



Multivariate analysis and ecological risk assessment of potentially toxic metals in soils contaminated by automobile battery wastes at Kosofe area of Lagos, Nigeria

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Abstract

This research work studied the multivariate analysis of potentially toxic metals in soils from the vicinity of automobile battery-workshops in Kosofe Local Government Area of Lagos, Nigeria. Representative soil samples were collected from ten selected locations where charging, refilling, repair and disposal of automobile batteries had been taking place. The samples were digested with aqua regia and analyzed for potentially toxic metals (Cd, Pb, Ni, Cr, Zn and Cu) using the flame atomic absorption spectrophotometer under optimized conditions. The physicochemical properties of the soils (pH, %organic matter, cation exchange capacity, and particle size distribution) were determined using standard analytical methods. The original results obtained were then subjected to multivariate analysis using the principal component analysis to identify the correlation between the physicochemical parameters and the pseudo-total concentration of the potentially toxic metals. The ecological risk assessment of the potentially toxic metals was done using Hakanson's proposal. The results of the analysis showed that the soils in the study area were severely contaminated with Pb, Cd and Cu. The results of the principal component analysis showed that PC1 explained 33.06% of the total variance which exhibited a high positive loading on Pb, Zn, Cr and Cu while PC2 explained 26.69% of the total variance which exhibited a high positive loading on Cd, Ni, Cr and Cu. The results of the ecological risk assessment revealed that the soils around the study area were severely contaminated with Pb, Cd and Cu and these could have both natural and anthropogenic sources.

Keywords: Heavy metal, potentially toxic metal, lead pollutant, automobile battery, principal component analysis, risk assessment.

Introduction

There is no generally accepted definition of a potentially toxic metal. However, a potentially toxic metal, otherwise known as a heavy metal, is often times defined in terms of specific gravity. In this context, heavy metals are defined as chemical elements, usually metals and metalloids, with specific gravity that is at least five times that of water and which are normally associated with pollution and toxicological problems¹. The term heavy metal, however, is often broadly applied to include other metallic elements that are potentially toxic even if they do not meet the strict chemical definition². The toxicity of potentially toxic metals can be attributed to the fact that these metal contaminants are not degradable into non-toxic forms, hence plants and animals find it difficult to get rid of the metals when exposed to their body³. While some potentially toxic metals (e.g. copper, nickel and zinc), in low concentrations are vital to plants and animals as components of enzymes, proteins and pigments, others such as chromium, nickel, cadmium and lead can be mobilized by biochemical processes which make them potential soil and water pollutants that can ultimately impact negatively on food chains^{4,5}.

Potentially toxic metals get into the environment either from natural sources which includes volcanic eruptions, weathering of rocks, and leaching into water bodies due to the action of winds, or from anthropogenic sources (human activities) which include but are not limited to the repair, charging and disposal of automobile batteries, smelting or processing of large quantities of metallic ores, metal wedding, indiscriminate disposal of electronic wastes and industrial effluents as well as the use of pesticides containing compounds (salts) of potentially toxic metals⁵. Kosofe Local Government Area is one of the important commercial nerve centres in Lagos, Nigeria which gained its popularity as a result of a wide variety of human economic activities that take place there, such as the ones named above. In the present study, therefore, we have investigated the concentration of potentially toxic metals in soils from selected locations where the soil has been contaminated by automobile battery wastes to ascertain the level of contamination arising from these anthropogenic activities. Automobile battery wastes, in this study, refer to scraps and spilled electrolytes of automobile batteries. The specific objectives of this study are to determine the pseudo-total

concentration of the selected potentially toxic metals (Cd, Cr, Ni, Pb, Zn and Cu) in the soils contaminated by scraps and spilled electrolytes of automobile batteries, to evaluate the correlations between the physicochemical parameters of soil samples and the heavy metals using principal component analysis, as well as to assess the ecological risk involved in the generation and release of these contaminants into the environment.

Materials and methods

Sample collection and preparation: Ten surface soil samples were collected from a depth of 0-5 cm from ten different locations in Kosofe Local Government of Lagos, Nigeria, in September 2011.

