Chemical speciation and mobility study of some heavy metals in soils around municipal solid waste dumpsites in Benin City metropolis, Nigeria

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Received: 1 July 2019 / Accepted: 14 November 2019 / Published online: 21 November 2019
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Abstract

This paper examined chemical fractionation of selected heavy metals (Cu, Pb, Mn and Ni) in soils around municipal solid waste dumpsites in Benin City, Nigeria, using the multi-step phase-selective extraction schemes for metal speciation. Total concentration levels of the heavy metals were done using atomic absorption spectrophotometry. The results showed that the analysed heavy metals were more abundant in their stable fractions with the residual fraction dominating the non-bioavailable fractions. The potentially mobile and bioavailable fraction of Cu ranged from 21 to 40%, of Pb ranged from 20 to 30%, of Mn ranged from 16 to 30%, while that of Ni ranged from 18 to 29% in soils around the studied dumpsites. The percentage of bioavailability/mobility of the analysed heavy metals in soils around each studied dumpsite were in the order: dumpsite (I), Pb > Cu > Mn > Ni; dumpsite (II), Cu > Ni > Pb > Mn; and dumpsite (III), Cu > Mn > Pb > Ni. The relative low mobility factors shown by each heavy metal in the studied sites were quite in agreement with the low bioavailable fractions recorded from their fractionation analysis. The overall result shows that large fractions of the analysed heavy metals were in geochemical forms and not readily released into soil solution for bioavailability.

Keywords Bioavailable · Dumpsite · Geochemical form · Heavy metals · Soil

1 Introduction

The increasing awareness of the potential hazards of large-scale contamination of the environment with heavy metals arising from rapid unplanned industrial, agricultural and human domestic activities or practices such as unlawful wastes disposal system and other anthropogenic sources which introduces heavy metals into soils has highlighted the need for continuous monitoring of the concentration levels and evaluation of the effects of the geochemical forms and the mobility of these contaminants in the environment [17, 20]. High concentration levels of heavy metals in soils and sediments have been known to be undesirable to the habitats, thereby posing serious environmental degradation.

Soils serve as the most absorptive sink for solid wastes; hence, they are very rich in micro- and macro-nutrients for the growth and survival of living organisms directly or indirectly. This gives credence to the view that the contamination and pollution of soils by heavy metals from solid wastes pose high risk to living and non-living components in the environment [28]. The toxicity of heavy metals in soils is determined largely by its chemical or geochemical forms. Large fractions of heavy metals in soils are associated with the solid phases of the soil. The problem of heavy metal soil pollution arises when these metals are mobilised into soil solution by different solubility reactions of ions or compounds of these metals in soils and then taken up by plants or transported to surface or ground water. However, total concentration levels of heavy metals in soils

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give little or no information about their sources, forms or phase, mobilization and bioavailable fraction [16, 23]. This means that the total concentration levels of heavy metals in the environment do not represent their geochemical forms, toxicity and their overall characteristics most often. In order to overcome the above-mentioned obstacles, it is important to analyse and evaluate each metal geochemical fraction to fully understand their actual and potential environmental effects based on their geochemical forms [37].

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 [4, 19]. These affect their behaviour, geochemical forms, bioavailability and mobility. However, not all the reactions in soil chemical and biological processes are equally important for each metal element, but the bioavailability and mobility of metals could be affected by other soil physicochemical properties like pH [39]. Heavy metals are also easily influenced by environmental factors such as surface run-off, atmospheric deposition and anthropogenic pollutants; hence, they may be sensitive indicators for monitoring changes in the environment [24]. Soil is a complex body composed of different components. The composition and proportion of these soil components have a great influence on soil properties [9]. The availability and movement of fraction of metals in soils is also determined by soil components to which the metal is associated with [3]. Soils within and around municipal solid waste dumpsites in most urban areas in Nigeria were found to be contaminated and polluted with heavy metals. This is because solid wastes dumpsites across cities in Nigeria consist primarily of metals, plastic and rubber materials, textiles, glass, food scraps, vegetable matter, damage batteries, tyres, contagious solid wastes coated with heavy metals which could introduce metals into soils, and so on [5].

The studied dumpsites are located along Benin-Agor road and Benin-Lagos express road, in Benin City. Cu, Pb and Ni are among the common metals present in road run-off and automobile exhaust fumes or emission. Hence, the sources of these metals in the environment are also from road transportation which includes leaded gasoline, tire wear, lubricating oil and grease, bearing wear, engine parts, brake emission and diesel fuel [15]. Cu, Pb and Ni were then considered in this study because of the close proximity of the studied dumpsites to high vehicular traffic. Also, Cu and Mn are amongst the heavy metals which occur naturally in the environment (soil), and they serve as plant nutrient, depending on their concentration levels in soils.

Literature research revealed that only few studies have been conducted on the chemical speciation and mobility study of heavy metals in contaminated sites like municipal solid waste dumpsite in Benin City metropolis, Nigeria. Most of the studies conducted centred on soil heavy metal contamination and pollution levels. Unlike many other urban towns in Nigeria such as Lagos, Warri, Agbor, Akure and Port Harcourt, where studies relating heavy metals speciation and mobility study have been investigated, there is little information in the literature on the heavy metal speciation, bioavailability and mobility study in soils around municipal solid waste dumpsites in Benin. Hence, this study was conducted. The aim of the study is to evaluate the different geochemical forms of Cu, Pb, Mn and Ni in soils around some major municipal solid waste dumpsites in Benin City metropolis and to assess the bioavailable fraction and mobility of these metals from their geochemical forms using chemical fractionation analysis.

2 Materials and methods

2.1 Study area

This study was carried out in Benin City metropolis between January and April 2018. The City is the capital of Edo State, Nigeria, and is located in the south-south geopolitical zone of Nigeria, bounded by latitudes 6°15'N to 6°30'N and longitudes 5°30'E to 5°45'E and area of about 500 square kilometres. The climatic condition falls within the Rain forest type and similar to other parts of southern Nigeria with annual rainfall generally high, ranging from 2000 to 2400 mm. The city is underlain by sedimentary formation [2]. The soil formation is made up of top reddish clay capping highly porous freshwater bearing, loose pebbly sands and sandstone with local thin clays and shale interbeds which are considered to be of weathered surfaces to white in the deeper fresh surfaces. Limonitic coatings are responsible for the brown reddish–yellowish colour [1, 2, 22].

