Elena V. Shabanova[1], Ts. Byambasuren[2,3], G.Ochirbat[3], Irina E. Vasil'eva[1], B. Khuukhenkhuu[3] and Alexei T. Korolkov[2]

[1] A.P. Vinogradov Institute of Geochemistry SB RAS, Irkutsk, Russia

[2] Irkutsk State University, Irkutsk, Russia

[3] Institute of Physics and Technology of MAS, Ulaanbaatar, Mongolia

*** Corresponding author:** tsagaanbyambasuren@gmail.com

RELATIONSHIP BETWEEN MAJOR AND TRACE ELEMENTS IN ULAANBAATAR SOILS: A STUDY BASED ON MULTIVARIATE STATISTICAL ANALYSIS

ABSTRACT. This article focuses on the relationships between major (Si, Al, Mg, Fe, Ca, Na, K, S, P and Ti) and potentially toxic trace (Ag, As, B, Ba, Bi, Co, Cd, Cr, Cu, F, Ge, Mo, Mn, Li, Ni, Pb, Sb, Sn, Sr, Tl, V and Zn) elements in Ulaanbaatar surface soils and also sources of the trace elements in the soils distinguished by the methods of multivariate statistical analysis. Results of exploratory data analysis of 325 Ulaanbaatar soil samples show the accumulation of Ca, S, B, Bi, Cu, Mo, Pb, Sb, Sn, Sr and Zn in urban soils. The major elements were grouped by cluster analysis in tree associations characterizing main soil fractions: sandy P-(K-Na-Si), clayey (Mg-Ti-Fe-Al) and silty (S-Ca). The factor analysis shows that silty fraction is enriched in major elements of both natural and anthropogenic origin. The principal component analysis from 32 variables extracted nine principal components with 82.49% of the cumulative explained variance. The results of cluster and factor analyses well agree and reaffirm the enrichment causes of potentially toxic elements are a coal combustion at thermal power stations (B, Bi, Ca, Mo, S and Sr) and traffic emissions (Cu, Pb, Sn and Zn). Spatial distributions of trace elements in the districts of Ulaanbaatar city were obtained by ordinary kriging. It is illustrated that the different principal components define the various origins and patterns of accumulation of trace elements in soils. The supplementation of data set by the concentration of organic carbon and the species of elements could help to identify the sources of such elements as P, Ni, Al, Fe, Ca, Ba, Bi, Cr, Zn, Sr and Sb in urban soils more completely.

KEY WORDS: urban surface soils; major and trace element; clayey, silty and sandy fractions; multivariate statistical analysis; ordinary kriging

CITATION: Elena V. Shabanova, Ts. Byambasuren, G.Ochirbat, Irina E. Vasil'eva, B. Khuukhenkhuu and Alexei T. Korolkov (2019) Relationship between major and trace elements in ulaanbaatar soils: a study based on multivariate statistical analysis. Geography, Environment, Sustainability, Vol.12, No 3, p. 199-212

DOI-10.24057/2071-9388-2019-18

INTRODUCTION

Environmental pollution is a worldwide problem that humanity is facing today. It is well known that the soil pollution can affect human health. Soil is considered as a dynamic ecosystem, able to accumulate and transport many components (including trace elements). Some of those trace elements are natural components of the environment and are healthy for humans, animals and plants. However, if the concentrations of these elements are significantly elevated in ecosystems, they are recognized as harmful. Different anthropogenic (wastes from different industries and transportation) and natural (soil-forming processes) sources influence the soil composition and the ability of soil for self-restoration (Kabata-Pendias 2011). The urban soils are much more vulnerable to pollution due to a low capacity of natural self-purification processes.