The soils were adequate to serve as representative samples and the locations from which they are collected are Agiliti, Alapere, Gidan-kwali, Ikosi-Ketu, Ketu, Kosofe/Mile 12, Ogudu, Ojota, Owode-Onirin and Shangisha. A sample was also collected from a site free of anthropogenic activities to serve as the control sample. The samples were collected on the site in clean black polyethylene bags, knotted tightly and labeled properly and then taken to the laboratory. In the laboratory, the samples were air-dried for seven (7) days and then crushed using a carnelian mortar, sieved through a 2mm mesh sieve to obtain fine particles (< 2 mm fraction). All experimental studies, except particle size distribution analysis, were done on this fraction.

Digestion, extraction and heavy metal analysis: The digestion of the soil samples was done in triplicates in a 100 ml Khedjal

flask using 2 grams of each sample and 20 ml *aqua regia*, heated on a hot plate for 2 hours in a fume hood. The supernatant extracts were obtained by filtration using Whatman No. 42 filter paper and made up to the mark in a 50 ml standard volumetric flask. Certified Reference Material (reference soil sample) was also treated alike to ensure that the experimental procedure was under control. The sample extracts were preserved in a refrigerator prior to analysis by a Flame Atomic Absorption Spectrophotometer (Perkin-Elmer, Analyst 400) which measured the pseudototal concentration of the potentially toxic metals.

Physicochemical analysis: The physicochemical parameters of the samples were determined using standard analytical methods. The pH values of the soils were measured with a pH meter using a soil-to-CaCl₂ suspension. The percent total organic carbon (%TOC) and percent organic matter (%OM) of the soils were determined by the Walkley-Black method⁶, while the cation exchange capacity and particle size distribution were determined using standard methods as described elsewhere^{7,8}.

Multivariate analysis (principal component analysis): The original experimental results obtained were subjected to multivariate statistical analysis. The associations exhibited by the physicochemical parameters *vis-a-vis* the pseudo-total concentration of the potentially toxic metals were studied using principal component analysis (PCA) and applying varimax with Kaiser Normalization rotation method. The PCA was performed with principal components that have eigenvalues greater than 1, using the SPSS version 15.0 software.

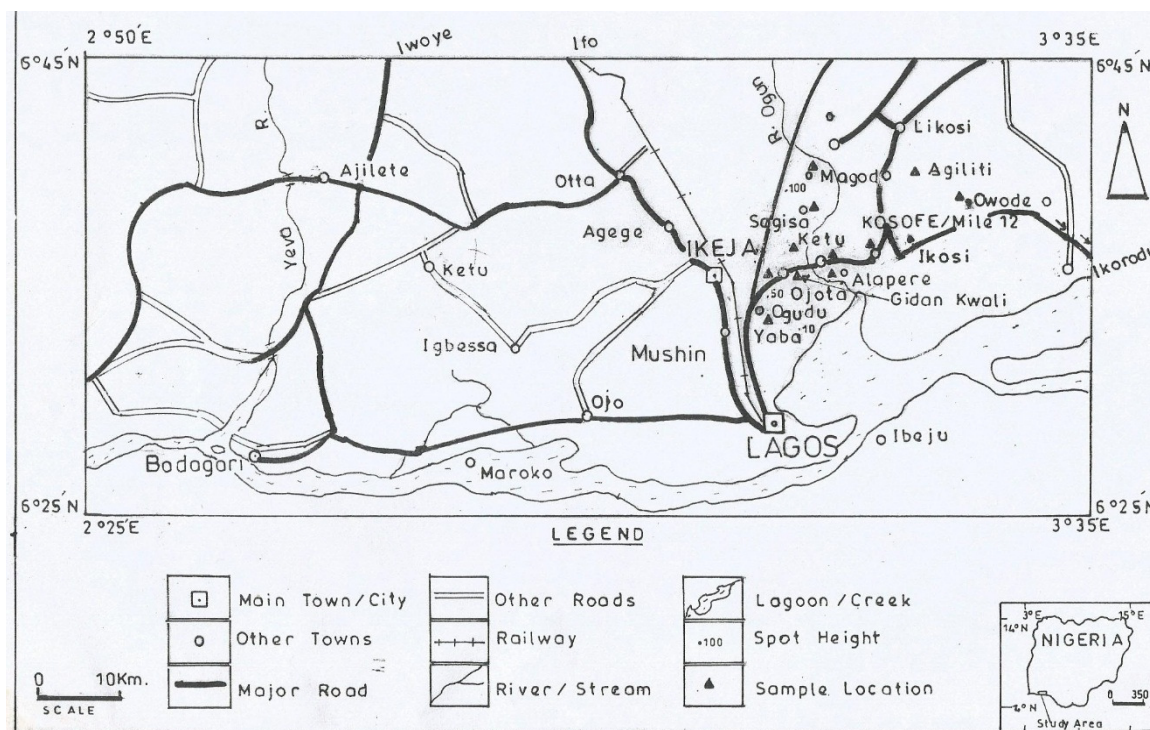


Figure-1: Location map of the study area.

