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Chemometric Evaluation of Heavy Metals in Agricultural Soil through PCA and CA Multivariate Statistical Approaches

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ABSTRACT
Concentration of heavy metals (Mo, Ni, Pb, Zn, Cu, Cd and As) along with other physicochemical parameters such as pH, temperature, electrical conductivity (EC), total dissolve solids (TDS) and organic matter (OM) in fifteen agricultural sites of Bareilly were investigated in this study. The average concentrations of heavy metals in studied soil samples were found as 25.28, 14.67, 11.96, 147.4, 135.6, 4.79 and 0.0024 mg/kg for "Mo, Ni, Pb, Zn, Cu, Cd and As" respectively. Multivariate analysis (PCA, CA) and correlation matrix used in this study provided important tools for better understanding of the source identification and dynamics of these contaminants. The PCA applied on the studied heavy metals identified two components. Among them PC1 was loaded with Mo, Pb, Zn, Ni and Cu. These were related to different anthropogenic sources (agricultural applications and vehicle emissions). PC2 was loaded with As and Cd which were related to natural and agrochemical sources. A positive correlation was observed by Pearson correlation coefficient among Pb, Mo, Cu, Ni and Zn. Negative correlation was observed for As with other metals, while positive for Cd. Temperature and organic matter showed positive relations with most of the metal when compared with other physicochemical parameters. pH had positive but weak correlation with Pb and As.
Keywords: *Heavy metals, Principal components, Cluster analysis, Correlation matrix*

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INTRODUCTION

Heavy metals can severely destruct the environment due to their toxicity and ability to persist and bio-accumulate in surroundings [1]. However the heavy metals are present naturally in soil, some anthropogenic activities such as uncontrolled emission from industries, mining process, use of waste water in irrigation and overuses of agrochemicals (fertilizers and pesticides), vehicle emissions and the combustion of fossil fuels constantly increasing the concentrations of heavy metals in agricultural soils [2], which is a highest concern because of food safety, health hazards as well as its damaging effects on soil ecosystems [3]. The physicochemical properties of soil such as pH, temperature, organic matter and salinity are the most significant parameters regulating the accumulation and the availability of heavy metals in soil [4]. Hence it is required to assess the relationship among these parameters and heavy metal concentrations in soil along with identification of their source. Principal component analysis (PCA) and cluster analysis (CA) are useful statistical approaches to determine common patterns in data distribution resulting in reduction of datasets and serving its interpretation [5]. PCA has been commonly used to identify the source of different pollutants. It can excellently decrease the number of variables and effectively explore the relationships among different variables [6]. Usually, if the correlations between heavy metals is significant then it is said to be the source of heavy metals is common, whereas weak correlations indicate different origins. CA is often coupled to PCA to provide groupings of different variables according to distances or similarity indices [7-11]. Therefore these two approaches will help to identify the heavy metal sources and allocate natural or anthropic origin of pollutant. Bareilly is an agricultural city and roadside agricultural regions are often being used for crop production, such as rice, bajra, maize, and sugarcane. Bareilly has a gross cropped area of 533.287 '000 ha. Determination of heavy metals in roadside agricultural soil is now an increasing demand due to bio-amplification of heavy metals in the food chain and their potential health impact. Therefore, the objectives of this study were (i) to measure the concentrations of heavy metals (As, Cd, Cu, Pb, Mo, Ni, Zn) in roadside agricultural soils of Bareilly; (ii) to determine correlations between heavy metals and other physicochemical parameters and (iii) to define their natural/anthropogenic sources using multivariate statistical methods. It is expected that the study would provide a baseline data regarding the distribution, accumulation, and sources of heavy metals in agriculture soil of Bareilly city.

MATERIALS AND METHODS

The study area and sampling sites

Bareilly is a district situated in Northern U.P, India. It is lying between 78°23'E longitude East and 28°10'N latitude North and spreading in 4120 km^2 (Fig. 1). The weather of Bareilly is humid with an average annual temperature of 25° C (77° F) and average monthly temperature range from 14° C to 33° C (58° F to 92° F). The average rain fall is nearly 1714 mm. The three agricultural regions were selected for sample collection. A total of 45 samples were collected from these area.

