Speciation Analyses and Mobility study of Zn, Cd and Cr in Soils around Municipal Solid Waste Dumpsites in Benin City

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Abstract – The mobility of zinc (Zn), cadmium (Cd) and chromium (Cr) in soils around municipal solid waste dumpsites in Benin metropolis, Nigeria was assessed using sequential chemical extraction procedure for metal speciation. Total concentration levels of heavy metals were carried out using Atomic Absorption Spectrophotometry (AAS). Results from the chemical fractionation analyses showed that the analysed heavy metals were more abundant in their non-bioavailable fractions amongst the defined geochemical forms with the residual fraction dominating the stabile fractions. The potentially mobile and bioavailable fraction of Zn varied from 26 to 40%, Cd also varied from 15 to 35% while Cr spanned from 14 to 30% in soils around the studied dumpsites. The percentage bioavailability / mobility of the analysed heavy metals in soils around each studied dumpsite were in the following order: dumpsite (I), Zn > Cd> Cr; for dumpsite (II), the order was, Zn > Cd > Cr while the order in dumpsite (III) was, Zn > Cr > Cd. The relative low mobility factors observed by each analysed heavy metal in the studied sites coupled with their comparatively high concentration in the residual fraction, indicates low mobility, lability and bioavailability for the analysed metals in soils around the studied dumpsites.
Keywords: Dumpsite; Soil; Heavy Metals; Bioavailability; Mobility; Benin City

1 INTRODUCTION

High concentration levels of heavy metals in soils and sediments have been known to be undesirable to the habitats thereby posing serious environmental degradation. Soil is the primary recipient of solid wastes, reservoir of nutrients and water for plants and animals. Its contamination and degradation from wide anthropogenic activities such as unplanned industrialization, unlawful or improper wastes disposal system has far reaching effects on the entire living components of the ecosystem and the environment [1]. The presence of toxic metals in soils can severely inhibit the biodegradation of organic matters [2], [3], [4].

During transportation of soil minerals, heavy metals undergo numerous changes in their forms as a result of mineral precipitation and dissolution, adsorption and desorption reactions, ion exchange, aqueous complexation, redox reaction, biological mobilization and immobilization [5], [6], [7] which affect their behaviour, bioavailability and mobility. Changes in their chemical forms (speciation) and bioavailability are however possible. It is generally recognised that the particular behaviour of heavy metals in the environment is determined by their specific physicochemical forms rather than their total concentration because the knowledge of total content of heavy metals present in soils provides little or no information about their potential behaviour, origin, mode of occurrence, mobilization, bioavailability and transport of these metals [8], [9]. Soil is relatively heterogeneous in terms of its physical, chemical and biological characteristic, hence heavy metals are associated with various soil components in different ways and these associations also determine their mobility and availability [10], [11]. The soils around municipal solid waste dumpsites are considered to be contaminated by heavy metals since these wastes dumpsites across Cities in Nigeria consists primarily of metals, plastic and rubber materials, textiles, glass, food scraps, vegetable matter and other solid wastes like damage electrical appliances, metallic materials and steels coated with heavy metals which could introduces metals into the soils [12].

The aim of the present study is to investigate the different chemical forms of Zn, Cd and Cr in soils around some major municipal solid waste dumpsites in Benin City metropolis and to assess the association, bioavailability and mobility of these metals as well as their environmental contamination risk between the different geochemical phases based on chemical speciation.

2. MATERIALS AND METHODS

2.1 Study Area

The study area is within Benin City metropolis. The City is the capital of Edo State, Nigeria and is located in the south-south geopolitical zone of Nigeria; bounded by latitudes 6^0 15′N to $6^0$30′N and longitudes 5^o30′E to 5^o45′E and area of about 500 square kilometres. The climatic condition fall within the Rain forest type and similar to other parts of southern Nigeria with annual rainfall generally high ranging from 2000 – 2400 mm. The City is underlain by sedimentary formation described by [13]. Benin City falls within the tropical equatorial zone dominated by dry season (November-March) and wet season (April – October). The climate is influenced by two prevailing air masses; the S.W. Monsoon wind and the N.E trade wind. The former prevails during the wet season and the later during the dry season. The effects of the dry N.E trade winds are most noticeable from December to February when they usher in the dry and dusty harmattan [14], [15], [16].

The map of Benin showing soil samples collection points and a table showing sampling sites description with their geographical position coordinates are presented in Figure 1 and Table 1 respectively.

