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Chemometric Approach to Analysis and Environmental Risk Assessment of Potentially Toxic Metals: A Case Study of Soils from Metal Welders' Workshops

Cornelius C. Ahanotu [1, *], Aderonke O. Oyeyiola [2] and Kehinde O. Olayinka[2]

[1*] Department of Science Laboratory Technology, Imo State Polytechnic, Umuagwo, Owerri, Nigeria

[2]Department of Chemistry, University of Lagos, Akoka-Yaba, Lagos, Nigeria

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ABSTRACT

The analysis of potentially toxic metals in soils and the environmental risk assessment was presented in this study. Ten representative surface soil samples were collected from ten different locations in Kosofe Local Government Area of Lagos, Nigeria where soils have been contaminated by metal particulates from metal cutting and welding operations. The samples were digested with *aqua regia* and the concentration of the potentially toxic metals (Cd, Pb, Ni, Cr, Zn and Cu) was measured using the flame atomic absorption spectrophotometer (FAAS) 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. Multivariate analysis of the original results obtained was carried out using the principal component analysis (PCA) to identify how the physicochemical parameters of the soils correlate to the concentration of the potentially toxic metals, while the ecological risk assessment was done using the model proposed by Hakanson. The results of the analysis showed that there was serious contamination of the soils in the study area with Pb, Cd and Cu. The results of the principal component analysis showed that the first factor, PC1 explained 36.95% of the total variance which exhibited a high positive loading on Ni, Zn, Cd and Cr while the second factor, PC2 explained 23.67% of the total variance which exhibited a high positive loading on Ni, Cd and Cr and the sources of these heavy metals could be both natural and anthropogenic. The results of the ecological risk assessment show that there is high ecological risk resulting from the release of Cd and Cu into the environment in majority of the sample locations.

1. Introduction

According to the Agency for Toxic Substances and Disease Registry [1], heavy metals are a group of metals and metalloids associated with contaminations and are potentially toxic to humans and animals. It is on account of their potential toxicity that heavy metals are sometime referred to as potentially toxic metals. Some of these chemical elements are described as essential since they play some important roles as components of vital biochemical or enzymatic activities in human body (e.g Fe, Mn, Mo, Cr, V, Zn), while some others are described as non-essential with no biological, chemical and physiological importance in man [2]. Examples of the non-essential heavy metals are Pb, Cd, Hg, Ni and As [3]. Studies have shown that chemical and metallurgical industries are the most important sources of potentially toxic metals in the environment. Metallurgical activities such as steel cutting and welding, especially the electric arc welding have been found to contribute to toxic metal contamination of the surrounding soil [4].Contamination by heavy metals refers to cases where the quantities of these elements in the soils exceed the maximum allowable concentrations, and this potentially harmful to biological life at such locations. When introduced into the environment, these heavy metals can find their way into the food chain and accumulate in vital organs to threaten animal and human health [5]. Potentially toxic metals are extremely persistant pollutants i.e. they are non-biodegradable and non-thermodegradable and their accumulation readily reaches trophic levels [6]. They can be biomagnified in the food chains and become increasingly hazardous to humans and aquatic life. Kosofe Local Government Area of Lagos, Nigeria harbours a wide range of artisans and workmen among whom are metal welders and other metallurgical workmen whose activities generate metal dusts and scraps that contain these heavy metals. It is for this reason that this study investigates to assess the level of contamination arising from the concentrations of these potentially toxic metals in the selected locations to prevent risks to life [5,7]. The specific objectives of this study, therefore, are to determine the pseudo-total concentration of the potentially toxic metals (Cd, Cr, Ni, Pb, Zn and Cu) in the soils contaminated by metal particulates from metal cutting and welding operations, to investigate the correlations or relationship between the physicochemical properties of soil samples and the heavy metals using principal component analysis as well as to ascertain the level of ecological risk associated with the production and release of these contaminants into the immediate environment.