Region 1 (R1) = Bareilly - Nainital road (NH530): Site S1, S2, S3, S4, S5

Region 2 (R2) = Bareilly - Faridpur road (NH30): Site S6, S7, S8, S9, S10

Region 3 (R3) =Bareilly - Lucknow road: Site S11, S12, S13, S14, S15

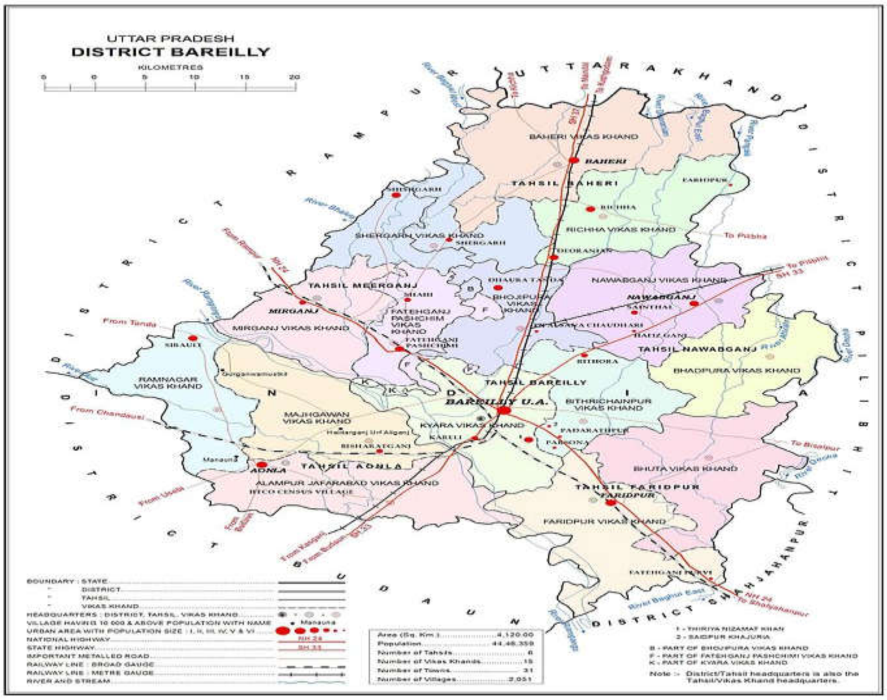


Fig1. Map showing the study area

Sampling and analytical procedures

Soil samples were collected from the uppermost 2 cm soil using a trowel. In laboratory, soil samples were oven dried at 60° C and screened through a sieve having a pore size of 2 mm. The hydrogen ion concentration (pH), temperature, electrical conductivity (EC), total dissolved solids (TDS) in collected samples were analyzed by pH/EC meter (Oakton, Multi-parameter PCSTestr™ 35), while organic matter (OM) has been analyzed by Walkley-Black method [12]. Nitric–perchloric acid digestion method was performed for digestion of soil samples, following the procedure suggested by AOAC [13]. Soil samples were analyzed for metals like ''Mo, Ni, Pb, Zn, Cu, Cd and As'' against their standard curve through Atomic Absorption Spectrophotometer (ECIL 4141). The manufacturers' protocol was followed for the same.

Statistical analysis

Minitab 19.0 software was utilized for the descriptive and multivariate statistical analysis.

Descriptive analysis

Descriptive data such as mean, standard deviation (SD), minimum and maximum concentrations, skewness, variation coefficient (CV) etc. was carried out. SD, CV and skewness were used to reveal the degree of distribution of different heavy metals. In addition, correlation coefficients were calculated to determine the relationships among different variables [11, 14]. For the analysis of correlation coefficients, Pearson's product-moment correlation coefficient (r) was used.

Multivariate analysis

Principal component analysis (PCA) has been used to identify the sources of heavy metals on studied sites [6, 11, 14, 15], while Cluster analysis (CA) used to identify different geochemical groups by clustering the samples with a similar heavy metal content [11, 14]. The Ward's method of linkage and Euclidean distance (similarity measure) were used in CA analysis, as they provide better separation between different clusters [11].

RESULTS AND DISCUSSION

Status and descriptive analysis of physico-chemical parameters and heavy metal concentrations in agricultural soil

Table 1 and 2 summarizes the concentrations of physicochemical and heavy metal contents in agricultural soil. Table 3 summaries the pollution status of different sites. The mean concentration of pH was 7.6 (Range 6.4 - 8.8) and that of temperature was 25.03° C (Range 22 - 31° C). EC (Range 25.6 - 183 µS/cm) and TDS (Range 9.78 - 129 ppm) have mean concentration of 103.99 µS/cm and 69.43 ppm respectively. The percent organic matter had the mean concentration of 3.75 % (Range 0.69 - 7.99 %). The average concentrations of heavy metals were found as 25.28 mg/kg (Mo), 14.67 mg/kg (Ni), 11.96 mg/kg (Pb), 147.4 mg/kg (Zn), 135.6 mg/kg (Cu), 4.79 mg/kg (Cd), and 0.0024 mg/kg (As). The range of heavy metals were observed as: Mo (27.09 - 53.37 mg/kg), Ni (14.89 - 41.32 mg/kg), Pb (0.57 - 37.7 mg/kg), Zn (10.27 - 290.5 mg/kg), Cu (4.16 - 355.12 mg/kg), Cd (0.18 - 9.66 mg/kg) and As (0.001 - 0.004 mg/kg).

Table 1: Physicochemical parameters of agricultural soil

Sites	Samples	Parameters				
		pH	Temp. °C	EC µS/cm	TDS (ppm)	Organic matter %
Region 1 (R1)						
S1	1	7.5	29	140	96	5.14
	2	7.0	28	99	32	5.09
	3	7.2	30	121	73	4.44
S2	4	7.6	30	69	28	3.55
	5	7.2	31	115	83	2.81
	6	7.1	30	94	66	2.02
S3	7	7.5	30	83	58	3.87
	8	7.2	31	77	54	3.75
	9	7.4	31	135	100	5.29
S4	10	7.2	29	107	82	4.34
	11	7.2	30	110	77	3.98
	12	7.2	30	178	122	2.38
S5	13	7.2	31	156	98	7.21
	14	7.2	29	177	81	7.45
	15	8.5	28	183	129	7.99
Region 2 (R2)						
S6	16	8.2	23	109	83.2	5.21
	17	8.4	23	72.4	49.6	4.05
	18	8.2	22	81.7	56.9	4.78
S7	19	8.8	23	55.6	38.7	6.32
	20	8.5	24	64.4	41.7	6.15
	21	8.4	23	103.2	72.4	5.74
S8	22	7.9	23	46.9	34.5	3.04
	23	8.1	23	68.4	42.8	3.66
	24	7.6	22	80.1	61.9	2.84
S9	25	7.2	23	35.7	21.4	1.92
	26	7.8	22	32.5	17.2	1.67
	27	7.6	22	25.6	9.78	1.24
S10	28	8.5	22	77.4	55.6	0.69
	29	7.1	23	58.2	40.1	1.02
	30	7.9	23	93.7	62.8	0.77

Region 3 (R3)						
S11	**31**	7.2	23	120	90.1	6.01
	32	7.5	22	131	106	5.76
	33	7.4	22	91.4	68.4	5.28
S12	**34**	7.1	23	102	76.2	1.16
	35	7.3	24	86.2	50.4	1.22
	36	7.5	22	112	81.7	1.71
S13	**37**	8.1	22	97.1	64	4.11
	38	7.4	22	139	92	4.78
	39	8.6	22	121	83.6	5.36
S14	**40**	6.9	22	154	105	2.98
	41	7.2	23	127	96.1	3.06
	42	7.9	22	115	85.5	3.59
S15	**43**	8.5	23	147	98.2	2.01
	44	7.5	23	132	74.7	1.56
	45	8.1	23	156	84.5	1.67

