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A Chemometric Approach for the Distribution and Source Identification of Heavy Metals in Tannery Contaminated Soil

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ABSTRACT: Heavy metals in the environment may reach to toxic levels to humans and animals due to tannery effluents, but there is insufficient information about heavy metals pollution and distribution by tanneries. The distribution and sources of heavy metals in soils of Challawa industrial estate area were evaluated using multivariate statistical analysis after determining metals concentrations by atomic absorption spectroscopy. The results of the Principal Component Analysis and Hierarchical Cluster Analysis suggested that variation in heavy metals concentrations are largely related to tannery operations. The Linear Discriminant Analysis revealed that soils around the tanneries and dumpsites are having high contents of Cr, Pb, and Zn. The metal concentrations showed significant difference ($P < 0.05$) between tannery and control soil samples. This confirmed the contamination of soils with toxic heavy metals at specific sites of the tanneries, and indicated the need to monitor and remediate to safeguard the environment.

Keywords: Soil, Heavy Metals, Chemometric, Tanneries, Pollution

I. INTRODUCTION

Soil is the major part of the ecosystem which serves as a domain for humans, plants and animals [1]. At the same time, it is the most threatened part due to the contamination arising from human activities especially industrialization. Variation in soil properties makes it difficult to identify and measure the extent of the pollution. The pollutants have different sources reaching the level that could be harmful to humans and other biota [2]. Most studies done so far revealed that elevated levels of metals in soils are due to anthropogenic input [3-5]. Tanneries are major sources of metal pollutants and contribute to solid wastes in the environment [6-8]. Tanneries have been identified as the major contributors for pollution from the variety of chemicals used. The pollutants in soil and tannery effluent are mostly Cr and some other heavy metals. In tannery operation, about 40,000 tones of basic chemicals and 15,000 tones of chromium as chromiumsulphateare used. Significant portion of metals find their way to the environment rendering the soil neither suitable for agriculture nor for any other beneficial use [9].

In areas with concentration of tanneries, underground water gets polluted due to discharge of effluent. Indiscriminate discharge of chemicals and tannery waste expose the workers and nearby residents to various heavy metals hazards. Plants absorb significant quantity of toxic metals which could be of health threat to humans [10-12]. Exposure to metals causes lung infection and respiratory disorder, kidney failure and damage to central nervous system among others [13].

Soil research needs complete knowledge about soil quality and any likely sources of contamination. Sometimes erroneous conclusions are drawn about soil pollution level and distribution of metals in soil [1]. As the pollutants from tanneries contain complex heavy metal pollutants [14], analysis of metal levels by considering only mean values and other measures of central tendency may not yield perfect data on the variations and metal distributions. Hence there is need to accurately study the heavy metal distribution by appropriate choice of chemometric techniques. Multivariate statistical analyses are widely applied to analyze the extent of variations of the metal pollutants, and identification of sources of environmental contamination [15-18].

According to Sena *et al.,* 2002, unsupervised methods of multivariate analysis are best utilized in analyzing contaminated soil. Principal Component analysis (PCA), Factor Analysis (FA), Hierarchical Cluster Analysis (HCA) and Linear Discriminant Analysis (LDA) have been commonly applied for several exploratory evaluations of soil pollutants. PCA is an unsupervised pattern recognition technique that provides information on the most significant parameters that describe the larger variation in the entire data set [19]. PCA excludes less significant parameters with minimum loss of information and identifies the unobservable, latent pollution sources [20]. FA interprets the principal components (PCs) that are not readily explained and this is achieved by rotating the significant PCs through varimax rotation [16]. HCA is a multivariate technique that classifies similar samples or sites into clusters based on their similarities. Clusters are formed sequentially, the most similar clusters are first grouped and the similarity decreases when the subclusters get merged into a single group [21]. LDA is a supervised pattern recognition technique commonly used to support PCA/FA, and HCA as a confirmatory analysis. It determines the parameters that discriminate between the samples or groups [22]. These techniques try to reveal more accurate information about metal distribution and their sources in the soil.

The objectives of the present study arise due to the explanations given above which identify the most important pollutants in tannery contaminated soil, and the source identification of the metals could show some lead for rehabilitation of the soil. This study that utilizes multivariate analysis techniques to evaluate the distribution and map the sources of metal pollutants in soil of Challawa industrial estate area is the first of its kind which would assist in pollution assessment, and environmental management.

