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Contamination Assessment of Potentially Toxic Metals in Road-Side Surface Soils Along Iwo-Ibadan Expressway, Nigeria

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Abstract: This study was carried out to assess the contamination levels of road-side surface soils by potentially toxic metals due to their persistence and bioaccumulative nature in the ecosystem. Surface soils were sampled at various equidistance points along Iwo-Ibadan expressway, Nigeria and were then digested and analyzed for elemental concentrations using Atomic Absorption Spectrophotometer. Zn (72.91 mg/kg) had the highest mean concentration followed by Pb (54.66 mg/kg), Mn (31.32 mg/kg), Fe (12.16 mg/kg), Cd (11.92 mg/kg) and Cu (4.06 mg/kg). Variation in the elemental levels across the sampling points was a reflection of the variation in traffic density. The results of the contamination factor and geoaccumulation index indicated varying degrees of contamination. The modified degree of contamination and the pollution load index suggested that the road-side surface soils are contaminated with the metals. Cluster analysis indicated that the metals are associated with car components and vehicular emissions. It is therefore recommended that strict regulations be put in place against the use of leaded gasoline as vehicular fuels. Adequate and frequent monitoring of highway contamination by metals as a result of their bioaccumulative tendencies is also suggested.

Keywords: Contamination; Road-side, Soil, Toxic Metal, Vehicular Emission

1. Introduction

Heavy metals enlist a relatively large series of elements with specific density over 5 g/cm^3 and relative atomic mass above 40. Environmental pollution by metals became extensive with the fillip in mining and industrial activities during the last two centuries. The current worldwide mine production of Cu, Cd, Pb and Hg is considerably huge [1]. These pollutants, ultimately derived from a growing number of diverse anthropogenic sources, have had enormous impact on different ecosystem [2-3]. Fifty-three of the ninety naturally occurring elements are heavy metals [4]. Of these, Fe, Mo and Mn are important as micronutrients, while Zn, Ni, Cu, Co and Cr are toxic elements, but have importance as trace elements. Ag, As, Hg, Cd, and Pb have no known function as nutrients, and seem to be toxic to plants and microorganism [5]. The majority of the heavy metals are toxic to the living organism and even those considered as essential can be toxic if present in excess. The heavy metals can impair important biochemical process posing a threat to human health, plant growth and animal life [1, 6-8]. Heavy metals are an important toxicity source for soils. Heavy metal contamination of soil is based on three main sources: road traffic (automobiles), industrial activities, and weathered materials [9-10]. In terms of roadside soil, the most effective contaminant source is vehicle traffic. Ward et al. [11] reported that heavy metal pollution from automotive emissions affects roadside surface soils. Roadside soils often show a high degree of contamination that can be attributed to motor vehicles. Various researchers have found that the concentrations of the metals Pb, Cu, Zn, Cd and Ni decrease rapidly within 10 to 50 m from the roadsides [12-13]. According to Panek and Zawodny [14], pollution of roadside soils and plants by combustion of leaded petrol products is localized and usually limited to a belt of several metres wide on either side of the road, and that for similar topography and vegetation, the level of pollution decreases with the distance from the road. Due to their cation exchange capacity, complexing organic substances, oxides and carbonates have high retention capacity for heavy metals. Hence contamination levels increase continuously as long as the nearby sources remain active. Nevertheless, some heavy metals attached to the soil particles can be removed from the soil surfaces and get translocated elsewhere by the action of water and wind [15-17]. Heavy metals found in roadside dust are significant environmental pollutants of growing concern in recent years, that public and scientific attention has increasingly focused on its contamination and effects on human and other living creatures [18]. The release of heavy metals is one of the most significant environmental problems caused by anthropogenic activities such as urban road construction, quarrying, agriculture, waste incinerations, sewage disposal, bush burning, vehicle exhausts, industrial discharges, oil lubricants, automobile parts [19], corrosion of building materials, atmospheric deposition [20] and particulate emission [21]. The presence of heavy metals has been considered as useful indicators for contamination in surface soil, sediment and dust environments [22]. These metals are bio-accumulative and there are possibilities that these metals can reach a critical value where human health is threatened [23]. Several contributions to road-side soil pollution by heavy metals arise from various anthropogenic inputs including vehicular emissions. Due to the potential toxicity and bioaccumulative ability of these metals, the need therefore arises to assess the possible contamination of these metals in road-side surface soils.