When studying the urban soils with wide spatial variations of features, lower buffer capacity and fertility loss, it is important to know both the concentrations of chemical elements and the geochemical structure in order to understand the relationships between soil and underlying rocks, and also to reveal the potential pollutants (Norra et al. 2006; Maurice 2009; Zinkutė et al. 2011; Chai et al. 2015; Byambasuren et al. 2018). In addition, the major element composition of soils is useful for studying the geochemical barriers, where mechanisms of trace element fixing by minerals are conditioned by sorption and oxidation-reduction processes, and by formation of new minerals-carriers (Vodyanitskii 2008; Kosheleva et al. 2015). However, many studies are limited by a narrow set of trace elements despite the clayey, silty or sandy fractions affect the soil elemental composition and the trend of biogeochemical processes (Norra et al. 2006; Maurice 2009; Zinkutė et al. 2011). Nowadays, the methods of multivariate statistical analysis are widely used to identify the sources of environmental pollution and to reveal the relationships between elements in the soil cover (Norra et al. 2006; Wong et al. 2006; Chen et al. 2008; Chai et al., 2015; Luo et al. 2015; Steinnes and Lierhagen 2018; etc.). Besides multivariate statistical analysis is often employed to develop measures for soil fertility improvement by the geostatistical modeling of under study areas mapping (Armstrong 1998; Facchinelli et al. 2001; Lee et al. 2006; Christensen et al. 2018; etc.).

Like in other big industrial cities, the surface soils of Ulaanbaatar city (Mongolia) are exposed to a strong anthropogenic impact due to the growth of the urban population and number of industries, industrial and domestic wastes, and thus have to be subject of continuous environmental monitoring. Therefore, the aim of the present study was to investigate and interpret the relationships between major (Si, Al, Mg, Fe, Ca, Na, K, S, P and Ti) and potentially toxic trace (Ag, As, B, Ba, Bi, Co, Cd, Cr, Cu, F, Ge, Mo, Mn, Li, Ni, Pb, Sb, Sn, Sr, Tl, V and Zn) elements of Ulaanbaatar surface soils to identify the sources of element supply into urban soils. The study included:

statistical description of sets containing 32 elements representing the urban surface soils;

revealing the relationships between major elements via the cluster analysis;

interpretation of relationships between major and trace elements with the Pearson's correlation coefficient;

use of factor analysis to identify the groups of elements demonstrating similar behavior;

revealing possible sources of element supply into the soil using the spatial methods of geostatistical modeling.

OBJECTS AND METHODS

The present study investigated soils from Ulaanbaatar city in Mongolia. The city lies at an elevation of about 1300-1500 m above the sea level in north central Mongolia, in an intermountain basin, drained by the Tuul River (106º55 E and 47º55 N). The climate is sharply continental with large amplitude fluctuations in annual and daily temperatures. Nowadays, the area of the city is 4704.4 sq. km; it refers to the Khangai soil-bioclimatic province, the Prekhentei (Cis-Khentei) district with chestnut and dark-chestnut soils under eluvial and trans-eluvial positions and alluvial stony-pebble soils in accumulative landscapes of river valleys. Carbonate dark-chestnut soils are neutral in reaction and poor in humus (2-3%) with carbonate-free upper horizons in the soil profile and occurs in the valley of the Tuul River and on the south slopes of Chingeltei Uul with wormwood-herb-grass communities (Gerasimov et al. 1984; Kasimov et al. 2011).

The parent rocks here include the Archean granites, Carboniferous metamorphic shales and Neogene mottled clays often containing readily soluble salts and gypsum, sand and conglomerates. The Quaternary pebbly sand-loamy alluvial deposits predominate in the river valleys. The shales and clays are enriched in Fe, Mn, Cr, Co, Pb, Ni and Ti; while granites, sandy sediments and river alluvium are poor in these elements; Mn, Mo, V, Co and Pb contents are at the Clarke level (Batkhishig 1999; Vasilyeva et al. 2013).

Ulaanbaatar city currently is an integrated industrial-transport-residential area with the population of 1 417 396 people (Capital statistics 2018). The central area of the city is occupied by multi-storied buildings (residential houses, buildings for different industrial enterprises and institutions), while most of the city's outskirts are occupied by unplanned ger (yurt) districts. Such ger residences lack sanitary conditions and accessible transportation; gers are heated with firewood or coal, being an important source of air pollution.

In total 325 soil samples subjected to different anthropogenic impact were collected in Ulaanbaatar using a non-regular sampling network in 2010-2011 (Vasilyeva et al. 2013; Byambasuren et al. 2018): close to thermal power plants, highways, residential areas and parks (Fig.1). The samples were collected and prepared using the normative documents (ISO 2008). The atomic-emission spectrometry with a.c. arc discharge (Vasil'eva and Shabanova 2012) was used to determine concentrations of 30 elements (Si, Al, Mg, Fe, Ca, Na, P, Ti Ag, As, B, Ba, Bi, Co, Cd, Cr, Cu, F, Ge, Mo, Mn, Li, Ni, Pb, Rb, Sb, Sn, Sr, Tl, V и Zn), while the concentrations of K