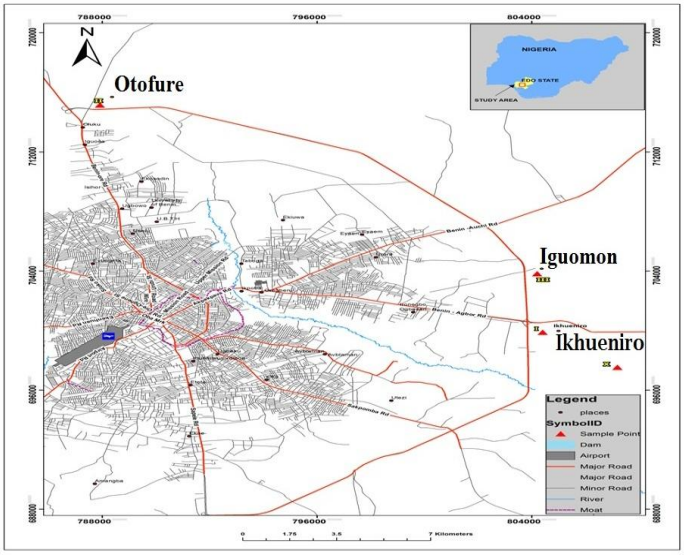

Fig.1 Map of Benin Showing the Sampled Locations

Table 1 Sampling Sites Description and Coordinates

Sampled sites	Location of Dumpsite	Type of waste	Age of dumpsite	Size of dumpsite	Coordinates (Latitude & Longitude)
Dumpsite (I)	Ikhueniro dumpsite; Ikhueniro community, Benin Agbor road (Bye pass) Benin City.	Domestic	15yrs	52,000 m^2	$6^0$19′28.261″ N$5^0$45′04.158″E
Dumpsite (II)	Otofure dumpsite; Otofure community, Oluku Bye pass, Benin City.	Domestic	Above 17yrs	37,500 m^2	$6^0$27′47.599″ N$5^0$36′10.397″E
Dumpsite (III)	Iguomon dumpsite; Iguomon community, Benin Lagos express way (Bye pass), Benin city.	Domestic	15yrs	58,560 m^2	$6^0$21′36.360″ N$5^0$44′58.085″E
Control site (X)	Farm land at Ikhueniro community, Benin Agbor road, Benin City	_	_	_	$6^0$18′11.394″ N$5^0$46′34.226″E

2.2 Sample Collection and Preparation

Composite soil samples were collected around three major municipal solid waste dumpsites in Benin City metropolis, using a stainless steel spade at depths of 0 – 15, 15 – 30 and 30 - 45cm, representing top soils, sub soils and bottom soils respectively. Three soil samples per point from the three depths were bulked together to form one composite sample. At each studied dumpsite, six different points were randomly chosen (50 metres away from the centre of each studied dumpsite) for sampling. The composite soil samples from the six different points in each studied dumpsite were labelled A, B, C, D, E and F for dumpsite (I); G, H, I, J, K and L for dumpsite (II); and M, N, O, P, Q and R for dumpsite (III), to give a total of eighteen (18) composite soil samples from the three studied dumpsites. The gradient (high and low gradient) and the direction of flow of erosion were also

considered for each sampling point. Control soil samples were also obtained in similar manner from a farm land in the adjoining area of the solid wastes dumpsite (500 metres away from the studied wastes dumpsite) to serve as control and was labelled sample 'X'. The control site was unaffected by dumping of waste materials. The geographical position coordinates of the sampled sites were identified and mapped using global position system (GPS). Soil samples collected were transferred into a black polythene bag, labelled properly and transported to the laboratory for analysis. Soil samples were air-dried for a period of two weeks in a well-ventilated space. Samples were homogenized by grinding in porcelain mortal and sieved through a 2mm (10 meshes) stainless sieve. The air-dried < 2mm soil samples were oven-dried at 105 ± 0.5°C to a constant mass, cooled and stored in labelled air-tight plastic Cans prior to analysis [17], [18].

2.3 Total Determination and Chemical Fractionation Analyses of Heavy Metals in Soil Samples

Total concentration levels of Zn, Cd and Cr in soils were determined in accordance with the USEPA method described by [19], [20]. 5 mL of aqua regia and 1 mL of 60 % perchloric acid were added to 2g of soil samples in a 150 mL digestion tube and digested on a heating digester until white fumes of perchloric acid appeared. In order to assess the geochemical forms and bioavailable Zn, Cd and Cr in soils, the five multi-step phase-selective sequential extraction procedure of [21] modified by [22], [9] was used. In the method, heavy metals were separated into five operationally defined fractions: Exchangeable (F_1), bound to carbonate (F_2), bound to Fe-Mn oxide (F_3), bound to organic matter (F_4) and residual fraction (F_5). 1g of the dried soil sample was weighed and extracted into five fractions as follows:

(i) Exchangeable(F_1): Eight (8) mL of 1M magnesium chloride solution (pH 7.0) was added to 1g of soil sample in a 50mL polypropylene bottle and the mixture was shaken in a mechanical shaker for 1hour.

