Research Article

Distribution Pattern of Metals in Atmospheric Settling Dust along Roads in Kano Metropolis, Nigeria

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The sequential extraction of Cd, Cr, Ni, Pb, Cu, and Zn in atmospheric dust particles collected along ten high traffic roads in Kano metropolis was carried out. Analyses of metals in the extracts were done using flame atomic absorption spectrometry (FAAS). The samples analyzed for metals indicated high levels of Cd, Cr, Ni, Pb, Cu, and Zn in the atmospheric dust samples. The sequential extractions that showed significant amount of Cd were associated with CO$_3^{2-}$ and Fe-MnO fractions especially during the dry seasons. For Cr and Ni, their occlusion in crystal lattice of the soil fraction exhibited the highest percentage. Pb in the particulate dust samples is significantly associated with the carbonate bound fraction with range of 8.81–64.69% across the season. The behaviour of Cu is quite different from other metals in that percentage fractions are higher in the organic bound. As for Zn, significant amounts were associated with the residue fractions ranging from 0.96 to 87.50% across the seasons. This study revealed contamination of the particulate dust with Cd and Pb; this implies health risks to human, living or carrying out daily activities along the corridors of these roads.

1. Introduction

The increase of health problems related to road dust arising from urbanization and industrialization has especially during the last two centuries gradually created a demand for more efficient vehicle-associated emission controls. According to Cho et al. [1], 50% of urban air particulate emissions are closely related to road traffic [1]. Studies have also reported association between traffic density, closeness to roads, and various respiratory symptoms in children [1–3].

From literature, motor vehicles are known to introduce a number of toxic metals into the atmosphere, which are later deposited on roadsides [4]. As a result of vehicle emissions, the deposition of heavy metals on the road may result in their incorporation into dust due to their size that ranges between 10$^{-9}$ and 10$^{-6}$ m [5]. Of all the types of dust found in the urban environment, one of the most highly toxic metals is dust from road. Since such dust may be inhaled via airborne or discharged into rivers by storm-water wash-off, dust from road may hence represent a major pollution source within the urban environment [6]. These activities release dust particulate which adversely affects human. Therefore, monitoring of particulate matter especially with heavy metals is imperative.

Based on the above facts, the present study aims to assess the distribution of metals (Cd, Cr, Ni, Pb, Cu, and Zn) species in atmospheric settling dust along roads using sequential extraction.

2. Materials and Methods

2.1. Study Area. Kano Metropolis is located between latitudes 11°59’59.57” and 12°02’39.57” N of the equator and between longitudes 8°33’19.69” and 8°31’59.69” E. The climate of the Kano is dominated by the migration of the intertropical convergence zone. Industrially, it is one of the most developed cities in Northern Nigeria, and tannery and textile
are some of its dominating industries [7]. Kano Metropolis attracts substantial number of immigrants being the seat of government and center of commerce, industry, and education. In the city, there are various large markets such as the City (Kurmi) Market, Sabon Gari Market, and Katin Kwari (cloth market) which attract people from all over the country. The major form of transportation within Kano Metropolis is by road. Most common transport modes used include cars, buses, motorcycles, and tricycles (Keke NAPEP).

2.2. Sample Collection and Pretreatment. Sampling of dusts for this study was conducted from December 2009 to September 2010 across four named seasons; cold and dry, hot and dry, warm and wet, and warm and dry. The criteria for selections of roads for the study were based on foreknowledge of the relative traffic density on each road and the desire to have each category of traffic density in different sections of the Metropolis. Samples were collected from 10 roadside locations (1–10) and a control site (C) all over the Metropolis as shown in Figure 1. These sites were mainly located in residential and commercial areas of the metropolis. Control samples were obtained from a small garden within a residential buildup area of farm center, which is not closer to any secondary or main road. Average temperature across the seasons is 31.5–36.6°C, 30.0–39.1°C, 30.5–33.9°C, and 30.1–39.5°C, respectively.

Atmospherically deposited particulates were sampled according to indirect method of air sampling described by Nabuloa [8]. Similarly, the traffic density was determined by manual counting according to Okunola et al. [9] as shown in Table 1.