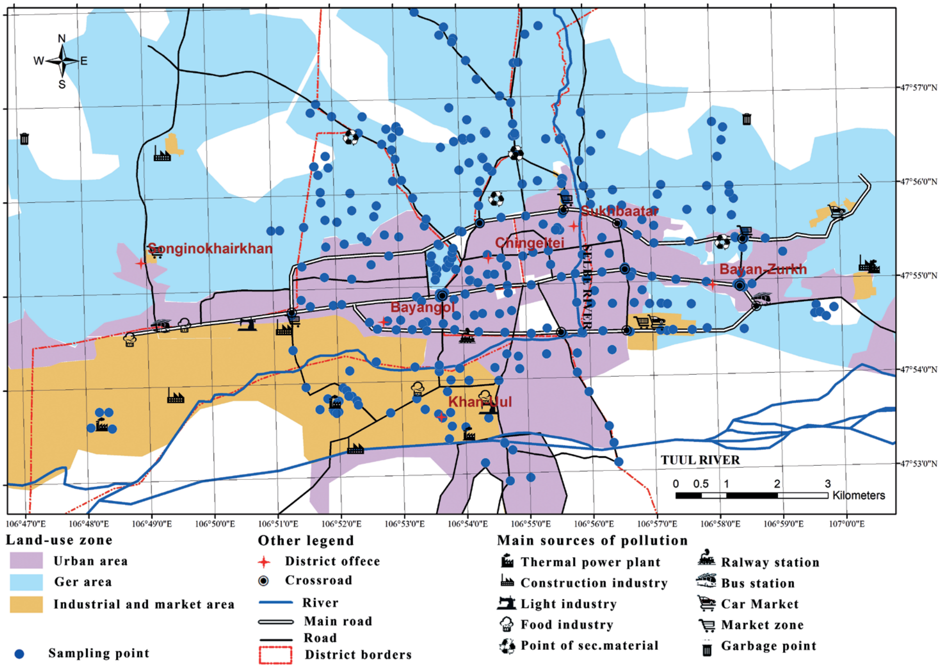

Fig. 1. Scheme of soil sampling with the characterization of different Ulaanbaatar districts

and S were defined by X-Ray fluorescence analysis (Gunicheva 2012).

This analytical information was sequentially treated by exploratory data analysis (calculation of minimum, maximum, median, average, geometric mean, coefficients of variation, skewness and kurtosis under 95 % confidence intervals); Shapiro-Wilk test (checking normality of each element concentration distribution in a set); cluster and factor analysis (classification of soil fractions in terms of major element composition and identification of soil pollution source). As the distribution of each element analyzed in the topsoil can be different from normal distribution, the analytical data were additionally transformed by Box-Cox method. The hierarchical relationships between major elements were described via the cluster analysis, where the Euclidian distance between primary transformed analytical data was used as a similarity measure and the distance between two clusters was calculated with Ward's method. Matrix of Pearson's correlation coefficients was calculated in order to describe the coupling strength between major and trace elements without identifying the causes and consequences of gotten geochemical associations. Factors describing the similarities and differences in the behavior of elements were distinguished by the principal component analysis. Amount of principal components (PC) was selected via Kaiser's criterion, i.e. the factors having eigen-values over 1 were taken into account. The normalized factor loadings (the varimax rotation strategy) increased the data interpretability. The spatial distributions of element groups (factors) were established by the ordinary kriging, where an index expressing the similarity degree of a PC to the association of elements in the sample was used. Some features of the land use and the geological structure of the territory of Ulaanbaatar city as well as the element distributions in the surface soil were taken into account when interpreting the geostatistics results and identifying sources of elements. The statistical procedures were calculated and generalized via Microsoft Office Excel 2013 and STATISTICA 13; the geostatistical modeling was done with ArgGIS 13.