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

2.2 Sample collection and preparation

Composite soil samples was collected from three government approved municipal solid waste dumpsites in Benin City metropolis, at depths of 0–15, 15–30 and 30–45 cm, representing top soils, sub soils and bottom soils, respectively. Soil samples were collected within 120 m × 120 m quadrants around each dumpsite. Each quadrant was

Fig. 1 Map of Benin showing 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 and longitude)
Dumpsite (I)	Ikhueniro dumpsite; Ikhueniro community, Benin Agbor road (Bye pass) Benin City.	Domestic	15 years	52,000 m ²	6°19'28.261" N 5°45'04.158" E
Dumpsite (II)	Otofure dumpsite; Otofure community, Oluku Bye pass, Benin City.	Domestic	Above 17 years	37,500 m ²	6°27'47.599" N 5°36'10.397" E
Dumpsite (III)	Iguomon dumpsite; Iguomon community, Benin-Lagos expressway (bypass), Benin city.	Domestic	15 years	58,560 m ²	6°21'36.360" N 5°44'58.085" E
Control site (X)	Farm land at Ikhueniro community, Benin Agbor road, Benin City	—	—	—	6°18'11.394" N 5°46'34.226" E

subdivided into 10 cells (12 m × 12 m), with each cell denoting a sampling point. A composite soil sample comprised at least six random samples was collected at each cell (100 m away from the centre of each studied dumpsite). Samples were extracted till an average depth of 45 cm by using stainless steel spade and an automatic core driller [7]. Three soil samples per point from the three depths were bulked together to form one composite sample. 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 composite soil samples from the three studied dumpsites. The gradient (high and low) and the direction of flow of erosion were also considered for each sampling point. For the purpose of control, soil samples were also obtained in similar manner from a farm land in the adjoining area of the solid wastes dumpsite (500 m away from the studied waste dumpsite), and it 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. They were air-dried for a period of 2 weeks in a well-ventilated space, homogenized by grinding in porcelain mortar and sieved through a 2-mm (10 meshes) stainless sieve. The air-dried < 2-mm soil samples were oven-dried at $105 \pm 0.5^\circ\text{C}$ to a constant mass, cooled and stored in labelled airtight plastic cans prior to analysis [7].

2.3 Determination of total concentration levels and chemical fractionation analyses of heavy metals in soil samples

Total concentration levels of Cu, Pb, Mn and Ni were determined in accordance with the USEPA method described by [21] and [14]. In order to assess the geochemical forms and bioavailable Cu, Pb, Mn and Ni in soils, the [40] five multi-step phase-selective sequential extraction schemes modified by [6] and [16] was adopted. In the method, heavy metals were separated into five operationally defined fractions. Two grams of the dried soil sample were weighed and extracted as follows:

Fraction I—Exchangeable fraction (F_1) Eight (8) mL of 1 M magnesium chloride solution (pH 7.0) was added to 1 g of soil sample in a 50 mL polypropylene bottle, and the mixture was shaken in a mechanical shaker for 1 h.

Fraction II—Metals bound to carbonates (F_2) Eight (8) mL of 1 M sodium acetate solution was added to the residue of F_1 and adjusted to pH 5.0 with glacial acetic acid

(concentrated). The resulting solution and mixture was agitated for 5 h in a mechanical shaker.

Fraction III—Metals bound to Fe-Mn oxides or reducible fraction (F_3) Twenty (20) mL of 0.04 M hydroxylamine hydrochloride in 25% glacial acetic acid was added to the residue of F_2 and the mixture was heated at $96 \pm 3^\circ\text{C}$ with occasional agitation for 6 h.

Fraction IV—Metals bound to organic matter or oxidizable fraction (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 $85 \pm 2^\circ\text{C}$ in a water bath for 2 h with occasional agitation. An additional 3 mL aliquot of the acidified 30% hydrogen peroxide was added, and the mixture was heated at $85 \pm 2^\circ\text{C}$ for 3 h with intermittent agitation. Subsequently, 5 mL of 3.2 M 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 min.

Fraction V—Residual fraction (F_5) The residue of F_4 from the previous extraction was transferred into a digested tube and digested with 5 mL of aqua regia and 1 mL of 60% perchloric acid until white fumes appeared. After cooling, it was filtered through a Whatman 1 filter paper into a 100-mL volumetric flask, and the volume was adjusted to mark with distilled water.

After each successive extraction process, centrifuging the mixture at 1500 rpm for 15 min effected the liquid–solid phase separation for easy decantation of the supernatant into a polypropylene bottle for metal analysis. The concentrations of heavy metals in the various supernatant 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 [27, 36], on the basis of Eq. (1).

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

2.5 Statistical analysis of data

One-way ANOVA ($p \leq 0.05$) was employed to evaluate the correlations of the mean concentration levels as well as

the geochemical forms of the analysed heavy metals fractions. Simple correlation coefficients and p values were calculated for all possible variable pairs. Various notable significant correlations were recorded and matrixes of correlation coefficient between different quantitative variables were also determined.

3 Results and discussion

The operationally defined geochemical forms of metals (exchangeable, carbonates, Fe-Mn oxides, organic matter and residual), summation of the forms, mean

Table 2 Correlation showing the effect of concentration levels of metals in soils on the distribution of the metals in their geochemical fractions

	<i>N</i>	<i>r</i>	sig.(2-tailed)
Sum of geochemical fractions of metals	72	0.999	0.000
Independent total concentration levels			