Tele:
E-mail address:cdibulo@gmail.com

2. Materials and Methods

2.1 Sample Collection and Preparation

From ten different locations of Kosofe Local Government Area of Lagos, Nigeria, were collected ten representative surface soil samples at a depth of 0-5 cm, in September 2011. The sample sites are all metal cutting and welding workshops situated at Agiliti, Alapere, Gidan-kwali, Ikosi-Ketu, Ketu, Kosofe/Mile 12, Ogudu, Ojota, Owode-Onirin and Shangisha. A control sample was also collected from an unpolluted site where human economic activities do not take place. The samples were collected on the site in clean black polyethylene bags, tightly knotted and properly labeled and then taken to the laboratory. In the laboratory, the samples were air-dried for seven (7) days and then homogenized using a carnelian mortar, sieved through a 2 mm mesh sieve to obtain fine particles (< 2 mm fraction). Except the particle size distribution analysis, all experimental studies were done on this fraction.

2.2 Digestion, Extraction and Heavy Metal Analysis

The soil samples (2.0 g each) were digested in triplicates using 20 ml of *aqua regia*, a mixture of nitric acid and hydroc hloric acid, optimally in a molar ratio of 1:3 by standard method to obtain the supernatant extracts which were respectively made up to mark in a 50 ml standard volumetric flask. Certified Reference Material (reference soil sample) was also digested in the same manner to ensure that the experimental procedure was under control. The sample extracts were refrigerated prior to analysis by a calibrated Flame Atomic Absorption Spectrophotometer (Perkin-Elmer, AAnalyst 400) which measured the concentration of the pseudototal potentially toxic metals.

2.3 Physicochemical Analysis

The soil pH was determined using a soil-to-$CaCl_2$ suspension with a pH meter. Other physicochemical parameters (total organic carbon and organic matter, soil cation exchange capacity, soil particle size distribution) were all determined using standard analytical methods which have been described elsewhere [8-10].

2.4 Multivariate Analysis

The large number of variables was reduced to a relatively smaller number of factors or principal components to aid the interpretation of the analytical data. This was done by subjecting the original experimental results to multivariate analysis. The correlations between the physicochemical parameters and the concentration of the potentially toxic metals in the soils were established by principal component analysis (PCA) using SPSS version 15.0 software and applying variance maximizing (varimax) rotation with Kaiser Normalization rotation method to determine the number of factors or principal components to be retained and also aid easy interpretation [11].

2.5 Ecological Risk Assessment

The model used for the ecological risk assessment of the potentially toxic metals has been previously described elsewhere by Hakanson [12]. According to Hakanson's model, the potential ecological risk index (PERI) comprises of three basic modules – contamination factor or degree of contamination (C^i_f), toxic response factor (T^i_r) and potential ecological risk coefficient (E^i_r) of a single element. These modules together with the potential risk index (RI) are connected by the following expression:

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

where $C_f^i = \frac{C_s^i}{C_n^i}$ and $RI = \sum E_r^i$

where i = the given potentially toxic metal (PTM)

C_s^i = measured concentration (in mg kg^{-1}) of the PTM in the soil sample

C_n^i = regional background concentration (in mg kg^{-1}) of the given PTM

3. Results and Discussion

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

The pH of the soils (Table 1) are near-neutral. With reference to the control sample, it can be observed that at the near-neutral pH, the soils have higher %organic matter and moderately high CEC values and accumulated significantly higher concentration of PTMs. This is in agreement with literature reports that higher %OM creates more exchange sites in the soil leading to high CEC values.

Generally, all the metals showed higher concentrations in the soils. The elevated concentrations of Cu in the samples can be attributed to the welding of copper-containing items and the use of solders and a wide variety of other items made of Cu. It has been reported by Alloway [13] and Lenntech [14] that when Cu enters the soils, it strongly binds to organic matter and minerals and therefore, cannot travel very far after its release. In a related study, Schmitt and Sticker [15] reported that which Cu is specifically fixed or adsorbed in soils and is one of the least mobile heavy metals at any pH value. This could be an explanation for the high concentration of Cu recorded in most of the samples.