Table 2. Heavy metal concentrations in agricultural soil

Sites	Samples	Heavy metals (mg/kg)						
Region 1 (R1)								
		Mo	**Ni**	**Pb**	**Zn**	**Cu**	**Cd**	**As**
S1	**1**	48.65	13.48	8.98	278.43	108.43	4.71	ND
	2	37.68	9.56	5.06	264.52	100.06	4.04	ND
	3	44.23	8.88	5.75	231.45	78.55	5.87	ND
S2	**4**	21.76	22.17	6.87	211.04	284.31	5.32	ND
	5	23.94	15.03	7.31	221.02	267.09	4.61	ND
	6	21.85	21.45	7.72	244.72	268.62	5.22	ND
S3	**7**	52.06	18.04	16.42	264.32	135.88	4.28	ND
	8	46.91	13.81	12.25	272.78	101.75	4.71	ND
	9	53.37	19.31	18.87	231.45	106.41	4.34	ND
S4	**10**	23.64	9.78	10.52	188.57	321.9	3.47	ND
	11	21.77	6.77	10.21	176.24	311.69	3.08	ND
	12	23.54	10.05	13.51	189.65	310.51	3.31	ND
S5	**13**	10.05	31.52	31.28	253.39	164.11	9.66	ND
	14	7.76	28.55	31.99	278.41	145.71	9.12	ND
	15	13.44	29.14	37.7	290.5	144.39	9.41	ND
Region 2 (R2)								
S6	**16**	51.28	12.67	30.22	201.56	140.27	6.48	ND
	17	49.13	14.01	31.07	206.31	127.22	5.07	ND
	18	23.05	10.36	35.45	211.67	146.21	6.79	ND
S7	**19**	39.06	18.49	12.56	178.22	291.03	5.09	ND
	20	33.76	12.42	12.52	161.06	301.32	4.18	ND
	21	33.02	13.65	10.23	177.02	257.78	5.65	ND
S8	**22**	41.21	9.16	16.49	232.66	145.06	3.86	ND
	23	37.82	9.78	14.85	231.81	120.08	3.34	ND
	24	34.41	10.05	12.38	210.32	121.87	3.01	ND
S9	**25**	27.52	10.04	21.57	186.23	121.18	7.34	ND
	26	27.67	12.57	26.69	156.05	132.47	7.56	ND
	27	28.02	12.01	21.33	177.03	120.34	6.21	ND
S10	**28**	23.63	35.11	14.78	128.45	337.24	2.66	ND
	29	27.05	32.67	10.44	121.26	341.65	0.87	ND
	30	26.86	26.84	10.17	137.28	355.12	1.54	ND
Region 3 (R3)								
S11	**31**	24.58	18.76	1.4	45.21	15.44	3.34	ND
	32	31.02	18.01	0.91	41.02	12.11	3.52	ND
	33	27.37	17.92	0.88	44.36	15.26	4.11	ND
S12	**34**	12.34	12.02	3.04	10.36	4.73	8.26	ND
	35	11.26	10.66	2.16	11.72	4.16	7.81	ND
	36	12.89	12.89	2.93	10.97	4.58	8.52	ND

S13	**37**	16.64	5.81	0.57	22.14	10.25	0.18	ND
	38	14.43	5.11	0.91	22.77	12.62	0.92	ND
	39	16.27	4.89	0.66	20.12	16.28	2.14	ND
S14	**40**	ND	6.28	0.79	17.14	14.65	1.21	ND
	41	ND	11.26	5.01	13.39	18.21	1.78	ND
	42	ND	12.01	4.96	10.27	14.72	2.36	ND
S15	**43**	5.65	11.73	4.11	10.88	20.46	6.09	0.004
	44	5.07	8.22	2.02	18.21	15.32	7.11	0.001
	45	5.89	7.13	2.67	19.6	15.87	7.26	0.002

*ND= not detected

Table3. : Minimum and maximum concentrations of heavy metals at different sites and their status in soil

Parameters	Min	Site	Max	Site	Permissible limit*	Status
pH	6.9	S14	8.8	S7	4-8.5**	Under limit
Temp° C	22	--	31	--	--	--
EC (µS cm^{-1})	25.6	S6	183	S5	4.0 ms/cm**	Under limit
TDS (ppm)	17.2	S6	129	S5	--	--
OM %	0.69	S10	7.99	S5	>0.86**	Good amount of organic matter
Zn (mg/kg)	10.27	S14	290.5	S5	300	Under limit
Cu (mg/kg)	4.16	S2	355.12	S10	100	Beyond limit in R1 and R2 region
Mo (mg/kg)	5.07	S5	53.37	S13	57#	Under limit
As (mg/kg)	0.001	S15	0.004	S15	20	Under limit
Cd (mg/kg)	0.18	S3	9.66	S5	3	Beyond limit except S10, S13, S14
Ni (mg/kg)	4.89	S3	35.11	S10	50	Under limit
Pb (mg/kg)	0.57	S3	37.7	S5	50	Under limit

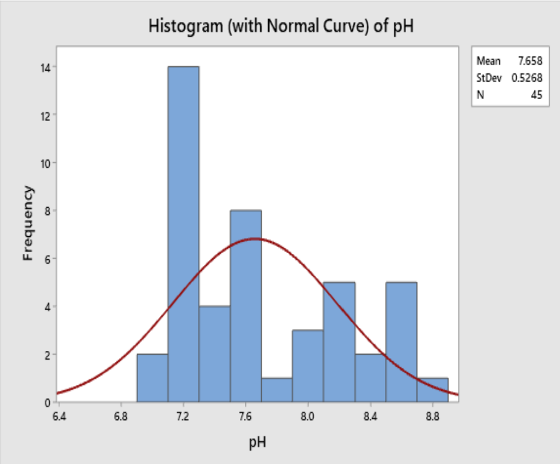
* According to WHO/FAO, 2001 [16] #According to USEPA, 1993 [17]; **International agricultural soil standards [18]

Table 4. Descriptive analysis (Data set 1)

