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Multivariate Statistical Analyses of Various Physico-Chemical Parameters and Selected Metals in Soil in Vicinity of Sugarcane Based Industrial Unit

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Multivariate analysis is a powerful tool to unravel the hidden aspects of a particular data set. The present investigation deals with the use of multivariate analysis (*i.e.* principal component analysis and cluster analysis) for exploring the sources of various studied parameters in the soil samples and also determines the pollution status of the soil in vicinity of a sugarcane based industrial unit located in Mandi Bahauddin, Pakistan. The industrial unit comprised of sugar mills and a few chemical industries producing methanol, ethanol etc. from the bye-products of sugar mills. A total of 36 soil samples were collected from the peripheral distance of 50, 100 and 150m from the industrial unit and analyzed for various physico-chemical parameters like pH, electrical conductivity, alkalinity, chloride, sulfide and sulfate. The selected metals (*i.e.* K, Mg, Co, Ni, Pb) were analyzed by flame atomic absorption spectrophotometer under optimum analytical conditions. The data thus obtained was subjected to univariate and multivariate statistical analyses. The results evidenced the contamination of the soil in vicinity of the industrial unit upto a critical distance of 150 m from effluent discharge point by heavy loads of chloride, sulphide, sulphate and almost all the selected metals. The correlation coefficient matrix revealed a number of strong positive relations among various metal pairs. Multivariate analysis evidenced the sources of metals to be present in various processes of sugar and other industries.

Key Words: Principal component analysis, Cluster analysis, Sugar industry, Metals, Soil, Multivariate analysis.

INTRODUCTION

Multivariate data analysis techniques [*i.e.* principal component analysis (PCA) and cluster analysis (CA)] have been used extensively to access the complex ecotoxicological processes, to trace the sources of various variables in the soil and to study the interdependency among these variables[1-10]. Principal component analysis reduces the dimensionality of a dataset consisting of a large number of interrelated variables thereby transforming it into a new set of orthogonal variables called the principal components (PCs). Mathematically, the principal components are computed from correlation coefficient matrix and are the linear combinations of the original variables and the eigenvectors.[11-14]

Cluster analysis (CA) is used to develop meaningful aggregations on the basis of a large number of interdependent variables. The resulting clusters exhibit high internal homogeneity and high external heterogeneity[15-17] of all the cluster analyses, hierarchical agglomerative cluster is most common approach which is based on the Ward's method for obtaining the normalized data set. Moreover, squared Euclidean distances are used here to measure the similarity of data set[18]. The results of cluster analysis support the finding of principal component analysis. Conjunction with CA and PCA provides a means for ensuring proper source identification for a given metal distribution pattern in water and sediment[19-22].

In recent years many studies have focused on multivariate methods for classifying the sampling sites, identify the latent pollution sources and distribution pattern of the measured data set[1, 23-28].

In view of these considerations, the present investigation also deals with the multivariate analysis of the data set obtained for soil samples collected from sugar cane based industrial unit located in Mandi Bahauddin, Pakistan. The industrial unit selected for the present investigation is located in the neighbourhood of residential colonies and agricultural lands. It comprises of sugar mills and some chemical manufacturing industries which are discharging voluminous amounts of wastewater containing heavy organic loads in addition to toxic trace metals. At present no treatment plant is working in the area to control the effluent discharge. The residents of this area are suffering from numerous health problems. The nauseating smell emanating from the solid and liquid wastes has also made their lives difficult. Moreover, the vast fertile lands are being devastated. It is therefore imperative to develop a strategy for monitoring the effluent being discharged by these industries.

Sugar industry is an agro based industry that discharges its effluents onto terrestrial and aquatic systems. This industry lacks high tech processes and thus the untreated effluents contain considerable amounts of organic and inorganic pollutants including sugar cane baggage, molasses, carbonates and bicarbonates *etc.*[29] It has also been characterized by high suspended and dissolved solids, BOD, COD, chloride, sulphate, nitrate, Ca and magnesium[30].