Ecological risk assessment: The potentially toxic metals were evaluated for Potential Ecological Risk Index (RI) using Hakanson's proposal⁹. This serves as a contamination control and was adopted as a diagnostic tool to assess the contamination of the study area arising from the concentration of these potentially toxic metals. This entailed sorting out sample site and substance to which special attention should be paid. According to Hakanson proposed that the potential ecological risk index (PERI) is formed by three basic modules—contamination factor or degree of contamination (C_f^i), toxic response factor (T_r^i) and potential ecological risk coefficient (E_r^i) of a single element. These modules together with the risk index (RI) were defined by Hakanson as follows:

$$E_r^i = C_f^i \times T_r^i$$

$$\text{Where, } C_f^i = \frac{C_s^i}{C_n^i} \text{ and } RI = \sum E_r^i$$

Where, i = the given potentially toxic metal (PTM), C_s^i = measured pseudo-total concentration (in mg kg⁻¹) of the PTM in soil, C_n^i = regional background concentration (in mg kg⁻¹) of the PTM.

Results and discussion

Physicochemical analysis: While Table-1 shows the results of physicochemical analysis, Table-2 shows the pseudo-total concentration of the potentially toxic metals (PTMs) in the soil samples, Table-3 shows the concentration of the PTMs in the Certified Reference Materials and Table-4 shows the correlation coefficient matrix for the PTMs and the physicochemical parameters of the soils.

The pH values of the soils (Table-1) are well below 7.0 except samples BS4 and BS9 which showed neutral pH. This implies that the soil samples are actually acidic and the acidity is due to the disposal of spoilt lead-acid accumulators as well as the spillage of the electrolytes in those sites. Consequent upon the low pH (acidic pH), the soil samples have low percent organic matter and low cation exchange capacities, and so accumulated low concentration of potentially toxic metals. This observation agrees with literature reports that at acidic pH value, the percent organic matter of the soil will be low and that will create few exchange sites leading to low CEC values. This observation is again supported by the low clay content. It has been reported in literature that as the soil pH decreases, the exchange sites of the soil will be less active, and will affect the CEC^{10,11}.

Concentration of potentially toxic metals: Lead had the highest concentration (Table-2) among all the metals investigated. This can be traced to the disposal of scrap automobile batteries or the spillage of their electrolytes during which Pb paste is released into the environment. Researchers have reported that low pH increases the mobility of metals through the soil, hence their lower concentration at the sample sites¹². Cadmium, chromium and nickel were not detected in most of the samples, indicating that the main contaminants in these soils are Pb, Zn and Cu. It has been reported in literature that the primary means of Cd removal from soils is adsorption mechanisms. The chemical behaviour of Cd in the soil environment, like all metals, is to a large extent dependent on the soil pH. Acidic conditions tend to increase the solubility of Cd and very little or no Cd will be absorbed by soil colloids, hydrous oxides or organic matter¹³. This explains why Cd content was below detection limit in about 40% of the samples.

Table-1: Mean values of physicochemical properties of soils contaminated by scraps and spilled electrolytes of automobile batteries.

Sample Location	Sample ID	pH	% Organic Matter	CEC (meq/100g)	Grain Size Distribution		
Agiliti	BS1	1.9	2.47	40.65	67.76	25.22	7.02
Alapere	BS2	4.2	3.36	24.36	67.73	25.59	6.68
Gidan-kwali	BS3	0.8	3.69	54.29	69.3	24.66	6.04
Ikosi-Ketu	BS4	6.8	3.69	42.93	64.38	29.08	6.54
Ketu	BS5	4.6	3.67	10.99	35.76	58.15	6.09
Kosofe-Mile 12	BS6	0.5	3.57	22.08	65.2	28.39	6.41
Ogudu	BS7	4.0	3.05	29.27	76.86	17.00	6.14
Ojota	BS8	4.1	2.91	28.41	73.7	20.25	6.05
Owode-Onirin	BS9	7.1	2.98	47.67	42.64	51.21	6.15
Shangisha	BS10	0.4	2.62	62.24	69.37	24.82	5.81
Control sample	CTR	6.3	0.309	2.46	64.4	24.7	10.9

CEC: Cation Exchange Capacity. Values are means of triplicate determinations.

