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RESEARCH ARTICLE

Chemical fractionation and mobility factor of some heavy metals in refuse dumpsite soil in Awka Metropolis, Anambra State, Nigeria

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Abstract: The geochemical forms of some heavy metals in refuse dump soils at Agu-Awka, Awka metropolis was studied in order to assess the mobility and bioavailability of the metals and hence their potential environmental risk. Exchangeable fraction (F1) contained the % fraction of 13.23% for Cd, 17.43% for Cr, 14.63% for Pb, 12.40% for Ni, 25.34% for Zn and 15.92% for Mn and these are in the order of Zn > Cr > Mn > Pb > Cd > Ni. The carbonate fraction (F2) contained the % fraction of 17.08% for Cd, 17.84% for Cr, 9.20% for Pb, 28.32% for Ni, 13.76% for Zn and 8.49% for Mn and these are in the order of Ni > Cr > Cd > Zn > Pb > Mn. Lead was predominantly associated with organic fraction with a result of 42.64% followed by chromium and manganese with the values of 22.48% and 20.00% respectively. The organic bound metals were in the abundance trend of Pb > Cr > Mn > Cd > Ni > Zn. The highest values of metal in Fe-Mn oxide phase was manganese with a value of 32.18%, followed by cadmium with the value of 21.76%. The values of the other metals bound to this phase were 17.52%, 16.64%, 13.99% and 12.90% for Zn, Ni, Cr, and Pb respectively. Zinc with the value of 32.20% was predominantly associated with the residual fraction. The other metals bound to this phase had their values to be 30.13% for cadmium, 28.24% for chromium, 20.61% for lead, 29.41% for nickel and 23.37% for manganese. The mobility factor values of the metals were relatively low and they followed the order of Ni > Zn > Cr > Cd > Mn > Pb. That notwithstanding, soils from studied area should be carefully monitored to prevent the release of these metals due to redox reactions which may make them available to plants through absorption.

Keywords: AAS, dumpsite, heavy metal, fractionation and mobility factor

1 Introduction

One major challenge that has persisted for long in our environment in Nigeria is the generation of refuse, its dumping and consequently its management. Anthropogenic contributions ranged from nutrition to industrialization, agricultural practices, transportation, education, commerce etc, have been largely responsible for the upsurge in refuse generation in the Nigerian society. The increase in the nation's population equally brings about a rise in the human practices responsible for the generation of refuse. This waste generated, without proper management can pose serious threat to human race as a result of its potentials to pollute the environment [1]. Just like in several other cities in Nigeria, Awka is plagued with many environmental challenges; one of the predominant ones being the inadequate discharge of refuse near residential areas and public places such as markets, churches, mosques, schools, hospitals etc, within the town. Some of these wastes are heavy metal bounds. These wastes are collected and dumped hugely without proper plans for management. This leads to potential accumulation of heavy metals on dumpsite soils. Soil is the major sink for heavy metals released into the environment and unlike the organic contaminants which are oxidized to carbon(IV)oxide by microbial actions, most metals do not undergo microbial or chemical degradation, and their total concentration in soils persist for a long time after their introduction [2, 3]. Its presence in soil used for cultivation, plants can easily take up some fractions from the soil and this can easily lead to phytotoxicity [4]. 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 [5]. High concentration levels of heavy metals in soils and sediments have been known to be undesirable to the habitants, thereby posing serious environmental degradation. Soil contamination with heavy metals is potentially damaging to the ecosystem health [6, 7].

Therefore, a better understanding and evaluation of the distribution and potential hazards of heavy metals in soils of heavily commercialized and industrialized city such as Awka are increasingly needed to ensure the safety of public health. Furthermore, excessive accumulation of heavy metals in soils may not only result in soil contamination, but also lead to elevated heavy metal uptake by plants, thus affect food quality and safety [8]. Heavy metals affect the physical and chemical properties of soil [9,10]. All this negatively affect soil establishment. Indeed, this has created a significant need for continuous monitoring of the concentration levels of these heavy metals [11,12]. Furthermore, it should be noted that the information provided by the total heavy metal concentration is limited since it does not give the specific forms of the heavy metals in the soil and their impact on the environment [13]. The particular behavior, mobility and bioavailability of these heavy metals in the soil are determined by their specific geochemical fractions and sequential extraction is the simplest method of identifying them. In this method, the components that are mobile in the soil are extracted first, followed by those that are more or less reactive. When changes occur in the oxidation status of soils and sediments, transformations of these metals between their soluble and insoluble chemical forms may occur [14]. This affects the mobility and plant availability of these metals [15].