II. MATERIALS AND METHODS

A. Study Area

The study was carried out in Challawa situated in Kano state in the northwestern part of Nigeria located on latitude 11° 54' 26.96″ N and longitude 8° 27' 55.81″ E. It is an industrial estate area comprising of large number of tanneries processing skin and hides, and surrounded by farms and residential houses as shown in Fig. 1. The sampling points indicated by letters R to Z are spread across the sampling site to study the extent of trend and distribution of some heavy metals. Activities being carried out for many decades in the area are predominantly industrial and small scale farming. Tanneries discharge the effluents into canals, and the solid wastes are droppedat dumpsite area of the industrial estate.

Fig. 1. Location of sampling sites in Challawa Industrial Estate.

B. Sampling and sample preparation

Samples were collected from each sampling point within 10 cm depth using a plastic scoop, and distance of 5 – 10 m was maintained between each sampling point (Table 1). To ensure accuracy and precision of the results, triplicate soil samples were collected from each point, placed inside polyethylene bags and brought to the laboratory. Similarly, soil samples were also collected from Challawa and Karfi towns as control for comparison. The samples were air dried, ground and sieved through 2 mm sieve [6].

Table 1: Coordinates of sampling points in Challawa Industrial Estate.

Code	Description	Coordinates
Q	Karfi Town	11º27´00.77″N, 9º09´00.16″E
R	Farm away from Tanneries	11º54´02.78″N, 8º28´50.28″E
S	Challawa Town	11º54´04.27″N, 8º27´34.36″E
T	Farm near dump site	11º53´33.87″N, 8º28´03.90″E
U	Dump site of Tanneries	11º53´44.84″N, 8º28´08.64″E
V	10 m away from U	11º53´44.45″N, 8º28´03.57″E
W	10 m away from V	11º53´41.72″N, 8º28´07.82″E
X	Vicinity of Tannery	11º54´09.43″N, 8º28´17.80″E
Y	5 m away from X	11º54´08.39″N, 8º28´19.06″E
Z	10 m away from X	11º54´07.19″N, 8º28´16.57″E

C. Chemical analysis

Heavy metals Pb, Cr, Cd, Mn, Fe, and Cu were analyzed in all the soil samples. The samples were digested using concentrated acids. Accurately weighed soil sample (0.2 g) was placed in a platinum crucible and heated on a hot plate with a mixture of 6 mL conc. HCl and 1 mL HF. After cooling the mixture, 5 mL HF and 1 mL conc. HCl were added. The mixture was heated on a sand bath to 200–230ºC until the acid evaporates to dryness. After cooling, 6 mL of 1M HCl was added and heated for 10 min. The resulting solution was filtered and made up to 25 mL mark with de-ionized water in a volumetric flask. Atomic absorption spectrophotometer (Varian 1200) with air acetylene flame was used for metal analysis [23].

D. Data analysis

Multivariate statistical analysis was carried out using JMP Pro 12. The PCA, FA, HCA, and LDA were used to explore the data matrix (30 × 6) of metals. For LDA, 20/30 of the data set was selected randomly for training and the remaining 10/30 for validation [18]. The standardized data sets of the metals were used for PCA/FA to minimize the influence of variables, and to prevent dominance of large size parameter in the data set. HCA was carried out on the data set using wards method which uses Euclidean distance as the measure of similarity and differences [24]. A discriminant function was computed in LDA using the eigenvalues to predict the group identity of the samples under consideration [25].

III. RESULTS AND DISCUSSION

A. Analysis of correlation coefficient

The correlation matrix of heavy metals obtained from Challawa industrial estate soil was analyzed. Table 2 shows a strong positive correlation between Fe and Cr, Pb, Cd and Zn.

Table 2: Correlation matrix of heavy metals in tannery contaminated soil from Challawa industrial estate Kano, Nigeria.

	Cr	Pb	Cd	Cu	Zn	Fe
Cr	**1.0000**					
Pb	0.3984	**1.0000**				
Cd	0.3936	0.3941	**1.0000**			
Cu	0.2779	-0.0522	0.0593	**1.0000**		
Zn	**0.5424**	0.3062	**0.8404**	-0.0051	**1.0000**	
Fe	**0.7417**	**0.5005**	**0.5481**	0.0188	**0.6949**	**1.0000**