$\alpha=0.05$

concentration levels (mg/kg), percentage (%) recovery, bioavailable fraction (%) and the distribution pattern (%) of Cu, Pb, Mn and Ni in the studied sites are presented in Tables 2, 3, 4, and 5 and Fig. 2. The variation that exists between the concentration levels of individual metal across all sampling points in the studied dumpsites could be due to factors such as direction of flow of erosion and gradient level (high and low gradient) that were considered across all sampling point in the studied sites when collecting soil samples. In most cases, the concentration level of each studied metal was higher in sampling point of low gradient and then lowers in point of high gradients which could be due to run-off of wastes and metals by erosion. The overall recovery rate which is the sum of five fractions from the sequential extraction procedure divided by the independent total concentration ranged from 90 to 99%. This signifies high reliability in the methods used for the sequential extraction procedures. The analysed heavy metals were mostly abundant in the residual and organic fractions in soils around the studied sites. This implies low mobility and bioavailability of the metals. It also indicates probably a low degree of pollution by the metals considered. The five geochemical forms are operationally defined by an extraction sequence that follows the order of decreasing solubility. Assuming that

Table 3 Geochemical forms of Cu (mg/kg) in soil samples from the studied dumpsites (I, II, III) and control (X) in Benin

Spots	F1	F2	F3	F4	F5	Sum	Mean conc. levels	Recov. (%)	Bioav. (%)
<i>Dumpsite I</i>									
A	0.56±0.11	1.11±0.04	1.38±0.07	1.95±0.07	3.08±0.16	8.09±0.44	8.30±0.44	97.47	20.67
B	0.63±0.01	1.07±0.06	1.23±0.04	1.83±0.02	2.99±0.02	7.74±0.04	8.27±0.06	93.57	21.94
C	0.92±0.01	1.31±0.02	1.55±0.02	2.03±0.02	3.32±0.02	9.14±0.04	9.96±0.04	91.77	24.45
D	0.85±0.06	1.14±0.04	1.61±0.01	2.13±0.03	3.25±0.03	8.99±0.11	9.23±0.15	97.39	22.16
E	0.74±0.03	1.23±0.02	1.59±0.02	1.99±0.03	2.51±0.04	8.08±0.04	8.30±0.26	97.35	24.44
F	0.93±0.10	1.31±0.03	1.78±0.01	2.16±0.02	2.71±0.03	8.89±0.07	9.73±0.15	91.37	25.19
<i>Dumpsite II</i>									
G	2.33±0.01	3.93±0.05	4.36±0.01	5.55±0.02	6.77±0.02	22.93±0.06	23.80±0.20	96.34	28.88
H	6.44±0.00	6.91±0.01	7.42±0.01	8.23±0.01	7.92±0.02	36.92±0.02	37.27±0.06	99.06	36.16
I	4.01±0.01	6.66±0.01	4.29±0.01	6.04±0.02	5.35±0.02	26.35±0.03	29.30±3.39	89.93	40.49
J	1.86±0.01	2.53±0.02	3.23±0.02	4.12±0.02	5.00±0.01	16.74±0.04	17.47±0.21	95.82	26.22
K	2.21±0.02	2.11±0.01	2.13±0.02	2.68±0.04	3.45±0.01	12.59±0.08	13.13±0.15	95.89	34.34
L	3.11±0.02	3.78±0.02	4.29±0.02	4.95±0.01	5.39±0.02	21.52±0.05	23.23±0.32	92.64	32.02
<i>Dumpsite III</i>									
M	2.12±0.04	2.29±0.04	2.00±0.02	2.91±0.03	2.58±0.01	11.90±0.13	12.40±0.46	95.97	37.06
N	2.68±0.09	3.69±0.03	5.72±0.04	7.67±0.03	8.12±0.06	27.88±0.20	29.03±0.25	96.04	22.85
O	2.93±0.04	3.71±0.04	4.54±0.04	5.07±0.04	5.76±0.05	22.01±0.17	23.17±0.21	94.99	30.17
P	0.88±0.01	1.22±0.02	1.42±0.02	1.88±0.02	2.11±0.01	7.52±0.05	7.63±0.06	98.56	27.96
Q	2.04±0.03	2.43±0.04	2.66±0.06	3.10±0.06	3.67±0.06	13.91±0.20	14.40±0.00	96.60	32.16
R	1.40±0.07	1.56±0.03	1.72±0.13	2.00±0.04	2.28±0.03	9.06±0.18	9.37±0.13	96.70	33.04
X	0.92±0.02	0.76±0.06	0.91±0.07	1.16±0.07	1.35±0.10	5.10±0.32	5.23±0.32	97.51	32.94

The values are Mean ± SD

Table 4 Geochemical forms of Pb (mg/kg) in soil samples from the studied dumpsites (I, II, III) and control (X) in Benin

Spots	F1	F2	F3	F4	F5	Sum	Mean conc. levels	Recov. (%)	Bioav. (%)
<i>Dumpsite I</i>									
A	0.14±0.00	0.25±0.01	0.35±0.02	0.52±0.03	0.65±0.04	1.92±0.10	2.03±0.15	94.58	20.42
B	0.32±0.02	0.39±0.01	0.50±0.01	0.67±0.02	0.75±0.01	2.62±0.03	2.80±0.00	93.57	26.99
C	0.29±0.01	0.43±0.03	0.49±0.01	0.59±0.02	0.76±0.01	2.57±0.03	2.70±0.00	95.19	28.16
D	0.35±0.01	0.48±0.00	0.59±0.01	0.73±0.00	0.89±0.01	3.02±0.02	3.30±0.00	91.52	27.30
E	0.57±0.01	0.81±0.01	0.97±0.02	1.23±0.01	1.57±0.03	5.13±0.02	5.60±0.00	91.61	26.79
F	0.31±0.00	0.55±0.02	0.86±0.03	1.12±0.02	1.32±0.02	4.15±0.04	4.33±0.01	95.84	20.67
<i>Dumpsite II</i>									
G	0.85±0.01	1.19±0.01	1.56±0.01	1.78±0.02	2.15±0.01	7.54±0.04	8.30±0.00	90.84	27.09
H	0.66±0.02	0.83±0.01	0.96±0.01	1.15±0.01	1.35±0.02	4.95±0.02	5.17±0.12	95.74	30.10
I	0.22±0.01	0.36±0.01	0.51±0.01	0.74±0.01	0.82±0.02	2.65±0.04	2.90±0.00	91.38	21.89
J	0.63±0.01	0.89±0.01	1.10±0.01	1.45±0.02	1.92±0.01	5.97±0.03	6.60±0.00	90.45	25.38
K	0.31±0.01	0.46±0.02	0.74±0.01	0.89±0.01	1.10±0.01	3.49±0.02	3.70±0.00	94.32	22.00
L	0.24±0.01	0.22±0.01	0.35±0.02	0.41±0.01	0.66±0.01	1.88±0.03	2.00±0.00	94.00	24.47
<i>Dumpsite III</i>									
M	0.15±0.02	0.18±0.03	0.29±0.02	0.33±0.02	0.41±0.07	1.36±0.15	1.43±0.23	95.10	24.26
N	0.45±0.03	0.38±0.06	0.57±0.05	0.71±0.01	0.86±0.02	2.97±0.09	3.13±0.12	94.89	27.95
O	0.37±0.02	0.55±0.03	0.62±0.01	0.83±0.02	0.97±0.03	3.35±0.09	3.63±0.21	92.29	27.54
P	0.11±0.03	0.18±0.03	0.21±0.04	0.31±0.02	0.34±0.03	1.15±0.15	1.23±0.21	93.50	25.22
Q	0.26±0.03	0.38±0.01	0.53±0.02	0.67±0.02	0.96±0.01	2.79±0.05	3.03±0.06	92.08	22.86
R	0.18±0.02	0.31±0.02	0.49±0.02	0.58±0.02	0.69±0.02	2.25±0.03	2.30±0.00	97.83	21.78
X	0.15±0.03	0.24±0.04	0.33±0.03	0.39±0.04	0.54±0.06	1.65±0.19	1.70±0.17	97.06	23.34