Variable	N	Mean	SE Mean	St Dev	Variance	Coef Var	Sum of square	Minimum	Q1
pH	45	7.6578	0.0785	0.5268	0.2775	6.88	2651.0800	6.9	7.2
Temp.	45	25.022	0.522	3.5	12.249	13.99	28714	22	22
EC	45	103.99	5.77	38.71	1498.3	37.22	552541.39	25.6	77.2
TDS	45	69.42	4.1	27.52	757.51	39.65	250202.77	9.78	50
OM	45	3.748	0.287	1.924	3.701	51.32	795.042	0.69	1.965
Mo	45	25.28	2.22	14.9	221.92	58.93	38520.5	0	13.16
Ni	45	14.67	1.14	7.63	58.16	51.99	12241.3	4.89	9.78
Pb	45	11.96	1.56	10.48	109.74	87.59	11265.51	0.57	2.99
Zn	45	147.4	14.6	97.9	9591.7	66.46	1399318.9	10.3	22.5
Cu	45	135.6	17.2	115.5	13331.3	85.14	1414254.3	4.2	15.7
Cd	45	4.787	0.361	2.42	5.858	50.56	1288.901	0.18	3.195
As	45	0.00016	0.0001	0.00068	0	432.45	0.000021	0	0

Table 5. Descriptive analysis (Data set 2)

Variable	Median	Q3	Maximum	Range	IQR	Mode	N for Mode	Skewness	Kurtosis
pH	7.5	8.1	8.8	1.9	0.9	7.2	11	0.61	-0.94
Temp.	23	29	31	9	7	23	15	0.75	-1.3
EC	103.2	132	183	157.4	54.3	115, 121, 156	2	0.06	-0.41
TDS	73	87.8	129	119.22	37.8	*	0	-0.16	-0.38
OM	3.75	5.25	7.99	7.3	3.28	1.67, 4.78	2	0.22	-0.78
Mo	23.94	36.1	53.37	53.37	22.88	0	3	0.17	-0.73
Ni	12.42	18.3	35.11	30.22	8.49	9.78, 10.05, 12.01	2	1.19	0.74
Pb	10.21	16.5	37.7	37.13	13.47	0.91	2	0.99	0.06
Zn	177	231	290.5	280.2	209	231.45	2	-0.3	-1.47
Cu	121.2	262	355.1	351	246.8	*	0	0.54	-1.02
Cd	4.61	6.64	9.66	9.48	3.44	3.34, 4.71	2	0.19	-0.63
As	0	0	0.004	0.004	0	0	42	4.96	26.11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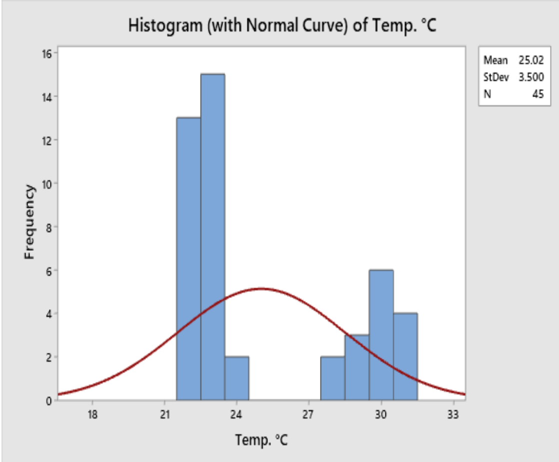
StDev 0.5268
N 45
Frequency
pH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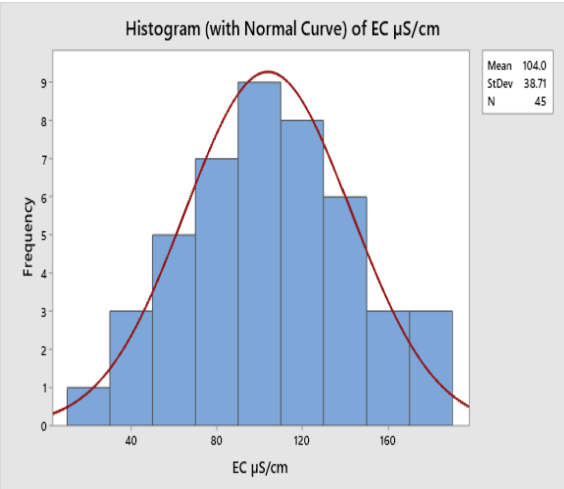
N 45
Frequency
Temp. °C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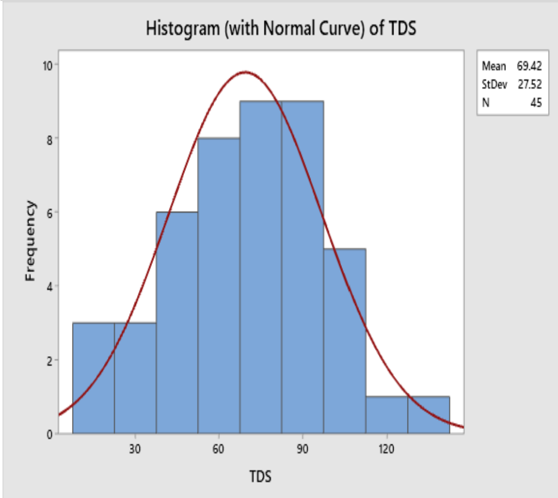
Mean 104.0
StDev 38.71
N 45
Frequency
EC µS/cm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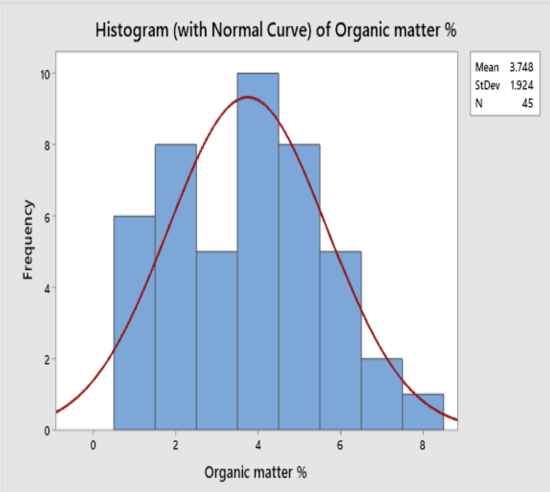
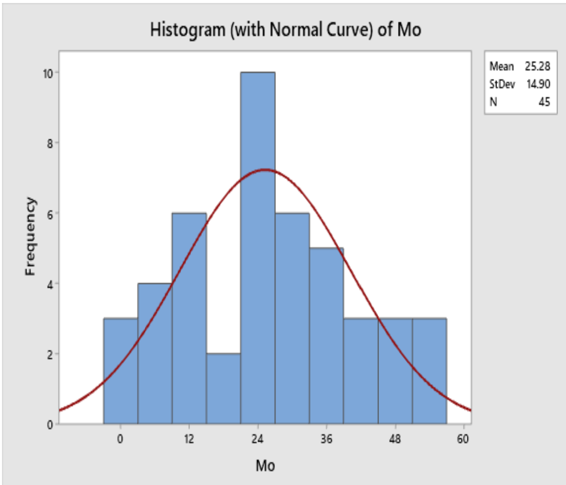
StDev 27.52
N 45
Frequency
TDS


