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ARTICLE

Discriminant analysis of concentrations of trace elements in Ulaanbaatar soil

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Abstract: In this work we investigated, through discriminant analysis, the spatial variability and pollution sources of potential toxic elements in Ulaanbaatar surface soil. The total concentration of potential toxic elements in urban surface soil samples, collected depending on pollution sources, were determined by using a rational scheme of chemical analysis of urban soils for ecological monitoring. It was found that the average concentration of B, Cr, Pb, Sn, Zn, Cu, Bi, Ag and Sb were all higher than their background values, while average concentration of Li, Ni, Co, V and Cd were comparatively lower. Urban surface soil samples had varying concentration levels of Ag, B, Bi, Cd, Cr, Cu, F, Ge, Mo, Pb, Sb, Sn and Tl, and identical levels of concentration of As, Co, Ni, Zn, Li, V and Mn. As per the results of the Kruskal–Wallis rank test, the surface soil in the *ger* (traditional round felt dwelling) area (A) and the main road (B) is highly polluted with Pb, Cu, Zn, Cr, MO, Sn, Bi, Ag and Sb. A stepwise selection of the spatial discriminant analysis shows that, Cr, Cu, Ge, Mo, Pb, Sb, Tl and V are most significant variables. These selected variables clearly discriminates the soil groups of the *ger* area (A) such as Khailaast, Chingeltei and Bayanzurkh, the main road (B) namely, along the central transport routes and in the vicinity of the bus stations and around the power plant and industrial area (C) with 71 per cent total success rate of classification.

Keywords: *Ulaanbaatar city, potential toxic elements, topsoil, discriminant analysis;*

INTRODUCTION

Ulaanbaatar is an independent administrative unit and the densely populated capital city of Mongolia, and is an integrated industrial, transport, and residential zone of the country. Therefore, like in any other large industrial cities, the surface soils of Ulaanbaatar city (Mongolia) are exposed to a strong anthropogenic influence due to the growth of the urban population and the number of industries, industrial and domestic wastes, and thus they must be subject to continuous environmental monitoring.

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Vol. 64 No 04(252) 2024
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In particular, the urban topsoil pollution with heavy metals and potential toxic elements has attracted the attention of researchers.

Soil contamination with potentially toxic elements (PTEs) (i.e., antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn)) has been widely reported and has led to growing concerns regarding severe negative effects on living organisms, including humans [1-3].

Numerous studies, aimed at studying the mechanical, elemental, and material composition of Ulaanbaatar urban soils [2-8], have been carried out. Although a large number of different researchers were involved in the above studies, soil ecological state assessments were conducted in the same urban area in the same time period, however during different periods. In addition, most works considered a rather narrow range of chemical elements without studying the behavior of these elements in the soil.

Our research team, during the period from 2010 to 2022, carried out the investigation of Ulaanbaatar soil pollution with heavy metals and potential toxic elements. The main objectives of this investigation during these periods were as follows: i) the implementation of index methods used worldwide in the assessment of urban polluted soils, such as individual (PI, Igeo) and complex (Zc and IPI) pollution indices [9, 10]; ii) the use of multivariate statistical analysis to identify the origin sources of potentially toxic elements in urban soil, and construct the distribution maps of pollution levels and pollution sources via geo-statistical modeling [11-14]; and, iii) create rational schemes for chemical analysis of soil and plant samples to obtain a reliable data [15].

The study of the spatial distribution of both heavy metals and potentially toxic elements in soil samples is extremely valuable in order to identify hot-spot areas and assess the potential sources of pollutants [16-18]. Therefore, the purpose of this research was to investigate, through discriminant analysis, the spatial variability and pollution sources of potential toxic elements in Ulaanbaatar surface soil in order to identify hot-spot areas and assess the potential sources of pollutants.

MATERIALS AND METHODS

Soil sampling

The studies were carried out in 2010, 2011, 2017, 2019 and 2022 years. Soil was the object of these studies, and a total of more than 620 mixed soil samples were collected using the "envelope" method with sides 1mx1m at a depth of 0-10 cm by irregular network. The standard envelope method (5mx5m) is effective in some contexts; its application in dense, built-up urban environments like Ulaanbaatar may face practical difficulties. Alternative sampling methods that are adapted to the complexities of urban space can provide more effective solutions for gathering accurate and representative data.