(ii) Metals bound carbonates (F_2): Eight (8) mL of 1M sodium acetate solution was added to the residue of F_1 and adjusted to pH 5.0 with concentrated acetic acid. The mixture was agitated for 5 hours in a mechanical shaker.

(iii) Metals bound Fe-Mn oxides (F_3): Twenty (20) mL of 0.04M hydroxylamine hydrochloride in 25% glacial acetic acid was added to the residue of F_2 and the mixture was heated at 96 ± 3°C with occasional agitation for 6 hours.

(iv) Metals bound to organic matter (F_4): Three (3) mL of 0.02 M nitric acid and 5 mL of 30% hydrogen peroxide were added to the residue of F_3 and adjusted to pH 2 with nitric acid. The mixture was heated to 85 ± 2°C in a water-bath for 2 hours with occasional agitation. An additional 3mL aliquot of the acidified 30% hydrogen peroxide was added and the mixture was heated at 85 ± 2°C for 3 hours with intermittent agitation. 5mL of 3.2M ammonium acetate in 20% nitric acid was added to the cooled mixture and the sample was diluted to 20 mL and stirred continuously for 30 minutes.

(v) Residual metals (F_5): The residue of F_4 from the previous extraction was transferred into a digested tube and digested with 5mL of aqua regia and 1mL of 60% perchloric acid until white fumes appeared. The tube was cooled and the side rinsed with distilled water and filtered through a Whatman 1 filter paper into a 100mL volumetric flask. The volume was made to mark with distilled water.

After each successive extraction process, centrifuging the mixture at 1500 rpm for 15minuts effected the liquid-solid phase separation. The supernatant was decanted into a polypropylene bottle for metal analysis while the residue was carried through the whole extraction process. Bulk scientific standard solution was used to calibrate the Atomic Absorption Spectrometer. Procedural blank samples were subjected to similar extraction method using the same amount of reagents. The concentrations of heavy metals in the various extracts were determined in a pre-calibrated acetylene flame Atomic Absorption Spectrophotometer (Bulk Scientific VGP 210). These procedures for soil sequential fractionation analyses were carried out on the eighteen (18) composite soil samples from the three (3) dumpsites soils and the control sample.

2.4 Mobility Factors

The mobility factors (MF) of metals in soils may be assessed on the basis of absolute and relative content of fraction weakly bound to soil components. In this study the mobility factor (MF) was calculated using five schemes extraction [23], [24], [6], on the basis of equation (1).

$$\mathrm{MF} = \frac{F_{1+F_2}}{F_{1+F_2+F_3+F_4+F_5}} \times \frac{100}{1} \quad (1)$$

3 RESULTS AND DISCUSSION

The geochemical forms, mean total concentration levels, percentage (%) recovery, percentage (%) bio-availabilities and percentage distribution pattern of Zn, Cd and Cr (mg/kg) in the studied sites are presented in Tables 2– 7. The analysed heavy metals were mostly abundant in their non-bioavailable fractions, implying low mobility and bioavailability of the metals.

3.1 Zinc (Zn)

The geochemical forms mean total concentration levels of Zn in soils around the studied dumpsites are presented in Table 2. The mean concentration levels of Zn ranged between 5.00 ± 0.17 and 37.93 ± 0.87 mg/kg against the control soil samples with mean levels of 3.97±0.15 mg/kg (Table 2).

Table 2 Geochemical forms of Zn (mg/kg) in soil samples from the studied dumpsites (I, II, III) in Benin