Table 5 Geochemical forms of Mn (mg/kg) in soil samples from the studied dumpsites (I, II, III) and control (X) in Benin

Spots	F1	F2	F3	F4	F5	Sum	Mean conc. levels	Recov. (%)	Bioav. (%)
<i>Dumpsite I</i>									
A	0.46±0.01	0.60±0.02	1.34±0.02	0.72±0.03	1.05±0.00	4.18±0.08	4.59±0.09	91.07	25.42
B	0.54±0.02	0.73±0.03	1.55±0.02	0.84±0.03	1.07±0.03	4.72±0.14	5.17±0.15	91.29	26.85
C	0.30±0.04	0.44±0.03	0.64±0.03	1.11±0.02	0.81±0.02	3.29±0.14	3.37±0.21	97.63	22.42
D	0.27±0.10	0.42±0.02	1.06±0.03	0.57±0.01	0.72±0.00	3.03±0.06	3.17±0.12	95.58	22.69
E	0.49±0.04	0.60±0.01	1.68±0.04	0.83±0.03	1.18±0.01	4.77±0.07	5.23±0.21	91.20	22.80
F	0.34±0.01	0.46±0.00	1.86±0.02	0.87±0.01	1.22±0.02	4.74±0.04	4.97±0.21	95.37	16.84
<i>Dumpsite II</i>									
G	0.97±0.00	1.57±0.02	2.32±0.01	1.74±0.02	2.08±0.01	8.65±0.02	9.27±0.31	93.31	29.26
H	0.88±0.01	1.29±0.01	1.82±0.02	1.43±0.02	1.95±0.03	7.38±0.07	8.03±0.21	91.91	29.44
I	0.45±0.02	0.41±0.02	1.04±0.01	0.64±0.01	0.93±0.02	3.46±0.03	3.77±0.21	91.78	24.78
J	0.55±0.02	0.70±0.02	0.96±0.01	1.75±0.03	1.34±0.01	5.30±0.02	5.67±0.12	93.47	23.58
K	0.15±0.01	0.23±0.01	0.29±0.02	0.56±0.02	0.75±0.03	1.97±0.06	2.13±0.15	92.49	19.19
L	0.12±0.01	0.20±0.01	0.30±0.02	0.41±0.02	0.49±0.02	1.51±0.07	1.57±0.12	96.18	21.05
<i>Dumpsite III</i>									
M	0.16±0.05	0.13±0.04	0.44±0.06	0.24±0.04	0.29±0.05	1.26±0.22	1.30±0.26	94.62	23.02
N	0.24±0.02	0.36±0.01	0.43±0.01	0.77±0.03	0.55±0.02	2.35±0.04	2.57±0.15	91.44	25.53
O	0.34±0.02	0.22±0.02	0.56±0.02	0.26±0.02	0.57±0.02	1.95±0.02	2.10±0.00	92.86	28.72
P	0.25±0.05	0.15±0.02	0.29±0.04	0.34±0.05	0.38±0.02	1.42±0.17	1.53±0.21	92.81	28.37
Q	0.33±0.02	0.29±0.02	0.34±0.03	0.47±0.04	0.68±0.07	2.11±0.17	2.17±0.21	97.23	29.38
R	0.25±0.01	0.28±0.02	0.58±0.01	0.23±0.02	0.49±0.01	1.82±0.03	1.97±0.06	92.39	28.96
X	0.12±0.02	0.14±0.02	0.19±0.02	0.25±0.02	0.31±0.02	1.02±0.08	1.10±0.17	92.73	25.74

The values are Mean ± SD

Fig. 2 Distribution pattern of the geochemical forms of Cu, Pb, Mn and Ni (%) in soils from the studied dumpsites (I, II, III) and control site (X), respectively

bioavailability is related to solubility, metal bioavailability decreases in the order: exchangeable > carbonate > Fe-Mn oxide > organic > residual [7].

The ANOVA test ($p \leq 0.05$) demonstrated the existence of significant difference in Cu, Pb, Mn and Ni concentration levels in soils between the studied dumpsites and the control site, indicating the contamination levels of the analysed metals. The coefficient of variability (CV) of the analysed heavy metals from the studied sites in this study could be ranked high in variation with Mn mean concentration levels having the highest coefficient of variation of 53%; Pb with 52%; Cu with 38%; and Ni with 35%. The correlation matrix computed shows that Cu mean concentration levels correlate positively and significantly with Pb mean concentration levels ($r = 0.485$) and also correlate positively and not significantly with the mean concentration levels of Mn ($r = 0.506$) and Ni ($r = 0.352$) in soils around the studied dumpsites. The mean concentration levels of Pb also correlate positively and significantly with the mean concentration levels of Mn ($r = 0.859$) and Ni ($r = 0.536$) in the studied sites. These positive correlations amongst heavy metals concentration levels tend to suggest same source and environment while the insignificant or not significant positive correlations between these metals may be due to possible contamination which may not indicate high values for others.