All soil samples were dried at room temperature in air-dry condition and manually cleared from the large inclusions, such as stones, glass, and plant roots; the samples were ground in a centrifugal ball mill (Fritsch, Germany) in order to homogenize them; they were passed through a 74-mm sieve and kept in paper packets before analysis [19-21]. The soils had undergone anthropogenic effect at varying levels: the thermal power plants, high congestion of traffic, residential areas (*Ger* district) and green zones of

Vol. 64 No 04(252) 2024
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the the urban households.

Chemical analysis

The total content and concentration of mobile forms of Ag, As, B, Ba, Bi, Co, Cd, Cr, Cu, F, Ge, Mo, Mn, Li, Ni, Pb, Rb, Sb, Sn, Sr, Tl, V and Zn were determined. In order to determine the elemental composition of soils, we used rational schemes for chemical analysis of samples of conjugated media "soil-plant", including X-ray fluorescence spectrometry (XRF) and atomic emission spectrometry with arc discharge (AES-DR) by applying the methods of evaporation of powder samples from the electrode channel and injection-spillage; atomic absorption spectrometry (AAS) in flame and electrothermal atomization variants, and flame atomic emission spectrometry (FAES) and atomic mission spectrometry with inductively coupled plasma (AES-ICP) [15].

Statistical analysis

The Kruskal–Wallis non-parametric ANOVA and median tests with multiple comparison procedures (at p = 0.05 level) were used to assess the differences between the mean values of the concentration of trace elements in soil groups. The Kruskal-Wallis test is a non-parametric statistical test and a powerful tool for analyzing non-normally distributed data, such as elemental distribution in soil, and comparing multiple independent groups when the assumptions for parametric tests are not satisfied.

Discriminant analysis was used for establishing the spatial relationships of elements in soils and for identifying the respective discriminative variables for each group as in the following equation [17, 18].

$$f(G_i) = k_i + \sum_{j=1}^{n} w_{ij} p_{ij}$$

where, *i is* the number of groups *(G); k_i* = the constant inherent to each group*; n* – the number of parameters used to classify a set of data into a given group; w_j – the weight coefficient, assigned by DA to a given selected parameter *(p_j)*.

All statistical analyses (basic statistics and discriminant analysis) for a graphical representation of soil quality data were applied using Microsoft Office Excel 2013 and Statistical 13 for Windows.

RESULTS AND DISCUSSION

Concentrations of elements in soils

The arithmetic means and standard deviations for presented row data of element concentration in the six soil groups (pollution sources) are summarized in Table 1 in which the values of microelement concentrations in the background soil samples (L) are also reported. Moreover, Table 1 demonstrates the estimations of Kruskal–Wallis (K-W) and medium tests to assess significant differences between the object (pollution source).

Exploratory statistical analysis showed that microelements in surface soils of Ulaanbaatar, as well as other large cities, have positively distorted distributions, i.e. there is one or more source of pollution within the city boundary.

The comparison of the surface soil elemental composition in Ulaanbaatar with a geochemical background value [22, 23], and most of the elements in Ulaanbaatar's surface soil are present at levels comparable to the natural geochemical background. However, certain elements, such as lead, copper, and zinc, show higher concentration, likely due to anthropogenic influences. Also our study shows that most of the potentially toxic elements, apart from F, are present in concentration below the maximum permissible value or standard levels [24]. Statistical features of microelement distribution in the surface soil of Ulaanbaatar indicate their

Vol. 64 No 04(252) 2024
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positively distorted distributions, which indirectly indicates to the presence of a point source of pollution [25].