Previously it has been shown that multi-element geochemical anomalies occur specifically in the vicinity of intensive industrial activity[31]. The industrial unit selected for the present investigation is quite old running for last 40-50 years. It is therefore quite imperative to study the metal pollution status of soil. Though soil constitutes a repository for anthropogenic waste containing trace metals but various biochemical processes mobilize these metals to water supplies and impact food chains in turn. No studies till today have been performed to evaluate the influence of sugar industry effluent on relevant environment.

Based on these considerations, the present investigation aimed at determining the present soil status in term of various physicochemical parameters and metal levels in vicinity of selected industrial unit. Moreover the inter-relationships of the trace metals in contaminated soils were determined by using multivariate statistical methods. Once the sources of selected metals in soil are traced, various control measures may accordingly be adapted to remediate the situation.

EXPERIMENTAL

Site description: Mandi Bahauddin is a fertile agricultural city located in central Punjab, Pakistan at about 244 meters from the sea level. It spans over an area of 2,673 square kilometers, most of which consists of plain fields irrigated by water from the Indus River and groundwater driven by tube wells. The temperature ranges for the area are about 39.5 ºC and 25.4 ºC with annual average rainfall of about 435 mm. Major crops and fruits of Mandi Bahauddin are sugarcane, wheat, rice, citrus and guava. The area inhabits about 879 industrial units comprising of sugar and flour mills, textile spinning, chip board and food colour manufacturing industries, *etc*. Due to high production of sugarcane, the city is also important for sugar production.

Sampling : A total of 36 soil samples each in 500 g portion were collected from 1-5 cm deep top-layer of soil in zip-mouthed high density polythene bags of appropriate size from the peripheral distance of about 50, 100 and 150 m from effluent discharge point with the help of plastic scoops (Fig. 1). For background analysis, the soil samples were also obtained from remotely located site having the same soil structure. Prior to sampling all the soil samples were cleaned manually for any foreign matter such as leaves, twigs and stones *etc*. All sample containers were duly labeled and transferred immediately to laboratory for analysis. For quality assurance all the samples were collected in triplicate following standard sampling guidelines[32].

Analysis of physicochemical parameters: In order to determine the physico-chemical parameters, the soil samples were air-dried, mechanically ground and sieved to obtain < 2 mm size fraction. This fraction was used to prepare the water

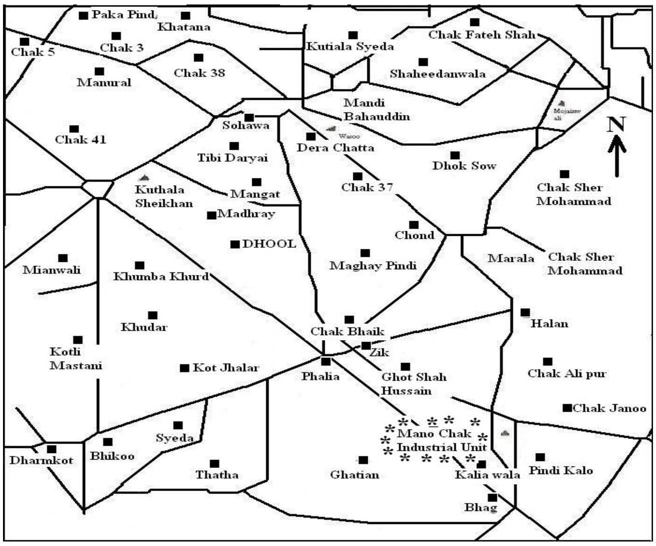

Fig. 1. Location map of sampling sites

extract of soil samples for the determination of pH, electrical conductivity, alkalinity and other parameters like Cl^-, S^{2-}, NO_3^- and SO_4^{2-} in accordance with standard methods [32].

