Study of Vertical Migration of Heavy Metals in Dumpsites Soil

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ABSTRACT

This study attempts to investigate the vertical migrations of heavy metals (Cu, Mn, Pb and Zn) in dumpsite soils with the view to elucidate the risk of contamination to the environment and to underscore the factorial effects of pH and organic matter on the migration of heavy metals in the dumpsite soils within Maiduguri metropolis, Nigeria. Soil samples were randomly collected by depth profile (0-5cm, 5-50cm and 50-100cm). Heavy metals were determined by ICP-OES technique, pH meter was used and titrimetric method for organic matter (OM) determinations. Results show contamination of the dumpsites in comparison with reference site and indicated high downward migration of heavy metals. The relationships between metal concentrations against pH and % OM respectively show antithetical relationships. The result of this study shows that there exists risk for the environment due to notable migration of heavy metals across depth profile and that the migrations were also observed to be highly correlated with organic matter content.

Keywords: municipal dumpsites, soil contamination, metal migration, ICP-OES, maiduguri metropolis.

1. INTRODUCTION

The proliferation of open and unsafe dumpsites containing multiple disposals of domestic, municipal, industrial and medical wastes is common practice in most cities in Nigeria. These dumpsites have become feeding ground for diseases breeding animals especially rats, birds, and stray animals; thereby contributing greatly to their nourishment and growth [1, 2]. Another problem of these waste dumps is air pollution which sometimes results in temporary limitations on movement of people and consequently slowing economic activities in urban areas [3]. Furthermore the random deposition of these wastes, consequently leads to adjacent lands getting enriched in trace metals and salts. Thus dumpsite soils eventually become the repository for metals released from municipal waste sludge and several similar wastes deposited on it [4, 5]. The severe problems associated with these are the infiltration of leachate into the surrounding environment, subsequent contamination of the land and groundwater [6]. Heavy metals once introduced to the environment by one particular method may spread to various environmental components, which may be caused by the nature of interactions occurring in this natural system. Heavy metals may chemically or physically interact with the natural compound, which changes their forms of existence in the environment. In general they may react with particular species, change oxidation states and precipitate [7]. Heavy metals may be bound or sorbed by particular natural substances, which may increase or decrease mobility [8]. Another environmental problem with heavy metals is that they are unaffected during degradation of organic waste and have toxic effects on living organisms when exceeding a certain concentration. Therefore, leachate quality may vary from time to time and site to site due to variables such as waste composition, temperature, moisture content, climatic changes etc. Many soil chemical and biological reactions are controlled by the pH of the soil solution in equilibrium with the soil particle surfaces [9].

In this study, we not only attempt to investigate the vertical migrations of heavy metals in soil [10, 11], with the view to elucidate the risk of contamination to the environment [12, 13], but to also underscore the factorial effects of pH and organic matter as they affect the migration of heavy metals in the dumpsite soils within this study area.

2. METHODOLOGY

Study Sites and Sample Collection

The study was conducted in Maiduguri, Borno State Nigeria at coordinates: latitude 11°51'N and longitude 013°05'E. Dumpsites located in three different districts of Maiduguri metropolis comprising, Bulunkutu (B), Meri (M) and Zajeri (Z) were identified and selected on the basis of divergent concomitant factors such as population density, variety of waste and magnitude of dumpsite. A fourth location was also selected as a Reference site (REF) at the outskirt of Maiduguri metropolis, which is also unaffected by farm practice. Sub-sampling clusters of six at each site were also generated to achieve analyte sampling representation.

Soil samples were collected randomly [14] from the dumpsites and the reference site using depth calibrated soil auger. The sampling depths are surface level (0-5cm), 5-50cm and 50-100cm [15]. Samples were collected in clean polythene bags.