2.3. Quality Assurance. All apparatus including glassware and plastic tubes were sterilized according to Adnan et al. [10]. All reagents used were of analytical grade, and the instrument working calibration was made by diluting the commercial Scharlau Japan stock solution (1000 mg L⁻¹) standard with distilled-deionized water. The detection limits for metal analysis were 0.01 mg L⁻¹ for Cd, Cr, Cu, Ni, and Pb and 0.05 mg L⁻¹ for Zn.

2.4. Metal Extraction of Atmospheric Settling Dust. Total metal assessment was done according to Ogunfowokan et al. [6], while sequential extraction was done using Finžgar et al. [11] method. The method modified Tessier et al. [12] method.
Table 1: Mean traffic density/hour.

<table>
<thead>
<tr>
<th>Sampling site code</th>
<th>Sampling site</th>
<th>Number of motorcycles</th>
<th>Number of vehicles</th>
<th>Number of trucks/lorries</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aminu Kano</td>
<td>1902 ± 12</td>
<td>2634 ± 10</td>
<td>196 ± 2</td>
<td>4732</td>
</tr>
<tr>
<td>2</td>
<td>Zoo</td>
<td>2011 ± 20</td>
<td>1504 ± 8</td>
<td>121 ± 5</td>
<td>3636</td>
</tr>
<tr>
<td>3</td>
<td>Dan Agundi</td>
<td>1206 ± 15</td>
<td>1935 ± 12</td>
<td>216 ± 2</td>
<td>2831</td>
</tr>
<tr>
<td>4</td>
<td>Kofar Nassarawa</td>
<td>1323 ± 13</td>
<td>1801 ± 19</td>
<td>46 ± 2</td>
<td>3170</td>
</tr>
<tr>
<td>5</td>
<td>Rimi Market</td>
<td>3005 ± 10</td>
<td>2008 ± 14</td>
<td>25 ± 2</td>
<td>5038</td>
</tr>
<tr>
<td>6</td>
<td>Sani Abacha</td>
<td>6857 ± 23</td>
<td>1292 ± 13</td>
<td>207 ± 2</td>
<td>8357</td>
</tr>
<tr>
<td>7</td>
<td>Ibo Road</td>
<td>2464 ± 13</td>
<td>1845 ± 19</td>
<td>35 ± 5</td>
<td>4344</td>
</tr>
<tr>
<td>8</td>
<td>Court/FRance</td>
<td>2651 ± 18</td>
<td>1041 ± 9</td>
<td>16 ± 2</td>
<td>3708</td>
</tr>
<tr>
<td>9</td>
<td>Kofar Mazugal</td>
<td>1995 ± 21</td>
<td>2836 ± 12</td>
<td>149 ± 2</td>
<td>4180</td>
</tr>
<tr>
<td>10</td>
<td>Zungeru/Airport</td>
<td>1443 ± 11</td>
<td>2366 ± 17</td>
<td>198 ± 3</td>
<td>4007</td>
</tr>
<tr>
<td>C</td>
<td>Farm Center</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Table 2: Concentrations (μgg⁻¹) of metals in samples collected from different sites across the seasons.