Analytical Methodology: In order to extract the metals from soil samples, wet digestion method of US-EPA was used; whereby air dried soil was digested by using conc. HNO_3 and H_2O_2 and subsequently diluted up to 50 mL. This solution was used for aspiration on atomic absorption spectrophotometer for the estimation of various metals[33]. All chemicals and reagents used were of spectroscopic grade with a certified purity of 99.9 %, procured from E. Merck (Germany). Pyrex glassware was used for the processing and preparation of samples. Hitachi atomic absorption spectrophotometer Model -AA5000, equipped with Zeeman background correction facility was used under optimum analytical conditions as provided by manufacture for the estimation of selected metals. Standard reference material (NIST, SRM1573a, TL) was used periodically to check the accuracy of the results and the precision of the instrument. Normally, the corresponding results matched within ± 0.5 %.

Statistical analysis: The analytical data obtained were processed for detailed statistical analysis. Basic statistical parameters such as mean, median, mode, standard deviation, skewness and kurtosis were computed along with correlation analysis, while multivariate statistics in terms of principal component analysis and cluster analysis was also carried out to trace the various sources of metals and physico-chemical parameters in soil. STATISTICA software was used to conduct relevant statistical analysis of the data[34].

RESULTS AND DISCUSSION

Mandi- Bahauddin is one of the main cities of Punjab, Pakistan comprising of various industrial units. The industrial unit selected for present investigation comprises of sugar mills and chemical industries producing ethanol and acetic acid *etc*. from molasses obtained as a by-product of sugar mill. Moreover, a nullah flows across this industrial unit which is a dumping site not only for almost all the industrial wastewater of the city but also for domestic sewage discharges. It is not bound

TABLE-1
BASIC STATISTICS FOR PHYSICO-CHEMICAL PARAMETERS OF SOIL SAMPLES (N = 36)

	Moist. Content %	pH	Conduct.	Alkalinity	Cl^-	SO_4^{2-}	NO_3^-	S^{2-}
			µS/cm	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Minimum	1.000	7.9	996	199.2	2.380	7.000	34.56	54.00
Maximum	24.00	8.4	1582	309.8	6.430	21.00	47.30	80.00
Range	23.00	0.5	586	110.6	4.050	14.00	12.74	26.00
Mean	6.790	8.2	1169	262.7	4.420	16.17	42.90	69.00
Median	2.750	8.2	1099	265.6	4.800	18.50	46.98	71.50
S.E.	2.260	0.05	53.50	7.950	0.470	1.490	1.770	2.740
S.D.	7.830	0.17	185.3	27.55	1.640	5.170	6.130	9.490
Kurtosis	0.880	-1.26	0.800	1.990	-1.710	-1.100	-1.650	-1.400
Skewness	1.480	0.22	1.240	-0.760	-0.220	-0.810	-0.810	-0.500
Variance	61.38	0.03	346	759.2	2.690	26.70	37.58	90.18

by any concrete lining rather it has a porous mud lining through which the seepage of hazardous materials may take place to nearby lands and subsequently to groundwater.

The soil was dark brown and grayish in colour with texture varying from sandy to loamy. The basic statistics for physico-chemical parameters of soil samples are presented in Table-1. Soil pH values varied from 7.9 to 8.4, which indicated the alkaline nature of the soil. The alkaline pH makes the trace metals present in the soil to be less mobilized, less biodegradable and more persistant. Consequently, there are lesser chances for the contamination of food chain [35]. Thus the metals like Pb, Co and Ni are persistent in soil at this high pH but a change of conditions from alkaline to acidic nature would cause the release of bulk of metals that will ultimately leach to groundwater thereby contaminating it. No definite trend of the variation of pH with distance from the effluent sources was observed.

Electrical conductivity values of water extract of soil samples varied between 996 and 1582 µS/cm signifying a larger proportion of solublized cations and anions most likely to be produced from the effluents spreading over the adjoining land. The situation is more aggravated by leaching from nearby nullah. The alkalinity ranges from 199.2 to 309.8 mg/kg with mean value of 262.7 mg/kg. The chloride content with a mean value of 4.42 mg/kg present in the soil was due to salt rocks and also from the use of Cl^- bearing salts in sugar processing. The collected soil samples were also found to be rich in sulphate and sulphide (*i.e.* 16.17 mg/kg and 69.00 mg/kg respectively). The sources of these anions was traced in sugar refining process whereby large amounts of SO_2 were used. The nitrate in the soil was present at a mean level of 42. 9 mg/kg.