Determination of Heavy Metals

Heavy metals (Cu, Mn, Pb and Zn) in the soil samples were determined by the ICP-OES methodology [16, 17]. Soil samples preparations, prior to determination of metals, was carried out according to Method 3050B [18]. The homogenized samples were subjected to oven-drying and sieved through an equivalent USS #10 sieve. One gram (1g) portions of soil sample were separately digested by refluxing in 10ml 1:1 HNO₃ for 10mins. This procedure was repeated with additional 5 ml of conc. HNO₃ until digestion was completed. The evaporated (5 ml) was treated with 2ml water and 3ml 30% H₂O₂ in 1ml sequential aliquot addition until bubbling subsided. The digest was further reduced to 5ml and refluxed in 10ml conc. HCl for 15mins. This was filtered and made up to 100ml volume. The Aglient 710 Series ICP-OES (USA),
operational with SPS auto-sampler was used for the determination of heavy metals. Samples were analyzed under the instrumental operating conditions: RF Power 1.0 kW, Outer argon flow 12.0 L/min, Intermediate and Inner argon flow 1.0 L/min and the Nebulizer uptake rate (mL/min) 1.0. Standards calibration curves for the metal analytes already prepared covering the optimum working range stored in the system software was used to produce the computerized analysis report.

Determination of pH
Twenty grams (20g) of air-dried soil sample was weighed into a 50 cm³ beaker and 20 cm³ of distilled water was added. The mixture was allowed to stand for 30 minutes with occasional stirring using a glass rod. The pH was determined using model 3310 pH meter (Jenway Ltd, Dunmow, UK). The pH meter and electrode was calibrated with buffer solutions of pH 7 and 4 for the determinations. The electrode of the calibrated pH meter was inserted into the partly settled suspension and the pH recorded [19].

Determination of Organic Matter
Soil organic matter was determined by the titrimetric method described by [20]. Samples were ground to pass through 0.5mm sieve after which they were weighed in duplicate and transferred to 250 cm³ Erlenmeyer flasks. Exactly 10 cm³ of 1M potassium dichromate was pipetted into each flask and swirled gently to disperse the soil followed by addition of 20 cm³ of concentrated, sulphuric acid. The flask was swirled gently until soil and reagents are thoroughly mixed. The mixture was then allowed to stand for 30 minutes on a glass plate to allow for the oxidation of potassium dichromate to chromic acid. Distilled water (100 cm³) was added followed by addition of 3-4 drops of ferroin indicator, after which the mixture was titrated with 0.5M ferrous sulphate solution. A blank titration was similarly carried out.

The % organic carbon is given by the following equation:

\[
\text{Mass (g) of air-dried soil} = \frac{M_1 e_1 K_2 Cr_2 O_7 - M_2 e_2 FeSO_4}{0.0031 x 100} \times F
\]

\[
F = \text{Correction factor (1.33)}
\]

\[
M_1 = \text{mole of K}_2\text{Cr}_2\text{O}_7
\]

\[
e_1 = \text{volume of K}_2\text{Cr}_2\text{O}_7
\]

\[
M_2 = \text{mole of FeSO}_4
\]

\[
e_2 = \text{volume of FeSO}_4
\]

\[
\% \text{ Organic matter in soil} = \% \text{ Organic carbon} \times 1.729
\]

Data Analysis
Data obtained were analysed using Analyse-it® v. 2.22 [21], statistical software for Microsoft Excel. Results are presented as mean ± standard deviation. Statistical variations were considered significant at p<0.05.

3. RESULTS

Copper (Cu)
The result of Cu concentrations across depth profile at the different dumpsites including the REF site is shown in Figure-1. The result revealed a steady downward increase in Cu concentration in all the dumpsites as well as the REF site. The highest concentration of Cu was observed at 100cm depth in dumpsite B (1.65±0.35 mg/kg) and the lowest concentration at the REF site (0.38 ± 0.25 mg/Kg). The concentrations of Cu was higher in all the dumpsites than in the at the REF site. The results was subjected to 1-way Analysis of variance (ANOVA), and indicated that there was no statistically (p<0.05) significant difference in the concentrations across the sampled depths. However by post-hoc test with Dunnnett error protection, the result of ANOVA showed significant variations between all dumpsites against the REF site.