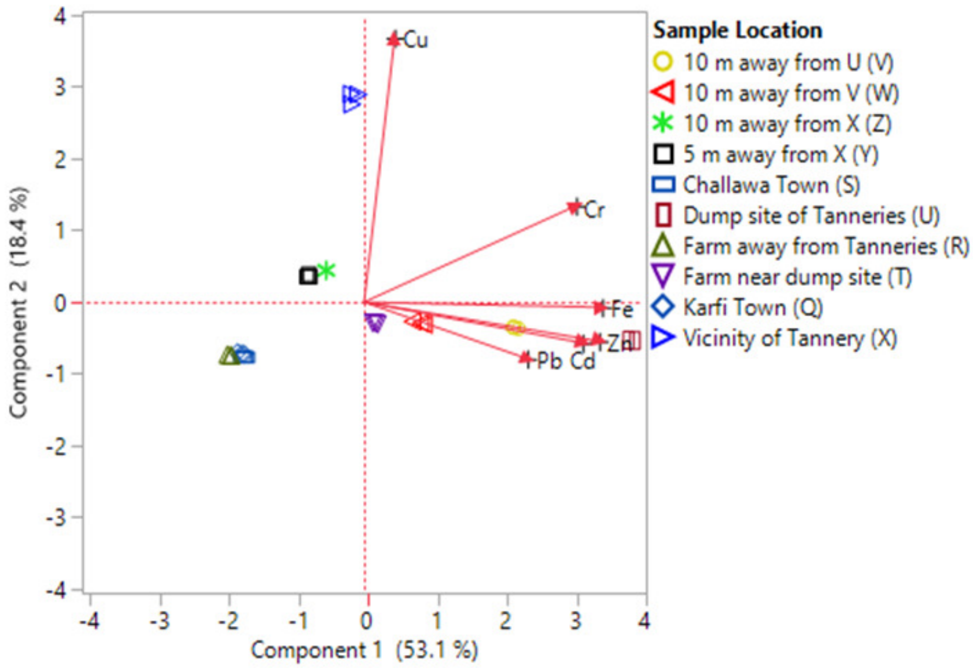

Fig. 2. PCA bi plot of heavy metals in tannery contaminated soil.

This indicates that Fe has a strong association with other metals and shares a common source. Both Cr and Cd are positively correlated with Zn and Fe. This suggests the influence of tannery discharge on the soil metal content. Cu has no correlation with any other metals, indicating other possible source of Cu in the tannery waste.

B. Source identification

PCA was to compare the variations in composition pattern of heavy metals in the soil. Six principal components (PCs) were obtained (Table 3), and two PCs with eigenvalue > 1 were subsequently retained for further analysis [21,26]. The Eigen value is the measure of importance of PCs, the PCs with the largest Eigen value are the most important and explain the larger variation in the data set. The first and second PC accounted for 71.5 % of the total variance in the soil dataset. The first PC accounting for 53.11 % of the total variance is strongly correlated with Cr, Cd, Zn and Fe. The high loadings exhibited on these metals can be interpreted as due to the influence of tannery operations. The chemicals used by tannery for skin and leather processing are similar to the toxic heavy metals present in the environment [27-29].

Table 3: Result of the principal component analysis for the tannery contaminated soil.

Variable	PC1	PC2	PC3	PC4	PC5	PC6
Cr	**0.49996**	0.32963	0.26459	**-0.46219**	**-0.63011**	-0.13079
Pb	0.33904	-0.19306	**0.69452**	**0.57452**	-0.03249	0.18519
Cd	**0.45330**	-0.13904	**-0.46079**	**0.42832**	-0.13935	**-0.59998**
Cu	0.06321	**0.90368**	-0.08217	0.34537	0.20836	0.09961
Zn	**0.48770**	-0.13343	**-0.44898**	-0.02941	-0.04870	**0.73453**
Fe	**0.49412**	-0.01738	0.16425	-0.39077	**0.73260**	-0.19791
Eigen Value	3.18	1.10	0.81	0.59	0.19	0.10
Variability (%)	53.11	18.39	13.56	9.90	3.25	1.78
Cumulative (%)	53.11	71.50	85.07	94.97	98.22	100

Values in bold reveals strong loading

A similar finding about the abundance of Cr, Fe and Zn in tannery contaminated soils was reported in Pakistan [29]. The second PC which accounted for 18.39 % of the total variance has strong correlation with only Cu. Cu in tannery is mostly used as preservative and in dyes in tanning process [30].

By observing the scores and loadings (Fig. 2), it is evident that dumpsite of tanneries (U) and its surroundings (V and W) are loaded with heavy metals derived from tannery operations. Exposure to the toxic heavy metals involves high risk in these locations [18]. The scores on PC2 show that vicinity of tanneries (X) are loaded mainly with Cu. Cu has been listed as a metal of great concern by tannery industry [14]. This further confirms abundance of toxic heavy metal in the study area, and relates it to tannery operation.

