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# Heavy Metals Contamination of Road-Deposited Sediments

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**Abstract: Problem statement:** Impact of anthropogenic activities on man and his environment as a result of the growing rate of urbanization in Bida, Nigeria is of a great concern. Street sediments that accumulate along pavements in urban environments have the potential to provide considerable loadings of heavy metals to receiving waters and water bodies, particularly with changing environmental conditions. The objective of this research was to evaluate the streets sediment contamination in Bida, Nigeria. **Approach:** Fifty five sediment samples were collected from four roads that experience intense traffic conditions and analyzed in the laboratory for some heavy metals by atomic absorption Spectrophotometric method and multivariate statistical techniques. **Results:** The overall decreasing metal concentration order was: Pb > Mn > Fe > Zn > Cu > Cr > Ni > Cd. Significantly positive correlation was only found between Cd and organic matter (r = 0.580). Factor analysis shows that road deposited sediment quality data consists of four major components accounting for 77.11% of cumulative variance of the contamination: Ni, pH and silt + clay; Cr, Fe and organic matter; Mn and Zn and finally Cu and Pb. Discriminant analysis revealed that the first two Discriminate Functions (DF1 and DF2) contain 90.61% information for Cu, Pb and Ni accumulation. **Conclusion:** This study concluded that the concentrations of all metals measured in Bida can be considered to present a low level of contamination and that multivariate statistical analysis is a useful tool in understanding contaminants relationships.

**Key words:** Anthropogenic, environment, multivariate, discriminant analysis, heavy metals

## INTRODUCTION

The presence of Metal pollutants in road-deposited sediments plays an important role in dictating urban storm water quality. Cities and Towns under various geographical, geological, climatic and sociological conditions are usually considered as big sources of pollutants irrespective of specific types of men activities (Mielke, 1994; Tiller, 1989). Established research has shown that sediments and dusts transported and stored in the urban environment have the potential to provide considerable loadings of heavy metals to receiving waters and water bodies, particularly with changing environmental conditions (Pereira *et al*., 2007).

Street sediments that accumulate along pavements in urban environments originate mainly from natural and anthropogenic sources. Heavy metals from natural sources vary significantly within catchments and may include materials transported by water from surrounding soils, pollutants from dry and wet atmospheric deposition and biological materials from vegetation. Significant quantities of particulate matter can also be attributed to anthropogenic sources such as industrial processes, abrasion of vehicular components and their exhaust emissions, incinerators, power plants and foundry operations, tyre and road surface wear (Sutherland and Tolosa, 2000; Pagotto *et al*., 2001).

These deposits as street sediment have become an important medium for the study of anthropogenic pollutants and their possible sources (Ferguson and Kim, 1991; Watts and Smith, 1994; De Miquel *et al*., 1997; Naqerotte and Day, 1998; McAllister *et al*., 2000; 2005). Urban street sediments have limited residence times and therefore provide a record of recent accumulations (Pereira *et al*., 2007; Pagotto *et al*., 2001; Sutherland and Tolosa, 2000; Sutherland, 2003). The aim of this study was to examine the extent of heavy metal contaminations in Bida road-deposited sediments. The use of statistical analysis as a useful tool for better understanding of the relationships among the studied parameters was also discussed.

## MATERIALS AND METHODS

**Studied area:** Bida town lies at 9°06′N and 6°01′E on the Nupe sandstone formation which consists of plains with ironstone capped hills or mesas. The scenery is fairly uniform since lithology and rock structure are not the existence of large areas of fadama. The northern edge of the town consists of a broken off plateau. From the foot of two flat-topped hills the town sweeps down into the plain. The town is drained by the Chicen and Mussa streams with the third stream Landzu, which flows right across the heart of the town. Bida is in the low basin that is formed by the valleys of the two rivers, Niger and Kaduna (Mahvi *et al*., 2005).

**Sediments sampling:** Fifty five sediment samples were collected from four roads that experience intense traffic conditions in Bida Town with the aid of stainless spoon, washed with soap and rinsed with distilled water after each sampling (Awofolu, 2005). These roads are BCC-Idi road, Govt. College-Post Office road, Banwuya road and Mokola road. Three sampling sites were designated on each road except Mokola road that had two sites.