Table 1. Mean values of physicochemical properties of soils contaminated by metal particulates from metal cutting and welding operations

Sample Location	Sample ID	pH	% Organic Matter	CEC (meq/100g)	Grain Size Distribution		
Agiliti	WS1	7.9	2.31	20.97	62.86	31.70	5.44
Alapere	WS2	8.0	2.59	71.55	47.80	46.50	5.70
Gidan-kwali	WS3	7.9	4.12	29.57	79.60	13.6	6.80
Ikosi-Ketu	WS4	7.4	4.28	59.22	78.95	15.07	5.98
Ketu	WS5	7.1	4.02	53.78	67.78	25.35	6.87
Kosofe-Mile 12	WS6	7.8	6.90	44.39	64.52	29.55	5.93
Ogudu	WS7	7.7	3.98	17.27	74.21	19.12	6.67
Ojota	WS8	6.7	5.31	79.72	89.79	5.88	4.33
Owode-Onirin	WS9	6.9	3.48	24.63	74.44	18.72	6.84
Shangisha	WS10	7.6	2.69	7.41	74.79	19.83	5.38
Control sample	CTR	6.3	0.309	2.46	64.40	24.70	10.90

WS – Welder's Shop

CEC – Cation Exchange Capacity

Values are means of triplicate determinations

Table 2. Concentration of potentially toxic metals in the soil contaminated by metal particulates from metal cutting and welding operations, presented as mean ± standard deviation

Sample ID	Concentration of Potentially Toxic Metals (mg kg^{-1})					
	Cd	Cr	Ni	Pb	Zn	Cu
WS1	0.75±0.11	5.04±1.09	1.05±0.25	82.5±10.4	87.5±2.48	5.53±1.78
WS2	0.94±0.09	5.97±1.53	1.79±0.12	24.0±0.35	149±0.71	20.0±3.54
WS3	3.22±0.39	2.75±0.53	6.30±1.95	175±4.24	61.2±8.84	106±0.14
WS4	2.77±0.14	18.6±3.03	3.31±0.79	46.7±6.93	154±10.6	90.6±14.4
WS5	1.85±0.04	1.61±0.51	4.23±0.27	43.8±1.56	56.2±14.1	74.3±1.70
WS6	3.68±0.72	16.1±2.62	4.29±0.57	29.1±0.35	137±13.4	36.4±2.26
WS7	1.59±0.02	18.5±3.3	4.71±1.43	36.8±1.91	190±7.07	87.4±6.36
WS8	0.60±0.18	12.6±2.78	0.59±0.02	151±27.9	128±1.41	226±0.04
WS9	1.90±1.06	12.1±0.42	0.97±0.35	51.1±2.97	38.7±5.30	27.0±6.72
WS10	0.75±0.11	20.2±0.14	1.51±0.06	29.5±3.54	134±1.41	34.5±7.50
CTR	B.D	B.D	B.D	0.98±0.02	43.9±0.08	6.98±0.10

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

Table 3.Concentration of the PTMs in the Certified Reference Material

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

Note: Values are means of triplicate determinations

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	.237	1.00										
Ni	.795	.072	1.00									
Pb	.208	-.166	.269	1.00								
Zn	.089	.723	.195	-.157	1.00							
Cu	.086	.196	.178	.693	.241	1.00						
%OM	.726	.469	.531	.342	.371	.528	1.00					
CEC	.189	.024	.073	.291	.296	.566	.531	1.00				
pH	.432	.217	.542	.105	.477	-.221	.272	.064	1.00			
Sand	.158	.381	.126	.605	.016	.772	.382	.053	-.341	1.00		
Silt	-.135	-.313	-.115	-.557	.064	-.725	-.301	.031	.430	-.989	1.00	
Clay	-.178	-.502	-.097	-.409	-.519	-.430	-.588	-.552	-.517	-.238	.089	1.00

[a] This matrix is not positive definite

3.1 Multivariate Analysis (Principal Component Analysis)

Table 4 below presents the physicochemical properties of the soils and Table 5 presents the eigenvalues of the factors after variance maximizing (varimax) rotations of the original variable space. Four principal components contained 86.87% of the total variance in the data, and were used to correlate the variables. Using Kaiser criterion with eigenvalue greater than 1 [11], only the first four principal components are retained. Subsequent eigenvalues are all less than 1 and are therefore rejected.