<table>
<thead>
<tr>
<th>Metal</th>
<th>SN</th>
<th>Site</th>
<th>Site</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>A</td>
<td>19.78</td>
<td>36.96</td>
<td>61.28</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>19.78</td>
<td>56.57</td>
<td>44.50</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>24.57</td>
<td>70.98</td>
<td>28.68</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>8.74</td>
<td>27.61</td>
<td>22.06</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>134.75</td>
<td>71.91</td>
<td>80.67</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>236.61</td>
<td>34.66</td>
<td>43.73</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>327.14</td>
<td>47.98</td>
<td>53.85</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>254.85</td>
<td>38.81</td>
<td>47.55</td>
</tr>
<tr>
<td>Cr</td>
<td>A</td>
<td>133.71</td>
<td>167.49</td>
<td>189.05</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>90.35</td>
<td>135.22</td>
<td>151.23</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>127.53</td>
<td>182.75</td>
<td>196.28</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>61.59</td>
<td>80.89</td>
<td>95.18</td>
</tr>
<tr>
<td>Ni</td>
<td>A</td>
<td>26.51</td>
<td>50.71</td>
<td>44.51</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>16.15</td>
<td>39.16</td>
<td>40.21</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>20.54</td>
<td>53.87</td>
<td>51.28</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>13.30</td>
<td>23.91</td>
<td>21.51</td>
</tr>
<tr>
<td>Pb</td>
<td>A</td>
<td>153.98</td>
<td>295.82</td>
<td>259.85</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>2312.28</td>
<td>11711.20</td>
<td>2371.19</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>2083.70</td>
<td>8781.65</td>
<td>2263.52</td>
</tr>
<tr>
<td>Cu</td>
<td>A</td>
<td>211.52</td>
<td>1261.07</td>
<td>201.82</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>2312.28</td>
<td>11711.20</td>
<td>2371.19</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>2083.70</td>
<td>8781.65</td>
<td>2263.52</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The total concentrations of Cd, Cr, Ni, Pb, Cu, and Zn for the samples are presented in Table 2. In each case the presented value is a mean observed in three determinations. Analysis of variance revealed significant difference (P < 0.05) in the contents of the studied heavy metals across sites across the studied seasons. The concentrations across the seasons varied to great extent among the samples: 5.05–25.99, 7.01–32.90, 1.57–8.72, and 2.77–13.86 μgg⁻¹ for Cd; 19.57–171.43, 24.14–220.51, 8.48–72.16, and 19.55–87.57 μgg⁻¹ for Cr; 26.54–24.35, 21.37–32.59, 38.00–254.70, and 66.67–134.50 μgg⁻¹ for Ni; 90.71–1067.03, 127.05–1408.13, 61.19–641.36, and 133.42–231.52 μgg⁻² for Pb; 15.80–204.73, 20.09–269.77, 13.60–99.24, and 26.02–133.27 μgg⁻¹ for Cu; and 2314.36–2353.03, 2087.39–17403.54, 213.04–3514.65, and 154.95–2029.84 μgg⁻² for Zn for cool and dry season,
hot and dry season, warm and wet season, and warm and dry season, respectively. Irrespective of sampling site, the distribution of total metals in the atmospheric particulate dust samples generally followed the order: Cd < Cr < Cu < Ni < Pb < Zn. Highest concentration of Cd, Cr, and Zn was found in site 8, while highest concentration of Ni, Pb, and Cu was found in sites 1, 5, and 4, respectively. Also, highest concentrations of all studied metals were recorded in hot and dry season with exception of Zn that has highest concentration recorded in cool and dry season. In general, highest concentrations of metals studied were recorded in dry seasons. This could be due to low moisture content of samples during this season. Comparing the data of control site to the studied sites, lower concentrations of metals were obtained from control site.

Correlation analysis indicates positive significant correlation ($P < 0.05$) between Zn and Cr (hot and dry season), and Zn: Cd and Cr (warm and wet season, and warm and dry season). Positive correlation of metals indicates common source of metals.

The distribution of heavy metals Cd, Cr, Ni, Pb, Cu, and Zn in the six fractions, water soluble (FI), exchangeable (FII), carbonate bound (FIII), Fe-Mn oxide (FIV), organic bound (FV), and residual (FVI), for all studied samples is summarized in Figures 2–24. The results obtained showed that the amounts of heavy metals extracted from each fraction vary widely among the sites across seasons ($P < 0.05$).

Significant amount of Cd was associated with carbonate and Fe-Mn oxide fractions especially during the dry seasons as shown in Figures 2–5. Highest percentage of Fe-Mn oxide was obtained in site 3 during the warm and wet season. Averagely, Cd distribution among the geochemical fractions of the particulate dust in the four seasons was
For Cd (Figures 5), the residual fraction exhibited the highest percentage ranging from 82.07 to 92.78% in site 9 in dry season. The low level of Cd in water soluble and exchangeable fractions of the samples may be an indication that leaching of Cd from the particulate dust may not occur readily. The patterns of Cd distribution among the fractions of the atmospheric particulate dust in the four seasons are:

- warm and dry season: FIII > FVI > FIV > FI > FII
- cool and dry season: FIII > FIV > FV > FII > FII
- hot and dry season: FVI > FV > FIV > FIII > FII > FI
- warm and wet season: FVI > FV > FIV > FII > FIII > FII

