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Co-Relation and Variability of Metal in Surface Soil of Rapidly Industrialized Area of Rohtak District

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ABSTRACT

Heavy metal concentration in soil of industrial area of Rohtak District was measured to access the soil quality and statistical methods were applied for comparing heavy metal accumulation. Soil samples from different sites of industrial area, Hisar Road Rohtak were analyzed by atomic absorption spectrophotometer to find concentration of selected heavy metal namely: Cu, Zn, Pb, Cd and Ni. Optimized the instrument settings and nebulizer controls for each element so that characteristic concentration of metal is ±20 % of manufacturer specifications, precision of 10 measurements is ≤5% (preferably ≤2%) the optimization process. A coefficient of variance of replicates was less than 2% for all elements. PCA shows first three components of 10 assessed contribute for 62.71% of overall variability in data. PC1 shows high loading of pH, TDS, conductivity and Cd which was might be due to anthropogenic or industrial and traffic activities; PC2 shows high loading of Pb, Zn, and Ni and moderately loaded by Cu which was might be due to geogenic sources and supplemented by solid waste disposed by industries.; PC3 shows high loading of Zn, Cu which was due to variation in geochemical nature of the soil. The most likely source for accumulation of heavy metal in soil near to industries was local industrial activities supplemented by vehicular emissions. The Pearson correlation coefficients of these metal under $p < 0.01$, such as Pb, Zn, Cd, Ni and Cu suggests that contamination takes place due to anthropogenic activities besides the natural components of the soil. There is positive correlation between few metal like Pb ($r=0.383$, $p=0.01$), Cd ($r=0.397$, $p=0.01$) with pH of the soil. A significant positive correlation ($P \leq 0.001$) between metal and different parameters in our case further substantiates this view.

Keywords: Industrialization; Surface soil samples; metal contamination.

INTRODUCTION

The native concentration of heavy metal depends upon geological parent material composition [1]. But the soil quality deteriorates due to various anthropogenic activities. Most of the problems of soil contamination are associated with large amount solid waste containing heavy metals which are disposed on the soil near to industries and vehicular emission on nearby roads[2-3]. The composition of dumps varies from site to site and also depends on peculiarity of the neighborhood. Moreover the soil quality variation greatly influences the availability of metal in the soil. Industrial activities, mining, fossil combustion, waste spills, power generation are the main source of metal contamination in the soil [4-7]. As soil is a dynamic and complex system where any change in the physicochemical characteristics would severely alter the fate of heavy metals in soil. Among the various parameters, pH, TDS and conductance are construed of primary importance which affects the metal concentration in industrial soil and have adverse effect on human health. Thus industrial soil near city is becoming knowledge of parameters governing environmental qualities of urban settings which plays vital role not only in sustainable attainment of human habitats but also understanding the potential influences on human health [8-10].In last few decades many soil surveys were conducted and were reported in scientific literature [11-12].However, in developing countries like India very few such research works have been carried out.

In environmental and geochemical exploration studies, the chemical analysis of such soil samples find important application. Wet chemical methods were used for analysing samples for present study. This is mainly due to better detection limit obtainable from intrumental method like AAS [13-15]. The aim of the present study was to examine physiochemical properties and heavy metal levels in the soil near to industries and also to establish the contamination status of the soil as a result of anthropogenic activities. The knowledge of heavy metal accumulation in soil, origin of these metals and their possible interaction with soil properties are priority objectives in this study. Statistical analysis is important tool for interpretation of data [16-18]. Some selected statistical methods were applied to find the most significant factors for controlling distribution of heavy metal in soil and to identify the possible origin of these metals in soil collected from industrial area, Hisar road Rohtak (Haryana).