Figure-1. Cu concentrations (mg/kg) at Dumpsites by depth.

Lead (Pb)
Figure-2 shows the result of Pb concentrations across depth profile and at the different sites. The result showed the presence of Pb in samples from all the sites. Pb was highest at dumpsite B (1.74±0.06 mg/kg) and the lowest at site Z (1.29±0.60mg/kg). The result also indicated an increase at 100cm depth in all sites. ANOVA result shows no significance across depth profile, but by sites, only site B showed significantly higher concentrations than the reference sites.

Data Analysis
Data obtained were analysed using Analyse-it® v. 2.22 [21], statistical software for Microsoft Excel. Results are presented as mean ± standard deviation. Statistical variations were considered significant at p<0.05.
Manganese (Mn)
The results of Mn is presented in Figure-3 and revealed that Mn was highest in concentration at dumpsite B (1.72±0.24 mg/kg) and the lowest at the REF site (1.01±0.01 mg/kg). Similar to Cu and Pb, the concentration of Mn was also observed to be accumulated at 100cm depth level. However, ANOVA of the results indicated that there was no statistically (p<0.05) significant difference in the concentrations across the sampled depths. However by post-hoc test with Dunnett error protection, the result of ANOVA showed significant variations between all dumpsites against the REF dumpsite.

Zinc (Zn)
Figure-4 shows the results of Zn with the highest mean concentration at dumpsite B (1.80±0.01 mg/kg) and the lowest at the REF location (1.09±0.35 mg/kg). It could be observed that Zn shows almost constant concentrations in all the locations (surface and 50cm depth). Similar to Cu, Pb and Zn, ANOVA of the results indicated that there was no statistically (p<0.05) significant difference in the concentrations across the sampled depths. However by post-hoc test with Dunnett error protection, the result of ANOVA showed significant variations between all dumpsites against the REF dumpsite.

Heavy Metals by Depth Profile
Figure-5 represents the overall status metal migration irrespective of dumpsite by depth profile. All metals showed higher concentration at the lower level. Higher concentrations of heavy metals were observed at the lower layer (100cm). Zinc showed the highest concentrations at all levels. Similarly, ANOVA results for pair wise test at p<0.05, show that there was only a significant variation in Cu concentrations between 0-5 and 50-100cm depth levels. Pb also showed significant variation in concentrations at all levels except 5-50 and 50-100cm depth levels while, the pair wise test for Mn showed significant variation in concentrations between 5-50 and 50-100cm depth levels. In contrast, Zn concentrations are not significant between all depth levels.

Inter-Metal Correlation Analysis
Inter-metal concentration correlation analysis was conducted using Pearson correlation coefficient (r) values, to determine the level of association of pairs of metals across the different depth levels. Table-1 shows that a perfect positive correlation value (r = 0.9) was recorded between Pb and Zn. Other metals revealed low (r = 0.3) to moderate (r = 0.6) level of association as their concentrations determination proceeded depth wise.
Soil pH and Organic Matter
Table 2 presents the results of soil pH and % OM at the different dumpsites and across the various depth levels of sampling. The results revealed that pH levels varied only slightly from one dumpsite to another and the average pH range from 11.05±1.09 to 8.72±0.72. Despite the fact that pH level was generally higher at the REF dumpsite (10.4±0.54) and lowest at dumpsite M (9.66±0.31), and that there were generally a decreasing trend of pH across depth levels, the results of ANOVA for these revealed no significance (p<0.05) in the variations. The average results of organic matter show diverse variations between locations and ranged from low (REF, 4.3%) to high (B, 21.8%). However, the results of % OM across depth profile indicated a general increase downwards at each site. ANOVA results for the variations of % OM between dumpsites was markedly significant, but the variations across depth levels show no significance. Figures 6 and 7 illustrate the relationships between metal concentrations and pH, and metal concentrations and % OM respectively. The Figures illustrated antithetical relationships; while metal concentrations tend to increase as pH increases the reverse was the case between metal concentrations and % OM.