The distribution of selected metals in soil near industrial unit are depicted in Table-2 as of basic statistical parameters

TABLE-2
BASIC STATISTICAL PARAMETERS FOR THE DISTRIBUTION OF SELECTED METALS (mg/kg) IN SOIL (n = 36)

	K	Mg	Ni	Co	Pb
Minimum	1788	3475	29.00	30.00	27.00
Maximum	5088	4888	69.00	45.50	49.00
Range	3300	1413	40.00	15.50	22.00
Mean	3561	4347	40.46	35.13	37.04
Median	3838	4363	36.00	35.75	37.25
Mode	2888	3475	29.00	37.00	29.00
S.D.	1240	516. 5	14.30	4.463	7.518
S.E.	358	149	4.127	1.288	2.170
Kurtosis	-1.498	-0.798	1.220	1.448	-0.993
Variance	1538365	266736	204.4	19.92	56.52

i.e. mean, median, Standard deviation, standard error, skewness and kurtosis *etc*. All the studied metals *i.e.* K, Mg, Ni, Co and Pb were present at much enhanced levels than their background concentrations (Fig. 2). Among all the metals Mg was present at highest mean level of 4.347 g/kg. It was followed by K, being present at mean level of 3.561 g/kg. Both of these metals were present at 100 folds elevated levels than the background concentrations. The mean Co level observed was thrice as greater as its NEQS value (10 mg/kg). This concentration was too high to cause any health or environmental effect. The comparison indicated that the soils in the adjoining area of the industries had accumulated multi-fold elevated levels of all selected metals with concentrations far exceeding the limit laid down by the world health authorities. These results were parallel to the previous studies[36].

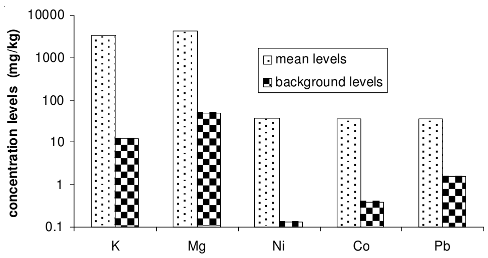

Fig. 2. Comparison of mean metal levels in soils with the background levels

Among the trace metals, Ni was present at highest mean concentration of 40.46 mg/kg against the maximum concentration of 69 mg/kg. Cobalt was observed at mean levels of 35.13 mg/kg. As such Ni and Co are not used in any of the processing of the industrial unit, so either they may have a soil base origin or may leach from nearby nullah. It has also been observed that high cobalt concentration in soils usually leads to high nickel levels which are more toxic than cobalt[37]. The raw material of sugar industry *i.e.* sugarcanes take along with them the residues of various pesticides Since sugarcane is used in bulk, a considerable amount of soil from grown fields is also transported along with them. This soil may be rich in various metals. To date no data are available regarding the metal pollution status of the soil of the area. As monitoring forms the initial step for any remediation strategy, the metal pollution status of soil in this area was determined for the present investigation.

The lead levels in soil ranged from 27-49 mg/kg with mean concentration of 35.88 mg/kg against the background concentration of 1.58 mg/kg. Chemical reagents like lead subacetate used in raw sugar polarization and biocide lead arsenate used for preservation of molasses and other sugar products are potential source of the high concentration of lead in the soil. A larger portion of lead is also contributed from vehicular emissions. Ultimately these enhanced lead levels may lead to probable contamination of groundwater and also the food chain.

All this data evidenced the contamination of the soil in the vicinity of the industrial units by both macro and micro elements which were present in the order: Mg > K > Ni > Pb > Co. This amply signified random intrusion of high levels of metal contaminants from effluent, molasses and other anthropogenic source into the soil. The metal data was found to be random with significantly dissimilar mean and median concentration levels. The standard deviation (SD) values showed a very high dispersion around the mean metal concentrations.