2. Materials and Methods

2.1. Study Area, Sampling, Sample Storage and Preparation

The study area is between Iwo in Osun State and Ibadan in Oyo State. Iwo is a host of a private tertiary institution while Ibadan is the largest city in Nigeria and host of several tertiary institutions. Ibadan is situated on latitude 7°24’39”N and longitude 3°54’21”E. It has a population of 5,580,894 million according to the National Population Census in 2006. It is situated within the tropical forest zone but close to the boundary between the forest and the derived savanna. Surface soil samples were collected from ten (10) different sampling points along Iwo-Ibadan expressway. The samples were collected by scooping the soil samples into air tight containers and labeled accordingly. The surface soil samples were air-dried; rocks and pebbles were removed before pulverization using a mortar and pestle. The pulverized soil samples were then passed through a 500 µm filter sieve to achieve uniform particle size.

2.2. Metal Analysis

Pulverized soil samples (1.0 g) each was pretreated using 10 mL Aqua regia (mixture of concentrated HCl and HNO_3 acids in the ratio 3:1, British Drug House, BDH Analar grade). This was then heated on a hot plate at 70°C to near dryness and then cooled, and 5 mL of 2 M HCl was added. This was filtered into 50 mL volumetric flask and made up with double distilled water [24]. The filtrates were analyzed for the metals (Zn, Mn, Cu, Cd, Pb and Fe) using Atomic Absorption Spectrophotometer, Model PG 990 at Bowen University, Iwo, Osun State, Nigeria. Blank determination was also carried out.

2.3. Quality Assurance and Quality Control

All the glassware and sample bottles were cleaned using the procedure of Laxen and Harrison (1981). The containers were thoroughly washed with detergent rinsed with water, soaked in 10% HNO_3 for 48 hours. Thereafter, they were thoroughly rinsed with distilled water and by doubly distilled water and then kept dried at 105°C in the oven. All analyses were performed in triplicates.

Recovery analysis was done to ascertain the accuracy of the method/analytical procedure used by spiking 1 g each of two different soil samples with 5.0 µg/g standard mixture of the heavy metal solutions (Pb, Cu, Cd, Fe and Zn). Standard metal solutions were used to fortify the sample with the specified metal, digested and taken for AAS analysis. The percentage recovery (% R) for the potentially toxic metals was determined as given below:

$$\% R = [(C - C') / A] \times 100 \quad (1)$$

Where C = heavy metal concentration in the spiked soil sample, C′ = heavy metal concentration in the unspiked sample and A = the amount of heavy metal used for spiking [24].

2.4. Data Treatment

For the interpretation of the geochemical data the following statistical methods were used: Descriptive statistics (mean, range, standard deviation and coefficient of variation) were performed in addition to contamination factor, geo-accumulation index, pollution load index and modified degree of contamination to interpret the obtained data. Cluster analysis was used to identify the possible sources as well as the correlation among the analyzed potentially toxic metals [25-29].

3. Results and Discussion

3.1. Result of Recovery Analysis

The reliability of the analytical procedures adopted in this study was tested in terms of sensitivity, recovery, precision and accuracy. Table 1 shows the values for % recovery for the analyzed metals under experimental conditions used. The recoveries of metals in spiked sample were between 84.5 –

95%. Since the mean percentage recoveries for all analyte were within an acceptable range (70-110%); this gives credence to the reliability of the results of this study.

