Assessment of Cd and Zn in Roadside Surface Soils and Vegetations along Some Roads of Kaduna Metropolis, Nigeria

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Abstract: To identify the concentrations of heavy metals in roadside environment, samples of roadside soils and vegetation were collected from 30 sites of 24 minor and major roads in Kaduna metropolis across two seasons. Subsequently, the concentrations of Cadmium (Cd) and Zinc (Zn) in the samples were analyzed using atomic absorption spectrophotometer. The mean concentration of Zn (mg kg\(^{-1}\) d.w.) in soil ranged from 45.37-237.96 and 24.21-123.14 for dry and wet season, respectively. While Cd mean concentration (mg kg\(^{-1}\) d.w.) in soil ranged from 1.96-6.80 and 0.38-2.44 for dry and season, respectively. Concentration of Zn in plant (mg kg\(^{-1}\)) ranged from 27.78-185.19 and 15.43-138.89 for dry and wet season, respectively while concentration (mg kg\(^{-1}\) d.w.) of Cd ranged from 4.88-14.63 and 4.88-9.76 for dry and wet season, respectively. The Zn concentrations in both soil and plant leaves were found to be within ICRCL and FAO/WHO recommended limits, respectively. While Cd concentrations were found in excess of ICRCL and FAO/WHO recommended limits, respectively, this indicates potential health risk for human through the food chain. Comparative study showed that Cd and Zn values for soil and plant leaves were found high in the study area than the control area. This suggests that automobiles are a major source of these metals in roadside environment.

Key words: Heavy metals, roadside, surface soils, vegetation, Kaduna, metropolis

INTRODUCTION

The pollution of soils and vegetation by trace metals from automobile sources is a serious environmental issue (Akbar et al., 2006). This is due to the health implications of their presence, since they are non-essential metals that are not required for any function either by plants or animals. These metals are released during different operations of the road transport such as combustion, component wear, fluid leakage and corrosion of metals. Lead, cadmium, copper and zinc are the major metal pollutants of the roadside environments and are released from fuel burning, wear out of tyres, leakage of oils and corrosion of batteries and metallic parts such as radiators etc. (Dolan et al., 2006).

Elevated concentrations of trace metals as a result of human activities have been recorded since ancient times (Nriagu, 1996). However, excessive releases of toxic trace metals into the roadside environment and the associated health implications only became apparent in the 1960s when anthropogenic lead contamination of the roadside environment was documented. Today, studies of roadside environment have developed into a global phenomenon with few geographical boundaries due to their growing environmental and health awareness (Li et al., 2005). Studies have shown that metal pollutants can be harmful to the roadside vegetation, wildlife and the neighboring human settlements (Turra and Maynard, 2003; Awofolu, 2005). Kaduna may not be an exception to the foregoing trace metals concentration problem.

Kaduna metropolis a rapidly growing city with present population estimated to be home to 1,652,844 people, compare with 993,600 in 1991 census (TWG, 2007). With increase in population
MATERIALS AND METHODS

Sampling Sites Description

Twenty sites of fourteen major roads were selected for soil and fresh plant leaf samplings as shown in Fig 1. These were chosen for the study because they have the heaviest traffic in the city (>2000 vehicle per day). Also, 10 low traffic roads (<2000 vehicle per day) were selected as control sites. The low traffic roads were located in areas of low traffic density with little commercial and industrial activities.

Sample Collection

All soil and plant (Sida acuta Burm. f. commonly known as broom weed) samples were collected in the month of April 2006 for the dry season and in the months of July and August 2006 for the wet season. According to Markert (1993) and Wittig (1993), the basic criteria for the selection of a species as a biomonitor are that it should be represented in large numbers all over the monitor area, be easy to sample and there should be no identification problems. Sida acuta Burm. f. embodies all these criteria. Fresh leaves of Sida acuta Burm. f. were randomly taken from the vicinity of the sampled area where soil samples were collected, using a clean stainless steel pair of scissors. Surface soil samples at 3 m distance from each road were collected with the aid of stainless steel spoon washed with soap and rinsed with distilled water after each sampling (Awofola, 2005). Ten subsamples of 20 g each were collected from each side of the road at a sampling site. The sub-samples for each sampling location were then placed in a cellophane bag (Bangbose et al., 2000). To get the composite samples of each site, bulked procedure was adopted to standardize the samples. A conning and quartering method was applied repeatedly to reduce the sample volume (Jackson, 1958). Representative sample collected from each site sample was then labeled and taken to the laboratory for processing/pre-treatment and analysis. The soil sampling spots was cleared of debris before sampling (Chimuka et al., 2005). Samples from the control sites were collected following the same procedure.
Fig. 1: The road network in Kaduna metropolis showing the sampling points