The correlation of the effect of the concentration levels of the analysed heavy metals in soils on the distribution of metals in the various geochemical fractions showed that the distribution was dependent on the total amount of the analysed metals present in the soil (Table 2).

Table 2 showed an r_{pb} of 0.999 and p value of 0.000 at alpha level (α) of 0.05. The r_{pb} value of 0.999 shows a very high correlation of total concentration levels of analysed metals and the concentration in their various geochemical fractions. The p value of 0.000 shows that there is a significant relationship between metal concentration in various geochemical fractions and total concentration levels, since the alpha value is greater than the p value (Table 2).

3.1 Copper (Cu)

The overall mean concentration levels of copper in soils around the studied dumpsites varied between 7.63 ± 0.06 and 37.27 ± 0.06 mg/kg. The geochemical forms of copper in soils around the studied sites are presented in Table 3 and the distribution pattern for Cu, Pb, Mn and Ni fractions in Fig. 2.

Copper was mostly associated with the residual and organic fractions with averages of 28.8% and 23.6%, respectively, in soils from the studied dumpsites. On the average, percentage of total Cu associated with different geochemical fractions in the soil from the studied

dumpsites was in the following order: residual > organic matter > Fe-Mn oxides > carbonate > exchangeable fraction. The exchangeable fraction of Cu in soils around the studied dumpsites ranged from 7 to 18% with an average of 12.3%, the bound to carbonates fraction 13–25% with an average of 16.6%, Fe-Mn oxide-bound fraction 16–21% with an average of 18.6%, organic matter bound fraction 21–28% with an average of 23.6% while the residual fraction 20–38% with an average of 28.8%. The dominance of Cu in the residual and organic fractions in this study corroborates the findings of [6], who reported Cu residual and organic fractions of 26.2% and 25.8%, respectively, in contaminated soil in Nigeria, while [8] reported that highest amount of Cu was found in residual fraction ranging from 45.4 to 65.6% in dry and wet seasons in sediments of Agbabu bitumen deposit with a very low potentially bioavailable fraction of 0.6%. This present study shows that 32% Cu was potentially bioavailable.

The high levels of Cu in this fraction (residual or inert) may be due to the high level of sand particles (loamy sand) from the physicochemical properties of the parent soil and the presence of acid-resistant mineral and organic materials [14]. Heavy metals interact with soil organic matter through different mechanisms, which affect their bioavailable fraction. The metal may have also co-precipitated with different silicate species as a result of their adsorption into the mineral lattice [25]. The high level of Cu also associated with the organic fraction in soils around the studied dumpsites could also be due to the fact that copper can easily complex with soil organic matters because of the high formation of organo-Cu compounds with soil organic matter [10]. When the residual and organically bound fractions of Cu in each studied dumpsite were compared with one another, there were close similarities in their percentage levels and mean values.

For soils around dumpsite (I), the residual fraction of Cu ranged from 30 to 38% with an average of 35.0%, while organic matter fraction ranged from 22 to 25% with an average of 23.8%. For soils around dumpsite (II), the residual fraction of Cu ranged from 20 to 30% with an average of 25.5%, while the organic fraction ranged between 21 and 25%, with an average of 23.0%, while in soils around dumpsite (III), the residual fraction varied between 22 and 29% with a mean value of 26.0%, and the organic bound fraction ranged from 22 to 28% with an average of 24.0%. For the control site, Cu was also predominantly associated with the residual and organic fractions averaging 26% and 23%, respectively. The Fe-Mn oxide-bound fraction was 18%, carbonates bound fraction 15%, while the exchangeable fraction was 18%. The sum of the stable or non-bioavailable fractions of Cu was more than 70% in soils around dumpsite (I), more than 65% in soils around dumpsite (II) and more than 68% in soils around dumpsite

(III). This can be considered as a symptom of low mobility of Cu in soils around the studied dumpsites. The bioavailable fraction of Cu was in average of 32% in soils around the studied dumpsites.

Amongst the weakly bound (bioavailable) fractions of Cu, the carbonates bound fraction appears to be more abundant, amounting to 54% of the sum of these fractions in soils around the studied dumpsites. 21–25% of Cu was potentially bioavailable in soils around dumpsite (I), 26–40% of Cu was potentially bioavailable in soils around dumpsite (II), while 23–37% of Cu was also potentially bioavailable in soils around dumpsite (III). The bioavailable fractions of Cu in the control site were 33%. The residual fraction of Cu in the control site was also more abundant amongst the stabile fractions while the exchangeable fraction was more abundant in the bioavailable fractions.

3.2 Lead (Pb)

The mean concentration levels of lead in soils around the studied dumpsites varied between 1.23 ± 0.21 and 8.30 ± 0.00 mg/kg (Table 4). Lead was largely present in the residual fraction in soils around the studied dumpsites, ranging from 27 to 35% with an average of 30.9% (Fig. 2). This high level of lead in residual fraction indicates lithogeneous origin.

Lead distribution in various geochemical fractions depended on the total Pb content in the soil. As the total concentration levels in the soils increased, the percentage of total Pb in residual, organic and Fe-Mn oxide fractions increased. The results of this study suggest that as the extent of Pb contamination in soils increased, more Pb was associated with the residual and organic fractions, which decreased the potential Pb mobility and bioavailability in these soils. But the findings of this study do not corroborate with the findings reported by [29] on the levels and speciation of heavy metals in contaminated soils from an industrial area in Southern Nigeria which shows that as the extent of Pb contamination in soil increased, more Pb was associated with the non-residual fractions, which increased the potential Pb mobility and bioavailability in soils.