Table 1. *Analytical Results for Calibration Curve and Percentage Recovery (% R).*

Metals	Amount spiked (mg/kg)	Amount recovered (mg/kg)	% Recovery
Pb	5.0	4.25	85
Cu	5.0	4.75	95
Cd	5.0	4.35	87
Zn	5.0	4.225	84.5
Fe	5.0	4.45	89

3.2. Elemental Analysis

The levels of the elemental composition of the road-side surface soils of the study area are presented in Table 2. Variations existed in the levels of the potentially toxic metals in the road-side surface soils. Zinc had the highest mean concentration while Copper had the least mean concentration. Sampling point A had relatively high levels of Zinc and Lead. This indicated a direct contribution of traffic pollution to the road-side soils as a result of the closeness of sampling point A to the edge of the road. According to previous studies, the levels of metals in road-side surface soils is dependent on the distance from the road and is considered an indicator of traffic-related pollution [30-32].

Table 2. *Levels of Toxic Metals in Road-Side Surface Soils (mg/kg).*

Samples	Zn	Mn	Cu	Cd	Pb	Fe
A	298.05	2.45	2.05	0.85	152.05	ND
B	46.35	14.45	0.95	0.15	65.95	ND
C	3.9	14.5	3.95	20.85	8.95	5
D	34.85	96.1	10.05	ND	4.55	1.55
E	162.5	50	1.2	0.45	52.25	ND
F	3.9	2.35	3.7	ND	3.7	2.7
G	32.5	5.65	1.65	5	103.65	ND
H	4.15	16.95	5.55	6.15	21.55	1.55
I	69.95	33.05	10.05	ND	61.05	ND
J	72.95	77.75	1.45	50	72.95	50
Range	3.90 – 298.05	2.35 – 96.10	0.95 – 10.05	ND – 50	3.70 – 152.05	ND - 50
Mean±SD	72.91±29.20	31.32±10.44	4.06±1.09	11.92±5.05	54.66±15.16	12.16±4.90
CV (%)	40.05	33.33	26.84	42.36	27.73	40.29

ND = Not detected.

The variation that existed in the different sampling points could be due to the action of wind across the sampling points. Most particulates carrying traffic-related elements like Zn, Pb, Cu, Cd, emitted from vehicles are usually deposited on road-side surface soils not more than 0–5 m, however, some can be carried a longer distance by wind. The variation could also be a reflection of traffic density at some points than the others. The relatively high concentration of Lead is a cause for concern because leaded gasoline has been verboten in Nigeria since 2005. Nevertheless, it is perceived that some marketers are still in the business of selling blends of the leaded gasoline with unleaded gasoline, which might be a reason for the high levels of Pb. However, crude oil contains Pb, alongside the other metals as geogenic impurities [33]. In contrast, the sources of Cu, Zn and Cd are car components, tyre abrasion, lubricants, industrial and incinerator emissions [34-35]. The soil contents of Fe were found to be almost independent on the distance from the road. This could be an indication that they were not directly related to traffic pollution, they could be a reflection of their natural sources or the background concentration of the study area. Generally, the levels of the metals in the road-side surface soils follow the order: Zn > Pb > Mn > Fe > Cd > Cu.

Figure 1 is a figure showing the hierarchical cluster analysis of the investigated metals in the road-side surface soils. Three major clustering groups are shown in the dendrogram. Group A showed a clustering relationship between Pb and Zn. Group B showed a clustering relationship between Fe and Mn. Group C showed the closest inter-element clustering between Cd, Fe and Cu. Inter-element clustering relationships are known to indicate common sources and/or similar background levels. Cd and Cu, for instance, are elements known to be associated with engine parts and motor oil. The clustering relationship between Fe and Mn could be attributed to natural sources or similar background levels in the study area.