Table 5. Eigenvalues of factors after varimax rotations

PC	**Eigenvalues**		
	Total	**% of Variance**	**Cumulative %**
1	4.434	36.954	36.954
2	2.829	23.573	60.527
3	1.745	14.541	75.068
4	1.416	11.802	86.870
5	.839	6.988	93.858
6	.502	4.182	98.040
7	.127	1.055	99.095
8	.098	.814	99.909
9	.011	.088	99.997
10	.000	.003	100.000
11	2.57E-016	2.14E-015	100.000
12	-2.60E-017	-2.17E-016	100.000

Extraction method: Principal Component Analysis

A close look at the correlation coefficient matrix in Table4 will reveal that Cd had a strong positive correlation to Ni (r = 0.795) and to %OM (r = 0.726). The strong correlation of Cd to Ni in these soils could be as a result of cutting and welding Cd-plated metals in those sites since cadmium does not corrode easily and is sometimes used as a metal coating.Nickel is also used as a metal coating and so when such metals are cut and/or welded, the metal dust (contaminant) is likely to contain Ni. The highest concentration of Ni was obtained in sample WS3, which was collected at Gidan-kwali metal scrap dumpsite, Ojota New Garage, where a wide range of anthropogenic economic activities take place such as automobile repairs, battery waste disposal, metal welding, dumping of plastics and electronic wastes (e-wastes), burning of wastes, etc. There is a positive correlation of Zn to Cr (r = 0.723). This could be as a result of contamination from the disposal and/or welding of alloys containing Cr (e.g. chrome steel) and Zn (e.g. brass, bronze, Babbitt metal, etc.). Most Pb in the soil come from human activities which include the burning of fossil fuels, making building or construction materials when it is alloyed with Cu, Zn, Mg, Mn and Sn. This could be an explanation to the positive correlation of Cu to Pb (r = 0.693). There was a significant positive correlation of %OM to Cd (r = 0.726), to Ni (r = 0.531) and to Cu (r = 0.528), indicating that the availability of these PTMs in the soils depends on the organic matter content. The positive correlation of CEC to Cu (r = 0.566) and to %OM (r = 0.531) shows that higher %OM leads to greater CEC of the soils and significant Cu adsorption. Sand showed a positive correlation to Pb (r = 0.605) and to Cu (r = 0.772) whereas the correlation of percent silt to Pb, Cu and percent sand were all negative (r = -0.557, -0.725 and -0.989 respectively), indicating that Pb and Cu concentration will increase when there are higher sand and lower silt contents. Clay content has no effect on Cr, Zn, %OM, CEC and pH as its correlation with these parameters are all significantly negative. The positive correlation of pH to Ni (r = 0.542) could be explained by referring to the results in Table 1 which shows that the pH of the soil are near-neutral, and at such pH, the soil has exchange sites that become more active to adsorb most of these metals.

The variance maximizing (varimax) orthogonal rotations of the original variable space extracted two principal components (factors), PC1 and PC2. Figure 1 below shows the plot of the factor loadings. The first factor, PC1 with 36.95% of the variance was observed to be positively correlated to Ni, Zn, Cd, Cr, pH, %organic matter and CEC with high loadings indicating that these parameters have a common origin. There is a fair correlation of PC1 to Pb, Cu, sand and silt contents and a negative correlation to clay content. The second factor, PC2 with 23.57% of the variance showed a positive correlation to Ni, Cd, Cr, CEC, %organic matter, Pb, Cu and sand, and a negative correlation to clay, silt and pH.

