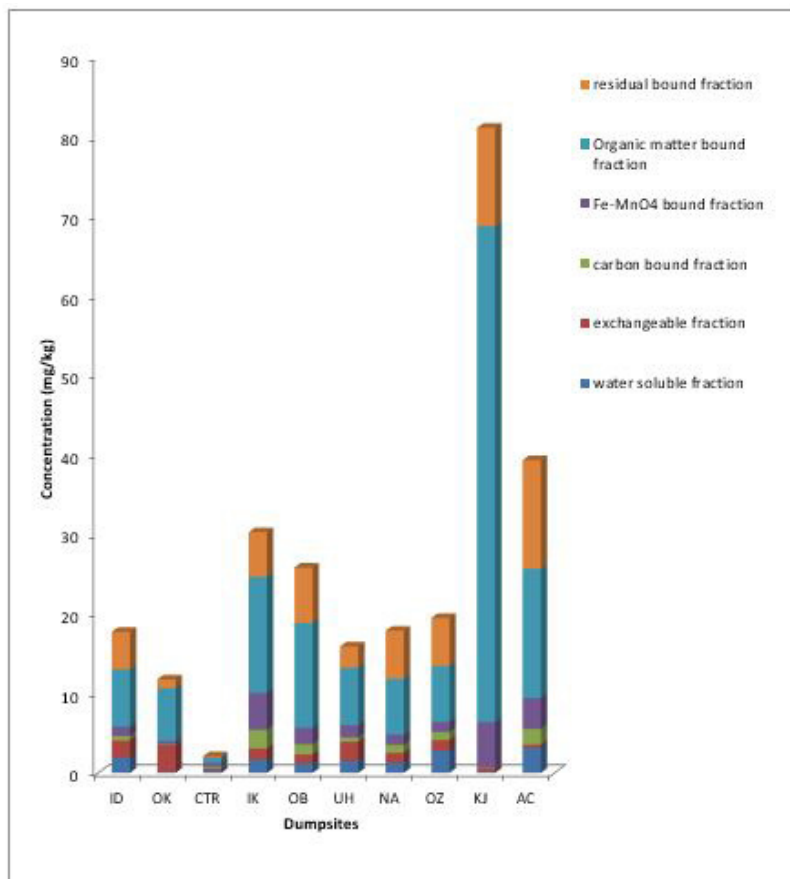


Figure 10: Lead concentrations in fractions of soil samples during dry season

Zinc (Zn) fractionation in dumpsite soils

The chemical partitioning of Zn into different fractions was dominated by Fe-MnO₄ fractions across both wet and dry season. However, organic matter bound and residual fractions in the selected dumpsites also showed appreciable results across the seasons as presented in Figs. 11 and 12. This could be linked with preferential incorporation of Zn into silicate lattice as suggested by [14]. Also, the high Zn values in the organic matter bound fractions may be connected to the ease of complexation between the metal and natural organic matters. In addition, Zn contents being high in the Fe-MnO₄ fractions could be due to high association or retention ability of the mineral crystal structure. This is attributed to dumpsite composition and its bioavailability in the soil. In the wet and dry season, relatively high mobility values are shown in tables 2 and 3.