EXPERIMENTAL SECTION

2.1 Site description

Rohtak district is located in Haryana; 70 km northwest of New Delhi and 250 km south of the Chandigarh (state capital) at the NH 10. Average annual rainfall in Rohtak city is 458.5mm (18.0 inch). Rohtak's climate shows extreme variation in temperature. In the winter months (November to January), the temperature does not usually fall below freezing point whereas, in summer (April to July), the day temperature generally remains between 30 °C and 40 °C occasionally going up to 48 °C on a few days. For present study 4 different sites of industrial area on Hisar road Rohtak were selected. The site selected for the present study includes small scale industries located on Hisar road Rohtak:

- Site-R: Precision Fasteners Private Limited (PFPL)
- Site-S: Chemical Industry (CI)
- Site-T: Battery cases synthesising industry (BCSI)
- Site-U: Paint industry (PI)

2.2 Soil sampling

64 Soil samples from four different sites were collected quarterly in a year at surface level (5, 10, 15 and 20 cm depths) so as to cover industrial area near Hisar road, Rohtak. At each site, a 50-meter tape was laid parallel to the road (on both sides) of industry. Three quadrates (0.5 × 4 m) were placed at equal distances along the 50-meter tape in each zone. Samples from three quadrates of a zone were mixed together to make a composite sample representative of that zone of a particular site. The soil samples were taken from each quadrate at two points with a stainless steel auger from the top 5–20 cm of the soil. Large stones and plant materials were removed from soil samples. Samples were kept in a thoroughly pre-cleaned polyethylene bottles.

2.3 Reagent

To prepare standards all chemicals of high purity analytical reagent grade were used. For both extraction and acid digestion procedures, Conc.HNO_3, Conc.HCl and H_2O_2 were used. The solutions were prepared by using double distil water. The sample flasks and digestion vessels were soaked into 10% HNO_3 before digestion for 24 hours and then washed with double distil water.

2.4 Digestion procedure

The soil samples were dried at 110^0 C for 3 hours, ground to pass through a 2 mm mesh sieve and homogenized for analysis. A procedure recommended by environmental protection agency (EPA 3050B) was used as conventional extraction method. 1g of soil sample was heated to 95^0C with 10ml of 50% HNO_3 without boiling. After cooling the sample, it was refluxed with repeated addition of 65% HNO_3 until no brown fumes were given off by the sample. Then the solution was allowed to evaporate until the volume was reduced to 5 ml. After cooling 10 ml of 30% H_2O_2 was added slowly without allowing any losses. The mixture was refluxed with 37% HCl at 95^0C for 15 minutes. Distilled water was added and filtered. A clear solution was used for AAS measurement after dilution to 50 ml. The total extraction procedure was lasted for 100-200 minutes.

2.5 Sample analysis
Atomic absorption spectrophotometer (EC Electronics Corporation of India Limited AAS Element AAS-4141) equipped with deuterium lamp for background correction was used for determination of heavy metal concentration in soil. The hollow cathode lamps for Cu, Zn, Cd, Pb, and Ni were employed as radiation source. The flame used was air/acetylene. The parameters for determination of metal concentration were according to the detailed provided in table-1. The quality control was monitored using 10% sample blanks and 10% of sample replicates in each set of sample replicates. A coefficient of variance of replicates was less than 2% for all elements. Optimize instrument settings and nebulizer controls for each element so that characteristic concentration of metal is $\pm$ 20 % of manufacturer specifications, precision of 10 measurements is $\leq$ 5% (preferably $\leq$2%) the optimization process.

pH was determined in soil suspension (soil : double distil water, 1:5 w/v) using Eutech Instruments pH-510 meter while Conductance and TDS were measured by microprocessor based Conductometer [19-24]. Bulk density was determined by cylindrical core method [25] and following formula was used to find bulk density.

$$\text{Bulk density (mg/m}^3\text{)} = \frac{\text{Mass of dry soil (g)}}{\text{Volume of the core (cm}^3\text{)}}$$

Percentage of organic carbon was determined by Walkley and Black method [26].