The samples were collected once every month for five months during the rainy season from May to September 2009. All the samplings were performed three days after the rain. Samples collected were stored in sealed polythene bags and transported to the laboratory for pre-treatment and analyses.

**Laboratory analysis:** The soil samples were air-dried, mechanically ground using a stainless steel roller and sieved to obtain <2 mm fraction. A 20-30 g sub sample was drawn from the bulk soil (<2 mm fraction) and reground to obtain <200 μm fraction using a mortar and pestle. This fine material was used to determine organic carbon and total metal content in soil. The <2 mm fraction was used to determine pH (1: 5 soil water extract and particle size analysis using methods outlined by Rayment and Higginson (1992). Organic carbon was determined by the modified Walkley and Black method by Damian and Damian (2007).

Soil samples were digested in a mixture of concentrated nitric acid ($HNO_3$), concentrated Hydrochloric acid (HCl) and 27.5% hydrogen peroxide ($H_2O_2$) according to the USEPA Method 3050B for the analysis of heavy metals (USEPA, 1996). A reagent blank was run for each set of six samples.

The extracts were analyzed by atomic absorption spectrophotometer (Perkin Elmer, Model No. 2380).

**Statistical analysis:** In order to quantitatively analyze and confirm the relationship among soil properties (pH, OM and silt + clay) and heavy metal content, a Pearson's correlation analysis was applied to dataset.

Principal Component Analysis (PCA) was adopted to assist the interpretation of elemental data. This powerful method allows identifying the different groups of metals greatly variable. An important feature of the scenery is that correlate and thus can be considered as having a similar behavior and common origin (Tahri *et al*., 2005). It should be noted that parametric statistical tests require the data to be normally distributed. Therefore, it was checked if the data came from a population with normal distribution by applying Shapiro-Wilk's test (significance level, $\alpha = 0.05$). The non-normal data were transferred logarithmically to ensure normal distribution.

All the statistical analysis were performed using SPSS for Windows (release Ver.11, Inc., Chicago, IL).

## RESULTS AND DISCUSSION

A close look at the Table 1 shows that high mean metal concentrations were found for all the metals except Cd. Average Pb concentration was 59.67 mg $dm^{-3}$ followed by Mn, Fe, Zn, Cu, Cr and Cd at 17.18, 15.66, 13.89, 11.67, 8.57 and 1.69 mg $dm^{-3}$ respectively. The variability in range of all the metal distributions as compared with their means respectively is an indication of a pollution of the sediment with that metal ion. The decreasing trend of average metal levels was as follows:

$$Pb > Mn > Fe > Zn > Cu > Cr > Ni > Cd$$

The mean and median were used as estimates of central tendency. Standard errors of the mean were all small. The distribution of original data for Ni, Fe, Mn, Zn, Cu and Cd are positively skewed while Cr and Pb were negatively skewed. Despite this skewness, the mean and median values are quite similar for Fe and Cd with medians having smaller values than means. This indicates that measures of central tendency are not dominated by outliers in the distribution. The effect of extreme outliers is greater for the distribution of Cr, Ni, Mn, Zn and Cu values. In each case, test for normality were conducted using the test based on analysis of the combined effects of skewness and kurtosis. The substantial difference in the symmetric parameters in the case of Zn, Cu and Cd indicated a non-normal distribution, thus supporting a possibility of random infiltration of the metals from some anthropogenic sources. Large standard deviations in the case of Pb, Cu, Mn and Zn levels revealed their randomly fluctuating concentration levels in the sediment.

Among significant variables that controls or influences the distribution and concentrations of heavy metals in the environment are the grain size of sediments and organic matterv (Lin *et al*., 2002; Huang and Lin, 2003; Lakhan *et al*., 2003). The degree of correlation between trace metals and organic matter and size distribution is often used to study the origin of many metal (Jumbe and Nandini, 2009). To verify this relationship in this study, correlations between all the metals and the parameters mentioned were carried out.