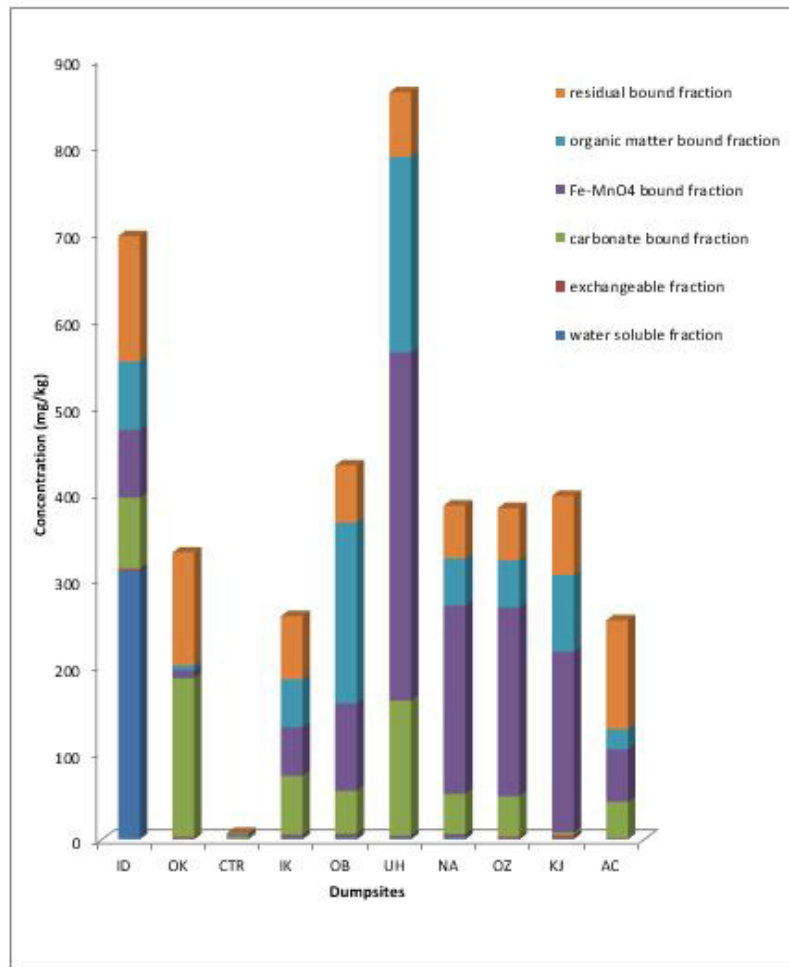


Figure 11: Zinc concentrations in fractions of soil samples during dry season

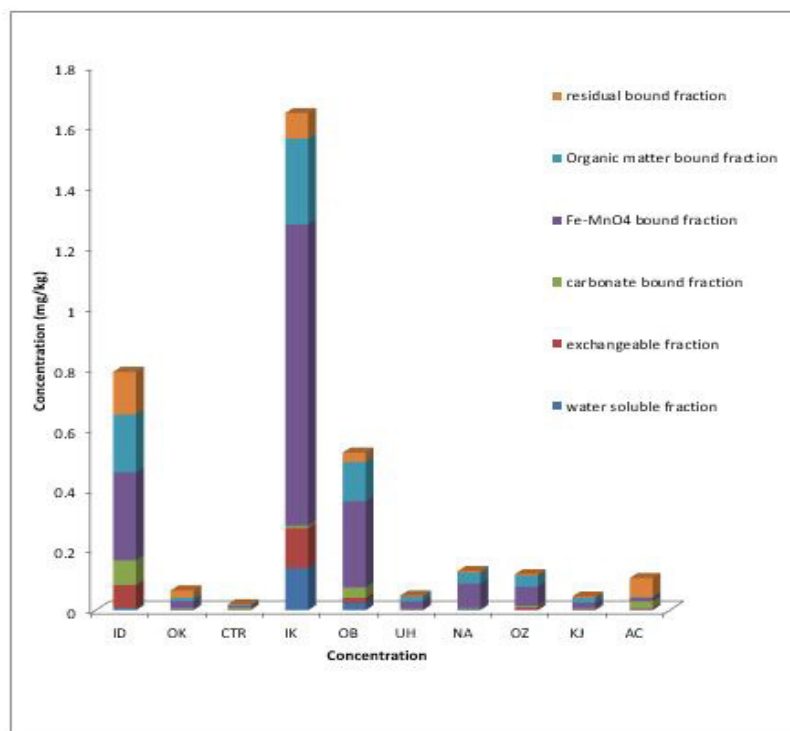


Figure 12: Zinc concentrations in fractions of soil samples during wet season

Chromium (Cr) fractionation in dumpsite soils

Cr was found relatively high in the residual fractions for IK, OB, UH, NA, and AC (dry season) and ID, IK, OB, UH, NA and AC (wet season) across the dumpsites studied. Also appreciable amount was present in the oxidizable organic matter bound fractions as shown in figs. 13 and 14. This shows the effectiveness of organic matter bound fractions as a scavenger of Cr in soil. A number of studies on chemical partitioning of Cr in soil have shown that it is mainly bounded to the oxidizable phase, occurring as organic complexed metal species. This is attributed to Cr having affinity for