**Determination of some Physico-Chemical Parameters of Roadside Soil**

Soil pH and electrical conductivity were measured in a 1:2 soil to water ratio (Hendershot et al., 1993). Particle size distribution was determined by the hydrometer method as described by Bougoucos (1951). Soil organic matter was determined by the wet oxidation method of Walkley and Black (1934). The exchangeable cations were extracted by 0.1 mold m$^{-3}$ BaCl$_2$ and subsequently determined by AAS Hendershot et al. (1993).
Digestion of Samples

Soil samples from each site were homogenized and air dried in a circulating air in the oven at 30°C to a constant weight and passed through a 2 mm sieve. Five gram of soil samples were placed in
100 mL beaker. Three milliliters of hydrogen peroxide (30%) was added following previously described
procedure by Shriadah (1999). This was left to stand for 60 min until the vigorous reaction ceased.
75 mL of HCl (0.5 m) solution was added and the content heated gently at low heat on hot plate for
about 2 h. The digest was then filtered into 50 mL standard flask. Triplicate digestion of each sample
together with blank was also carried out. Then the quantification of metallic content of digested
samples was carried out with the flame atomic absorption spectrophotometry model AA 650.

Plants samples were properly rinsed with distilled-deionized water to remove any attached soil
particles, cut into smaller portions then placed in large clean crucible where they were oven dried at
100°C for 48 h. The dried plant samples were ground into fine particles using clean acid washed mortar
and pestle. The procedure according to Awofolu (2005) was used for digestion of plant
sample. 0.5 g of sieved leaf samples were then weighed into 100 mL beaker. A mixture of 5 mL
concentrated Trioxonitrate (iv) acid and 2 mL Perchloric acid was added and this was digested on low
heat using hot plate until the content was about 2 mL. The digest was allowed to cool, filtered into
50 mL standard flask using 0.45 um Millipore filter kit. The beaker was rinsed with small portions
of double distilled water and then filtered into the flask. Triplicate digestion of each sample was carried
out together with blank digested without the plant sample.

Quality Assurance

Quality control test was conducted on soil and plant samples in order to evaluate the experimental
procedures and efficiency of atomic absorption spectrophotometer. This was done by spiking the
pre-digested soil and plant samples with multielement metal standard solution (0.5 mg L⁻¹ of Cd and
5 mg L⁻¹ of Zn) (Awofolu, 2005).

RESULTS AND DISCUSSION

Method Validation

The validity of the procedures used for sample treatment and analysis was tested by spiking
experiment. The recoveries of soil were 105.6 and 107.8% for Cd and Zn, respectively. The recoveries
for those of plant leaves were 100.0 and 102.2% Cd and Zn, respectively. Recoveries from soil
samples were generally higher than plant samples with Zn in soil sample having the highest recovery
overall. The recovery results were in good agreement with expected values. Therefore, the recovery test
and reproducibility of the method were found satisfactory to validate the experimental protocol.

Soil Physicochemical Properties

Generally, all samples from the study sites were dominated by high average percentage sand
fraction followed by clay and finally silt. Table 1 and 2 showed the seasonal variation of the soil
physico-chemical properties. Soil pH varied from 7.7-8.2, indicative of an alkaline environment.
Electrical conductivity values ranged from 0.18-0.42 mS cm⁻¹ and suggest non-saline growing

Table 1: Physicochemical properties of the studied soils

<table>
<thead>
<tr>
<th>Properties</th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>pH</td>
<td>7.52</td>
<td>8.34</td>
</tr>
<tr>
<td>EC (mS cm⁻¹)</td>
<td>0.20</td>
<td>1.80</td>
</tr>
<tr>
<td>OM (%)</td>
<td>0.27</td>
<td>1.76</td>
</tr>
<tr>
<td>CEC (meq/100 g)</td>
<td>2.34</td>
<td>3.55</td>
</tr>
</tbody>
</table>

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conditions in the study area. Percentage of organic matter was generally low in the study area. Cation exchange capacity values obtained in this study were lower than range of 10.2-27.2 mequiv/100 g reported in a similar study (Mohammed et al., 2005). Analysis of variation between seasons revealed no significant differences (p>0.05) for pH, Electrical Conductivity (EC) and Cation Exchange Capacity (CEC) between study and control areas, significant variations (p<0.05) were observed for Organic Matter (OM) of study and control areas. Significant variations in properties between seasons could be attributed to wash-out process during rains while non-significant variation in some properties could be due to anthropogenic sources.