Spots	F1	F2	F3	F4	F5	Sum	Total	Recov. (%)	Bioav. (%)
Dumpsite I									
A	2.63±0.00	3.89±0.01	2.13±0.02	3.36±0.01	4.15±0.01	16.17±0.03	17.04±0.27	94.89	40.35
B	2.81±0.01	3.81±0.02	2.32±0.01	3.14±0.06	4.04±0.03	16.18±0.05	16.49±0.03	98.12	41.07
C	1.36±0.02	1.51±0.03	1.94±0.03	2.49±0.04	2.01±0.01	9.32±0.09	9.76±0.05	95.49	30.83
D	1.45±0.02	1.66±0.03	1.90±0.02	2.37±0.02	2.92±0.02	10.30±0.07	11.24±0.21	91.63	30.19
E	1.97±0.01	2.17±0.00	2.45±0.03	2.87±0.01	3.24±0.03	12.69±0.07	14.08±0.17	90.13	32.59
F	2.81±0.02	3.63±0.03	3.93±0.01	5.03±0.02	7.27±0.04	22.67±0.10	23.17±0.06	97.84	28.41
Dumpsite II									
G	6.12±0.02	7.85±0.04	6.75±0.02	7.14±0.04	8.71±0.02	36.57±0.12	37.93±0.87	96.41	38.20
H	5.32±0.01	5.06±0.01	5.53±0.01	6.54±0.02	6.07±0.01	28.51±0.02	30.37±1.01	93.88	36.39
I	2.08±0.02	2.52±0.02	3.39±0.01	5.09±0.01	4.16±0.00	17.25±0.04	18.93±0.06	91.13	26.68
J	1.24±0.01	1.71±0.00	2.05±0.02	3.56±0.01	2.72±0.02	11.29±0.04	12.20±0.17	92.54	26.15
K	2.17±0.02	1.81±0.02	1.96±0.02	2.37±0.02	2.85±0.02	11.16±0.08	12.13±0.32	92.00	35.66
L	0.89±0.02	1.14±0.02	1.39±0.02	1.71±0.01	2.26±0.02	7.38±0.06	7.57±0.15	97.49	27.47
Dumpsite III									
M	0.91±0.03	1.07±0.03	1.31±0.02	1.43±0.02	1.57±0.04	6.29±0.13	6.93±0.21	90.76	31.48
N	1.10±0.02	1.38±0.01	1.60±0.02	2.66±0.02	1.93±0.03	8.67±0.03	8.83±0.15	98.19	28.60
O	1.52±0.01	1.97±0.02	1.78±0.01	2.04±0.02	3.40±0.03	10.74±0.02	11.47±0.25	93.19	32.57
P	0.59±0.07	0.68±0.02	1.04±0.02	1.19±0.01	1.35±0.02	4.85±0.12	5.00±0.17	97.00	26.19
Q	1.30±0.06	1.41±0.04	1.48±0.05	1.81±0.02	2.26±0.04	8.26±0.20	8.93±0.15	92.50	32.81
R	0.81±0.02	0.81±0.01	0.92±0.02	1.18±0.02	1.51±0.02	5.24±0.04	5.57±0.06	94.08	30.97
X	0.60±0.04	0.49±0.03	0.63±0.02	0.86±0.03	1.03±0.05	3.60±0.15	3.97±0.15	90.68	30.19

The values are Mean ±S.D

Table 3 Distribution pattern of the geochemical forms of Zn (%) in soils from the studied dumpsites (I, II, III) and control (X)

Spots	F1	F2	F3	F4	F5	Bioavailability (%)
Dumpsite I						
A	16	24	13	21	26	40.35
B	17	24	14	19	25	41.07
C	15	16	21	27	22	30.83
D	14	16	18	23	29	30.19
E	16	17	19	22	26	32.59
F	12	16	17	22	32	28.41
Mean	15.0	18.8	17.0	22.0	26.7	33.91
Dumpsite II						
G	17	21	18	20	24	38.20
H	19	18	19	23	21	36.39
I	12	15	20	30	24	26.68
J	11	15	18	32	24	26.15
K	19	16	18	21	26	35.66
L	12	15	19	23	31	27.47
Mean	15.0	16.6	18.7	24.8	25.0	31.76
Dumpsite III						
M	14	17	21	23	25	31.48
N	13	16	18	31	22	28.60
O	14	18	17	19	32	32.57
P	12	14	21	25	28	26.19
Q	16	17	18	22	27	32.81
R	15	15	18	23	29	30.97
Mean	14.0	16.0	19.0	24.0	27.0	30.44
X	17	14	18	24	29	30.19

The residual and organically bound fractions of zinc were the dominant fractions amongst the defined geochemical species in soils around the studied dumpsites (Table 3). The mean percentages of the residual and organically bound fractions Zn were 26.2% and 23.6% respectively. The residual fraction ranged between 21% and 32% with averages of 26.7%