2.6 Statistical analysis
For statistical analysis, the data was processed by using SPSS PASW statistics 17 and help in assisting inter-elemental relationship among heavy metals. This helps in identifying the groups of metal that correlate and have similar behavior and origin. In order to quantitatively analyze and confirm the relationship between soil properties and metal concentration Pearson's correlation was applied to the data set. Correlation analysis and PCA, based on the correlation matrix, were applied on the data set by using MATLAB and SPSS PASW statistics 17 respectively. The aim of using PCA was to ascertain any patterns in the soil samples in relation to these chemical characteristics, and then to make a preliminary conclusion for finding the possible relationship between heavy metal concentrations and soil properties.

RESULTS AND DISCUSSION

3.1 Concentration of heavy metal in industrial soil
The descriptive statistics of the heavy metal concentrations are summarized in Table-2 after eliminating some abnormal concentrations. High level of Zinc was observed at site -S;Cu at site –T; Pb at site - S; Ni at site –R whereas Cd at site - U. Especially, Zn (629.5mg Kg^{-1}), Cu (7270mg Kg^{-1}), Pb (3449mg Kg^{-1}), Ni (497.15mg Kg^{-1}), and Cd (34.7mg -1Kg) data showed significant increase in concentration than threshold value of Indian Regulatory limit of metal in soil as shown in Table – 3. Such extremely high levels of metal concentration in the soil can found in many industrial areas and waste disposal dumps. This results from localized additions and accidental spillages of concentrated materials [27]. The concentrated metal can be leached into surface water or ground water, taken by plants, which may later affects the human health [28-30].

3.2Physiochemical properties of selected sites
The detailed descriptive summary of all physiochemical parameters was provided in table-4.The soil pH was from 6.61 to 9.39 at site R; 7.1to7.9 at site S; 7.89 to 11.4 at site T; 7.13 to 8.32 at site U whereas electrical conductivity varies from 0.37 to 4.32 mS at site R; 0.34 to 3.03 mS at site S; 0.54 to 6.67 mS at site T; 0.69 to 3.43 mS at site U. TDS was from 0.25 to2.59 ppt at site R, 0.33 to 1.95 ppt at site S, 0.34 to 4.43 ppt at site T, 0.45 to 2.24 ppt at site U. The soil samples were alkaline in most of soil samples as they generally have pH>7. It was reported that pH is an important factor which influences the cation mobility and also regulates the solubility of heavy metal in soil [31]. Most of metal ion tends to be available at acidic pH. Higher soil pH is not favorable for transference of heavy metal from surface soil (0-20 cm) to subsoil (20-40 cm). The mean bulk density of soil inside and outside the industry was found to be 1.097gm $cm^{-3}$and 1.027gm cm^{-3}. Percentage of organic carbon varies from 0.01 to 0.84.

DISCUSSION

4.1 Correlation analysis:

The concentration of heavy metal in soil and their impact on ecosystem was influenced by various parameters such as parent material, climate and anthropogenic activities [32]. Correlation analysis between soil heavy metal concentration and soil parameters will help to trace the origin of elevated levels of heavy metals in soil.

The pH of the soil is greater than 7while% of organic carbon varied from 1.02 to 1.5.In the 64 soil sample, all heavy metals showed no significant relationship except Pb and Zn as summarized in table – 5. TDS has statistically significant linear relation with conductivity, pH, Cu and Cd; out of which conductivity, pH and Cu has positive relation whereas Cd has negative relation. The significant relationships between concentration of heavy metals and different parameters of soil were further substantiated by performing correlation analysis. The correlation coefficients between soil samples and different physiochemical properties as mean of different sampling periods and places were calculated for each metal separately (table-2 and table-4). As seen in table-5 there is positive correlation between few metal like Pb ($r=0.383$, $p=0.01$), Cd ($r=0.397$, $p=0.01$) with pH of the soil. While these relations are not statistically significant for Zn($r=0.005$), Cu($r=0.049$) and Ni ($r=0.243$). Positive relationships between metal content and soil parameters are expected results as pH of soil helps in percolation of metal ion in soil. It was found that TDS of soil shows positive correlation with Cu metal only ($r=0.402$, $p=0.01$), whereas conductivity has positive correlation with Cu ($r=0.396$, $p=0.01$). Few metals like Zn, Pb shows relationship which might be due to association with indigenous clay minerals and constant vehicular emission near to industries.