The residual fraction of metals is considered the most stable, less reactive and less bioavailable since it is incorporated in the crystal lattices of clay minerals and silicates, hence not readily released into solution [38]. The fraction represents a measure of the degree of soil heavy metal pollution. The smaller the percentage of metals presents in residual fraction, the greater the degree of pollution of the area [13]. Similar levels of Pb in residual fraction have been reported by [14], ranging from 37 to 39% in soils cultivated with oil palm in Benin City, and in an earlier report, [8] reported much higher levels of

residual fraction of Pb ranging between 93.3 and 95.9% in sediments of Agbabu Bitumen deposit area, Nigeria, while [6] also reported 43.6% residual fraction of Pb in contaminated soil from an automobile spare parts market in Nigeria, which is also higher than the average of 30.9% reported in this present study. The high levels of Pb in residual fraction (27–35%) observed in this present study may also be due to the presence of acid-resistant mineral and organic matters, since heavy metals interact with organic matter through various mechanisms [6]. The residual fraction of Pb in soils around dumpsite (I) ranged from 29 to 34% with an average of 30.8%, around dumpsite (II) 27 to 35% with an average of 31.0% and varied between 29 and 34% in soils around dumpsite (III) with an average of 31.0%.

The organically complexed Pb fraction was next to the residual fraction in terms of relative abundance. The organic matter fraction varied between 22 and 28% with an average of 24.9% in soils around the studied dumpsites. Fe-Mn oxide fraction of Pb ranged between 14 and 16% with an average of 19.6% in soils around the studied dumpsites. The dominance of residual and organic fractions (inert or stabile) of Pb over other fractions have been reported by [6] and [8]. The organically complexed fraction of Pb in dumpsite (I) varied between 23 and 27% with an average of 25.2%, in dumpsite (II) it was 22–28% with an average of 24.5%, while in dumpsite (III) it varied between 24 and 27% with an average of 25.0%. The dominance of the stabile fractions of Pb over the bioavailable fractions could also be due to the formation of Pb phosphates particularly pyromorphites in soils which has implicated for immobilizing Pb and thereby reducing its bioavailability [11, 34]. The relative abundance in the residual, organic and Fe-Mn oxide fractions of Pb in soils around the studied dumpsites showed that Pb is less available and immobile in the studied dumpsites environment. The association of lead with Fe-Mn oxide fraction is due to the formation of stable complexes. The carbonates fraction of Pb ranged between 12 and 17% with an average of 14.5%, while the exchangeable fraction varied between 7 and 15% with an average of 10.6% in soils around the studied dumpsites.

Generally, the total Pb associated with different defined geochemical fraction in soils around the three studied dumpsites was in the following order: residual > organic fraction > Fe-Mn oxide > carbonate > exchangeable bound fraction. The residual and organic matter fractions were also the dominant fractions of Pb in the control soils with an average of 33 and 24%, respectively. The bioavailable fraction of Pb in soils around dumpsite (I) ranged from 20 to 28%, around dumpsite (II) it ranged 21–30%, while around dumpsite (III) ranged from 21 to 28%. The control sample had 23% bioavailable fraction.

3.3 Manganese (Mn)

The mean concentration levels of Mn in soils around the studied dumpsites ranged between 1.30 ± 0.26 and 9.27 ± 0.31 mg/kg against 1.10 ± 0.17 mg/kg in the control soil (Table 5). The residual and Fe-Mn oxide fractions contained the predominant species of Mn in soils around the studied dumpsites. The residual fraction varied from 23 to 38% with an average of 26.8%, while the Fe-Mn oxide-bound fraction 15 to 39% with an average of 26.6% in soils around the studied dumpsites.

Manganese distribution in various geochemical fractions also depended on the total Mn content in soils from the studied dumpsites (Table 5). As the total concentration levels in these soils increased, the percentage of total Mn in Fe-Mn oxide and residual fractions increased. Hence, the potential Mn mobility and bioavailability in these soils were reduced.

High levels of Mn in residual fraction have been reported by [31], ranging from 14.96 to 39.71% with an average of 24.43% in soils around automobile waste dumpsites in Nigeria, with potentially bioavailable fractions varied between 28.41 and 50.83%, which is higher than the range of 16.84 to 29.44% observed in this present study. In an earlier study, [13] had reported higher residual level of Mn in Fe-Mn oxide fraction as 54.81% in sediments of Diobu River, Port Harcourt, Nigeria. The high levels of Mn in non-bioavailable form signify that Mn could be embedded in the crystal lattices of clay minerals and silicate which is usually in an insoluble form such as in the ionic compounds of Mn^{2+} and Mn^{4+} and not readily released into solution which is capable of forming MnO_2 and MnO_4 [26].

The Fe-Mn oxide fraction forms the second most important species of Mn in this study, almost equivalent to the residual fraction of Mn in soil matrix of the studied dumpsites. The levels of Mn in this fraction ranged from 15 to 39% with an average of 26.6% in soils around the studied dumpsites. The association of Mn in Fe-Mn oxide fraction is similar to the reports by [31], who reported Mn levels in the Fe-Mn oxide-bound fraction in the range of 13.24–31.77% with an average of 19.38% in soils around automobile waste dumpsites in Northern part of Niger Delta, Nigeria, and [16] reported higher range of 13.38–55.06% of Mn in Fe-Mn oxide-bound fraction in mechanic waste dumps, Niger Delta, Nigeria.

The association of manganese with Fe-Mn oxide fraction may be attributed to its interference in the crystal of Fe oxide precipitate leading to its reduced occlusion. Moreover, the higher concentration of Mn associated with this fraction is as a result of the metal being adsorbed to the Fe-Mn colloids, and it is thermodynamically unstable under anoxic conditions. This shows that Fe-Mn oxides

fraction can locate heavy metals from solution through processes such as ion exchange, sorption, aqueous complexation and co-precipitation [39, 41].

The changes in the concentration levels of the geochemical forms of metals from one soil location to another could be influenced by the system or mechanisms in which the mineral precipitation/ dissolution, adsorption/ desorption and aqueous complexation reactions are affected by changes in specific combinations of both environmental parameters and soil physicochemical properties such as pH, cation exchange capacity, organic matter, oxidation and reduction reaction potentials. In soils around dumpsite (I), level of Fe-Mn oxide-bound fraction varied from 19 to 39% with an average of 32.2%, around dumpsite (II) it was 15–30% with an average of 22.5%, while around dumpsite (III) also 16–35% Fe-Mn oxide-bound fraction of Mn with an average of 25%. Although this Fe-Mn oxide-bound fraction may be considered relatively stable, slowly mobile and poorly available, but it could change with variations in redox and pH conditions and could become more soluble under acidic conditions and less soluble under oxidizing conditions [7, 30]. The organic fraction forms the third most important species of Mn in this study. The percentage levels ranged from 13 to 34% with an average of 21.8% in soils around the studied dumpsites. The report of [31] also showed that organic fraction of Mn varied between 13.36 and 29.91% with an average of 19.38% which is similar to that of this present study.