Table-2: Pseudo-total Concentration of potentially toxic metals in the soils contaminated by scraps and spilled electrolytes of automobile batteries, presented as mean \pm standard deviation.

Sample ID	Pseudo-total Concentration of Potentially Toxic Metals (mg kg ⁻¹)					
	Cd	Cr	Ni	Pb	Zn	Cu
BS1	B.D	2.52 \pm 1.48	B.D	49.0 \pm 28.7	117 \pm 21.3	10.3 \pm 2.46
BS2	B.D	2.55 \pm 0.46	B.D	36.2 \pm 12.3	96.2 \pm 16.2	22.0 \pm 6.10
BS3	281 \pm 0.23	6.62 \pm 0.11	0.96 \pm 0.41	51.9 \pm 10	50.6 \pm 16.5	106 \pm 0.07
BS4	B.D	5.47 \pm 1.41	0.15 \pm 0	197 \pm 27.9	132 \pm 5.66	27.4 \pm 0.71
BS5	0.20 \pm 0	6.00 \pm 0.90	B.D	569 \pm 41.4	122 \pm 12	95.8 \pm 12.3
BS6	B.D	7.91 \pm 0.13	B.D	140 \pm 5.66	94.0 \pm 1.98	71.8 \pm 5.37
BS7	1.21 \pm 0.05	0.43 \pm 0	B.D	180 \pm 28.6	38.1 \pm 1.70	7.60 \pm 1.13
BS8	1.01 \pm 0.3	B.D	0.05 \pm 0	221 \pm 32.7	36.0 \pm 0.21	5.28 \pm 0.05
BS9	1.81 \pm 0.06	B.D	0.60 \pm 0.18	165 \pm 0.71	20.0 \pm 5.30	29.2 \pm 1.56
BS10	0.76 \pm 0.02	B.D	0.16 \pm 0.02	182 \pm 18.2	40.6 \pm 2.33	8.18 \pm 1.08
CTR	B.D	B.D	B.D	0.98 \pm 0.02	43.9 \pm 0.08	6.98 \pm 0.10

*Values are means of triplicate determinations. *B.D – below detection limit.

Table 3: Concentration of the PTMs in Certified Reference Material

	Concentration of the PTMs in mg Kg ⁻¹					
	Cd	Cr	Ni	Pb	Zn	Cu
Certified PTM conc.	< 0.74	43.2 \pm 3.0	50.2 \pm 5.2	387 \pm 25	177 \pm 11	111 \pm 5
Measured PTM conc.	0.76	41.5 \pm 3.5	47.2 \pm 7.0	384 \pm 21.0	174 \pm 9.2	109 \pm 5.5

*Values are means of triplicate determinations.

Multivariate analysis (principal component analysis): Table-4 shows the correlation coefficient matrix for the metals studied and the physicochemical properties of the soils, while Table-5 shows the eigenvalues of the factors after variance maximizing (varimax) rotations of the original variable space for the soil samples. The variables are correlated with four principal components in which 87.98% of the total data variance were found. Kaiser criterion with eigenvalue greater than unity was used to select and retain only the first four principal components as the significant ones¹⁴. This gives the reduced dimensionality of the descriptor space as four.

From the correlation coefficient matrix in Table-4, it can be observed that Ni had a strong positive correlation to Cd ($r = 0.879$). A good positive correlation was also found between CEC and Cd ($r = 0.548$) and between CEC and Ni ($r = 0.599$), indicating that Cd and Ni were the most exchanged cations among the PTMs studied. These trends also show that the sample sites investigated must have been contaminated by spilled electrolytes from Ni-Cd accumulators.