Factor analysis was applied on the data set to understand how many variates are important to explain the observed variances in the data. PCA was used to generate the factors by rotating the PCs to reduce the contribution of less significant variables [16]. This approach produces a small number of factors that account for nearly the same amount of information as the original set of variables[21]. The varimaxrotation of the PCs gives two factors (Eigen value > 1) with the corresponding parameter loadings as shown in Table 4. Similarly, Fig. 3 reveals that factor 1 accounted for 52.10 % of the total variance and was positively correlated with Cr, Pb, Cd, Zn and Fe. This factor may illustrate anthropogenic source of pollution due to heavy metals associated with tannery operations. Second factor explains 19.40 % of the total variance and was positively correlated with Cu and Cr.

Table 4: Varimax rotated component matrix for the tannery contaminated soil.

Variable	Factor 1	Factor 2
Cr	**0.716583**	**0.472520**
Pb	**0.630579**	-0.098991
Cd	**0.822228**	-0.008997
Cu	-0.047181	**0.954930**
Zn	**0.881785**	0.007055
Fe	**0.872738**	0.129185
Eigen Value	3.13	1.16
Variability (%)	52.10	19.40
Cumulative (%)	52.10	71.50

Significant factor loadings are bold

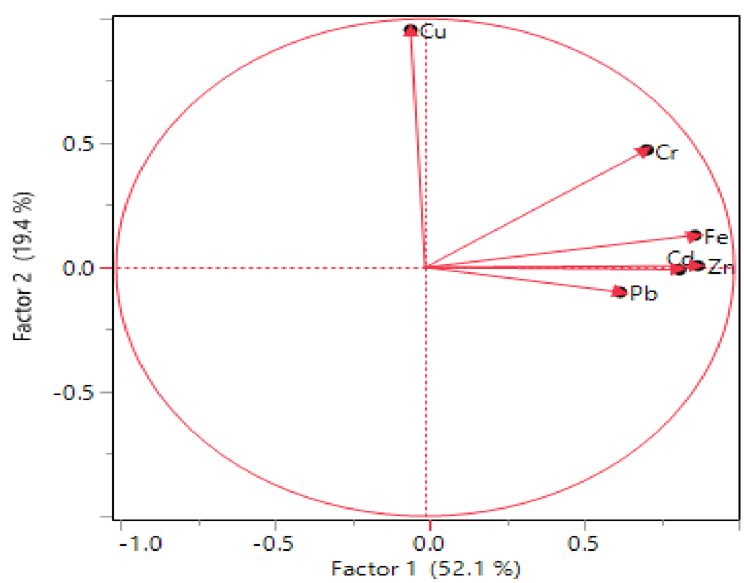

Fig. 3. Factor loading plot of heavy metals in tannery contaminated soil.

This factor may be related to tannery operation and other industrial source of the metal pollutants. The results of FA has confirmed and supported the metal sources and distributions in the tannery soil using PCA.

C. Spatial similarity and grouping

Application of two-way HCA on the data set sorted out the sampling sites based on similarity in the metal distribution as shown in the concentration pattern (Fig. 4). The dendrogram indicates three clusters, and sub-clusters with corresponding levels of metal concentrations. The observed clustering suggest that variations in metal concentrations originated from the level of pollution due to tannery operations. The extent of pollution at the sampling locations increases from cluster 1 to 2, and sites in cluster 3 are the most polluted with Cr, Fe, Zn, Cd and Pb. In a similar study to determine soil quality and properties in farms, HCA was successfully applied to verify the similarity pattern among the plots [31]. Hence, the influence of heavy metals on the sites can be observed and studied by HCA.