For Cr (Figures 6–9), the residual fraction exhibited the highest percentage ranging from 82.07 to 92.78% in site 9 in dry season. The low level of Cr in water soluble and exchangeable fractions of the samples may be an indication that leaching of Cr from the particulate dust may not occur readily. The patterns of Cr distribution among the fractions of the atmospheric particulate dust in the four seasons are:

- cool and dry season: FVI > FV > FIV > FIII > FII > FI
- hot and dry season: FVI > FV > FIV > FIII > FII > FI
- warm and wet season: FVI > FV > FIV > FII > FIII > FII
- warm and dry season: FIII > FVI > FIV > FV > FII > FI.
The Ni similar to Cr was concentrated in the residual fraction with exception of warm and wet season as shown in Figures 10–13, ranging from 7.62 to 72.73%. The organic fraction was second in proportion ranging from 0.00 to 56.92%, followed by Fe-Mn oxide, carbonate, exchangeable, and water soluble. Based on the result found, the profile obtained for Ni was:

- cool and dry season: FVI > FV > FIV > FIII > FI > FII,
- warm and dry season: FVI > FV > FIV > FIII > FI > FII,
- warm and wet season: FV > FII > FIV > FVI > FI > FII,
- hot and dry season: FVI > FV > FIV > FIII > FI > FII.

Pb in the particulate dust samples is significantly associated with the carbonate bound fraction with range of 8.81–64.69% across the season as shown in Figures 14–17, which suggested that Pb had a preference for carbonate fractions at
On the average percent of total Pb associated with different fractions across the site was in the following order:

- cool and dry season: $F_{III} > F_{VI} > F_{IV} > F_{V} > F_{I} > F_{II}$,
- hot and dry season: $F_{III} > F_{VI} > F_{IV} > F_{V} > F_{I} > F_{II}$,
- warm and wet season: $F_{III} > F_{VI} > F_{IV} > F_{V} > F_{I} > F_{II}$,
- warm and dry season: $F_{III} > F_{VI} > F_{IV} > F_{V} > F_{I} > F_{II}$.

The behaviour of Cu is quite different from other metals in that percentage fractions are higher in the organic bound ranging from 3.62 to 89.62% (Figures 18–21). Based on the result found, the profile obtained for Cu was

- cool and dry season: $F_{V} > F_{VI} > F_{I} > F_{II} > F_{III}$,
- hot and dry season: $F_{V} > F_{VI} > F_{I} > F_{II} > F_{III}$,
- warm and wet season: $F_{V} > F_{VI} > F_{I} > F_{II} > F_{III}$,
- warm and dry season: $F_{V} > F_{VI} > F_{I} > F_{II} > F_{III}$.
As for Zn, significant amount of Zn was associated with the residue fractions ranging from 0.96 to 87.50% across the seasons (Figures 22–25). Zn association with the chemically reactive fractions such as Zn in water soluble and exchangeable forms generally represented less than 10% of the total fractions of Zn in the samples. The distribution of Zn among the particulate dust fractions across the seasons is

cool and dry season: FVI > FIV > FIII > FV > FI > FII,
hot and dry season: FVI > FIV > FIII > FV > FII > FI,

warm and wet season: FVI > FIV > FIII > FV > FI > FII,

warm and dry season: FIV > FII > FV > FVI > FII > FI.

Heavy metal speciation studies are important since slight changes in metal availability and in environmental conditions can cause these elements to be toxic to animals and plants [13]. From the results presented above, Cd was found in its highest proportion in the form bound to Fe-Mn oxide (60.31%) in site 3 sample.
The highest percentage of this fraction is relatively high and constitutes a large portion of nonresidual Cd. Heavy metals wrapped by Fe-Mn oxides or precipitated as hydroxide have been reported by Wang et al. [14].

Metals bound to Fe-Mn oxides would be released under reductive conditions [15] and therefore are unstable under anaerobic condition. Similar to this study, Feng et al. [16] reported high percentage of Cd in carbonate and Fe-MnO fractions. Also, Cd in samples agrees with the findings of Harrison et al. [17], Baron et al. [18], and Yusuf [19]. The high amount of Cd associated with nonresidual fractions shows that it may be easily transferred into the food chain. The minor role for organic fraction in the fractionation of Cd in this study is consistent with the low adsorption constant of Cd to organic matter [20] and with evidence that Cd does not appear to form strong organic complexes [21].