Histogram (with Normal Curve) of Organic matter %
Mean 3.748
StDev 1.924
N 45
Frequency
Organic matter %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Mean 25.28
StDev 14.90
N 45
Frequency
Mo

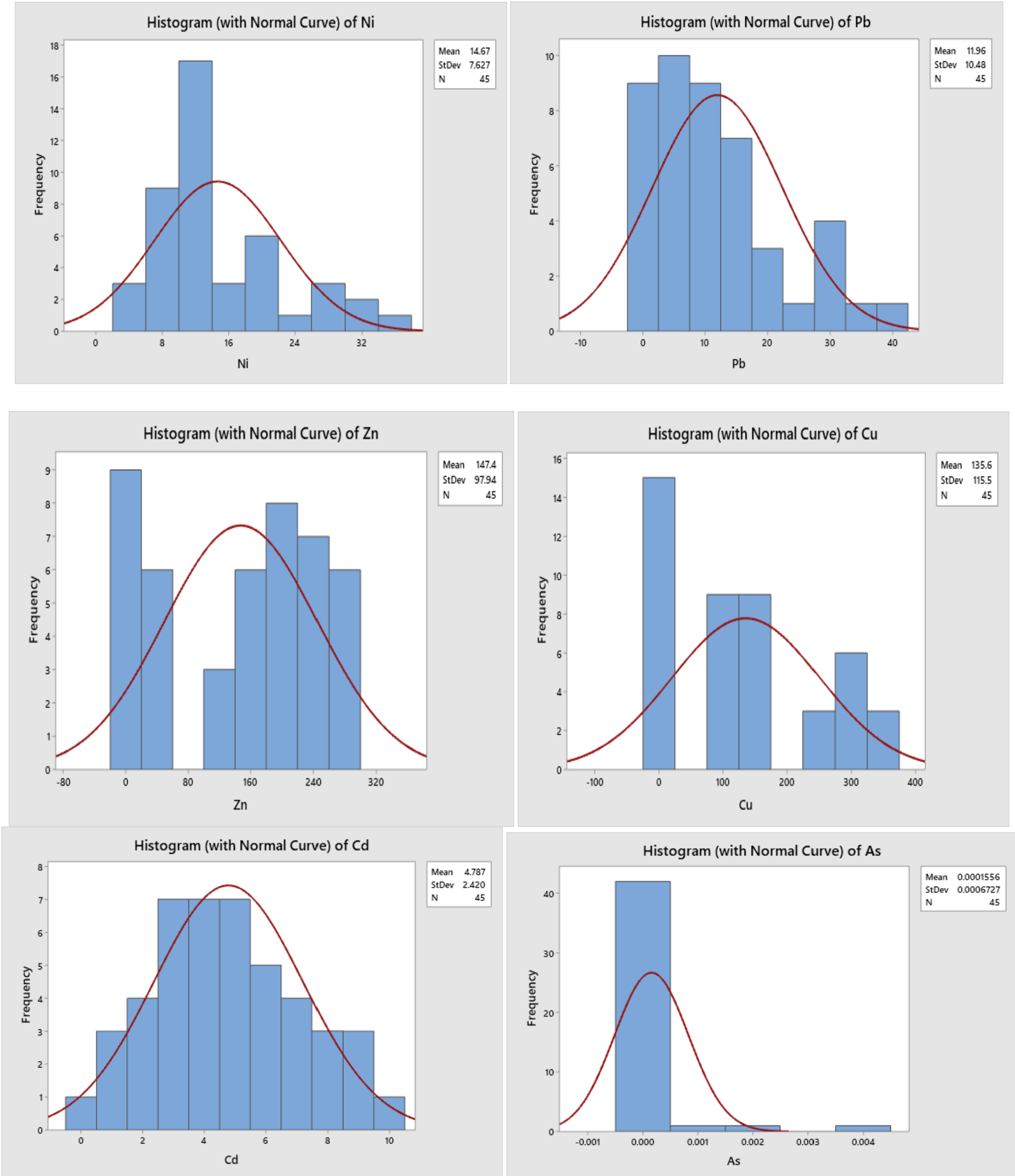


Fig 2. Graph showing mean concentrations of different parameters and skewness of the curve

Correlation analysis

Table 6 summarizes the Pearson's correlation coefficients (r) for the ecological parameters and heavy metals. The results showed that Mo and Pb were weakly and positivity correlated with temperature and organic matter (OM %), while negatively correlated with electrical conductivity (EC) and total dissolved solids (TDS). Ni is positively correlated with all factors except pH. There was a slight correlation observed between Mo, Ni, Cd, Cu and Zn with pH. A significant correlation was found between Zn, temperature and organic matter (OM). Cu was negatively correlated with EC, TDS and organic matter, while positively with pH and temperature. Cadmium (Cd) exhibited a significant relationship with pH, temperature, EC and OM %. Arsenic (As) had positive correlation with pH, EC and TDS, while negative with temperature and organic matter. Correlation coefficients among the heavy metals are also given in table 6. A good correlations were observed between many of the heavy metals. For instance, Pb concentrations was significantly correlated to most of the metals, especially Mo, Cu, Ni, Zn and Cd.