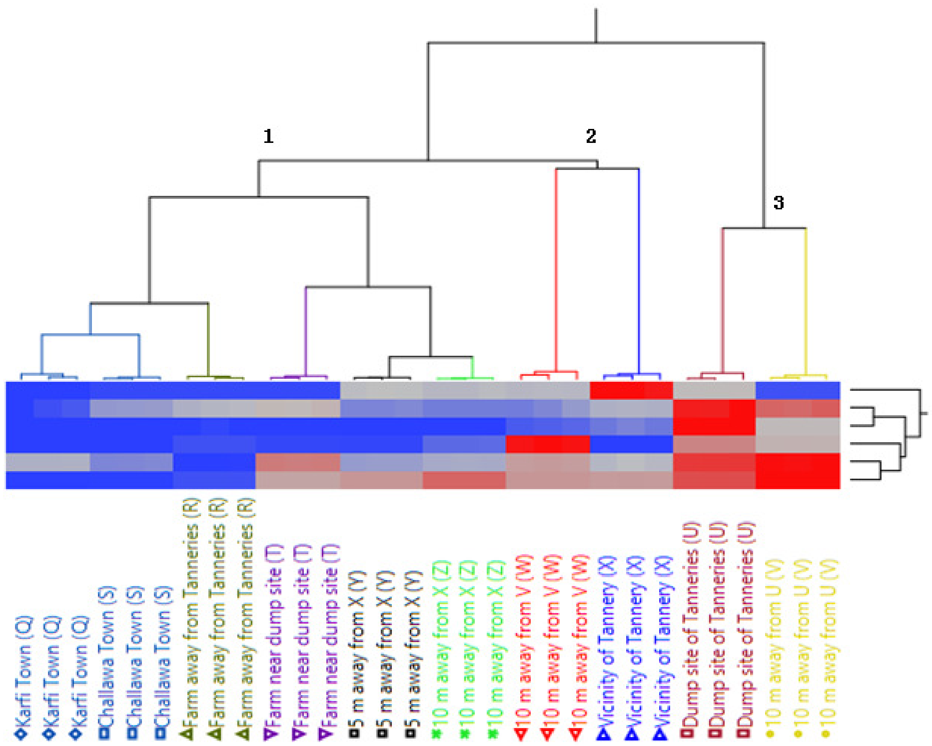

Fig. 4. Dendrogram of various soil sampling locations.

D. Linear discriminant analysis

LDA was successfully applied on the data to determine the parameters which distinguish contaminated soil from the control. Accurate prediction with R^2 = 1.00 was achieved without mis classification in the validation set. Contaminated soil was completely separated from the control in the direction of canonical 1 (Fig. 5), in which Cr, Pb and Zn were associated with the tannery contaminated soils, while Fe was mainly associated with the control soil sample. This indicates that tannery operations introduce toxic heavy metals to the environment there by polluting the soil and the surrounding environment [32-34]. Hashem *et al.* 2017 reported that hair burning and liming in tannery operation is the major source of Pb, As, Zn, Mn and Fe.

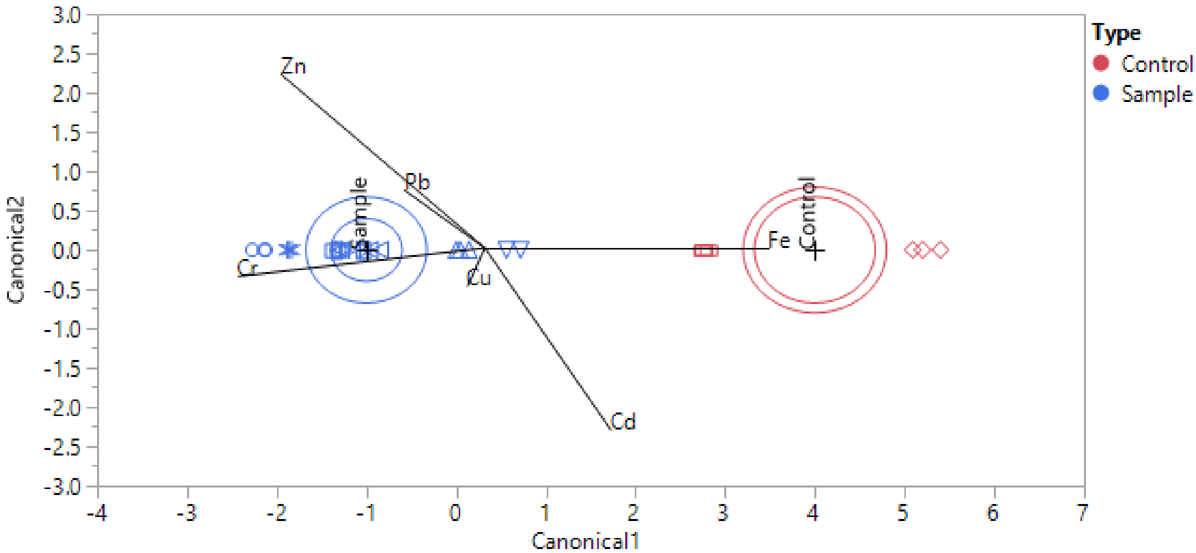

Fig. 5. Canonical plot for the discrimination of tannery contaminated and control soil samples.

IV. CONCLUSION

There is significant variation in the heavy metal concentrations in tannery contaminated soils of Challawa industrial estate. The analysis by PCA, FA, and HCA indicated that these variations are due to the tannery operations in the area. According to LDA results Cr, Zn and Fe are metals that discriminate the tannery contaminated soil from control soil and Cr, Pb and Zn predominated tannery contaminated soil. The reason being indiscriminate dumping of tannery solid waste and discharge of effluent. The study demonstrated the practical application of chemometric techniques to identify the distribution and sources of heavy metals polluting the soil. It also gave information about the variations in the study sites so that effective monitoring and management of soil pollution could be done.

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