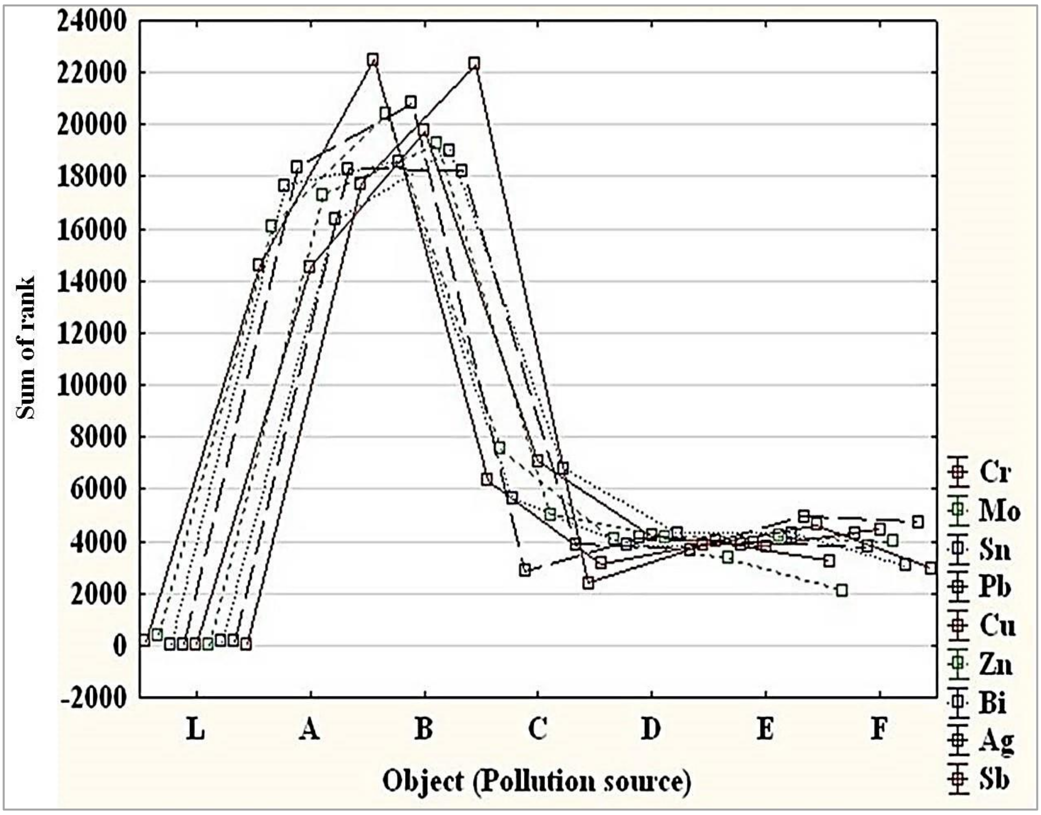

Figure 1. The Kruskal–Wallis rank sum

From the results in Table 1 it is evident that the average concentration of all elements, except Sn and Zn (by median test), is significantly different in six groups of soils and background soil samples. The presence of elevated concentration and high standard deviation among the B, Cr, Pb, Sn, Zn, Cu, Bi, Ag and Sb indicate that the soils are polluted by these microelements due to combustion fuel and traffic emission similarly like in other densely populated cities around the world.

In order for a correct interpretation of the environmental situation and classification of sources of microelements entering urban soils using multivariate statistical analysis, the structure of analytical and geochemical data should contain information on the macro-and microelement composition, as well as pH and Corg.

Adding to the data structure pH and Corg allows for a more complete characterization of the sources of such elements as P, Ni, Al, Fe, Ca, Ba, Bi, Cr, Zn, Sr and S [25].

Highly contaminated soil is prevalent in areas with *gers* and the main road area, which is confirmed in Figure 1, because the Kruskal–Wallis rank sum is greater in the *ger* and the main road areas than in other areas. The sum of Kruskal-Wallis ranks is greater for the *ger* areas and main road than other areas (Figure 1) because the highly contaminated soils are prevalent in these same areas.