Different types of sequential extraction procedures have been used for similar studies; however, in this study, the Tessier extraction method was adopted. This extraction method mostly involves the chemical separation of heavy metals into the following 5-steps fractions (F1-F5): Exchangeable fraction, bound to carbonate fraction, bound to Fe-Mn oxide fraction, bound to organic fraction and residual fractions [16]. Many research has been carried out on the speciation of heavy metals in dump site soils in different parts of Nigeria [17,18] to mention but few, including Awka and its environment, but there is need to occasionally re-assess the pollution levels with reference to heavy metal pollutants of such highly industrialized and commercialized area. Hence, this study was conducted. The aim of the study is to evaluate the different geochemical forms of Cd, Cr, Pb, Ni, Zn and Mn in soil of waste dumpsites in Awka City and to assess the bioavailable fraction and mobility factors of these metals using chemical fractionation analysis.

2 Materials and Methods

2.1 Description of the Study Area

The study site is Agu-Awka waste dumping site. The dumpsite contains mixtures of both organic and inorganic waste materials such as food wastes, papers, cardboards, metals, engine oils, tins, glass, ceramics, battery wastes, textile rags, plastics, sewage night-soils and other miscellaneous materials such as bricks, ash, fine dust, rubber and wood wastes. These wastes have been dumped and allowed to accumulate for years due to inadequate waste management in the state. The dumpsite is located between the latitude of 6^o13'30" N and longitude of 7^o06'0" E of Anambra state, Nigeria. Figure 1 and 2 show the map of Awka indicating the geographical locations of the sampling areas.

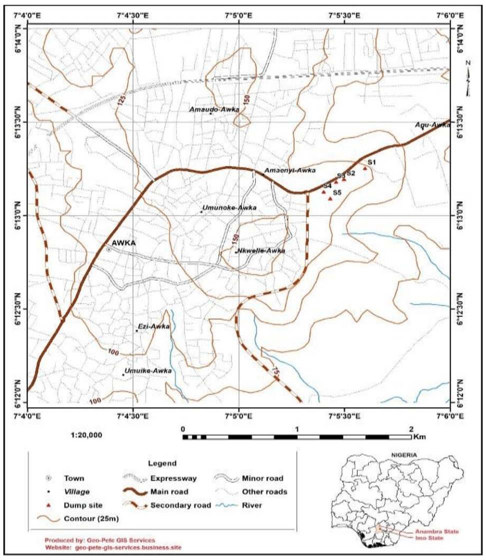

Figure 1 Map of Awka showing the Study sites

Figure 2 The study sites

2.2 Sample collection and preparation

The soil samples after removing the overlying wastes were collected from refuse dump site at Agu-Awka at the depths of 0–20 cm using soil spade and shovel. At site for sampling, five sub-sites soil as shown on the map above were taken for the purpose of random sampling and pooled together to obtain a composite sample. Wastes, nylons, plastics and stones were manually sorted out and removed to some extent. They were bagged and transported home. The soil was air dried for eight days, ground and sieved through a 2 mm sieve. These were stored in well labelled polythene bags and taken to the laboratory for analysis.

2.3 Fractionation analyses of heavy metals in soil samples

Sequential extraction was done as described by [16] with modification as described by [19] replacing percloric acid with aqua regia. All extracts were analyzed using AAS (FS240AA).

F1 Exchangeable: To 1 g of amended soil sample, 8 mL of 1 M $MgCl_2$ was added with pH adjusted to 7.0 with agitation for 1hr before centrifuging for 15 mins. The supernatant was filtered into a polypropylene bottle for AAS analysis, while the residue was used for further extraction.

F2 Carbonate bound: 1 M NaOAc (8 mL) was added to the residue obtained from the exchangeable fraction above and then adjusted to pH 5.0 with concentrated acetic acid and agitated for 5 hrs. The mixture was then centrifuged at 15 rpm for 15 mins. The supernatant was filtered into a polypropylene bottle for AAS analysis.

F3 Fe-Mn Oxides: 20 mL of 0.0 4M $NH_2OH.HCl$ in 25% HOAc was added to the residue obtained from the carbonate bound fraction and placed in water bath for 6 hours at 96±3^{o}C. The mixture was then centrifuged at 1500 rpm for 15 mins before the supernatant was filtered into a polypropylene bottle for metal analysis.

F4 Bound to organic: 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2.0 was added to the residue obtained from the step above and mixture was heated to 85±2^{o}C for 2 hours. About 3 mL of 30% H_2O_2 was later added and mixture heated to 85±2^{o}C for 3 hours before centrifuging at 1500 rpm for 15 mins. The supernatant was filtered into a polypropylene bottle for metal analysis.