**Concentration of Metals in Soils and Plants**

Zn and Cd show higher mean concentrations in the study than in the control samples except for Cd in plants sample (Control – 11.38 and Study – 8.29 mg kg⁻¹). This suggests the possibility for Cd and Zn, that in some cases, other sources are responsible, such as wear out of tyres, leakage of oils and corrosion of batteries and metallic parts such as radiators. For the study soil and plant samples, the mean concentrations of Cd and Zn were found in the following decreasing order: Zn and Cd (Table 3, 4). Other researchers have reported similar trends in related studies (Lagerwerff and Specht, 1970; Ward et al., 1977; Fatok, 1996; Chimuka et al., 2005; Okunola et al., 2007). In general, the results showed that there was decrease in concentrations of Cd and Zn in soil and plant samples between the dry and wet seasons. According to Fatoki (1996), seasonal variation can also cause significant differences in the levels of metals found on roadside soil and plant. In support, analysis of variation performed between dry and wet season revealed significant differences (p<0.05) in Cd and Zn in both samples for the study area, while no significant differences (p>0.05) were found.
Table 4: Heavy metal concentrations in control roadside surface soil and plant samples

<table>
<thead>
<tr>
<th>Properties</th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Cd Soil</td>
<td>1.96</td>
<td>9.80</td>
</tr>
<tr>
<td>Cd Plant</td>
<td>9.76</td>
<td>14.63</td>
</tr>
<tr>
<td>Zn Soil</td>
<td>41.66</td>
<td>140.74</td>
</tr>
<tr>
<td>Zn Plant</td>
<td>27.78</td>
<td>92.59</td>
</tr>
</tbody>
</table>

Transfer factor (Plant/soil)

|             |            |            |
| Cd          | 2.83       | 3.25       |
| Zn          | 0.64       | 0.98       |

Table 5: Correlation matrices between metals in soil and plant samples of study sites

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Soil Cd</th>
<th>Soil Zn</th>
<th>Plant Cd</th>
<th>Plant Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry season</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil Cd</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil Zn</td>
<td>0.325</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plant Cd</td>
<td>-0.176</td>
<td>0.263</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Plant Zn</td>
<td>0.402</td>
<td>0.760**</td>
<td>0.259</td>
<td>1.00</td>
</tr>
<tr>
<td>Wet season</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil Cd</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil Zn</td>
<td>0.477*</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plant Cd</td>
<td>0.221</td>
<td>0.307</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Plant Zn</td>
<td>-0.131</td>
<td>0.685</td>
<td>-0.209</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*Significant correlation at p<0.05. **Significant correlation at p<0.01

in Cd and Zn in both samples for the control area. The marked differences with Cd and Zn results obtained in this study could be attributed to wash-out process of deposited metals by rains (Chimuka et al., 2005).

An attempt was made to investigate any relationship between the metals in the soil, metals in soil to that found in the plant and metals in plant. The correlation coefficient as shown in Table 5, revealed that positive correlation between Cd and Zn in soil in both dry and wet seasons, respectively. Negative correlation was observed between plant Cd and soil Cd, positive correlation between plant Cd and soil Zn, plant Zn and soil Cd, plant Zn and soil Zn for both dry and wet seasons. Although inverse relationship was observed between plant Zn and soil Cd in wet season. Positive correlation between metals in both samples suggest similar source of these metals while negative correlation suggest another source of contamination other than motor traffic. This finding suggest interaction between Cd and Zn during dry season in both plant and soils were in corroborate with the results of McKenna et al. (1993) in relation to the known geochemical association between the two metals. The correlation between trace metals in soil to that in plant is very important from the human health aspect (Chimuka et al., 2005).