PMAS
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Table 1.Total element concentration (mg/kg) with standard deviation depending on object (pollution source) and K-W test and median test

	L	A	B	C	D	E	F	K-W test		Median test	
								H	p	χ^2	p
Li	38.50±5.91	24.29±4.32	21.95±4.73	21.92 ± 7.10	22.1±4.54	26.04 ±5.94	25.26±4.05	45.57	0.00	37.66	0.00
B	34.75±8.61	59.02 ± 19.54	51.58 ± 13.55	49.53 ± 15.31	59.67±23.04	66.96 ±42.45	50.04±6.26	27.56	0.00	22.69	0.00
Mn	682.5±44.25	598 ± 122.26	566.83 ± 96.52	859.61 ± 975.85	797.14 ± 1079.85	611.15±117	700.43 ± 117.60	29.58	0.00	25.18	0.00
Ni	43.25 ± 13.37	36.69 ± 8.34	32.8 ± 6.46	37.85 ± 14.30	32.05 ± 5.75	36.58 ± 10.31	38.56 ± 7.17	25.32	0.00	22.05	0.00
Co	18.00 ± 4.83	12.95 ± 3.14	10.43 ± 2.76	13.45 ± 6.36	10.35 ± 2.06	12.79 ± 5.27	13.55 ± 3.27	53.03	0.00	39.01	0.00
V	83.25 ± 10.62	69.3 ± 11.69	62.21 ± 11.35	68.11 ± 29.76	62.67 ± 7.59	70.54 ± 15.26	68.78 ± 10.28	31.95	0.00	31.35	0.00
Cr	38.5 ± 4.35	50.45 ± 17.18	55.46 ± 16.48	133.31 ± 193.08	51.26 ± 13.11	52.88 ± 18.71	50.17 ± 9.78	39.46	0.00	25.27	0.00
Mo	1.93 ± 0.41	2.44 ± 0.99	2.58 ± 1.63	6.86 ± 4.36	2.8 ± 1.25	2.59 ± 2.07	1.86 ± 0.49	68.59	0.00	39.43	0.00
Sn	2.78 ± 0.62	6.51 ± 9.56	4.71 ± 1.31	6.95 ± 4.68	6.99 ± 7.45	5.19 ± 2.66	5.24 ± 1.36	23.1	0.00	12.42	0.05
Pb	18.5 ± 4.04	87.89 ± 181.86	54.37 ± 24.08	42.34 ± 22.49	65.14 ± 35.54	66.31 ± 55.35	51.13 ± 18.26	23.98	0.00	15.62	0.02
Cu	23.25 ± 4.19	50.86 ± 133.74	40.47 ± 13.16	65.27 ± 28.83	68.19 ± 104.57	46.69 ± 40.86	42.09 ± 8.60	58.05	0.00	49.45	0.00
Zn	60.00 ± 10.51	142.57 ± 66.74	140.89 ± 103.35	157.23 ± 58.71	159.05 ± 76.00	205.92 ± 296.39	138.78 ± 38.55	17.59	0.01	7.94	0.24
Bi	0.53 ± 0.01	0.69 ± 0.16	0.68 ± 0.10	1.09 ± 0.58	0.81 ± 0.33	0.7 ± 0.16	0.64 ± 0.08	43.17	0.00	32.22	0.00
Cd	1.31 ± 0.62	0.87 ± 98.64	0.71 ± 0.32	1.29 ± 0.66	0.80 ± 0.56	0.81 ± 0.30	0.72 ± 0.15	44.99	0.00	28	0.00
F	487.5 ± 145.22	480.48 ± 98.65	422.36 ± 95.86	739.62 ± 392.47	440 ± 73.21	473.85 ± 114.96	520.43 ± 105.63	47.91	0.00	36.49	0.00
Ag	0.095 ± 0.02	0.26 ± 0.21	0.29 ± 0.90	0.24 ± 0.31	0.45 ± 0.64	0.34 ± 0.34	0.29 ± 0.16	19.08	0.00	19.54	0.00
Sb	1.17 ± 0.24	3.97 ± 3.81	3.82 ± 2.67	2.48 ± 2.11	8.01 ± 21.34	4.23 ± 3.89	2.75 ± 1.32	34.21	0.00	15.46	0.02
As	11.75 ± 1.5	11.7 ± 6.48	9.11 ± 2.35	16.82 ± 12.36	9.81 ± 1.90	11.88 ± 6.54	9.04 ± 1.88	39.1	0.00	33.52	0.00
Tl	1.025 ± 0.23	0.8 ± 0.27	1.5 ± 9.04	1.39 ± 0.51	0.64 ± 0.17	0.67 ± 0.21	0.87 ± 0.31	58.27	0.00	33.83	0.00
Ge	1.11 ± 0.24	2.09 ± 0.74	1.71 ± 0.46	1.79 ± 0.62	1.82 ± 0.64	2.12 ± 1.26	1.84 ± 0.34	39.17	0.00	23.26	0.00