humic substances which are a fraction of natural organic matter chemically active high in complexing such metals. This is in agreement with the studies of Brew (2010) and [14]. In the wet season high mobility values were obtained at OB (60%), CTR (38.0%), AC (25.0%), OK (24.0%) and OZ (16.0%): while in the dry season high values were obtained at AC (26.0%) OB (22.0%), OZ (19%) and IK (16%) as presented in table 2 and 3 respectively. This result indicates high bioavailability and mobility, thus these dumpsites would be contaminated by Cr. Trend of mobility in the dumpsites during the rainy season is given as OB > CTR > AC > OK > OZ > IK > NA > KJ > ID > UH while in the dry season follows the order: AC > OB > OZ > IK > NA = CTR > ID = OK > KJ > UH.

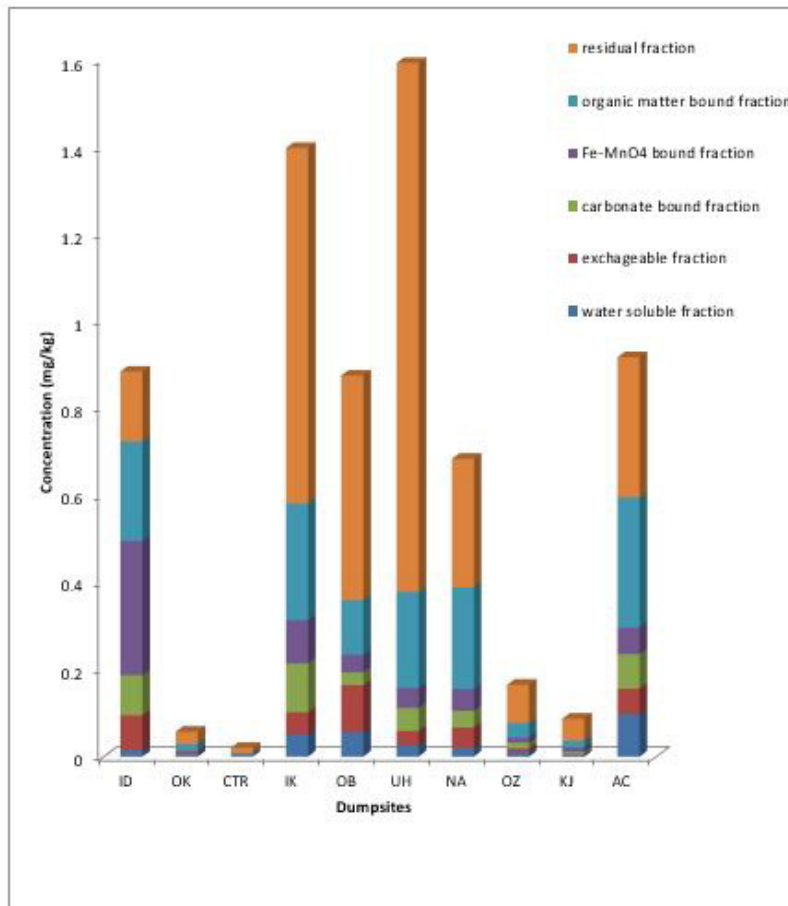


Figure 13: Chromium concentrations in fractions of soil samples during dry season