The percentage of the composition of total Mn in the carbonate fraction ranged from 10% to 18% in the studied dumpsites with averages of 13.2% in soils around dumpsite (I), 14.2% in dumpsite (II) and 13.0% in dumpsite (III). Higher levels of Mn in carbonate fraction had earlier been reported by [32] in a range of 13–25% in sediments of Rapel reservoir, Chile. The exchangeable fraction of Mn ranged from 7 to 18% in soils around the studied dumpsites with averages of 9.5% in dumpsite (I), 10.3% in dumpsite (II) and 15.0% in dumpsite (III). The levels of Mn in carbonates and exchangeable fractions in this study suggest that Mn is most likely present in the soluble carbonates, which may occur in small amounts and dissolve during the organic acid extraction and also available on the exchange site.

The bioavailable fraction of Mn in soils around dumpsite (I) ranged from 16.84 to 26.85%, in soils around dumpsite (II) the fraction was 21.05–29.44%, while in soils around dumpsite (III), it was 23.0–29.38%. The residual and the Fe-Mn oxide-bound fractions dominate the stabile (non-bioavailable) fraction of Mn which amounts to more than 65% in this study. The amount of Mn associated with the different geochemical fractions in soils around the studied dumpsites was in the following order; residual > Fe-Mn oxide > organic > carbonate > exchangeable.

3.4 Nickel (Ni)

The mean concentration levels of nickel in soils around the studied dumpsites varied between 1.00 ± 0.00 and 5.13 ± 0.06 mg/kg (Table 6). Nickel was predominantly associated with the residual and organic fractions averaging 33.5% and 24.7% respectively in soils around the studied dumpsites from the chemical fractionation analyses.

The residual form of nickel varied from 25 to 42% in soils around the studied dumpsites with averages of 35.8% in dumpsite (I), 31.8% in dumpsite (II) and 33.0% in dumpsite (III). The organic fraction of nickel ranged between 18 and 29% in the studied dumpsites with averages of 25.7% in dumpsite (I), 23.3% in dumpsite (II) and 25.0% in dumpsite (III). The predominance of the inactive forms of nickel in residual fraction is consistent with other reports of contaminated soils. [16] reported higher range of 52–85% in soil profiles at automobile mechanic waste dumpsite in Niger Delta, Nigeria, while [31] reported lower range of 10.12–34.38% with an average of 22.24% in soils around automobile waste dumpsites in Niger Delta, Nigeria. [13] also reported higher levels of nickel in residual form (55.29%) in sediments of Diobu River, Port Harcourt, Nigeria, which is commonly occluded by silicate during soil weathering [23, 35]. High levels of soluble nickel were

also found in Kaolin soil [33]. The organic fraction of nickel varied from 18 to 29% in the studied dumpsites soils with averages of 25.7% in dumpsite (I), 23.3% in dumpsite (II) and 25.0% in dumpsite (III). Nickel in Fe-Mn oxide-bound fraction varied from 14 to 22%, averaging 17.7% in dumpsite (I), 17.2% in dumpsite (II) and 18.0% in dumpsite (III). The levels of nickel in Fe-Mn oxide fraction depend on how much Mn oxide is absorbed in a given soil sample because Ni^{2+} could substitute for surface manganese in mixed valence Mn oxides [12, 18]. The exchangeable nickel varied from 6 to 22% in soils around the studied dumpsites with averages of 8.8% in dumpsite (I), 13.8% in dumpsite (II) and 10.0% in dumpsite (III). The carbonate fraction of Ni also ranged from 8 to 22% in the studied dumpsites soils with averages of 11.8% in dumpsite (I), 13.5% in dumpsite (II) and 14.0% in dumpsite (III).

The percentage sum of the weakly bound (bioavailable) fraction of nickel ranged from 18.61 to 27.01% for soils around dumpsite (I), 21.08 to 43.01% in soils around dumpsite (II) and 18.82 to 28.65% in soils around dumpsite (III), but the carbonate fraction was dominant in the bioavailable or weakly bound fractions.

The mean levels of total nickel associated with different geochemical forms in soils around the studied dumpsites were in the following order: residual

Table 6 Geochemical forms of Ni (mg/kg) in soil samples from the studied dumpsites (I, II, III) and control (X) in Benin