There are also strong positive correlations of Zn to Cr ($r = 0.657$) and Cu to Cr ($r = 0.830$) and these indicate that the main sources of these PTMs were identical. The concentration of these PTMs seems to be influenced by anthropogenic factors. Studies by several scholars have revealed that soil behaves as a long-term sink for Cu and Zn especially when fertilized with manure and chemical fertilizers¹⁵⁻¹⁷. Based on the foregoing, it is reasonable to conclude that long-term fertilization with manure and chemical fertilizers is the main source of Zn, Cu and Cr contaminants in the soils around the study area. A significant positive correlation also existed between %OM and Cr ($r=0.613$) and between %OM and Cu ($r=0.550$). As organic matter decomposes, the concentration of metals in compost and thus, in the soil to which it has been applied may increase. A study by Papafilippaki and coworkers showed that organic matter plays a significant role in the availability and mobility of the potentially toxic metals (especially Cu and Zn) in soils¹⁸. The extractable forms of these metals are strongly affected to the organic matter content. A significant positive correlation can also be found between percent silt and Pb ($r = 0.666$), indicating

that Pb concentration increases as the silt content increases. Lead showed no significant positive correlation with other parameters and this indicates that the main source of Pb is the Pb-acid batteries. Percent clay had a strong negative correlation

to %OM ($r = -0.877$) and to CEC ($r = -0.589$), indicating that these parameters are not affected by the presence of clay in the soils. The pH of the soils had no correlation to any of the parameters.

Table-4: Correlation coefficient matrix^a for the PTMs and the physicochemical parameters of the soils.

	Cd	Cr	Ni	Pb	Zn	Cu	%OM	CEC	pH	Sand	Silt	Clay
Cd	1.00											
Cr	-.069	1.00										
Ni	.879	.177	1.00									
Pb	-.096	.233	-.196	1.00								
Zn	-.642	.657	-.381	.275	1.00							
Cu	.325	.830	.486	.379	.287	1.00						
%OM	.241	.613	.261	.429	.372	.550	1.00					
CEC	.548	-.061	.599	-.188	-.216	-.022	.363	1.00				
pH	-.153	-.329	-.104	.145	-.017	-.298	-.238	-.359	1.00			
Sand	.043	-.202	-.129	-.625	-.209	-.444	-.149	.201	-.413	1.00		
Silt	.000	.228	.157	.666	.214	.471	.245	-.132	.368	-.994	1.00	
Clay	-.378	-.250	-.259	-.431	-.064	-.292	-.877	-.589	.358	.053	-.165	1.00

^aThis matrix is not positive definite.

Table-5: Eigenvalues of factors after varimax rotations.

PC	Eigenvalues		
	Total	% of Variance	Cumulative %
1	3.967	33.058	33.058
2	3.202	26.687	59.774
3	2.096	17.463	77.207
4	1.293	10.772	87.979
5	.686	5.716	93.696
6	.507	4.225	97.920
7	.173	1.441	99.361
8	.062	.517	99.878
9	.012	.096	99.974
10	.003	.026	100.000
11	1.47E-016	1.23E-015	100.000
12	3.63E-017	3.02E-016	100.000

E=Extraction method: Principal Component Analysis.

After varimax orthogonal rotations of the original variable space, two principal components (factors) were extracted. Figure-1 shows the plot of the factor loadings. It can be seen from the figure that the first factor (PC1) with 33.06% of the variance was strongly and positively correlated to Pb, Zn, Cr, Cu, %OM, and percent silt, thereby suggesting that these parameters have an identical source. PC1 is also fairly and positively correlated to Ni and pH and negatively correlated to Cd, CEC, sand and clay. The second factor PC2 with 26.69% of the variance was found to correlate positively to Cd, Ni, Cr, Cu, CEC, %OM and sand. Cd, Ni and CEC together have high loadings. PC2 is also negatively correlated to Zn, Pb, silt, pH and clay.

Ecological risk assessment: The analytical results of the ecological risk coefficients (E_r^i) and the potential risk indices (RI) of the selected PTMs for the two soil sample types are presented in Table-6.

The regional background concentration and the toxic-response factors for the different PTMs are shown in Table-7 while the grades of ecological risk coefficients, risk indices and classifications of risk intensity are described in Table-8. In this study, the regional background concentration of the different PTMs in the soil and their toxic-response factor were culled from the National Oceanic and Atmospheric Administration

(NOAA) Screening Quick Reference Tables (SQuiRTs)¹⁹, except that of Cr which was given by Holmgren *et al.*²⁰.