Significant correlations suggest a common source [7, 19]. A very weak positive correlation was found between Mo and Ni (r=0.040). This may suggest that these heavy metals in soil were came from unrelated sources. Cd was negatively correlated with Mo (r= -0.084) and Cu (r= -0.129). On the contrary, arsenic (As) exhibited negative or non-significant correlations with all other metals except Cd (r=0.174).

Table 6. Pearson correlation coefficient (r*) among physicochemical parameters and heavy metal concentrations

Variables	pH	Temp.	EC	TDS	OM	Mo	Ni	Pb	Zn	Cu	Cd
Temp.	-0.462										
EC	-0.158	0.307									
TDS	-0.104	0.211	0.921								
OM	0.180	0.279	0.364	0.334							
Mo	0.117	0.26	-0.42	-0.336	0.207						
Ni	0.028	0.237	0.045	0.03	0.133	0.04					
Pb	0.250	0.19	-0.1	-0.133	0.308	0.288	0.38				
Zn	-0.038	0.662	-0.138	-0.212	0.353	0.631	0.321	0.665			
Cu	0.110	0.367	-0.255	-0.24	-0.04	0.285	0.462	0.317	0.539		
Cd	0.030	0.2	0.108	-0.023	0.118	-0.084	0.178	0.483	0.248	0.129	
As	0.263	-0.137	0.265	0.185	-0.234	-0.312	-0.147	-0.193	-0.321	-0.24	0.174

(*0.05>P, Cl=95%)

0.0 to ± 0.20 : no or slightly correlated
±0.20 to ± 0.40 : weak correlation
±0.40 to ± 0.70 : real significant correlation
± 0.70 to ± 1.00 : high or very high correlation [20]

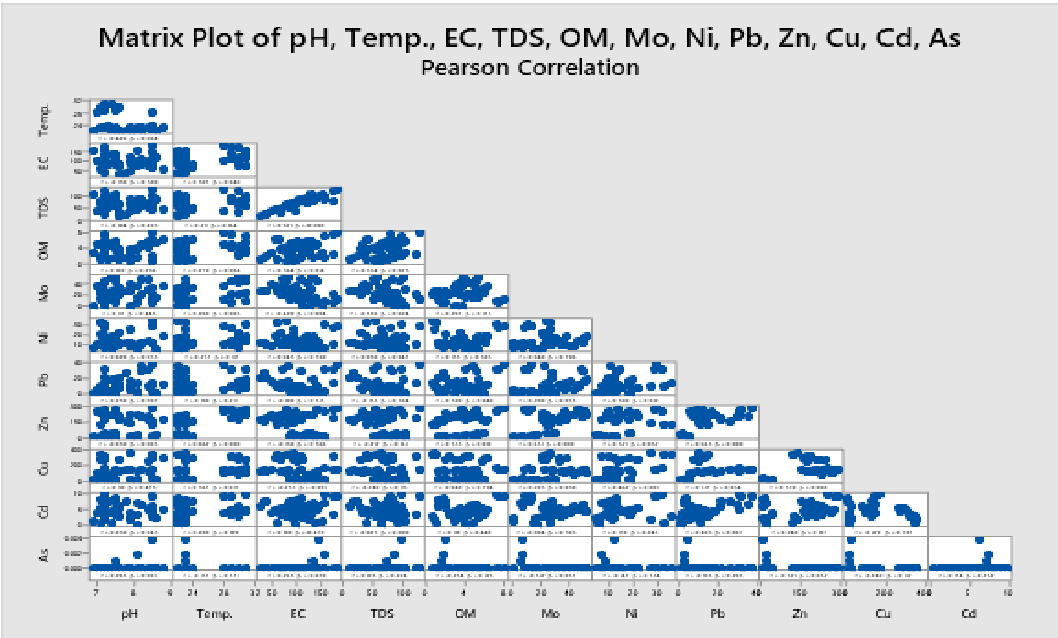


Fig 3. Correlation matrix plot for different studied variables

Multivariate Analysis

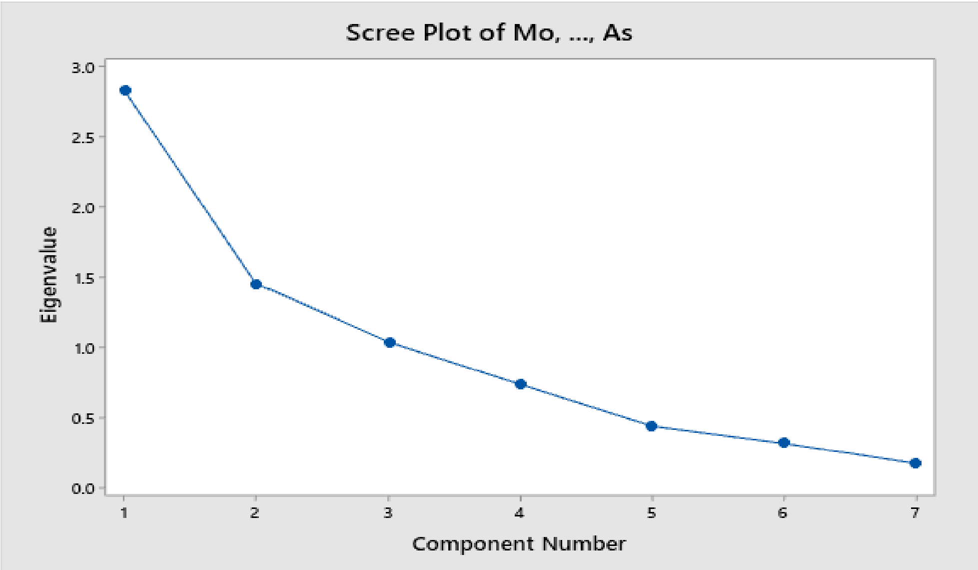
Principal Component Analysis:

By the evaluation of eigenvalues and eigenvectors from the correlation matrix, the number of important principal components and their variance percentage can be determined (Table 7). The first two eigenvalues revealed 61.3 % of the total variance, indicating that they are the most significant components. The first component revealed 40.5 % of the total variance and had the highest loads of Mo, Ni, Zn, Pb and Cu. Second component had the highest loads of As and Cd showing 20.8 % of the total variance. The factor loadings are presented along with the variance percentage by each component in table 7.