RESULTS AND DISCUSSION

Table 1 shows statistical features in trace element distribution in surface soils of Ulaanbaatar city. The concentrations of major (Si, Al, Fe, Mg, Ca, Na, K, P, S, Ti) and trace (F, Ba, Sr, Li, P, B, Mn, Ni, Co, V, Cr, Mo, Cu, Pb, Zn, Ge, As, Sn, Sb, Ag, Tl, Bi, Cd) elements vastly varied. Concentrations of major elements (Si, Al, K and Ti) appear to be similar to the geochemical background in Mongolia (Vasilyeva et al. 2013) while the concentrations of other elements exceed their regional background values. The regional background values of the majority of the above elements are significantly different from their abundances in the lithosphere due to specific features in geology and landscape (Soil cover… 1984). The ratio of an average concentration of element in urban soil to regional background value of the same element more than 1 suggests the existence of some local anomalies on geochemical barriers which could, in certain conditions, lead to the enrichment by this element, i.e. a combination of higher concentrations and wide element variations suggests an anthropogenic or pedogenic origin of the element (Wei et al. 2010). Therefore, the available data for the urban soils indicate the accumulation of Ca, Na, S, B, Bi, Cu, Mo, Pb, Sb, Sn, Sr и Zn and removal of Mg, V, Co and Cd.

Sets of initial data for all elements (Table 1) demonstrate the consistency of median, average and geometric mean of total concentrations; a wide spread of data; asymmetric and sloping-like distributions. The Shapiro-Wilk test revealed the lack of normal distribution for elements throughout the city area. Such behavior is typical of urban topsoil with a layer thickness of about 50 cm, produced by mixing, filling or by burial of land surfaces in urban and suburban areas. The skewness significantly reduced for transformed data elements; though most elements (Si, Fe, S, As, B, Ba, Bi, Cr, Cu, Sb, Mo, Mn, Ge, Co, Li, V, Ba and Sr) still preserved the sloping-like shape of their distribution. The transformed data only for Al, Ca, Na, P, Ag, Cd, Ni, Pb, Sn, F and Sr can be regarded as normally distributed in terms of three criteria (skewness and kurtosis, calculated indictor of Shapiro-Wilk test at p>0.05).

The relationships of major elements in Ulaanbaatar soils were characterized by means of cluster and factor analyses. Both analyses revealed the same groups of elements [P-(K-Na-Si)]-[(S-Ca)-(Mg-Ti-Fe-Al)], which are related to certain soil fractions (Fig. 2). A group of elements P-(K-Na-Si) represents a sandy fraction. Sands formed as a result of mechanical weathering under dry climatic conditions of Mongolia often contain quartz, feldspar, clay and gypsum fragments (Gerasimov et al. 1984; Norra et al. 2006). Terrigenous clastic rocks with high content of sodium and potassium are mainly distributed in this area. Silicon in this association occurs as quartz and characterizes sandy soil. The presence of phosphorus in this group can be best explained by increasing phosphate adsorption of soils enriched in sodium at pH over 6.5 (Maurice 2009). The similarity in chemical composition of clayey and silty soil fractions complicates distinguishing the remaining major elements between fractions. It has been suggested that clayey fraction including the following group of elements (Mg-Ti-Fe-Al) predominates in the Ulaanbaatar topsoil. This fraction is hard to separate from the silty fraction that contains Ca and S. However, elements of (S-Ca) group could be of anthropogenic origin as well, as sulfur is regarded as an air pollutant in areas, which widely use combustion of brown coal (Amgalan et al. 2016). Nowadays, 90 % of electricity in Mongolia is produced by thermal power stations which burn brown coal with sulfur content varying from 0.2 to 3.2 wt. % (Erdenetsogt et al. 2009).

Table 2 shows correlation coefficients between major and trace elements. Positive correlation between Mn, Ba, Li, B, Ge and major elements of sandy and clayey fractions indirectly suggests a natural origin of these trace elements.