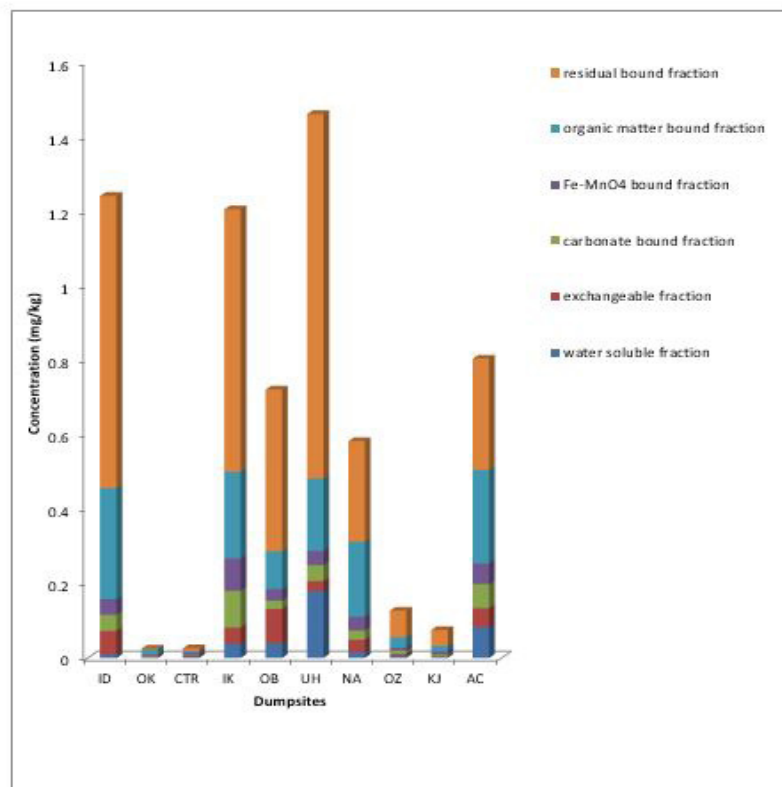


Figure 14: chromium concentrations in fractions of soil samples during wet season

Manganese (Mn) fractionation in dumpsite soils

Mn partitioning is dominated by the Fe-MnO₄ and organic matter bound fractions in the selected dumpsites and across the seasons as presented in Figs. 15 and 16. This could be linked with preferential incorporation of Mn into silicate lattice. Also, the high Mn values in the organic matter bound fractions may be connected to the ease of complexation and peptization between the metal and natural organic matter like humic fulvic acid. In addition, Mn contents being high in the Fe-MnO₄ fractions could be due to high association or retention ability of the mineral crystal structure. This is attributed to dumpsite composition. In the wet season, relatively high mobility values were recorded at CTR (42.0%), AC (27.0%) and ID (20.9 %) while in the dry season mobility values were high at OK (32.0%), AC (29 %) and IK (22.0%) as shown in table 2 and 3 respectively. The results obtained in this study for Mn is similar to that obtained by [18] where higher percentage of Mn was bounded to organic matter. The Order of mobility in the wet season is given as CTR > AC > IK > ID > OZ > KJ > OB > UH > OK > NA while dry season values are in the order OK > AC > IK > ID > CTR > OB > UH > KJ > NA = OZ.