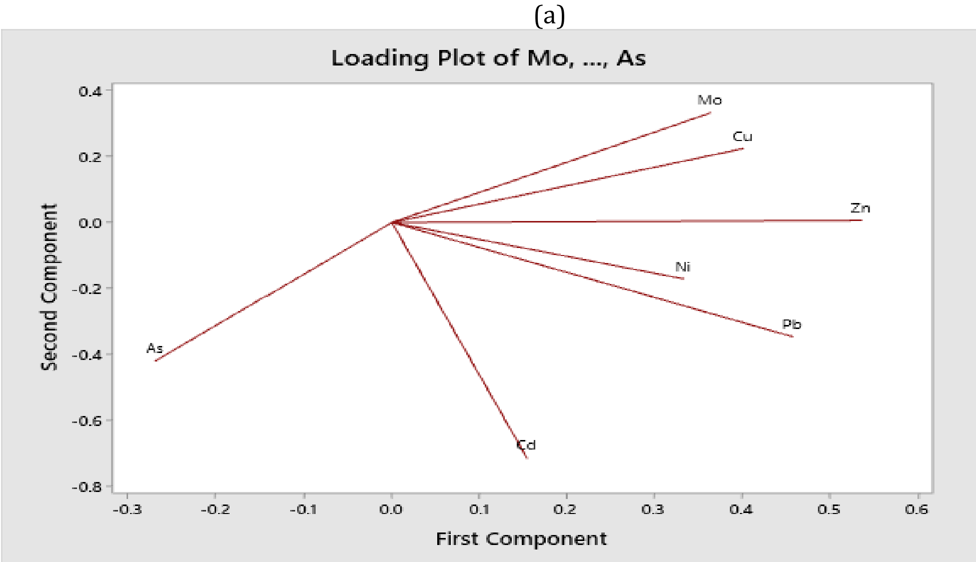
Table 7. Total variance and component matrixes (two factors selected) for heavy metals.

Heavy metal	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Mo	**0.365**	0.333	0.488	-0.306	-0.513	0.084	-0.392
Ni	**0.334**	-0.172	-0.659	0.112	-0.635	-0.064	0.075
Pb	**0.459**	-0.347	0.132	0.12	0.257	-0.7	-0.285
Zn	**0.536**	0.006	0.218	-0.173	0.108	0.08	0.786
Cu	**0.402**	0.224	-0.461	-0.344	0.498	0.321	-0.325
Cd	0.155	**-0.716**	0.215	0.157	-0.003	0.599	-0.186
As	-0.269	**-0.42**	-0.063	-0.84	-0.088	-0.176	0.049
Eigenvalue	2.8352	1.4565	1.00	0.7367	0.4409	0.3175	0.1732
Variance %	40.5	20.8	14.9	10.5	6.3	4.5	2.5
Cumulative %	40.5	61.3	76.2	86.7	93	97.5	100

*__Factors loading (The highest loadings are marked)__
*According to the Kaiser criterion, the first two components with Eigen values larger than 1.0 have dominant influences



(a)



(b)

Fig. 4 (a). The scree plot validation of the PCA confirms the choice of two PCs. (b). Presents a loading plot for two components, which clearly reveals the relationships among the seven heavy metals.

Cluster analysis(CA)

CA was used to confirm the results obtained from PCA analysis [21]. Figure 5 and 6 displays the results from CA analysis of heavy metals as a dendrogram created using hierarchical clustering and distances between clusters were presented in Figure 5 that shows two clusters. Cluster 1 is represented by Mo, Pb, Zn, Ni and Cu. Those are very well correlated with each other. Long-term application of fertilizers/pesticide and emissions from vehicle might be a main source of these heavy metals in the study area. Cluster 2 which is related with As and Cd in the study area. The examined results are in good accordance with the results of the PCA analysis.

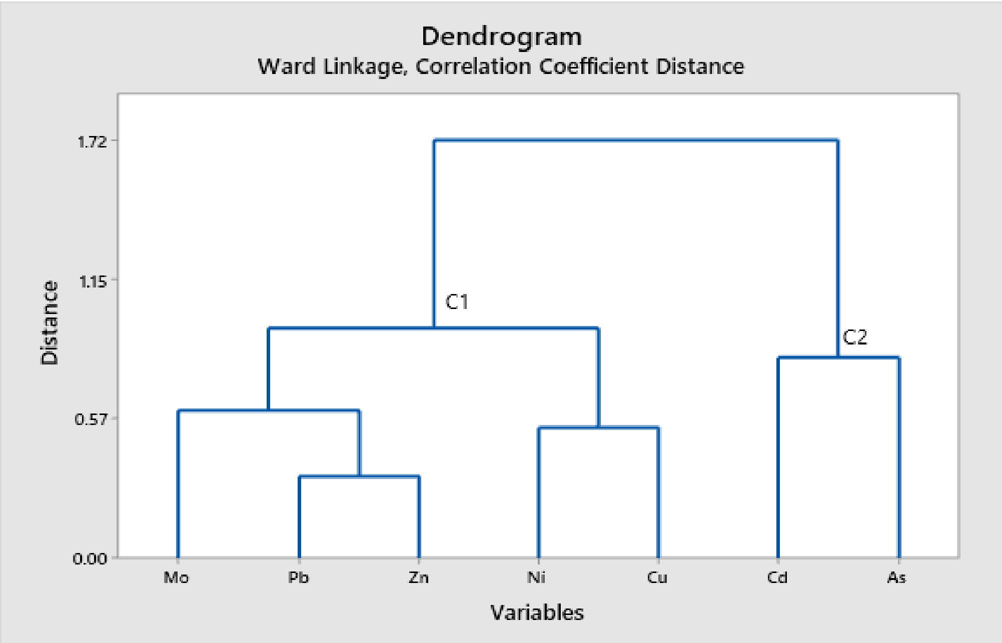


Figure 5. Hierarchical dendogram (Ward's method) for 7 heavy metals from cluster analysis Cluster 1 (Mo, Pb, Zn, Ni, Cu), Cluster 2 (Cd, As)