Spots	F1	F2	F3	F4	F5	Sum	Mean conc. levels	Recov. (%)	Bioav. (%)
<i>Dumpsite I</i>									
A	0.34 ± 0.01	0.26 ± 0.00	0.45 ± 0.02	0.75 ± 0.01	1.33 ± 0.00	3.14 ± 0.00	3.40 ± 0.00	92.35	19.17
B	0.53 ± 0.01	0.38 ± 0.02	0.75 ± 0.01	1.27 ± 0.02	1.94 ± 0.04	4.87 ± 0.04	5.13 ± 0.06	94.93	18.61
C	0.27 ± 0.05	0.37 ± 0.03	0.60 ± 0.03	0.91 ± 0.01	1.32 ± 0.02	3.47 ± 0.13	3.53 ± 0.15	98.30	18.44
D	0.13 ± 0.00	0.30 ± 0.02	0.41 ± 0.01	0.52 ± 0.01	0.66 ± 0.02	2.02 ± 0.02	2.23 ± 0.06	90.58	21.29
E	0.12 ± 0.02	0.25 ± 0.01	0.43 ± 0.01	0.52 ± 0.01	0.63 ± 0.03	1.94 ± 0.03	2.10 ± 0.18	92.38	18.97
F	0.35 ± 0.01	0.49 ± 0.00	0.57 ± 0.00	0.77 ± 0.02	0.93 ± 0.02	3.11 ± 0.03	3.34 ± 0.09	93.11	27.01
<i>Dumpsite II</i>									
G	0.48 ± 0.04	0.37 ± 0.04	0.58 ± 0.04	0.85 ± 0.05	1.13 ± 0.04	3.41 ± 0.19	3.57 ± 0.31	95.52	25.00
H	0.62 ± 0.02	0.65 ± 0.01	0.82 ± 0.01	0.97 ± 0.01	1.16 ± 0.02	4.22 ± 0.04	4.50 ± 0.00	93.78	30.09
I	0.13 ± 0.01	0.26 ± 0.02	0.33 ± 0.02	0.45 ± 0.01	0.68 ± 0.01	1.85 ± 0.01	2.00 ± 0.00	92.50	21.08
J	0.23 ± 0.11	0.18 ± 0.07	0.41 ± 0.06	0.58 ± 0.08	0.90 ± 0.05	2.31 ± 0.35	2.53 ± 0.42	91.30	17.83
K	0.27 ± 0.03	0.24 ± 0.02	0.32 ± 0.03	0.45 ± 0.01	0.55 ± 0.02	1.83 ± 0.10	1.93 ± 0.12	94.82	27.87
L	0.21 ± 0.01	0.19 ± 0.01	0.13 ± 0.02	0.17 ± 0.01	0.23 ± 0.02	0.94 ± 0.06	1.03 ± 0.06	91.26	43.01
<i>Dumpsite III</i>									
M	0.14 ± 0.02	0.21 ± 0.02	0.27 ± 0.03	0.38 ± 0.04	0.49 ± 0.04	1.50 ± 0.13	1.53 ± 0.15	98.04	23.49
N	0.14 ± 0.02	0.21 ± 0.02	0.34 ± 0.01	0.48 ± 0.02	0.69 ± 0.02	1.87 ± 0.04	2.07 ± 0.06	90.34	18.82
O	0.14 ± 0.03	0.22 ± 0.04	0.25 ± 0.03	0.32 ± 0.05	0.46 ± 0.03	1.39 ± 0.16	1.53 ± 0.21	90.85	25.87
P	0.12 ± 0.01	0.12 ± 0.00	0.16 ± 0.01	0.26 ± 0.00	0.32 ± 0.01	0.97 ± 0.02	1.00 ± 0.00	97.00	24.49
Q	0.16 ± 0.02	0.25 ± 0.02	0.32 ± 0.02	0.47 ± 0.02	0.44 ± 0.02	1.64 ± 0.02	1.70 ± 0.00	96.47	25.00
R	0.23 ± 0.00	0.28 ± 0.01	0.29 ± 0.01	0.39 ± 0.02	0.59 ± 0.03	1.78 ± 0.04	1.87 ± 0.12	95.19	28.65
X	0.09 ± 0.04	0.10 ± 0.02	0.14 ± 0.03	0.23 ± 0.05	0.29 ± 0.05	0.84 ± 0.18	0.87 ± 0.21	96.55	22.35

The values are Mean $\pm$ SD

Table 7 Analysis of variance (ANOVA) at $p \leq 0.05$ showing a significant difference among the geochemical fractions of analysed heavy metals

Source of variation	Sum of square	Df	Mean square	F-stat	F-tab (Sig.)
Between groups	3442.984	69	49.898	0.863	0.680
Within groups	115.695	2	57.848		
Total	3558.679	71			

 $\alpha = 0.05$

(33.5%) > organic (24.7%) > Fe-Mn oxide (17.6%) > carbonate (13.17%) > exchangeable (10.9%).

The low percentage of bioavailable fractions of the heavy metals were ascertained by studying their partitioning between and within groups of bioavailable and non-available fractions using one-way analysis of variance (ANOVA) ($p \leq 0.05$) as presented in Table 7.

The levels of heavy metals in bioavailable and non-bioavailable fractions showed significant difference between and among groups of the geochemical fractions of metals, indicating and confirming the low potential contamination risk in the soil.

The mobility factors (MF) described the potential mobility of metals as some metals are more strongly bound to the soil component than some. High MF values have been reported as symptoms of relatively high liability and biological availability of heavy metals in soil. The mobility factors of metals were independent of their total concentration levels in soil as presented in Table 8.

Table 8 showed an r_{pb} of -0.136 , and p value of 0.253 at alpha (α) level of 0.05 . The r_{pb} value of 0.136 shows a negative correlation of mobility factors and independent total concentration levels of metals in soils. The p value of 0.253 shows that there is no significant relationship between metal concentration levels and mobility factors since the alpha value is less than the p value (Table 8).

The mobility factors (MF) of the analysed heavy metals in soil around dumpsite (I) shows that Cu ranged from 20.67 to 25.19%, Pb 20.42 to 28.16%, Mn 16.84 to 26.85% and Ni 18.44 to 27.01%; soil around dumpsite (II) shows that Cu ranged from 26.22 to 40.49%, Pb 21.89 to 30.10%, Mn 21.05 to 29.44% and Ni 17.83 to 43.01%; soil around dumpsite (III) shows that Cu ranged from 22.85 to 37.06%, Pb 21.78 to 27.93%, Mn 23.02 to 29.38% and Ni 18.82 to 28.65%. The results are indicative of the relative reactivity of the metals with active sites. The low mobility factors observed for each analysed heavy metal

Table 8 The correlation effect of total concentration levels of analysed metals on their mobility factors in soils

	<i>N</i>	<i>r</i>	sig.(2-tailed)
Mobility factors			
	72	-0.136	0.253
Independent total concentration levels			

 $\alpha = 0.05$

in the studied sites agree 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 dumpsite (I): $Pb > Cu > Mn > Ni$; for dumpsite (II): $Cu > Ni > Pb > Mn$; for dumpsite (III): $Cu > Mn > Pb > Ni$.

4 Conclusion

The heavy metals fractionation results in this study showed that high percentage of the metals was found to be strongly bounded to soil components, in a form not readily released into solution for plant absorption. The distribution of metals in the defined geochemical fractions was dependent on the total concentration levels of analysed metals while mobility factors were not dependent on the concentration levels in soil. The low mobility factors observed in the studied heavy metals confirm the low biological availability of the analysed heavy metals in soils around each studied dumpsite and pose no danger to biota. The continuous injection of these metals into the ecosystem increases their concentration levels, consequently their toxicity.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests

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