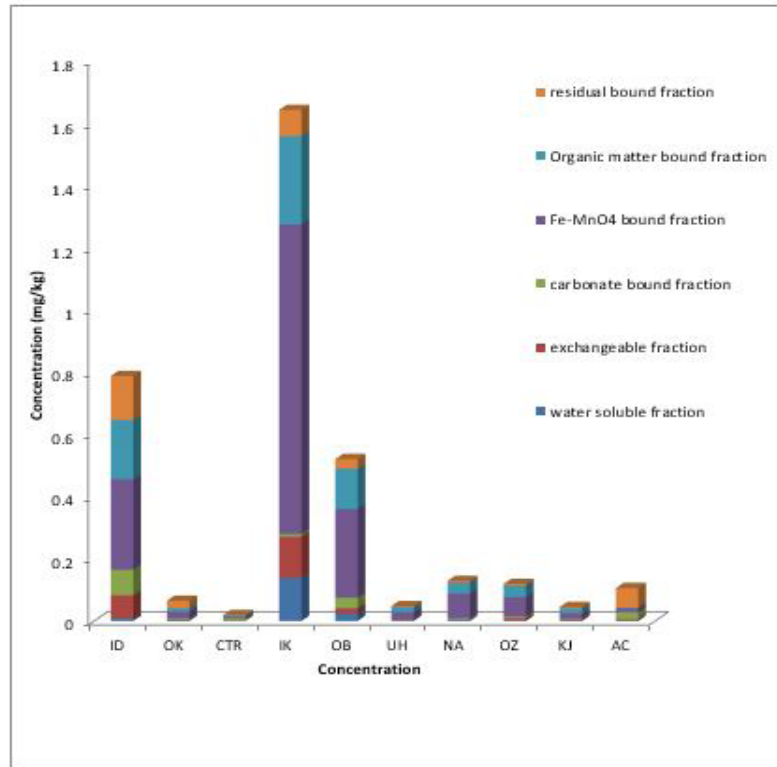


Figure 15: Manganese concentrations in fractions of soil samples during wet season

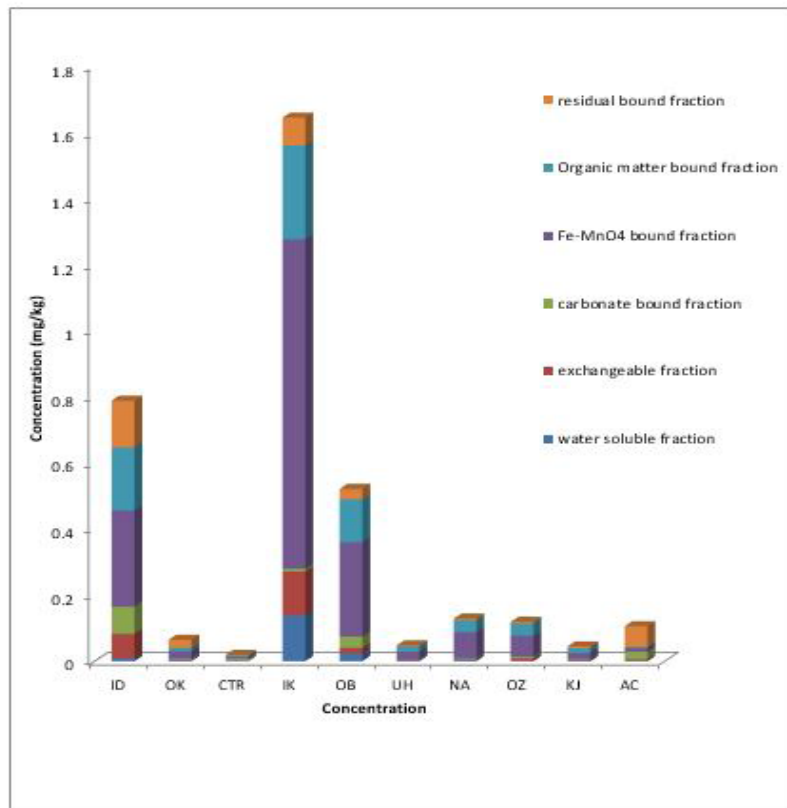


Figure 16: Manganese concentrations in fractions of soil samples during wet season

Conclusion

From these studies, mobility factors for all the metals varied significantly among the trace metals, dumpsites and seasons. Since trace metals recorded relatively high mobility factors in both wet and dry season. Hence they will be potentially available for plant uptakes and easily in soil solution. Considering these results obtained in this study, consumption of plants grown on these dumpsites should be discourage in order to avoid the risk of ingestion of the trace metals studied.

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Conflict of Interest

The authors declares that there is no conflict of interest

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