Nandram and Verloo in 1985 [33] showed that low solubility of Pb, Zn, Cd, and Cu at pH 6 to 6.5 and an increase by several orders at pH 2. Similarly, Pb, Cd, and Zn exhibited weak solubilities at slightly alkaline condition (pH 8) while at pH 3.3 solubility is higher [34]. Furthermore with regard to Cu, Brun etal. 1998 [35] reported decrease in extractable Cu with an increase in soil pH. In light of the above, the near neutral pH in our case perhaps facilitated more complexation of heavy metals with organic carbon, resulting in their accumulation in the top layers. Except for Ni, all the metals showed positive correlations with pH substantiating that the higher the pH, the more the metal retention is and vice versa. Although the mobility of Pb, Zn, Cd, and Mn showed significant positive correlations with pH and organic carbon, the trends were not uniform among all the sites.

Table-1: Parameters for measurement of metal concentration by AAS

Parameters	Pb	Zn	Ni	Cu	Cd
Lamp current (mA)	10	5	3.5	3	3.5
Wavelength (nm)	217	213.9	232	324.8	228.8
Linear Range (mg/l)	0.2-30	0.4-1.5	0.2-20	1.0-5.0	0.01-3
Slit Width (nm)	1.0	0-2	0.2	0-2	0.5
Integration Time(sec.)	3.0	2.0	2.0	2.0	2.0
*Detection Limit (mg/Kg)	0.1	0.005	0.04	0.02	0.005

**Metal concentration for Blank in AAS-4141*

4.2 Principal component analysis:

The data was processed for KMO and Bartlett's test (Table-6) to check the adequacy of the data analyzed. It was found that KMO value of 0.62 so the pattern of correlations which was relatively compact, can be analyzed and yield distinct and reliable factors. Bartlett's test of sphericity with an associated value of $p<0.001$ indicates that we can proceed for PCA analysis.

PCA was used to identify the origin of metal in the soil and % of variance of each of the metal and properties were shown in Table- 7. The results of the factor loaded with the quartimax rotation as well as the eigen values and communalities shows first three components contribute for 62.71% of overall variability in data. The number of principal components were found on the basis of Kaiser Normalization with Eigen value greater than one (figure-1). After varimax orthogonal rotation, these components are related to source of elements in studied samples shown in figure-2.

The first component (PC1) with variance of 29.972% showed loading of pH, conductivity, TDS and Cd which suggested that soil properties helps in accumulating Cd in the soil. Thus Cd accumulation was mainly due to anthropogenic or industrial activities such as improper disposal of solid waste of precision industry and solid carbon disposed on the surface of soil. Application of solid waste from precision industries and tyres abrasion [36] also results in increase in Cd in soil.

Table-2: Main descriptive statistics of metal concentrations of various industrial sites of Rohtak district (n = 64)

Description of various parameters		Pb (mg/Kg)	Cu (mg/Kg)	Zn (mg/Kg)	Cd (mg/Kg)	Ni (mg/Kg)
Site R	Minimum	209.25	3.95	1.50	10.35	52.80
	Maximum	832.50	5690.00	160.50	26.70	497.15
	Mean	451.92	1486.38	62.11	18.38	234.76
	Median	432.65	302.35	55.28	19.38	218.43
	Standard Deviation	211.19	1923.97	51.24	4.97	116.12
Site S	Minimum	174.05	77.25	49.20	13.45	37.05
	Maximum	3449.00	3354.50	629.50	29.75	247.80
	Mean	721.83	1130.18	224.66	18.32	125.20
	Median	400.48	354.73	123.90	17.33	113.55
	Standard Deviation	851.89	1174.49	212.35	3.77	71.53
Site T	Minimum	307.40	3.95	11.70	14.95	65.60
	Maximum	1977.00	7270.00	379.35	18.75	206.25
	Mean	934.14	1432.03	170.30	16.52	131.78
	Median	570.18	208.13	180.93	16.38	124.75
	Standard Deviation	682.48	2298.09	132.98	1.24	40.23
Site U	Minimum	149.40	14.40	9.35	15.00	72.00
	Maximum	878.50	1271.00	589.50	34.70	257.40
	Mean	389.17	502.89	192.12	18.78	154.33
	Median	339.58	417.55	129.90	16.58	148.70
	Standard Deviation	170.49	397.28	175.89	5.40	60.32