Correlation coefficients for the metals silt plus clay and organic matter were low except the correlation between organic matter and Cd (Table 2). One reason for this occurrence could be the fact that the analyzed grain sizes were not in the silt plus clay fraction. This result was unexpected, since heavy metals have a high affinity for organic and silt and clay fractions (Mihaly-Cozmuta *et al*., 2005; Zonta *et al*., 1994). This low correlation can be indicative of distinctive sources for these metals in these urban areas. Pereira *et al*. (2007) discovered that the particle size distribution for urban street sediments does not obey the laws of the hydrodynamics like materials found in natural environments such as beaches and rivers. For example, in urban environment particulate matter can be deposited in different ways and these include moving parts of vehicles, loads spilling from trucks, accidents, erosion of gardens and atmospheric deposition. They also noted that urban runoff travels down gradients in accordance with the urban landscape, specifically topography and slope gradients. The fine sediments are swept and flushed along its path, whereby the runoff eventually becomes highly enriched with heavy metals.

In contrary to Pereira *et al*. (2007) observations, some researchers (Ujevic *et al*., 2000; Zhang *et al*., 2001; Che *et al*., 2003; Avila-Perez *et al*., 1999) found organic matter to be associated with the highest concentrations of heavy metals.

In addition to correlation analysis, Factor Analysis (FA) of the studied road deposited sediment samples was performed in order to get an overall impression about assembling the samples in a multidimensional space defined by the chosen metals. The FA has emerged as a useful tool for better understanding of the relationships among the variables (e.g., metal concentrations in the present study) and for revealing groups (or clusters) that are mutually correlated within a data body. This procedure reduces overall dimensionality of the linearly correlated data by using a smaller number of new independent variables, called Varifactor (VF), each of which is a linear combination of originally correlated variables. The rotated Principal Component Loadings (Factors) are given in Table 3.

Four Factor Components (Eigen values>1) emerged accounting for 77.11% of cumulative variance. The first Factor loading with 25.93% variance showed higher loadings for Ni and silt + Clay and moderate loading for pH. The sediment physico-chemical properties such as pH and clay content could have contributed to Ni retention in the sediment, resulting in low mobility of the metal (Ong and Kamaruzzaman, 2009). Odero *et al*. (2000) found that high pH could result in precipitation of metals, however clay adsorbed heavy metals.

Factor loading with 21.80% of total variance, had higher loadings for Cr and Fe, along with significant contributions from organic matter. These could be conceived to mainly originate from domestic waste discharged in some of the areas and decomposition of vehicle and machine scraps apart from their natural occurrence. The third Factor had higher loadings for Mn and Zn at 17.32% of total variance, while the fourth Factor loading at 15.13% of total variance showed higher loadings for Cu and moderate loading for Pb. These might be due to soldering and battery charging activities going on in this area. Pb and Cu are integral components of the raw materials used in soldering wires and Pb accumulators (Odero *et al*., 2000). Also automobiles and paints are very important sources of Pb contamination in urban environments (Baptista Neto *et al*., 2000).

Table 1: Basic statistical parameters for the distribution of selected metals (mg $dm^{-3}$) in road sediment samples from Bida

| | Min | Max | Mean | Median | SD | SE | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|
| Cr | 3.00 | 12.00 | 8.57 | 9.00 | 2.34 | 0.59 | -0.74 | 0.63 |
| Ni | 1.00 | 18.00 | 7.89 | 8.00 | 4.26 | 1.06 | 0.31 | 1.21 |
| Fe | 9.20 | 26.70 | 15.66 | 15.35 | 4.19 | 1.05 | 1.04 | 1.97 |
| Mn | 1.20 | 80.00 | 17.18 | 7.15 | 21.92 | 5.48 | 1.91 | 3.70 |
| Zn | 3.40 | 70.00 | 13.89 | 9.60 | 15.60 | 3.90 | 3.48 | 13.00 |
| Cu | 3.33 | 97.00 | 11.67 | 6.24 | 22.83 | 5.71 | 3.96 | 15.76 |
| Pb | 7.22 | 88.80 | 59.67 | 78.15 | 35.17 | 8.79 | -0.79 | -1.43 |
| Cd | 1.33 | 3.44 | 1.69 | 1.42 | 0.67 | 0.17 | 2.40 | 4.55 |