Note: L- background soil, A- Ger districts, B-main road and car maintenance areas, C-power plant and industry, D-markets, E-dumpsites, F-greenery.

PMAS
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Vol. 64 No 04(252) 2024
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Spatial variability

Spatial variations in soil quality were evaluated through discriminant analysis. For this purpose, we first entered six groups of soil samples as grouping variables and microelements such as As, Co, Ni, Zn, Li, V, Mn, Ag, B, Bi, Cd, Cr, Cu, F, Ge, Pb, Mo, Sb, Sn, and just Tl as independent variables. The six groups characterize the following areas of (A) Ger districts (n=105), (B) main road and car maintenance areas (n=123), (C) power plant and industry (n=26), (D) markets (n=21), (E) dumpsites (n=26) and (F) greenery (n=23).

For this purpose, all soil samples were separated in six groups. The grouping and independent variables are microelements such as As, Co, Ni, Zn, Li, V, Mn, Ag, B, Bi, Cd, Cr, Cu, F, Ge, Pb, Mo, Sb, Sn and Tl. The six groups characterize the following areas: (A) Ger districts (n=105), (B) main road and car maintenance areas (n=123), (C) power plant and industry (n=26), (D) markets (n=21), (E) dumpsites (n=26) and (F) greenery (n=23).

The results of general discriminant functional analysis are summarized in Tables 2 and 3.

Table 2. Statistics of discriminant functional analysis among six groups of soil samples

Element	Wilks' λ	F-remove 5.299	p-value
As	0.1885	1.4937	0.1916
Co	0.1862	0.7419	0.5926
Ni	0.1881	1.3743	0.2338
Zn	0.1881	1.3450	0.2452
Li	0.1881	1.3439	0.2457
V	0.1903	2.0638	0.0699
Mn	0.1885	1.4800	0.1961
Ag	0.1957	3.8216	0.0023
B	0.1927	2.8423	0.0159
Bi	0.1913	2.4135	0.0363
Cd	0.1919	2.5817	0.0264
Cr	0.1968	4.1788	0.0011
Cu	0.2132	9.5159	0.0000
F	0.1926	2.8058	0.0171
Ge	0.1931	2.9959	0.0118
Mo	0.1994	5.0241	0.0002
Pb	0.2067	7.4205	0.0000
Sb	0.1991	4.9320	0.0002
Sn	0.1929	2.9259	0.0135
Tl	0.1954	3.7186	0.0028

A statistics summary of discriminant functional analysis shows that Wilks' λ is approximately 0.19182, F (140.20) = 4.0518 and p < 0.0000, which is indicative of the fact that independent variables significantly separated the soil samples. The obtained results clearly show that 6 groups of soil samples were different in the concentration level of Ag, B, Bi, Cd, Cr, Cu, F, Ge, Mo, Pb, Sb, Sn and Tl, and the same in the concentration level

Vol. 64 No 04(252) 2024
DOI: https://doi.org/10.5564/pmas.v64i04.3978

of As, Co, Ni, Zn, Li, V and Mn. The obtained results clearly distinguish 6 groups of soil samples having varying concentration levels of Ag, B, Bi, Cd, Cr, Cu, F, Ge, Mo, Pb, Sb, Sn and Tl within the constant concentration levels of As, Co, Ni, Zn, Li, V and Mn. Fluctuating of Wilks λ statistic from 0.186 to 0.213 indicates a lower degree of within-group variations for all of elements.

The relationship between microelements composition of soil groups were assessed by the squared Mahalanobis distance (Table 3).