in soils around dumpsite (I), 25.0% in soils around dumpsite (II) and 27.0% in soils around dumpsite (III). The organically bound fraction also ranged between 19% and 32% in soils around the studied dumpsites with averages of 22.00%, 24.8% and 24.0% in soils around dumpsite (I), (II) and (III) respectively. Fe-Mn oxides bound fraction varied between 13% and 21% in soils around the studied dumpsites with averages of 17.0%, 18.7% and 19.0% in soils around dumpsite (I), (II) and (III) respectively (Table 3). Fe –Mn oxide seems to play a major role in zinc accumulation in soil profile as precipitation and co-precipitation product [8]. The portion of zinc in soils and sediments strongly imparts its mobility in the environment. For this reason, severe zinc contamination tends to be confined to the region of the source. Hydrous Fe – Mn oxide and clay mineral have been noted as sorbents that control the behaviour of zinc [8]. The exchangeable and carbonate fractions ranged from 11% to 19% and 14% to 24% respectively with their percentage mean levels of 14.7% and 17.1% respectively in soils around the studied dumpsites (Table 3). The mean percentage of the total zinc associated with the different defined geochemical fractions in soils around the studied dumpsites (I, II & III) was in the following order: exchangeable (14.7%) < Carbonate (17.1%) < Fe-Mn oxide (18.2%) < organic (23.6%) < Residual bound fraction (26.3%) (Tables 2, 3 and 4). The control also had 29% residual fraction, 24% organic matter bound fraction, 18% Fe-Mn oxide fraction, and 14% carbonate fraction while the exchangeable fraction had 17% of zinc (Table 3). The bioavailable fractions also called the weakly bound fractions of Zn (Exchangeable and carbonate fractions) varied between 28.41% and 40.35% in soils around dumpsite (I), 26.15% and 38.20% in soils around dumpsite (II) and varied between 26.19% and 32.57% in soils around dumpsite (III) (Table 3). Amongst these fractions, the carbonate (F_2) was the dominant fraction. The percentage sum of the non-bioavailable fraction or the stabile fraction of Zn (F_3+F_4+F_5) was more than 65% in soils around the dumpsites studied. Ma and Rao [25], [26], [24] have all reported Zn to be strongly bound to the residual and organic fractions. When fractions of metals are mostly abundant in the residual fraction, it shows that the metals are less available and immobile.

3.2 Cadmium (Cd)

Total concentration levels and geochemical forms of cadmium in soils around the studied dumpsites are presented in Table 4. The chemical fractionation analyses shows that large amount of Cd in the contaminated soils around the studied waste dumpsites was associated with the residual and organically complexed fractions, with overall mean percentage of 31.8% and 24.9% respectively (Table 5). The high percentage amount of Cd found in the residual fraction is an important repository of Cd in the soil.

Table 4 Geochemical forms of Cd (mg/kg) in soil samples from the studied dumpsite (I, II, III) in Benin

Spots	F1	F2	F3	F4	F5	Sum	Total	Recov. (%)	Bioav. (%)
Dumpsite I									
A	0.33±0.01	0.54±0.01	0.92±0.00	1.46±0.02	2.13±0.02	5.39±0.04	5.90±0.00	91.36	16.17
B	0.14±0.00	0.29±0.01	0.41±0.01	0.86±0.01	1.02±0.02	2.73±0.04	2.93±0.02	93.17	15.81
C	0.23±0.01	0.43±0.02	0.58±0.01	0.78±0.02	1.35±0.03	3.37±0.07	3.82±0.07	88.22	19.58
D	0.53±0.01	0.64±0.01	1.08±0.01	1.26±0.03	1.46±0.02	4.97±0.05	5.14±0.05	96.69	23.54
E	0.70±0.00	0.83±0.01	1.09±0.00	1.36±0.02	1.72±0.02	5.69±0.03	6.24±0.06	91.19	26.84
F	0.88±0.01	1.01±0.02	1.14±0.02	1.32±0.01	1.92±0.02	6.27±0.06	6.79±0.02	92.34	30.14
Dumpsite II									
G	0.24±0.01	0.37±0.01	0.55±0.03	0.78±0.01	1.08±0.03	3.02±0.54	3.27±0.15	92.35	20.19
H	0.74±0.02	0.63±0.01	0.85±0.01	0.98±0.01	1.35±0.02	4.55±0.05	5.07±0.15	90.00	30.11
I	0.11±0.01	0.32±0.01	0.36±0.01	0.52±0.02	0.66±0.01	1.97±0.01	2.27±0.15	86.78	21.83
J	0.16±0.02	0.30±0.02	0.34±0.02	0.48±0.01	0.60±0.03	1.88±0.08	2.13±0.15	88.26	24.47
K	0.13±0.02	0.21±0.02	0.24±0.02	0.34±0.02	0.48±0.02	1.40±0.11	1.53±0.15	91.50	24.29
L	0.28±0.23	0.11±0.02	0.14±0.02	0.25±0.01	0.34±0.02	1.12±0.01	1.15±0.00	97.00	34.82
Dumpsite III									
M	0.16±0.02	0.25±0.03	0.31±0.01	0.42±0.02	0.61±0.02	1.75±0.08	1.83±0.15	95.63	23.43
N	0.27±0.03	0.25±0.03	0.45±0.02	0.61±0.02	0.75±0.02	2.32±0.11	2.53±0.21	91.70	22.32
O	0.23±0.02	0.28±0.01	0.36±0.02	0.43±0.02	0.62±0.02	1.91±0.03	2.03±0.06	94.09	26.56
P	0.11±0.01	0.15±0.01	0.16±0.02	0.23±0.01	0.32±0.01	0.96±0.02	1.00±0.00	96.00	26.80
Q	0.21±0.03	0.27±0.02	0.35±0.02	0.47±0.02	0.68±0.01	1.99±0.07	2.17±0.15	90.78	24.24
R	0.40±0.01	0.36±0.02	0.57±0.01	1.09±0.00	1.38±0.01	3.79±0.01	3.90±0.00	97.18	20.00
X	0.12±0.00	0.14±0.01	0.19±0.01	0.23±0.01	0.29±0.01	0.96±0.01	1.00±0.00	96.00	26.80