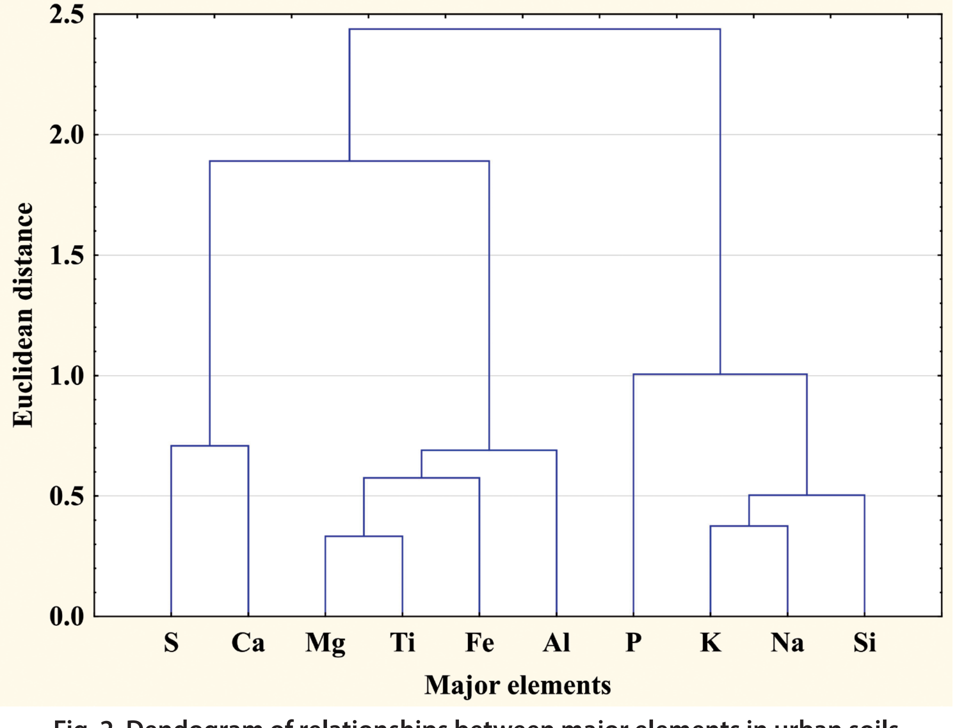

Fig. 2. Dendogram of relationships between major elements in urban soils

Table 1. Results of exploratory data analysis for each chemical element in the data set

Element	Measure unit	C_{BG}	Statistics of set of obtained concentrations					Statistics of data spread		Coefficients, describing data					
										Initial			transformed		
			μ	M	C_{GM}	C_{min}	C_{max}	σ	V	S	K	W	S	K	W
Si	% wt.	30	28.76	28.83	28.64	19.51	34.79	2.58	9	-1.19	3.65	0.00	0.18	2.42	0.00
Al		6.7	6.99	7.02	6.92	4.1	9	0.94	13	-0.47	0.6	0.15	0.00	0.19	0.77
Mg		0.9	0.68	0.66	0.65	0.21	1.12	0.21	31	-0.66	0.31	0.00	-0.02	-0.44	0.15
Ca		1.6	2.26	2.00	2.08	1.00	6.7	1.08	48	2.25	5.59	0.00	0.01	0.19	0.54
Fe		2.9	2.89	2.8	2.75	1.05	7.5	0.98	34	1.67	5.2	0.00	-0.01	1.23	0.33
Ti		0.38	0.37	0.37	0.35	0.11	1.00	0.13	35	2.55	11.68	0.00	0.02	3.68	0.00
Na		1.5	2.1	2.2	2.03	0.63	3	0.48	23	-0.96	1.11	0.00	-0.11	-0.09	0.31
K		2.2	1.99	2.08	1.95	0.64	2.69	0.38	19	-1.37	1.97	0.00	-0.12	0.45	0.01
P		0.105	0.12	0.098	0.1	0.038	0.32	0.058	51	1.4	1.85	0.00	0.01	-0.24	0.68
S		0.092	0.19	0.11	0.12	0.023	2.52	0.34	182	6.08	40.62	0.00	-0.11	1.76	0.30
Ag	ppm	-	0.29	0.18	0.2	0.05	10	0.61	208	13	202	0.00	0.00	0.04	0.35
As		12	11	9.7	10	2.6	64	6	55	5	35	0.00	-0.21	4.46	0.00
B		35	56	51	53	28	230	20	37	4	23	0.00	-0.1	1.36	0.00
Ba		700	671	705	656	364	1055	140	21	-0.1	0.9	0.00	0.05	1.15	0.00
Bi		0.50	0.72	0.68	0.7	0.4	3.6	0.25	35	6	57	0.00	-0.09	1.17	0.00
Cd		1	0.82	0.72	0.75	0.36	3.1	0.42	50	3	9	0.00	0.02	-0.14	0.25
Co		18	12	12	11	3.9	34	3.8	32	1	5	0.00	0.01	0.75	0.01
Cr		45	59	51	53	24	960	60	101	12	64	0.00	-0.18	2.08	0.00
Cu		25	48	39	41	17	1400	82	171	14	230	0.00	-0.11	1.12	0.00
F		450	479	450	459	240	2100	166	35	4	32	0.00	-0.05	0.58	0.06
Ge		-	1.9	1.7	1.8	0.85	6.8	0.69	37	3	15	0.00	-0.11	1.66	0.00
Li		32	23	22	23	10	49	5.1	22	0.9	2.4	0.00	0.01	0.92	0.01
Mn		710	629	580	594	360	5500	406	65	11	128	0.00	-0.16	1.26	0.00
Mo		1.9	2.8	2.3	2.5	0.6	17	2.2	76	4	19	0.00	-0.18	3.06	0.00
Ni		33	35	34	34	15	73	8.5	24	1.00	1.00	0.00	0.00	0.26	0.12
Pb		20	67	50	51	19	1370	110	164	10	110	0.00	-0.03	0.22	0.05
Sb		1.2	4.3	3	3.1	0.62	200	11	264	16	278	0.00	-0.16	2.55	0.00
Sn		2.8	5.7	4.7	5	2.7	96	6.1	106	11	156	0.00	-0.01	0.34	0.06
Sr		290	428	421	424	296	671	59	14	0.6	2.5	0.01	0.00	0.99	0.12
Tl		-	0.79	0.7	0.73	0.3	2.2	0.33	41	2.00	3.00	0.00	0.00	0.07	0.00
V		83	66	66	65	31	180	14	22	1.6	11.8	0.00	0.01	1.83	0.00
Zn		60	149	130	135	61	1600	115	77	10	110	0.00	-0.07	0.68	0.01