Table 2: Pearson correlation coefficient matrix for heavy metals in Bida Town streets sediments

| | Cr | Ni | Mn | Zn | Cu | Pb | Cd | pH | Organic matter | Silt + clay |
|---|---|---|---|---|---|---|---|---|---|---|
| Cr | 1.000 | | | | | | | | | |
| Ni | 0.214 | 1.000 | | | | | | | | |
| Mn | 0.033 | -0.214 | 1.000 | | | | | | | |
| Zn | -0.239 | -0.277 | 0.476 | 1.000 | | | | | | |
| Cu | 0.288 | 0.182 | -0.211 | -0.080 | 1.000 | | | | | |
| Pb | 0.138 | -0.120 | -0.034 | 0.280 | 0.189 | 1.000 | | | | |
| Cd | 0.106 | 0.265 | -0.234 | -0.159 | -0.104 | 0.228 | 1.000 | | | |
| pH | 0.138 | -0.269 | -0.351 | -0.276 | 0.346 | 0.270 | -0.360 | 1.000 | | |
| Organic matter | 0.357 | 0.136 | 0.222 | -0.010 | -0.126 | -0.013 | 0.502* | -0.228 | 1.000 | |
| Silt + clay | 0.320 | -0.448 | 0.201 | -0.059 | -0.094 | 0.330 | -0.332 | 0.580* | 0.049 | 1.000 |

*: Correlation is significant at the 0.05 level (2-tailed)

Discriminant analysis was also used to investigate whether the variations of the various metals along the road sediments had statistical significant concentrations. The discriminant analysis results for each of the six metals are summarized in Table 4.

For discrimination of the samples according to the sampling sites, the LDA yielded a 100% classification success when using all 10 originally available variables as revealed in Table 4. Since they are hierarchical, the first two Discriminant Functions (DF1 and DF2) contain almost 90.61% of total information and are well representing the sample categorization.

The statistical analysis of Table 4 shows that Cu and Pb are most important for DF1 while Ni as could be seen is very important for DF2. DF3 had Cd and Silt + Clay and DF4 is Ni and Silt+Clay. Nickel, Fe, Pb, Cd and Silt + Clay are the most important for DF5. The variable that is most important for DF6 are Ni, Fe, Cu, Pb, pH and Silt + Clay. Ni, Fe and Cd were found to be most important to DF7, however, the impact on the discrimination of road sediments (DF2-DF7) in Bida is pretty low (less than 10% altogether) since it is given by a combination of factors: Relative percentage valid for the given DF (e.g., 5.43% for DF2) and the value of the Standardized Discriminant Function Coefficient (SDFC).

Table 5 shows that the concentrations of all metals measured in Bida can be considered to present a low level of contamination and pose no serious threat to the ecosystems when compared to some location around the world.

Table 3: Varimax normalized rotated principal component loadings of selected metals and sediment properties

| | Factors | | | |
|---|---|---|---|---|
| | VF1 | VF2 | VF3 | VF4 |
| Cr | 0.190 | **0.810** | -0.114 | 0.246 |
| Ni | **0.726** | 0.454 | -0.281 | 0.148 |
| Fe | -0.497 | **0.743** | -0.209 | 0.179 |
| Mn | 0.135 | 0.189 | **0.773** | -0.235 |
| Zn | -0.056 | -0.259 | **0.859** | 0.213 |
| Cu | -0.127 | 0.088 | -0.234 | **0.772** |
| Pb | 0.306 | 0.032 | 0.296 | **0.697** |
| pH | **0.677** | -0.108 | -0.481 | 0.402 |
| Organic matter | 0.010 | **0.694** | 0.252 | -0.255 |
| Silt + clay | **0.885** | 0.264 | 0.019 | 0.074 |
| Eigenvalue | 2.593 | 2.180 | 1.732 | 1.206 |
| Total variance (%) | 25.930 | 21.800 | 17.320 | 12.060 |
| Cumulative (%) | 25.930 | 47.730 | 65.050 | 77.090 |