The distribution of different metals in soil samples as a function of distance from the industrial unit was an important segment of present study. A comparison of these metals showed that K and Mg were contaminating the soil to a greater extent (Fig. 3). Although K and Mg are macronutrients but their excess levels are hazardous for normal plant growth in alkaline soil because they compete with soil Ca for availability to plants. Comparatively lower concentration of Ni, Co and Pb were present at peripheral distance of 150 m. Fig. 3 also depicted that the soil from area adjacent to industrial zone was seriously affected by metals up to a distance of 150 m. The concentrations of heavy metals was found to decrease with the increase in the distance from the industry, pointing towards the industry as a potential source of these metals as reported earlier[38-40]. Some irregularities in this pattern were observed in case of Ni and K, which were attributed to the leaching effect of nullah. The total trace metal contents in soils were irregularly distributed as a function of distance.

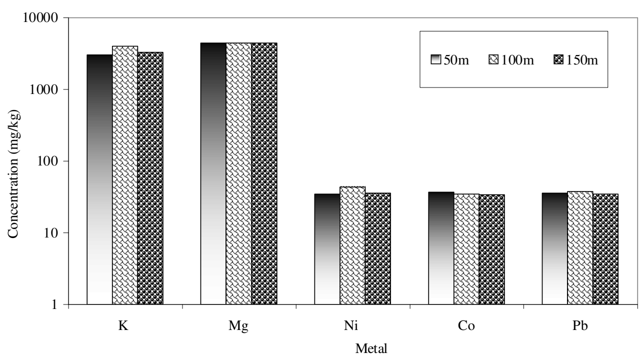

Fig. 3. Mean metal levels in soil as a function of distance from effluent discharge point

Correlation coefficient matrix pertaining to metal-to metal relationships in the soil is presented in Table-3. The metal-to-metal correlation coefficient matrix evaluation yielded r-values which were significant at ±0.279 at a probability of 0.05. A number of metal pairs were found to be mutually associated significantly and positively *i.e.* K and Mg (r = 0.721), K and Ni (r = 0.683) and Mg and Co (r = 0.686). This strong correlation pointed toward a common source for these metals. A weak positive relationship was also observed between the macro-elements and the micro-elements *i.e.* K-Co (r = 0.344) and Mg-Ni (r = 0.312). Naive correlation was identified for the two couples of heavy metals *i.e.* Ni-Co (r = 0.222) and Mg-Pb (r = 0.242).

TABLE-3

CORRELATION COEFFICIENT MATRIX FOR SELECTED METALS IN SOIL (n = 36)

	K	Mg	Ni	Co	
	1.000				
Mg	0.721	1.000			
Ni	0.683	0.312	1.000		
Co	0.344	0.686	0.222	1.000	
Pb	0.325	0.242	0.339	0.351	1.000

r-values > 0.279 or <-0.279 are significant at $p \leq 0.05$

The correlation coefficient values indicting the relationships among the metals and physico-chemical parameters in soil are enlisted in Table-4. Significant positive correlation was observed between moisture content, conductivity and metals and negative correlation with pH. This suggests that a humid soil environment tends to accumulate metals like K, Mg and Pb that formed strong positive correlations with r-values of 0.673, 0.544 and 0.458 respectively. Lead was also found to be significantly, positively correlated with sulphate of soil (r-value = 0.401).

TABLE-4

CORRELATION COEFFICIENT MATRIX FOR SELECTED METALS AND PHYSICO-CHEMICAL PARAMETERS IN SOIL (n=36)

	K	Mg	Ni	Co	Pb
Moist. content	0.673	0.544	0.358	0.351	0.458
pH	-0.781	-0.754	-0.300	-0.179	-0.326
Conduct.	0.592	0.459	0.221	0.221	0.001
Alkalinity	0.424	0.071	0.260	0.030	0.120
Cl^-	0.091	0.001	0.093	-0.249	-0.066
SO_4^{2-}	0.243	0.090	0.210	0.331	0.401
NO^-_3	0.185	0.001	0.212	-0.227	0.003
S^{2-}	0.239	0.005	0.291	-0.073	0.140

r-values>0.279 or <-0.279 are significant at $p \leq 0.05$

The varimax normalized principal component analysis was applied for factor loadings in soil samples according to standard procedure reported in the literature [24]. Accordingly two factors were extracted, together embodying more than 76 % of total variance (Table-5). The first factor represented a major contribution from K and Ni with an eigen value of 2.699 and a total variance of 53.99 %. Lead was another smaller contributor to this factor. Factor 2 with a cumulative eigen value of 3.80 accounted mainly for Mg and Co as the major contributors.