Table 2. Mean pH and Organic Matter (% OM).

<table>
<thead>
<tr>
<th>Dumpsite</th>
<th>DEPTH (cm)</th>
<th>pH</th>
<th>% OM</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0</td>
<td>11.05±1.09</td>
<td>4.15±0.76</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>10.21±1.37</td>
<td>4.36±0.43</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>9.96±0.83</td>
<td>4.42±0.92</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>10.34±1.33</td>
<td>21.68±4.88</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>10.17±1.45</td>
<td>21.87±5.11</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>10.02±1.59</td>
<td>21.88±4.82</td>
</tr>
<tr>
<td>M</td>
<td>0</td>
<td>9.9±1.22</td>
<td>15.93±3.14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9.66±0.91</td>
<td>16.65±2.56</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>9.42±1.33</td>
<td>17.04±5.22</td>
</tr>
<tr>
<td>Z</td>
<td>0</td>
<td>10.41±1.00</td>
<td>14.05±2.38</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9.87±1.21</td>
<td>14.3±1.78</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>8.72±0.72</td>
<td>14.42±2.54</td>
</tr>
</tbody>
</table>

Figure 5. Metal migration profile at dumpsites by depth.

Table 1. Results of Inter-Metal Correlation Analysis.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Mn</th>
<th>Zn</th>
</tr>
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<tbody>
<tr>
<td>Cu</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.3</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.3</td>
<td>0.9</td>
<td>0.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 6. Relationship of pH and Metal migration profile at dumpsites.

Figure 7. Relationship of % OM and Metal migration profile at dumpsites.
4. DISCUSSIONS

The contamination of the dumpsites was obviously indicated by the high concentrations of heavy metals and the downward migration against the reference site. This shows the presence of metal containing wastes contributing enormously to heavy metal pollution. The result of accumulated metals in soil showed that zinc has the highest value which is similar to other reports [11, 22]. All the heavy metals (Cu, Pb, Mn and Zn) determined showed higher concentration at dumpsite B, which is due to the fact that this dumpsite is close to the high way and a mechanical workshop that is likely to contribute to the increased level of heavy metals. The appreciable level of Pb at the REF site is unclear, but may be due to proximity to unknown previous activities that are not palpable to the deduction in this study. However, it is unlikely to consider the geology of the area as a factor, but the varying concentrations of all metals studied in this work are within the common range [23].

Heavy metal cations are said to be more mobile under acidic conditions [10]. The pH obtained in this study was generally alkaline; consequently the mobility of metal ions may not have been favored completely by the pH. However, there was correspondingly higher concentration of metals as the pH tends towards acidity. Other factors, such as gravity, resulting from reoccurrences of heavy rainfall and constant leaching may be attributable. Acidic conditions in soil often enhance the solubility of heavy metals such as Cu, Zn and Pb. Also, the behaviour of heavy metals in soil environments is dependent on the chemical speciation and the relative distribution of chemical forms of metals in soil solutions. These in turn influence the available and mobility of these metals in soils [23].

The concentrations of metals are observed to be favored by increase in % OM since it increases the rate of metal ion absorption. The decomposition of the organic components of waste by the action of microorganisms increases the level of organic matter in the dump soil. Organic matter acts as a major adsorbent for metals through the formation of chelates and renders them immobile [10]. Organic matter content of the dumpsites was also found to be higher than obtained from a farm land. This indicated that waste contaminated soils have relatively high organic matter content compared with that of non-waste contaminated soils [24]. The profiles of soil OM in this study are consistent with other studies [7, 25]. The antithetical relationships between pH and OM correspond to the results of other study [7].

In conclusion, the result of this study shows that there exists risk for the environment due to notable migration of heavy metals across depth profile. The migrations were also observed to be highly correlated with organic matter content than pH values.

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