Table 4: Standardized discriminate function coefficients

| | DF1 (65.31%) | DF2 (90.61%) | DF3 (96.04%) | DF4 (98.07%) | DF5 (99.40%) | DF6 (99.97%) | DF7 (100%) |
|---|---|---|---|---|---|---|---|
| Cr | -0.67 | 0.15 | 0.03 | 0.15 | 0.42 | 0.88 | 0.13 |
| Ni | -0.42 | **1.06** | -0.16 | **1.23** | **2.21** | **2.42** | **1.04** |
| Fe | 0.93 | -0.47 | 0.11 | -0.96 | **-2.63** | **-2.71** | **-1.20** |
| Mn | 0.03 | -0.46 | -0.30 | -0.08 | -0.10 | -0.96 | 0.54 |
| Zn | 0.66 | -0.05 | 0.57 | 0.43 | 0.56 | 0.79 | 0.46 |
| Cu | **1.29** | -0.19 | -0.14 | 0.12 | 0.79 | **1.48** | 0.72 |
| Pb | **1.03** | -0.10 | -0.76 | -0.22 | **-1.49** | **-1.36** | -0.45 |
| Cd | 0.59 | 0.41 | **1.07** | -0.22 | **1.38** | 0.97 | **1.20** |
| pH | -0.57 | 0.11 | -0.17 | -0.85 | -0.86 | **-1.65** | 0.31 |
| Organic matter | -0.21 | 0.31 | -0.43 | 0.45 | -0.82 | -0.56 | -0.11 |
| Silt + clay | 0.38 | 0.15 | **1.02** | **1.01** | **1.74** | **2.95** | 0.75 |

**Note:** The variables most important for discriminating classes are marked by bold faces

Table 5: Comparison of sediment in this Study and other documented sediment levels (mg $kg^{-1}$) around the world

| Location Panama | Mn | Zn | Cu | Pb | Ni | Cr | Fe | Cd |
|---|---|---|---|---|---|---|---|---|
| Punta Mala Bay[a] | 295 | 105.00 | 56.30 | 78.20 | 27.3 | 23.30 | 9827 | <10.00 |
| Toro Point[a] | 294 | 19.90 | 4.90 | 38.00 | 82.4 | 13.70 | 1885 | 6.60 |
| Galeta[a] | 143 | 10.90 | 4.00 | 32.50 | 74.0 | 12.80 | 1748 | 7.20 |
| Payardi[a] | 228 | 16.10 | 4.00 | 33.30 | 91.8 | 10.00 | 2094 | 7.50 |
| **Costa Rica** | | | | | | | | |
| Punta Portete[a] | 268 | 14.70 | 8.40 | 34.50 | 102.0 | 22.60 | 3225 | 7.30 |
| Punta Piuta[a] | 525 | 11.40 | 9.80 | 25.60 | 99.0 | 19.80 | 6118 | 6.00 |
| Colombia | | | | | | | | |
| Cienaga Grande[b] | 623 | 91.00 | 23.30 | 12.60 | 32.5 | 13.20 | 15593 | 1.92 |
| **Australia** | | | | | | | | |
| Port Jackson[c] | - | 145.000 | 62.00 | 180.00 | - | - | - | - |
| Port Jackson [c] | - | 351.000 | 102.00 | 443.00 | - | - | - | - |
| Hawksbury[c] | - | 94.000 | 18.90 | 26.40 | - | - | - | - |
| Port Hacking[c] | - | 10.300 | 1.10 | 2.50 | - | - | - | - |
| Queensland[d] | 103 | 23–56 | 1-12 | 36 9.0 | 0 1–72 | 1056.0 | 0.6 | - |
| **Brazil** | | | | | | | | |
| Clean Mangrove[e] | - | 24.200 | 3.82 | - | - | - | 2464.0 | 0.60 |
| Hong Kong | | | | | | | | |
| Clean Mangrove[f] | 96.00 | 43.000 | 2.60 | 31.20 | 2.90 | 1.20 | 1.08 | 0.320 |
| Present study | 17.18 | 13.890 | 11.67 | 59.67 | 7.89 | 8.57 | 15.66 | 1.670 |

[a]: Guzman and Jimenez (1992); [b]:Perdomo *et al*. (1999); [c]: MacFarlane and Burchett (2002) ; [d]: Preda and Cox (2002); [e]: Harris and Santos (2000); [f]: Tam and Wong (2000)

## CONCLUSION

In this study, correlation, factor and discriminant analysis were used for determining the environmental quality of road deposited sediments in terms of heavy metal accumulation and some soil properties. Correlation analysis shows a strong relationship between organic matter content on cadmium metal accumulation. Principal component analysis summarizes (reduces) the dataset into four major components representing the different sources of the elements. Using discriminant analysis, it was found that the metal concentrations are fairly well discriminated and correctly classified. This study generally concludes that the statistical methods can be a strong tool for monitoring of current environmental quality of road deposited sediments in terms of heavy metal accumulation and for predicating the future soil contamination.

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