Table- 3: Metal concentration in industrial soil

Metals	Selected average for soils (mg/Kg)*	Common Range for soils (mg/Kg)*	Threshold value**
Cu	30	2 - 100	30.0
Zn	50	10 - 300	200.0
Pb	10	2 – 200	100.0
Ni	40	5 - 500	80.0
Cd	0.06	0.01 – 0.70	0.07

**Source: (Lindsay, 1979; Murthy, 2008)*

***Maximum permissible concentration (mg/Kg) in Industrial soil as per Indian government*

Table-4: Descriptive summary of soil physiochemical properties of different industrial sites for collected samples (n = 64)

		TDS (ppt)	Conductivity (mS)	pH	%age OC	Bulk density (g/cc)
Site R	Minimum	0.25	0.37	6.61	0.44	1.26
	Maximum	2.59	4.05	9.39	0.46	1.34
	Mean	1.36	2.08	7.62	0.45	1.29
	Median	1.54	2.31	7.33	0.45	1.28
	Standard Deviation	0.83	1.27	0.84	0.01	0.03
Site S	Minimum	0.33	0.34	7.1	0.79	1.02
	Maximum	1.95	3.03	7.9	0.84	1.1
	Mean	1.01	1.50	7.41	0.81	1.06
	Median	0.96	1.44	7.37	0.81	1.07
	Standard Deviation	0.52	0.85	0.25	0.02	0.03
Site T	Minimum	0.34	0.54	7.98	0.79	1.25
	Maximum	4.43	6.67	11.4	0.84	1.40
	Mean	2.58	3.96	9.84	0.81	1.31
	Median	3.07	4.63	10.19	0.81	1.30
	Standard Deviation	1.42	2.16	1.15	0.02	0.07
Site U	Minimum	0.45	0.69	7.13	0.79	1.27
	Maximum	2.24	3.43	8.43	0.84	1.5
	Mean	1.10	1.82	7.95	0.81	1.39
	Median	0.98	1.81	8.14	0.82	1.41
	Standard Deviation	0.59	0.88	0.41	0.02	0.11

Table-5: Pearson's correlation between metal concentration and soil parameters

		Depth	TDS	Conductivity	pH	Pb	Cu	Zn	Cd	Ni
Depth	Pearson Correlation	1								
	Sig. (2-tailed)									
	N	64								
TDS	Pearson Correlation	-0.121	1							
	Sig. (2-tailed)	0.339								
	N	64	64							
Conductivity	Pearson Correlation	-0.13	.994**	1						
	Sig. (2-tailed)	0.306	0.000							
	N	64	64	64						
pH	Pearson Correlation	0.042	.709**	.711**	1					
	Sig. (2-tailed)	0.741	0.000	0.0000						
	N	64	64	64	64					
Pb	Pearson Correlation	-0.169	0.088	0.063	.383**	1				
	Sig. (2-tailed)	0.182	0.489	0.622	0.002					
	N	64	64	64	64	64				
Cu	Pearson Correlation	-0.07	.402**	.396**	0.049	-0.091	1			
	Sig. (2-tailed)	0.585	0.001	0.001	0.698	0.476				
	N	64	64	64	64	64	64			
Zn	Pearson Correlation	-0.159	-0.102	-0.123	0.005	.395**	0.039	1		
	Sig. (2-tailed)	0.21	0.423	0.334	0.968	0.001	0.762			
	N	64	64	64	64	64	64	64		
Cd	Pearson Correlation	0.103	-.441**	-.443**	-.397**	-0.1	0.028	-0.051	1	
	Sig. (2-tailed)	0.419	0.000	0.000	0.001	0.43	0.824	0.691		
	N	64	64	64	64	64	64	64	64	
Ni	Pearson Correlation	0.06	0.052	0.056	-0.243	-.285*	0.182	-0.187	0.008	1
	Sig. (2-tailed)	0.637	0.681	0.66	0.053	0.023	0.15	0.14	0.952	
	N	64	64	64	64	64	64	64	64	64

***. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed).*

Table-6: KMO and Bartlett's test of adequacy for factor analysis for data set of industrial soil (n = 64)

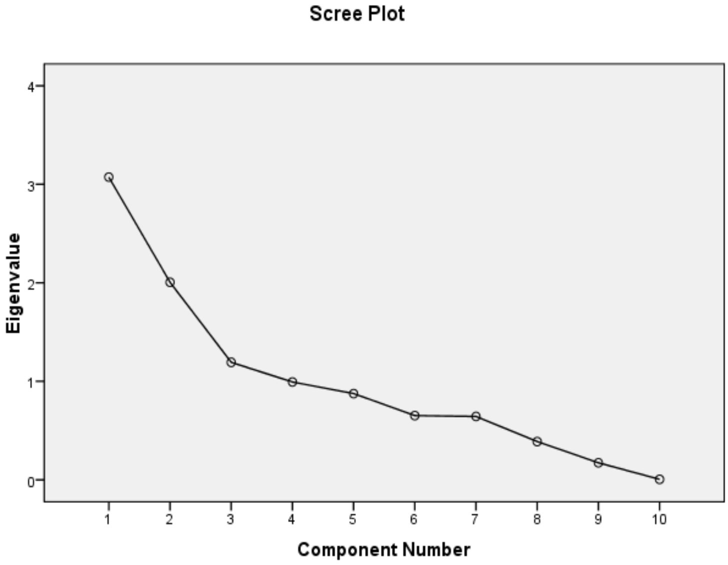
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.628
Bartlett's Test of Sphericity	Approx. Chi-Square	415.279
	Df	45
	Sig.	.000