F5 Residual Fraction Residue: from the organic bound extraction was digested with 8 mL of Aqua regia for 2 hours before collecting for analysis.

2.4 Determination of mobility factor

The mobility factor which is the percentage fraction of heavy metals that are mobile or available for plant absorption was calculated thus: $MF(\%) = \frac{F1+F2}{F1+F2+F3+F4+F5} \times 100$, where F1 = exchangeable fraction, F2 = bound to carbonate, F3 = bound to Fe-Mn Oxide, F4 = bound to organic, F5 = residual fraction.

2.5 Determination of the percentage factor

The fraction percentage is calculated using the equation:

$$\%\ \text{fraction(F)} = \frac{\text{concentration of each fraction}}{\text{sum of concentration of all fraction}} \times 100$$

2.6 Data Treatment

Results are presented as mean value ± standard deviation and analyzed by analysis of variance (ANOVA) using SPSS software package version 23.

3 Result and Discussion

Sequential extraction of these heavy metals (Cd, Cr, Pb, Ni, Zn and Mn) are presented in Table 1.

Table 1 Mean concentration (mg/kg) of heavy metals in the different fractions in the dumpsite soil (Mean ± SD)

Metals & fraction	Cd	% F	Cr	% F	Pb	% F	Ni	% F	Zn	% F	Mn	% F
F1	5.01±0.01	13.23	5.48±0.02	17.43	17.18±0.02	14.63	3.07±0.10	12.40	30.94±0.05	25.34	21.44±0.00	15.92
F2	6.47±0.03	17.08	5.61±0.02	17.84	10.80±0.00	9.20	7.01±0.01	28.32	16.80±0.00	13.76	11.44±0.06	8.49
F3	8.24±0.00	21.76	4.40±0.01	13.99	15.14±0.01	12.90	4.12±0.02	16.64	21.39±0.02	17.52	43.32±0.03	32.18
F4	6.73±0.02	17.77	7.07±0.03	22.48	50.05±0.07	42.64	3.27±0.03	13.21	13.63±0.01	11.16	26.93±0.02	20.00
F5	11.41±0.02	30.13	8.88±0.02	28.24	24.19±0.01	20.61	7.28±0.02	29.41	39.32±0.03	32.20	31.46±0.01	23.37
MF (%)	30.32		35.27		23.84		40.72		39.10		24.42	

Note: F1 = Exchangeable fraction; F2 = Bound to carbonates fraction; F3 = Bound to Fe-Mn oxides fraction; F4 = Bound to organic fraction; F5 = Residual fraction; MF = Mobility factor; F = Fraction

3.1 Cadmium (Cd)

Cadmium was present mostly in the residual fraction. The fraction of Cd in the residual fraction in these soil profiles is 11.41±0.02. Similar results have been reported by other researchers in literatures [20–23]. Followed by bound to Fe-Mn fraction. The fraction of Cd in the Fe-Mn oxide fraction is 8.24±0.00. The Fe-Mn oxides fraction is relatively stable but could change with variation in redox condition according to [21–24]. Then followed by bound to organic and carbonate fractions. The fraction of Cd in organic fractions and the carbonate fraction are 6.73±0.02 and 6.47±0.03 respectively, while the fraction of Cd in the exchangeable fraction is 5.01±0.01. The fraction of Cd in the exchangeable fraction indicates that Cd is potentially available to some extent in these soil profiles for plant uptake and its accumulation could be very dangerous.

3.2 Chromium (Cr)

In these soil profiles, Cr is in all the fraction however it is mostly found in the residual and organic fraction. The fraction of Cr in the residual fraction is 8.88±0.02. The organic bound fraction followed the residual fraction with 7.07±0.03 [21], suggested that Cr in the organic bound fraction might be due to its strong affinity for organic matter. On the other hand, according to [23] they also suggested that existence of Cr in the organic bound fraction results from the existing physicochemical conditions which include the pH and total organic carbon. Furthermore, the bound to carbonates and exchangeable fractions constituted 5.61±0.02 and 5.48±0.02 respectively, while the concentration of Cr in the Fe–Mn oxide is 4.40±0.01.

3.3 Lead (Pb)

Lead partition was predominantly in the organic bound fraction. The concentration of Pb in the organic fraction is 50.05±0.07. According to Ajala et al. (2014) [25], the high distribution of Pb in this fraction could be as a result of the strong complexes lead formed with humic minerals. The next dominant fraction of Pb in these soil profiles is residual fraction (24.19±0.01), followed by the exchangeable fraction with 17.18±0.02 of Pb. Metals in this fraction are soluble and easily released into biota. Therefore, the accumulation of Pb in this fraction calls for concern as Pb is one of the metals that constitutes the widest possible health risk to humans through the plant uptake dietary route [25, 26]. The fraction of Pb in the Fe-Mn oxide and carbonate fractions are 15.14±0.01 and 10.80±0.00 respectively.