Table 3. Squared Mahalanobis distance and F-values; df = 8.57

	A	B	C	D	E	F
A	0.000	5.273 p=0.000	24.770 p=0.000	2.781 p=0.000	1.228 p=0,228	3.065 p=0.000
B	1.980	0.000	22.132 p=0.000	1.363 p=0.138	2.421 p=0.0007	4.588 p=0.000
C	25.283	21.934	0.000	11.825 p=0.000	17.321 p=0.0000	12.839 p=0.000
D	3.381	1.617	21.653	0.000	1.763 p=0,024	3.505 p=0.000
E	1.254	2.400	28.342	3.228	0.000	2.561 p=0.000
F	3.456	5.037	22.379	6.793	4.464	0.000

The analysis of Mahalanobis distances separated the C group from all of other soil groups. This statistic for C ranged from 21.9 to 28.34. The soil samples from the *ger* districts have the highest level of similar element composition with the B and E groups with a squared distance of 1.254-1.980. The soil samples of the main road and car maintenance areas have the most identical element composition with the dumpsite area.

According to Table 3, the surface soils in (A), (B) and (C) areas are highly polluted with microelements. Therefore, in order to identify in detail which variable makes the highest contribution to discriminant between the group's soil samples in *ger* districts (A), main road area (B) and power plant and industry area (C), the stepwise discriminant analysis modes were performed on the Box-Cox transformed data. Therefore, the stepwise discriminant analysis modes via the Box-Cox transformed data of the soil samples from (A), (B) and (C) areas were performed to find in detail which variable makes the highest contribution to the discrimination between the groups. The results of modes of the discriminant function analysis are tabulated in Table 4.

The standard discriminant function analysis mode, constructed discrimination function including all 20 microelements, yielded the corresponding correlation matrix assigning correctly in 77 per cent of the cases. In forward stepwise mode, discrimination function using 17 variables rendered the corresponding classification matrix assigning in 76 per cent cases correctly. In backward stepwise mode classification, the function gave classification matrix with 71 per cent correct assignations by using 8 variables, such as Cr, Cu, Ge, Mo, Pb, Sb, Tl and V. Thus, spatial discriminant function analysis results indicate that Cr, Cu, Ge, Mo, Pb, Sb, Tl and V are the most significant variables to discriminate between the three soil groups.

PMAS
Proceedings of the Mongolian Academy of Sciences
Vol. 64 No 04(252) 2024
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As has been observed, some microelements with high total concentrations (particularly Sn, Zn and Bi) did not contribute to discrimination between the three sampling groups, because of the concentration of these elements is very close. This indicates a close relationship between the groups and consequently, the same origin for these elements in (A), (B) and (C) areas. In contrast, Cr, Cu, Ge, Mo, Pb, Sb, Tl and V have a different origin, caused by various sources.

Table 4. Results of the stepwise discriminant analysis for all data measurements and classification matrix

Elements	Standard mode			Forward stepwise mode			Backward stepwise mode		
	A	B	C	A	B	C	A	B	C
Ag	-163	-163	-164	-186	-186	-187			
As	884	882	885	-1298	-1300	-1297			
B	330694	330715	329821	207053	207058	206206			
Bi	1506	1507	1511	2712	2712	2716			
Cd	4194	4193	4194	3457	3455	3456			
Co	-12303	-12303	-12301						
Cr	-46832	-46830	-46757	-63784	-63713	-63060	122793.4	122864.2	123502.4
Cu	-342145	-342017	-341730	-288755	-288655	-288366	22387.3	22439.4	22753.1
F	700549	700584	701068	596394	596421	596914			
Ge	988	984	996	305	301	312	1122.1	1117.1	1125.9
Mo	9012	9014	9022	8840	8842	8850	-560.6	-558.6	-550.0
Ni	10509	10509	10504	2411	2411	2408			
Pb	22849	22846	22781	27168	27164	27099	-2189.9	-2199.9	-2265.2
Sb	2243	2243	2237	3035	3036	3030	-320.7	-320.2	-326.3
Sn	-23754	-23773	-23739	-17533	-17551	-17518			
Zn	208964	208888	208891						
Li	1055	1054	1053						
Tl	1796	1795	1799	-628	-628	-624	133.4	132.1	136.7
V	-14781	-14781	-14788	-19475	-19476	-19482	-204.3	-206.0	-210.2
Mn	86501140	86499695	86506975	82183763	82182265	82190357			
Constant	-3765878	-3765764	-3766466	-3575020	-3574909	-3575680	-63605.2	-63697.8	-64477.1
Correct %	72	79	88	71	76	88	65	72	88
Total	77			76			71		