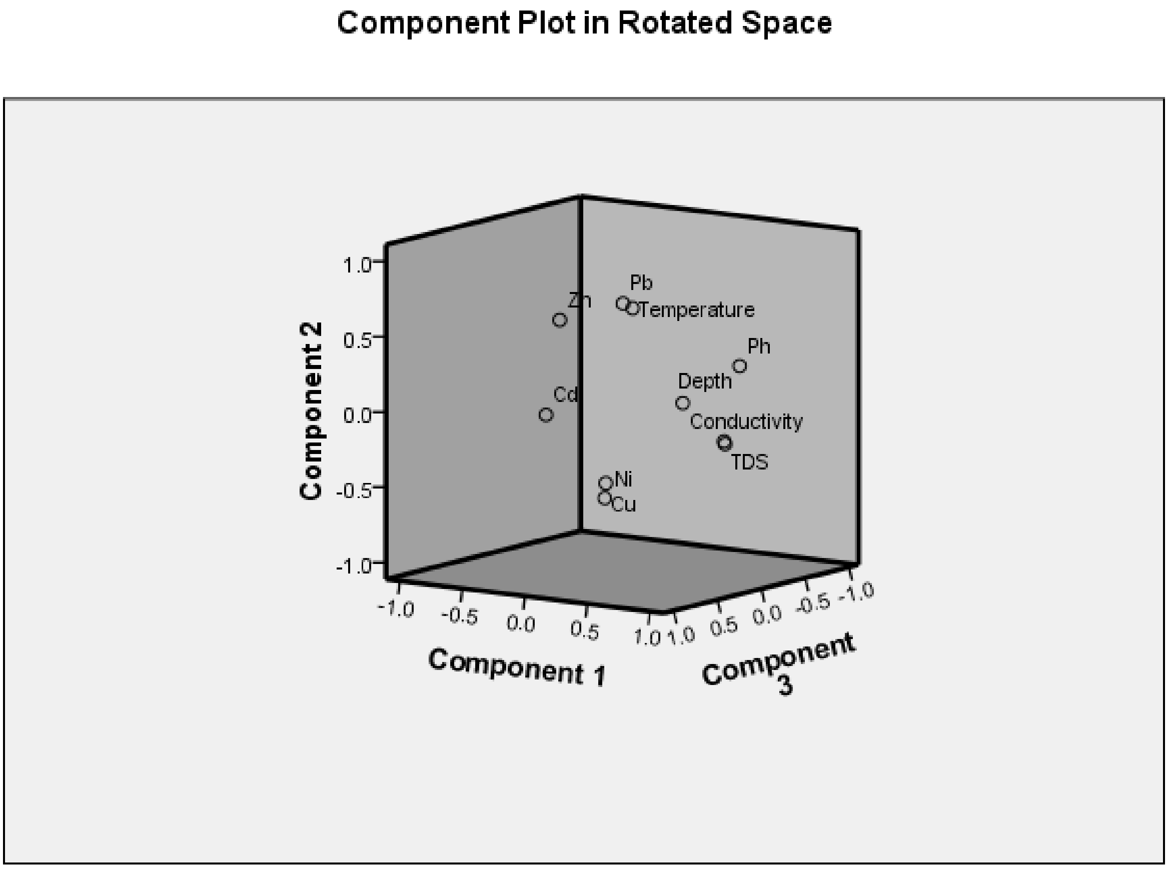
Table-7: Varimax-rotated component loadings of extracted factors and percentage of variance explained for industrial area of Rohtak district

	Component		
	1	2	3
TDS	.947	-.194	.015
Conductivity	.946	-.214	.007
Ph	.850	.325	-.314
Cd	-.590	-.067	.149
Pb	.266	.722	.132
Temperature	.067	.634	-.132
Zn	-3.235E-5	.620	.501
Ni	-.065	-.606	.191
Depth	-.161	-.142	-.713
Cu	.361	-.408	.590
Total	2.997	2.005	1.269
% of variance	29.972	20.052	12.686
Cumulative %	29.972	50.024	62.710

Extraction method: Principal component analysis

Fig.-1: Scree plot showing all rotated components





The second component (PC2) showed 20.052% of total variance and showed loading of Pb, Zn and Ni. It is also moderately loaded by Cu and pH. It suggested that these four elements were affected by anthropogenic industrial activities in addition to the original content of the soil. This component arises from different source such as solid waste of battery synthesizing industry which was supplemented by vehicular emission. The Pearson correlation coefficients of these metals under $p < 0.01$, such as Pb, Zn, Ni and Cu suggested that contamination takes place due to anthropogenic activities besides the natural components of the soil.

The third component (PC3) alone explained 12.686% of total variance of our result and showed loading of Cu, Zn with depth. This suggested that both metal have common origin and the value also suggested that contamination of these metals were not solely related to anthropogenic industrial activities but can be due to local anomalies and natural deposition of metal in soil.

CONCLUSION

PCA reduces the dataset into three major components representing the different origin of metal in the industrial soil. The solid waste dumped on the soil without pretreatment results in deposition of metal in the soil. PC1 with high loading of Cd, pH, TDS, conductivity is attributed due to anthropogenic or industrial and traffic activities. PC2 with high loading of four metals is attributed dominantly due to geogenic sources and supplemented by solid waste disposed by industries.PC3 is mainly due to variation in geochemical nature of the soil due to various parameters. A significant positive correlation ($P \leq 0.001$) between metal and different parameters in our case further substantiates this view.

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