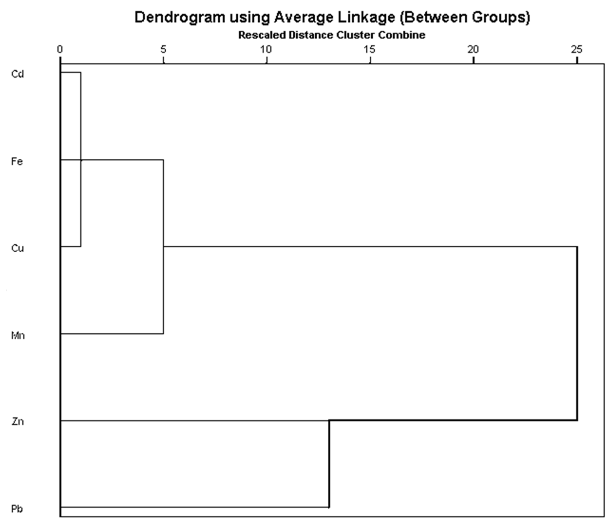

Figure 1. *Cluster Analysis of the Potentially Toxic Metals in the Road-Side Surface Soils.*

3.3. Contamination Indices of the Potentially Toxic Metals in the Road-Side Surface Soils

The indices of contamination of the investigated metals in the road-side surface soils are presented in Table 3. The road-side soils showed low contamination by Mn and Fe. Mn and Fe levels in the soils might be due to natural sources or other unknown sources rather than contamination arising from vehicular emissions. The road-side soils showed considerable contamination by Cu and very high contamination by Zn and Pb.

Table 3. *Indices of Contamination of the Potentially Toxic Metals in the Road-Side Surface Soils.*

Metal	Mean	Geochemical baseline	CF	I_{geo}
Zn	72.91	3	24.30	4.01
Mn	31.32	40	0.78	-0.93
Cu	4.06	0.8	5.07	1.75
Cd	11.92	N. A	N. A	N. A
Pb	54.66	5.3	10.31	2.78
Fe	12.16	1600	0.007	-7.62
mCd			8.09	
PLI			1.49	

CF = contamination factor, I_{geo} = Geo-accumulation index, mCd = Modified degree of contamination, PLI = Pollution load index.

The results of the geo-accumulation index indicated that the road-side surface soils were unpolluted with Mn and Fe, moderately polluted with Cu, moderately to strongly polluted with Pb and strongly to extremely polluted with Zn. The result of the modified degree of contamination showed that the soils exhibited very high degree of contamination, while the pollution load index indicated a deterioration of site quality by the investigated metals.

3.4. Comparison of Elemental Profiles of Road-Side Surface Soils with Other Studies

The elemental levels of the road-side surface soils were compared with other studies, and their results are presented in Table 4. Variations existed in the metal levels of this study and that of the other studies reported in Bosnia and Herzegovina [36] and Turkey [37]. The toxic metals (Zn, Mn, Cu, Pb and Fe) were all higher in the other studies. Cd level reported in this study was relatively higher. It has been reported that load on heavy metal contents in surface soils and their variability depend upon the traffic density and the distance [38-40].

Table 4. *Comparison of Elemental Profiles of Road-Side Surface Soils with Other Studies.*

Metal	This Study	Skrbic [36]	Isen et al. [37]
Zn	72.91	139	229.07
Mn	31.32	860	129.2
Cu	4.06	32.2	69.42
Cd	11.92	2.78	6.65
Pb	54.66	74.7	227.6
Fe	12.16	11801	113.8

4. Conclusion and Recommendation

Concentrations of potentially toxic metals were analyzed in road-side surface soils along Iwo-Ibadan expressway, Nigeria. Vehicular emissions as a function of traffic density was found to be a major source of the contamination by the metals. The relatively high Pb levels indicated that leaded gasoline is still in use in Nigeria despite its proscription since 2005. Cluster analysis grouped the metals according to their natural sources and anthropogenic inputs respectively. The indices of contamination indicated a deterioration of the road-side soils by the metals. Increased urbanization and the use of second-hand vehicles in the country necessitates a further monitoring of the elemental levels of the road-side. It is also recommended that strict regulations be enforced on the use of leaded gasoline in the country.

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