The values are Mean ±S.D

Table 5 Distribution pattern of the geochemical forms of Cd (%) in soils from the studied dumpsites (I, II, III) and control (X)

Dumpsite I

Spots	F1	F2	F3	F4	F5	Bioavailability (%)
A	6	10	17	27	40	16.17
B	5	11	15	32	37	15.81
C	7	13	17	23	40	19.58
D	11	13	22	25	29	23.54
E	12	15	19	24	30	26.84
F	14	16	18	21	31	30.14
Mean	9.2	13.0	18.0	25.3	34.5	22.01
Dumpsite II						
G	8	12	18	26	36	20.19
H	16	14	18	22	30	30.11
I	6	16	18	26	34	21.83
J	9	16	18	26	32	24.47
K	9	15	17	24	34	24.29
L	25	10	13	22	30	34.82
Mean	12.2	13.8	17.0	24.3	27.0	25.95
Dumpsite III						
M	9	14	18	24	35	23.43
N	12	11	19	26	32	22.32
O	12	15	19	23	32	26.56
P	11	16	17	24	33	26.80
Q	11	14	18	24	34	24.24
R	11	9	15	29	36	20.00
Mean	11.0	13.0	13.0	25.0	34.0	23.89
X	13	15	20	24	30	26.80

Association of Cd in the residual fraction does not generally constitute an environmental risk. The residual fraction (F5) had mean percentage levels ranging from 29% to 40% in the studied dumpsites with averages of 34.5%, 27.0% and 34.0% in soils around dumpsite (I), (II) and (III) respectively (Table 5). The levels of Cd in the organic bound fraction in soils around the studied dumpsites were next to those in the residual fraction ranging from 21% to 32% in soils around studied dumpsites with averages of 25.3%, 24.3% and 25.0% in dumpsite (I), (II) and (III) respectively (Table 5). This is an evidence of the influence of soil organic matter on Cd sorption. Fe-Mn oxide fraction had levels ranging from 13% to 22% in soils around the studied dumpsites, with an overall average of 17.7%. The carbonate fraction of Cd in soils around the studied dumpsites was a little higher than the exchangeable fraction amongst the bioavailable forms of Cd. The carbonate bound fraction accounted for 9% to 16% in soils around the studied dumpsites with averages of 13.0%, 13.8% and 13.0% in dumpsite (I), (II) and (III) respectively, while the exchangeable fraction accounted for 5% to 25% in soils around the studied dumpsites with an overall average of 10.8% (Table 5).

The percentage sum of the weakly bound fractions of Cd (Exchangeable and carbonate fractions) varied between 15.81% and 30.14% in soils around dumpsite (I), 21.83% and 34.82% in soils around dumpsite (II) and also varied from 22.32% to 26.80% in soils around dumpsite (III) (Table 5). The control soil samples had 30% residual, 24% organic, 20% Fe-Mn oxide, 15% carbonate while the exchangeable bound fraction had 13% (Table 5). The mean percentage of total Cd associated with different geochemical fraction in soils around the studied dumpsites was in the following order: F_5 (31.8%) > F_4 (24.9%) > F_3 (17.7%) > F_2 (13.3%) > F_1 (10.8%) (Table 5).

3.3 Chromium (Cr)

The results of the concentration levels and chemical fractionation of Cr in soils around the studied dumpsites are given in Table 6. From the results, it was observed that Cr was mostly bound to the residual fraction of soils around each studied dumpsite.