CONCLUSIONS

Most of the studied elements in Ulaanbaatar surface soil are comparable to the natural geochemical background, while lead, copper and zinc show higher concentrations, probably due to anthropogenic impact. Potentially toxic elements, with the exception of F, are present in concentrations below the maximum permissible value or standard levels.

Statistical features of microelements distribution in the surface soil of Ulaanbaatar indicate their positively distorted distributions, which indirectly indicates to the presence of a point source of pollution. For a correct interpretation of the environmental situation and classification of sources of microelements entering urban soils using multivariate statistical analysis, the structure of analytical and geochemical data should contain the information on the macro- and microelement composition, as well as pH and Corg. Adding to the data

Vol. 64 No 04(252) 2024
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structure pH and Corg allows for a more complete characterization of the sources of such elements as P, Ni, Al, Fe, Ca, Ba, Bi, Cr, Zn, Sr and S.

The samples found to be contaminated represented different areas of the city and different functional zones (industrial, transport, residential, recreational). For example, Sr was found to be hazardous in the soils of Bayanzurkh district; B – in the soils of the Bayangol, Bayanzurkh and Chingeltei districts; Mn – in the soils of the Bayanzurkh and Khan-Uul districts; F and V – in the soils of the Khan-Uul; Cr – in the soils of the Bayangol, Bgyanzurkh and Han-Uul districts; W – in the soils of the Bayangol, Bayanzurkh, Khan-Uul and Sukhbaatar districts.

The discriminant analysis had been used to evaluate and interpret spatial variations of Ulaanbaatar soil quality by using 20 trace elements in six soil groups characterizing the areas with gers, the main road and car maintenance areas, power plant and industry, markets, dumpsites and greenery space. The variations in the contents of Ag, B, Bi, Cd, Cr, Cu, F, Ge, Mo, Pb, Sb, Sn and Tl with a constant concentration levels of As, Co, Ni, Zn, Li, V and Mn had found in soil samples. The soil samples from three areas (*ger* districts, such as Khailaast, Chingeltei and Bayanzurkh, main road and car maintenance and dumpsites) have the most similar element composition. Additionally, the power plant and industry area is separated by the analysis of Mahalanobis distances from all other soil groups. It was found that some microelements with high total concentrations (particularly Sn, Zn and Bi) did not contribute to discrimination between the three groups (the *ger* districts, main road and power plants and industry areas), while the most significant variables are Cr, Cu, Ge, Mo, Pb, Sb, Tl and V.

The following main conclusions can be drawn:

- Soil samples from the areas with *gers*, main road and car maintenance, power plant and industry, markets, dumpsites and greenery were different with the concentration level of Ag, B, Bi, Cd, Cr, Cu, F, Ge, Mo, Pb, Sb, Sn and Tl, and had the same concentration level of As, Co, Ni, Zn, Li, V and Mn.
- According to the Kruskal–Wallis nonparametric ANOVA test, the main objects that pollute the Ulaanbaatar environment are the *ger* districts (A), especially in the Khailaast, Chingeltei, and Bayanzurkh districts, main road area (B) namely, along the central transport routes and in the vicinity of the bus stations, and power plants and the industrial area (C).
- Cr, Cu, Ge, Mo, Pb, Sb, Tl and V are the most significant variables to discriminate between *ger* districts (A), the main road area (B) and power plants and industrial area (C). As has been evidenced, some microelements with high total concentrations (particularly Sn, Zn and Bi) did not contribute to discrimination between the three sampling groups, as there is hardly any difference in the concentration of these elements.

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Vol. 64 No 04(252) 2024
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