Note. C_{BG} – regional background value; μ –average; M – median of data distribution; C_{GM} – geometric mean ; σ – scattering; V – coefficient of variation; S – skewness; K – kurtosis; W – calculated indicator of Shapiro-Wilk at $p > 0.05$.

A more significant correlation between elements of the clayey fraction and Mn and Li is found. The sources of these elements are carbonaceous metamorphic shales and Neogene mottled clays. The negative correlations between major elements ((Mg-Ti-Fe-Al) and (K-Na-Si)) and typical pollutants ((Pb-Sb-Ag-Cu-Zn-Sn) and (Ni-Co-V-As-F)-(Mo-Bi-Cd-Cr-Tl)) are mainly observed. Elements (Cu-Sb)-(Mo-Bi-Cd-Cr-Tl) show significant positive correlations with sulfur. Concentrations of the above trace element for 50-90% of samples are higher than the regional geochemical background and connected with sulfur. Thus, it can be suggested that the contamination by these elements are due to combustion of brown coal and automobile petroleum (Chou 2012; Chai et al. 2015). A positive correlation of P

Table 2. Correlations between major and trace elements (The significant correlations at the 0.05 level are marked in bold)

Major element Trace element	Si	Na	K	P	Al	Fe	Mg	Ti	Ca	S
Ag	-0.09	-0.22	-0.05	**0.61**	0.08	0.08	0.09	0.05	0.07	0.19
As	**-0.63**	**-0.44**	**-0.41**	-0.06	-0.20	0.30	-0.14	-0.23	0.09	0.24
B	0.07	0.16	**0.25**	0.04	**0.33**	**0.36**	0.22	0.11	-0.05	**-0.38**
Ba	-0.12	0.06	0.09	**0.31**	0.03	0.03	0.05	0.00	-0.08	0.12
Bi	**-0.32**	**-0.38**	**-0.32**	-0.11	**-0.29**	0.21	**-0.26**	-0.24	0.09	**0.46**
Cd	**-0.65**	**-0.39**	**-0.51**	0.12	**-0.36**	0.17	-0.19	**-0.41**	**0.35**	**0.58**
Co	**-0.67**	**-0.29**	**-0.29**	**0.41**	-0.07	**0.25**	0.12	-0.05	0.14	0.07
Cr	-0.02	**-0.41**	**-0.39**	-0.19	**-0.44**	0.02	**-0.39**	**-0.30**	-0.06	**0.50**
Cu	**-0.42**	**-0.41**	**-0.47**	-0.11	**-0.29**	0.06	**-0.26**	**-0.29**	**0.34**	**0.49**
F	**-0.76**	**-0.33**	**-0.36**	0.14	-0.20	**0.30**	-0.18	**-0.31**	0.10	0.24
Ge	0.03	-0.05	0.00	0.19	**0.30**	**0.33**	0.24	-0.06	0.14	-0.15
Li	**0.28**	0.09	**0.35**	**0.33**	**0.62**	**0.51**	**0.73**	**0.43**	**-0.33**	**-0.37**
Mn	-0.08	**-0.26**	-0.02	**0.31**	**0.40**	**0.72**	**0.75**	**0.48**	0.03	-0.19
Mo	**-0.34**	**-0.46**	**-0.60**	**-0.34**	**-0.48**	0.12	**-0.32**	**-0.57**	**0.34**	**0.73**
Ni	**-0.39**	-0.05	-0.17	**0.26**	0.03	0.08	0.01	0.06	0.22	0.16
Pb	**0.25**	-0.17	-0.09	0.15	0.06	-0.08	0.06	0.12	0.05	0.23
Sb	0.00	-0.23	**-0.25**	-0.22	-0.18	0.05	-0.11	0.00	-0.01	**0.28**
Sn	-0.08	**-0.27**	-0.24	0.02	-0.12	0.04	-0.15	**-0.25**	0.20	0.18
Sr	-0.11	0.10	-0.17	0.17	0.10	-0.14	-0.15	0.05	**0.37**	0.11
Tl	**-0.37**	**-0.31**	**-0.40**	0.01	**-0.37**	0.01	-0.22	**-0.45**	**0.32**	**0.45**
V	**-0.40**	-0.12	-0.12	**0.44**	**0.25**	**0.45**	**0.42**	**0.27**	-0.10	**-0.38**
Zn	-0.20	**-0.29**	**-0.34**	0.01	-0.09	0.18	0.02	-0.13	**0.25**	0.20