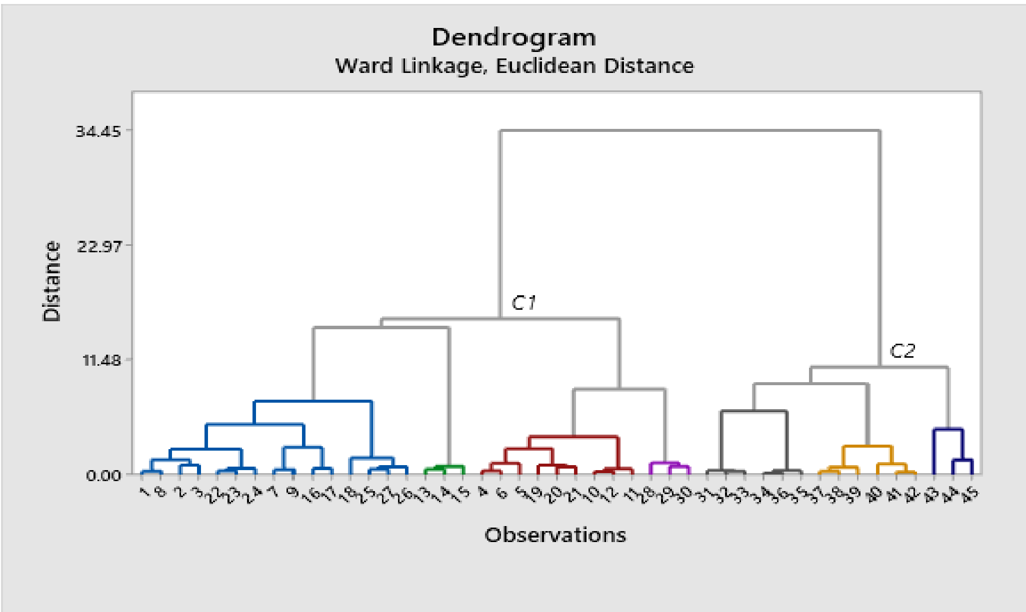


Fig 6. Showing clusters for sampling locations (Most of the sampling locations marked as C1) grouped in cluster 1.

Source identification of heavy metals

Table 7 and Figures 4 and 5 showed that the seven heavy metals could be grouped into the two categories: Group 1 (Mo, Pb, Zn, Ni, Cu) and Group 2 (Cd, As). In PCA analysis, the factor 1 showed the connection between Mo, Pb, Zn, Ni, Cu and presence of a mixed anthropogenic sources of these metals such as fuel combustion from vehicles, use of pesticides, biosolids, manure and fertilizers in agriculture. The application of various biosolids (e.g., livestock manures, composts, municipal sewage sludge) in agricultural land unintentionally leads to the accumulation of heavy metals (Mo, Pb, Zn, Ni, Cu) in the soil [22]. Mattigod and Page [23] have also suggested the probable source of these metals by application of biosolids. Yang and Cheng [24] proposed that the burning of oil in vehicles leads to emission of enormous amount of Ni and Cu in environment. There was also a report that Zn, Cu, and Ni are extensively used in tires and other parts of vehicle [25]. On the basis of these suggestions, it could hypothesize that the metals of Group 1 were also principally derived from vehicle emissions. The metals in Group 2 (Cd and As) were significantly correlated. The mean concentration of the Cd (4.787 mg/kg) was higher than the threshold limit in most of the samples (Table 3). Its primary source in soil is possibly from fertilizer applications. The mean concentration of the As was much lower than the acceptable limits, and its source appears to be related mainly from nearby soil. ICRCL [26] suggest the fertilizer application is a possible source of As and Cd accumulations in agriculture soils. There was a statement of Washington Department of Ecology (WDE) that more than 200,000 ppm of cadmium is present in raw ingredients of fertilizers [27] and the use of final products obtained from these raw ingredients presented 10,600 ppm of Cd. The report also notifies that Cd is not present in natural mineral sources that result to conclude that the fertilizer application is the main source of Cd in soil. Moreover Cd, can reach the soil by air through the burning of fossil fuels in rural areas situated near highways that pollute the ecosystem [28]. In a word, the metals in Group 2 mainly come from fertilizers, burning of fossil fuels and soil surface.

CONCLUSION

All the soil samples had the As, Pb, Ni, Zn and Mo concentration below the standard limit of 20 mg/kg, 50 mg/kg, 50 mg/kg, 300 mg/kg (WHO/FAO 2006) and 57 mg/kg (USEPA 1993) respectively. However the Cd concentration in all the samples was found above than permissible limit (3 mg/kg) except the site S10, S13 and S14. The concentration of Cu was found beyond the permissible limit govern by WHO/FAO (2006) in Region R1 and Region R2, except the region R3 which is quit lower among all studied soil samples. Hence there should be a proper monitoring and management of Cd and Cu in these soil. The sampling region 1 and 2 have the high concentration of heavy metals as compared to region 3 as the region 1 and 2 exposed to high traffic loads. On the basis of multivariate statistical analysis, the heavy metals were classified into two main groups according to their sources: (1) Mo, Pb, Zn, Cu, and Ni seems to have resulted from a variety of anthropogenic sources (2) As and Cd appear to be produced by fertilizer applications and natural sources.

According to Pearson correlation coefficient there was a positive correlation between Pb, Mo, Cu, Ni and Zn. Arsenic was found to negatively correlate with other metals except Cd. The results from Pearson correlation supports the results obtained from PCA analysis. Among all physicochemical parameters temperature and organic matter exhibited positive relations with most of the metals. Therefore, PCA and CA statistical methods can be a strong tool for monitoring pollution status of agricultural soils and for predicating the source of heavy metal pollution.

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