The high percentage of Cr (31.15–84.88%) across the seasons was found in the residual fraction, indicating that...
Cr shows little risk to environment. Metal in this fraction is mainly fixed in the primary and secondary minerals [22] and is chemically stable and biologically inactive. The greater the percentage of metals present in this fraction, the smaller the risk of the metal because this portion of metal cannot be released to the environment under normal conditions [14]. Furthermore, the stable nature of the metal and the fact that the metal are bonded firmly within a mineral lattice restricting the bioavailability of this metal [23]. The trend in Ni is similar to that in Ni in the fact that residual fraction is the major carriers of Ni in the atmospheric particulate dust. Similar trend was reported by Ma and Rao [24].

In a study by Flores-Rodriguez et al. [25] on the bioavailable and stable forms of atmospheric particulate dust, Fe-MnO and carbonate fractions of suspended solids are the most important in terms of metal binding, irrespective of heavy metal. This finding is in general agreement with the results of this study for Pb. Studies on the fractionation of atmospheric particulate dust have suggested that Pb has a high affinity for carbonates [16]. As such, Pb is generally considered to be relatively mobile with the dust particles, primarily as a result of its small soluble component. High amount of Pb in the carbonate fractions is also reported in other studies on roadside soils. Howard and Sova [26] noted, for example, a larger part of Pb in the carbonate fraction in the most heavily contaminated roadside soil.

The predominant form of Cu available in the entire fraction is organic fraction. The higher stability constant of Cu complexes with organic matter leads to higher organic fractions. Tessier et al. [12] indicated that Cu exhibits the highest stability constants for most ligand among the heavy metals studied. Based on this, Ho [27] suggested that the high affinity of organic ligands with heavy metals makes Cu in river sediments more stable, leading to the suppression of diffusion and dispersion of Cu; though dust samples were considered in this study, similar reasons could be responsible. However, under strong oxidizing conditions, Cu be leached into the environment [14]. In this fraction, the metal ion acts as the central ion, and the active organic matter group acts as the ligand or perhaps through the reaction of the sulphide ion and Cu. The organic fraction released in this step is hardly considered very mobile or available because the Cu is associated with stable high-molecular weight humic substances that decompose slowly [28]. A high percentage (3.62–89.62%) of Cu was found in the oxidizable fraction, indicating that high organic matter and sulphide absorbed Cu and played a significant role in controlling the mobilization of this element. Cu is usually reported to dominate in the organic and residual fractions [17, 24, 29, 30].

From the results, Zn fraction is considered to be occluded inside the crystalline structures and not readily available for plant absorption. The findings are different with that of Shuman [31], who reported that soil Zn was mainly associated with crystalline Fe-Mn oxide and with nonresidual extractable residual fraction, though atmospheric particulate dust was used in this study. Usero et al. [32] and Mashal et al. [33] using Tessier’s method found that Zn is bound to residual fraction. Maskall and Thornton [34] indicate that, in contaminated soils, Zn is mainly found in the residual fractions. The results for atmospheric particulate dust are similar, but with less association with Fe-Mn oxides and a higher percentage with the residual fraction. For Cr the residual fraction exhibited the highest percentage.

4. Conclusion

The atmospheric dust collected from roads in Kano Metropolis shows high concentrations of heavy metals which could lead to serious environmental hazards. Correlation analysis indicates common source of metals: Zn, and Cr (hot and dry season), and Zn: Cd and Cr (warm and wet season, and warm and dry season). The sequential extraction showed that significant amount of Cd was associated with carbonate and Fe-Mn oxide fractions especially during the dry seasons. For Cr and Ni the residual fraction exhibited the highest percentage. Pb in the particulate dust samples is significantly associated with the carbonate bound fraction with range of 8.81–64.69% across the season. The behaviour of Cu is quite different from other metals in that percentage fractions are higher in the organic bound. As for Zn, significant amount was associated with the residue fractions ranging from 0.96 to 87.50% across the seasons. This study indicated that air particle pollution due to metal such as Cd and Pb may possess serious health risks to the residents in this rapidly developing and populated city.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