Table 6 Geochemical forms of Cr (mg/kg) in soil samples around dumpsite (I) in Benin City

Dumpsite I									
Spots	F1	F2	F3	F4	F5	Sum	Total	Recov. (%)	Bioav. (%)
A	0.05±0.00	0.12±0.01	0.26±0.01	0.18±0.00	0.53±0.00	1.13±0.02	1.23±0.05	91.87	14.91
B	0.09±0.01	0.18±0.01	0.28±0.00	0.20±0.05	0.58±0.02	1.34±0.05	1.41±0.01	95.04	20.30
C	0.08±0.01	0.10±0.01	0.14±0.01	0.18±0.01	0.38±0.02	0.88±0.02	0.91±0.01	96.70	20.45
D	0.09±0.01	0.14±0.01	0.18±0.01	0.23±0.00	0.31±0.00	0.95±0.02	1.06±0.01	89.62	24.21

E	0.17±0.00	0.22±0.00	0.31±0.00	0.33±0.00	0.41±0.00	1.44±0.01	1.49±0.01	96.64	27.08
F	0.11±0.01	0.17±0.00	0.35±0.01	0.63±0.00	0.71±0.00	1.97±0.02	2.06±0.02	95.63	14.21
Dumpsite II									
G	0.63±0.05	0.74±0.06	1.27±0.05	1.06±0.12	1.44±0.05	5.14±0.34	5.60±0.36	91.79	26.65
H	0.25±0.01	0.36±0.01	0.49±0.01	0.66±0.04	0.75±0.02	2.51±0.05	2.60±0.00	96.54	24.30
I	0.37±0.01	0.56±0.01	0.63±0.02	0.77±0.02	0.94±0.02	3.23±0.11	3.43±0.25	94.17	28.44
J	0.13±0.03	0.20±0.03	0.31±0.02	0.35±0.01	0.51±0.03	1.49±0.13	1.60±0.17	93.13	22.00
K	0.14±0.02	0.21±0.01	0.33±0.02	0.52±0.01	0.67±0.04	1.87±0.10	1.97±0.15	94.92	18.72
L	0.14±0.01	0.18±0.02	0.23±0.02	0.31±0.03	0.39±0.03	1.26±0.09	1.37±0.12	91.97	25.60
Dumpsite III									
M	0.10±0.00	0.16±0.01	0.27±0.01	0.35±0.01	0.43±0.01	1.32±0.03	1.40±0.00	94.29	19.85
N	0.32±0.01	0.48±0.02	0.55±0.02	0.62±0.03	0.74±0.04	2.70±0.09	2.83±0.15	95.41	29.52
O	0.30±0.04	0.44±0.04	0.48±0.04	0.62±0.06	0.72±0.07	2.56±0.23	2.63±0.15	97.34	28.91
P	0.15±0.02	0.14±0.02	0.19±0.02	0.25±0.02	0.31±0.02	1.04±0.08	1.13±0.12	92.04	27.88
Q	0.14±0.01	0.20±0.01	0.35±0.03	0.48±0.02	0.61±0.05	1.77±0.10	1.83±0.12	96.72	19.10
R	0.21±0.03	0.27±0.02	0.33±0.03	0.46±0.03	0.59±0.05	1.86±0.15	1.90±0.17	97.89	25.81
X	0.13±0.02	0.17±0.02	0.22±0.02	0.26±0.01	0.33±0.02	1.12±0.08	1.17±0.06	95.73	27.03

The values are Mean ±S.D

Table 7 Distribution pattern of the geochemical forms of Cr (%) in soils from the studied dumpsites (I, II, III) and control (X)

Spots	F1	F2	F3	F4	F5	Bioavailability (%)
Dumpsite I						
A	4	11	23	16	47	14.91
B	7	13	21	15	43	20.30
C	9	10	18	20	43	20.45
D	9	15	19	24	33	24.21
E	12	15	22	23	28	27.08
F	6	9	18	32	36	14.21
Mean	7.8	12.2	20.2	21.7	38.3	20.19
Dumpsite II						
G	12	14	25	21	28	26.65
H	10	14	20	26	30	24.30
I	11	17	20	24	29	28.44
J	9	13	21	23	34	22.00
K	7	11	18	28	36	18.72
L	11	14	18	25	31	25.60
Mean	8.3	13.8	20.3	25.0	31.3	24.29
Dumpsite III						
M	8	12	20	27	32	19.85
N	12	18	20	23	27	29.52
O	12	17	19	24	28	28.91
P	14	13	18	24	30	27.88
Q	8	11	20	27	34	19.10
R	11	15	18	25	32	25.81
Mean	10.8	14.3	19.2	25.0	30.5	25.18
X	12	15	20	23	29	27.03