TABLE-5

VARIMAX NORMALIZED PRINCIPAL COMPONENT LOADINGS OF SELECTED METALS IN SOIL SAMPLES

	Factor 1	Factor 2
K	**0.862**	0.330
Mg	0.336	**0.846**
Ni	**0.912**	0.004
Co	0.0154	**0.928**
Pb	0.477	0.445
Eigenval	2.699	1.101
% Total Variance	53.99	22.01
Cumul. Eigen value	2.699	3.800
Cumul. %	53.99	76.01

Actually these metals are discharged simultaneously in the form of effluents and get accumulated onto the soil. A more detailed account of factors is shown by the cluster loading graph (Fig. 4).

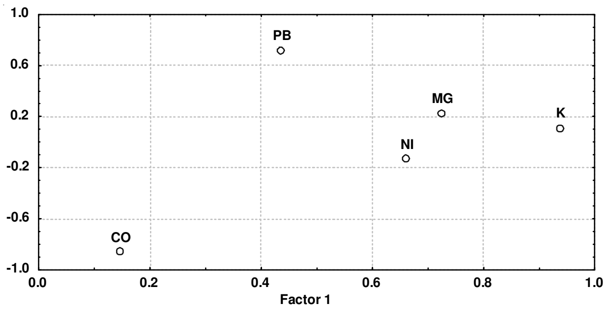

Fig. 4. Factor loading graph

Cluster analysis was used to separate the dataset into various groups on the basis of matrix of concentration values. The dendrogram (Fig. 5.) clearly showed two primary clusters, the first one presented Pb as an isolated source and the second one with K, Mg, Ni and Co. However, these two main clusters comprise heterogeneous grid squares when considering lithologies and activities. The second clusters were thus divided into sub-clusters, reflecting more natural groupings. In this way, it is interesting to analyze the distribution of the variables in sub-clusters based on their common origin.

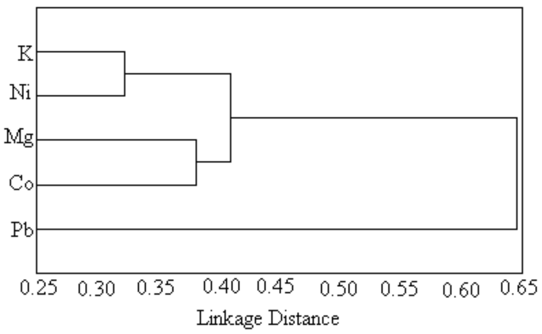

Fig. 5. Dendrograms of cluster analysis for metals in soil

The data set provided hereby not only identifies the potential pollutants arising from sugar cane based industrial units but also the determination of actual levels of heavy metals heterogeneously distributed in the soil provides baseline data for proper legislative and administrative measures towards the ensurance of regulated discharge of the industrial effluents.

Conclusion

This study highlights the metal pollution status of the soils in vicinity of one of the industrial unit of Mandi Bahauddin, Pakistan. The physico-chemical parameters studied characterized the soil as being highly alkaline in nature with high electrical conductance values. Moreover, all the selected macro and micro-elements *i.e.* K, Mg, Ni, Co and Pb were found at much enhanced levels than background levels. The sugar mills and other sugar based industries were therefore acting as the point sources for soil contamination by producing voluminous amounts of wastewater that is being dumped onto open lands. Another major source of these metals was found in leaching of metals from nearby nullah. The study also evidenced multivariate analysis as a powerful tool for studing the point sources for various metals. Thus there is a dire need to plan for a strategy for monitoring and remediation of the soil polluted by various trace metals and to trace the origin of various metals.

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