3.4 Nickel (Ni)

The speciation of Ni follows the order; Residual > carbonates > Fe-Mn oxide > organic > exchangeable with their fractions to be 7.28±0.02, 7.01±0.01, 4.12±0.02, 3.27±0.03 and 3.07±0.10 respectively. This finding is consistent with some researches [17, 20, 21, 27–33].

3.5 Zinc (Zn)

The speciation of Zn follows the order residual > exchangeable > Fe-Mn oxide > carbonate > organic. The fractions of Zn in the different profile are 39.32±0.03, 30.94±0.05, 21.39±0.02, 16.80±0.00 and 13.63±0.01 respectively.

3.6 Manganese (Mn)

The speciation of Mn follows the order Fe-Mn oxide> residual > organic > exchangeable > carbonate. The fraction of Zn in the different soil profile is 21.44±0.00, 11.44±0.06, 43.32±0.03, 26.93±0.02 and 31.46±0.01 for exchangeable, carbonate, Fe-Mn oxide, organic and residual fractions respectively.

3.7 Mobility factors (MF) of heavy metals in the soils

Mobility Factor is an important indicator of heavy metal mobility and bioavailability in soil. Generally, in any sequential extraction procedure, the early fractions are the most mobile and bioavailable fractions [**?**,19,34,35]. And the mobility factor value provides the relative mobility and bioavailability of these heavy metals in the contaminated dumpsite soil. Therefore; in this study, the results of the mobility factor are hence represented as 30.32%, 35.27%, 23.84%, 40.72%, 39.10% and 24.42% for cadmium, chromium, lead, nickel, zinc and manganese respectively. And they followed the order of Ni > Zn > Cr > Cd > Mn > Pb (Figure 3).

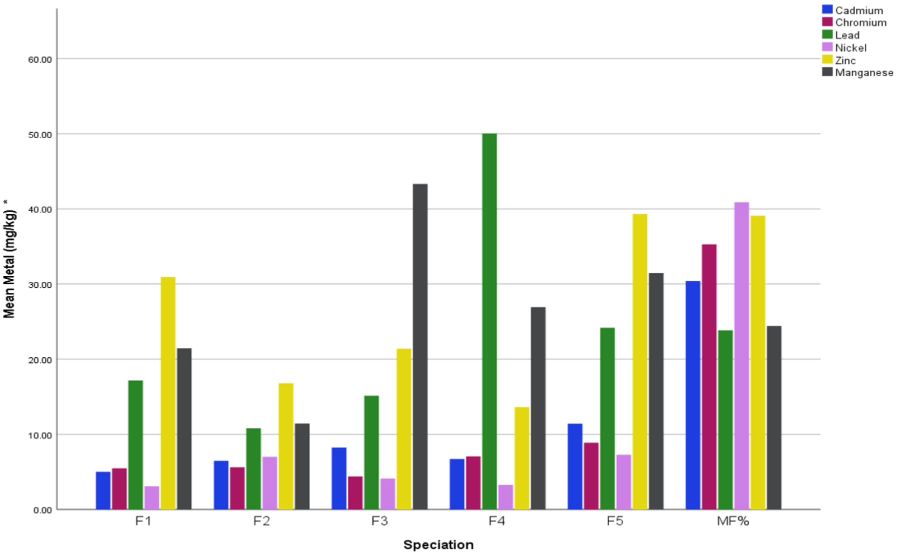

Figure 3 Chemical speciation and mobility factor of heavy metals in dumpsite soil

4 Conclusion

The chemical speciation of the metals among the five geochemical phases revealed that residual, organic and Fe – Mn oxide phases proved to be of most importance for the refuse dump soil examined in this study. This is because they contained significantly high amounts of all the metals analyzed. The predominant species of lead was associated with organic fraction while residual and carbonate fraction contained majority of nickel. On the other hand, the exchangeable fractions of zinc and manganese were also notably high. However, the mobility factors of all the metals studied are relatively low; notwithstanding it is the accumulation and persistence of these metals which can increase their concentration levels that is of great concern. On the other hand, since the early fractions, which are exchangeable and carbonate are the most mobile and most potentially available fractions, and iron-manganese oxide occluded and organic bound metals can be released under favorable conditions, the soils under study may pose some potential environmental risk. It is highly recommended that the refuse dump site be judiciously monitored; if possible a remediation scheme should be adopted.

Conflicts of interest

The authors declare that they have no conflict of interest.

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