Soil contamination was evident in both study and control areas, although ameliorated during rains. Cd concentration exhibited higher levels of contamination in study areas than the mean values of 1.3 mg kg⁻¹ (Ndikwure, 1984), 1.1 mg kg⁻¹ (Ho and Tai, 1988) and 0.75 mg kg⁻¹ (Jaradat and Mornani, 1999) in a similar studies. In absence of any major industry in the sampling sites, high levels of Cd could be due to lubricating oils and old tyres that are frequently used and the rough surfaces of the roads which increase the wearing of tyres. Similarly the level of Zn contamination in this study is small compared with 163 and 121.7 mg kg⁻¹ reported by Ndikwure (1984) and Jaradat and Mornani (1999). Although higher than 1.4 mg kg⁻¹ reported by Akbar et al. (2006). Cd and Zn are usually found in lubricating oils as part of many additives. Since no major industry exists in the study areas such as smelting operation, the primary sources of Zn are probably the attrition of motor vehicle, tyre rubber exacerbated by poor roads surfaces (Jaradat and Mornani, 1999). Positive correlation between soil Cd and soil Zn as shown in Table 5 also supported this. However the concentration were higher than 0-3 and within 0-250 mg kg⁻¹ critical limits (ICRCL, 1987) for Cd and Zn, respectively.
Table 6: Correlation matrices of heavy metals and physicochemical parameters of studied soil

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>EC</th>
<th>OM</th>
<th>CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry season</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.246</td>
<td>0.155</td>
<td>0.099</td>
<td>0.038</td>
</tr>
<tr>
<td>Zn</td>
<td>0.137</td>
<td>0.501**</td>
<td>0.156</td>
<td>-0.373</td>
</tr>
<tr>
<td><strong>Wet season</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>-0.043</td>
<td>0.286</td>
<td>-0.021</td>
<td>-0.155</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.456*</td>
<td>0.569**</td>
<td>0.158</td>
<td>0.149</td>
</tr>
</tbody>
</table>

Broad leaf vegetation are known to accumulate greater concentration of most heavy metals. The high accumulation of Cd in plants than soil could be attributed to foliar absorption of these metals via atmospheric emission. The concentration of Zn and Cd in the plants increased with the degree of contamination of the soil. Different plant species are known to accumulate different metals depending on environmental conditions, metal species and plant available forms of heavy metals (Chandrappa and Lokeshwari, 2006). Although forms of heavy metals were not determined in the present study. However, considerably higher concentrations of Cd are detected compared to 0.2 mg kg⁻¹ (FAO/WHO, 2001) maximum critical limit above which toxicity is possible. While Zn concentrations were within 60-400 mg kg⁻¹ toxic doses of Zn to plant (FAO/WHO, 2001).

Transfer Factors for Heavy Metals

Table 3 and 4 shows the transfer factor (TF) of Cd and Zn from soil to plant, which is one of the key components of human exposure to metals through the food chain. Transfer factors were determined for Cd and Zn to quantify the relative difference in bioavailability of metals to plants or to identify efficiency of plant species to accumulate a given metal. The transfer factors as suggested by Kloke et al. (1984) for Cd and Zn (1-10) were used as a generalized range for comparisons. These factors were based on the root uptake of metals and discount the foliar absorption of atmospheric metal deposits. No samples exceeded Cd and Zn suggested factor range as suggested by Kloke et al. (1984). Although the degree of accumulation of Cd is 2-3 fold higher than Zn. The reasons could be due to the nature of Cd, since Cd is known to be less retained by the soil than other toxin cations (Chandrappa and Lokeshwari, 2006) or the low organic matter contents (Table 1, 2) of soils sampled could have also enhanced soil-plant transfer of metals.

Influences of Some Soil Parameters on Metal Availability and Solubility

Positive correlations between parameters indicate a linear relationship of this parameter on solubility and mobility of metal ion. Negative correlations between physicochemical parameters and soil heavy metals could indicate an inverse relationship between the parameters (Table 6).

CONCLUSION

The present study has shown some Cd contamination of soil and plant samples in Kaduna metropolis. Cd and Zn values for soil and plant leaves were found high in the study area than the control area. This indicates that wear and tear of automobile parts could be responsible for the high concentration of these metals in the study area. Changes in concentration of both metals across the sampling periods might be due to wash-out process during rains. The Zn concentrations in both soil and plant leaves were found to be within ICRCL and FAO/WHO recommended limits, respectively. While Cd concentrations were found in excess of ICRCL and FAO/WHO recommended limits, respectively. The degree of accumulation shows that Cd is more than 2 folds higher than Zn. The reasons could be due to the nature of Cd, since Cd is known to be less retained by the soil than other toxin cations (Lokeshwari and Chandrappa, 2006) or the low organic matter contents (Table 1, 2) of soils sampled could have also enhanced soil-plant transfer of metals.
Further studies should consider variations in uptake between different species and the difference in plant uptake between soil and foliar mechanisms.

REFERENCES