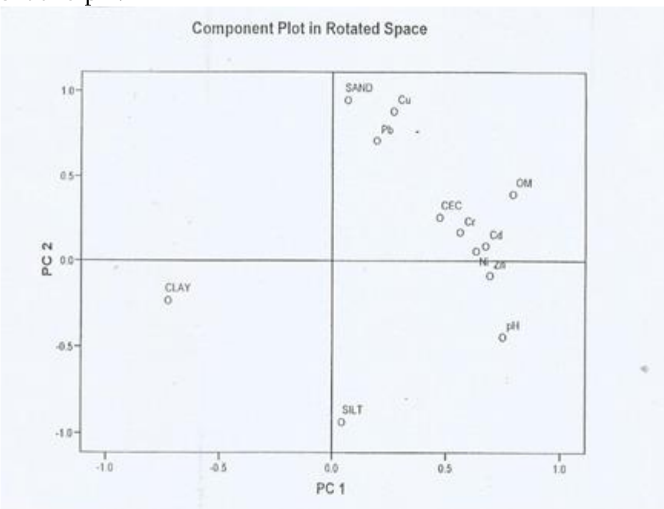

Figure 1. Plot of factor loadings

3.2 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.

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 Referenc Tables (SQuiRTs), except that of Cr which was given by Holmgren and his co-workers [16]. 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.

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

	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

Table 8. The grades of ecological risk coefficient, risk index and classification of risk intensity

E_r^i	RI	Grade of Risk Intensity
$E_r^i < 40$	RI < 150	Low
$40 \le E_r^i < 80$	150 ≤ RI < 300	Moderate
$80 \le E_r^i < 160$	300 ≤ RI < 600	Considerable
$160 \le E_r^i < 320$	RI ≥ 600	High
$E_r^i \ge 320$	-	Very high

In Table 6, the results show that Cd and Cu posed the highest ecological risk among all the PTMs investigated, with the risk coefficient ranging from 66.6 – 409.1 for Cd and 1.63 – 66.5 for Cu, which account for 72 – 98.1% of the risk index (RI). In two of the samples (MS3 and MS8), the risk coefficient of Pb exceeded 40 (the minimum risk coefficient for low risk intensity) and this indicated extreme pollution by Pb in those locations. The rest of the PTMs (Cr, Ni and Zn) showed a low potential ecological risk in all the soil samples investigated.

4. Conclusion

The results obtained from this study have shown that metal cutting and welding operations are potential sources of heavy metal contamination in the surrounding soils. The multivariate statistical analysis has also been found useful in classifying these PTMs in terms of their relationship with soil physicochemical properties and in identifying their probable origin in the soil. The results of the ecological risk assessment show that there is high ecological risk resulting from the release of Cd and Cu into the environment in majority of the sample locations.

Table 6: Ecological risk coefficients and risk indices of potentially toxic metals in the soil contaminated by metal particulates from metal cutting and welding operations

Sample Location	Sample ID	Ecological Risk Coefficient, E_r^i						Potential Risk Indices (RI)
		Cd	Cr	Ni	Pb	Zn	Cu	
Agiliti	WS1	83.22	0.27	0.08	25.08	1.82	1.63	112.10
Alapere	WS2	104.10	0.32	0.14	7.52	3.09	5.88	121.05
Gidan-kwali	WS3	358.23	0.15	0.49	54.67	1.28	31.12	445.94
Ikosi-Ketu	WS4	308.22	1.01	0.26	14.60	3.20	26.66	353.95
Ketu	WS5	205.23	0.09	0.33	2.74	1.17	21.86	231.42
Kosofe-Mile 12	WS6	409.11	0.87	0.33	9.09	2.85	10.71	432.96
Ogudu	WS7	176.34	1.00	0.36	11.52	3.96	25.71	218.89
Ojota	WS8	66.57	0.68	0.05	47.14	2.67	66.48	183.59
Owode-Onirin	WS9	210.99	0.66	0.08	15.98	0.81	7.95	236.47
Shangisha	WS10	83.34	1.09	0.12	9.22	2.79	10.14	106.70
Control sample	CTR	-	-	-	0.31	0.90	2.05	3.26

Declaration of Interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

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