The levels Cr in residual fraction varied from 27% to 47% in soils around the studied dumpsites with averages of 38.3% in dumpsite (I), 31.3% in dumpsite (II) and 30.5% in dumpsite (III) (Table 7). The high amount of Cr associated with the residual fraction could be due to the sandy nature of the parent soils (loamy sand) from the studied sites and

also Cr may have co-precipitated with various silicate species consequent to their adsorption into the mineral lattice [27], [28]. Similar association of Cr in residual fractions were reported by [20] on soils cultivated with oil palm in Nigeria institute for oil palm research (NIFOR) in Benin, Nigeria with an average of 35.0% Cr in the residual bound fraction; Osakwue and Okolie [29] in their reports on soils around Petrol filling stations in selected Areas of Delta State, Nigeria. The organically bound fraction of Cr ranged between 16% and 32% in soils around the studied dumpsites with averages of 21.7%, 25.0% and 25.0% in dumpsites (I), (II) and (III) respectively (Table 7). Fe–Mn oxide bound fraction of Cr ranges from 18% to 25% in soils around the studied dumpsites with an overall average of 19.9%. The bioavailable fractions of Cr in soils around the studied dumpsites (the exchangeable and carbonate fractions) were within the ranges of 4% to 14% and 9% to 18% respectively, with their overall averages of 8.9% and 13.4% respectively (Table 7). The order of the different defined geochemical forms of Cr in soils around the studied dumpsites is as follows: F1 (8.9%) < F2 (13.4%) < F3 (19.9%) < F4 (23.9%) < F5 (33.4%). The fraction of Cr that is associated with the residual and the organically complexed fractions in the control samples were also the dominant fractions amongst the defined geochemical forms with an average of 29% and 23% respectively (Table 7). The percentage sum of the weakly bound fractions (F1 + F2) which reflects the potential bio-availability of Cr ranged from 14.21% to 28.08% in soils around dumpsite (I), 18.72% to 28.44% in dumpsite (II) while soils around dumpsite (III) bioavailable fractions varied between 19.10% and 29.52%. Generally, bioavailability of weakly bound fractions of heavy metals can be altered by changes in pH, organic matter content and redox status of the contaminated soils [30].

The mobility factors (MF) described the potential mobility of metals as some metals are more strongly bound to the soil component than others. Low MF values have been reported as symptoms of relatively low liability and biological availability of heavy metals in soil. The mobility factors (MF) of the analysed heavy metals in the studied sites are presented in Table 8. The results are indicative of the relative reactivity of the metals with active sites.

Table 8 Mobility factors (%) of Zn, Cd and Cr from the studied dumpsites (I, II, III) and control (X)

Dumpsite I			
Spots	Zn	Cd	Cr
A	40.35	16.17	14.91
B	41.07	15.81	20.30
C	30.83	19.58	20.45
D	30.19	23.54	24.21
E	32.59	26.84	27.08
F	28.41	30.14	14.21
Mean	33.91	22.01	20.19
Dumpsite II			
G	38.20	20.19	26.65
H	36.39	30.11	24.30
I	26.68	21.83	28.44
J	26.15	24.47	22.00
K	35.66	24.29	18.72
L	27.47	34.82	25.60
Mean	31.76	25.95	24.29
Dumpsite III			
M	31.48	23.43	19.85
N	28.60	22.32	29.52
O	32.57	26.56	28.91
P	26.19	26.80	27.88
Q	32.81	24.24	19.10
R	30.97	20.00	25.51
Mean	30.44	23.89	25.81
X (Control)	30.19	26.80	27.03

The mobility and availability of heavy metals in soils are associated with the solubility of their geochemical forms and that if these metal fractions increases in the order of their extraction sequence; $F_1 < F_2 < F_3 < F_4 < F_5$, then the apparent mobility and potential availability will be low in the soils, which is an indication of their decreasing solubility from F_1 to F_5. The low mobility factors observed for each analysed heavy metal in the studied sites is quite in agreement with the low percentage of the weakly absorbed (exchangeable and carbonate) fractions recorded from their chemical fractionation analyses. The mobility factors (MF) in soils around each studied dumpsite are in the following order: For soils around dumpsite (I); Zn > Cd > Cr, for soils around dumpsite (II); Zn > Cd > Cr while MF for soils around dumpsite (III); Zn > Cr > Cd (Table 8). For the control site, the mobility factors (MF) of each metal were in the decreasing order of: Zn > Cr > Cd (Table 8).

4 CONCLUSION

Heavy metals chemical speciation results in this study gave an overall picture that high percentage of these metals were found to be strongly bounded to soil matrix, in a form not readily available for introduction into the soil solution for possible absorption. The overwhelming importance of the non-bioavailable fractions (residual, organic and Fe-Mn oxide bound) in this study illustrates clearly the difficulty of distinguishing between background and irregular levels of heavy metals contamination when only total metal analysis are performed. The low mobility factors observed in the studied heavy metals confirms the low biological availability of the analysed heavy metals in soils around each studied dumpsite and pose no danger to the ecosystem. The continuous injection of these metals into the environment increases their concentration levels, consequently their toxicity and bioavailable fractions.

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