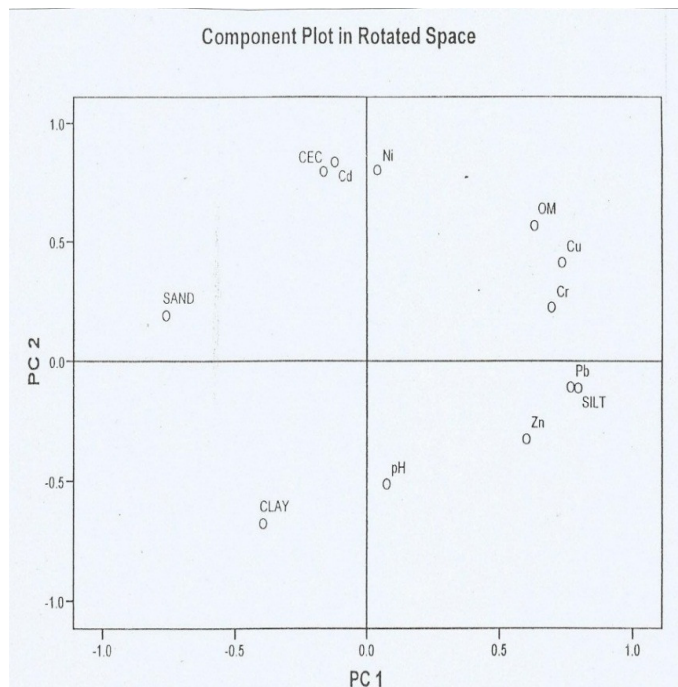


Figure 2: Plot of factor loadings.

Table-6: Ecological risk coefficients and risk indices of potentially toxic metals in the soil contaminated by scraps and spilled electrolytes of automobile batteries.

Sample Location	Sample ID	Ecological Risk Coefficient, E_r^i						Potential Risk Index (RI)
		Cd	Cr	Ni	Pb	Zn	Cu	
Agiliti	BS1	-	0.14	-	15.31	2.44	3.04	20.93
Alapere	BS2	-	0.14	-	11.32	2.00	6.48	19.94
Gidan-kwali	BS3	312.33	0.36	0.07	16.21	1.05	31.24	361.26
Ikosi-Ketu	BS4	-	0.30	0.01	61.51	2.75	8.06	72.63
Ketu	BS5	22.23	0.32	-	177.86	2.55	28.17	231.13
Kosofe-Mile 12	BS6	-	0.43	-	43.74	1.96	21.11	67.24
Ogudu	BS7	134.67	0.02	-	2.25	0.79	2.24	139.97
Ojota	BS8	112.32	-	0.01	69.05	0.75	1.55	183.68
Owode-Onirin	BS9	201.21	-	0.05	51.43	0.42	8.60	261.71
Shangisha	BS10	84.66	-	0.01	56.80	0.85	2.41	144.73
Control sample	CTR	-	-	-	0.31	0.9	2.05	3.26

Table-7: Regional background concentration (C_n^i) and toxic-response factor (T_r^i) of the selected PTMs¹⁹.

	Cd	Cr	Ni	Pb	Zn	Cu
C_n^i (mg kg ⁻¹)	0.27	37	13	16	48	17
T_r^i	30	2	1	5	1	5

Source: NOAA Screening Quick Reference Tables (SQiRTs).

Table-8: The grades of ecological risk coefficient, risk index and classification of risk intensity⁹.

E_r^i	RI	Grade of Risk Intensity
$E_r^i < 40$	RI < 150	Low
$40 \leq E_r^i < 80$	$150 \leq \text{RI} < 300$	Moderate
$80 \leq E_r^i < 160$	$300 \leq \text{RI} < 600$	Considerable
$160 \leq E_r^i < 320$	RI ≥ 600	High
$E_r^i \geq 320$	-	Very high

From Table-6, it could be observed that Cd and Pb posed the highest ecological risk among all the PTMs investigated, with the risk coefficient ranging from 22.2–312.3 for Cd and 2.25–177.9 for Pb, accounting for 56 – 98.7% of the risk index (RI). The other PTMs (Cr, Ni, Zn and Cu) showed a low ecological risk.

Conclusion

The results of this study have shown that the soils of the study area were contaminated by potentially toxic metals with Pb, Cd and Cu showing the highest ecological risk. This arises from the spillage of battery electrolytes and disposal of lead pastes on the surroundings, and as such these activities are not environmentally friendly.

This study, therefore, recommends that certain regulations and policies should be enacted by the Government to make provisions for battery recycling and safe disposal especially the lead-acid and nickel-cadmium batteries which contain not only Pb and Cd respectively, but also Hg and Ni which are equally toxic and hazardous. In the meantime, adequate measure should be taken by individuals to minimize the exposure of humans to these PTMs during their economic activities.

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