and Ca with trace elements Ni, Co, V, As, F and Ag characterizes them as pedogenic elements, which were involved into natural formation of surface soils during the sedimentation of organic substances.

The study of correlations between major and potentially toxic trace elements in surface soils via the factor analysis revealed nine principal components (PC) out of 32 variables (Table 3). Each PC considers not more than 24.5% of cumulative explained variance, which in total can account for 82.49% of the cumulative explained variance. Variance and cumulative explained variance for each factor varies from 7.79 to 1.01 and from 24.3 to 3.16, correspondingly. The coefficients of communality show the completeness of the description of each element (variable) via the distinguished principal components. For the majority of elements, except of Al, Ba, Bi, Ca, Cr, Fe, Ni, P, Sb, Sr and Zn, these coefficients are rather high; therefore the variables are well represented by the PCs. However,

Table 3. Results of factor analysis showing relative loading of total concentrations of major and trace elements of surface soils (The loadings over 0.45 are marked in bold)

Statistics	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9	Communality
Eigenvalue	7.79	5.08	3.25	2.37	2.13	1.90	1.57	1.30	1.01	
Cumulative explained variance (%)	24.33	40.22	50.38	57.78	64.43	70.37	75.28	79.33	82.49	
Element	Loading									
Si	**-0.829**	0.021	-0.033	0.035	0.123	-0.328	-0.201	-0.074	-0.013	0.94
Na	-0.349	-0.275	-0.258	0.194	0.295	*-0.428*	0.202	-0.331	-0.168	0.93
K	*-0.408*	-0.082	-0.232	0.304	0.340	**-0.462**	-0.316	-0.167	-0.190	0.89
P	0.185	0.227	-0.023	**0.822**	0.031	-0.137	0.076	-0.133	-0.035	0.84
Al	-0.180	**0.487**	-0.039	0.197	0.309	-0.403	0.093	-0.184	-0.099	0.77
Fe	0.307	**0.784**	0.048	-0.167	0.199	0.112	-0.160	0.209	0.017	0.86
Ti	-0.143	**0.547**	-0.105	0.143	-0.182	**-0.527**	0.118	-0.092	0.114	0.88
Mg	-0.009	**0.869**	-0.013	0.046	-0.013	-0.187	0.103	-0.282	0.028	0.95
Ca	0.142	0.020	0.279	-0.179	-0.116	0.183	**0.805**	-0.148	-0.038	0.86
S	0.110	-0.200	0.046	0.027	-0.247	**0.655**	0.193	0.373	0.290	0.96
Ag	0.022	0.184	**0.469**	**0.715**	-0.152	0.105	-0.001	0.205	-0.055	0.89
As	**0.778**	-0.054	0.110	-0.186	0.190	0.137	-0.056	0.164	0.263	0.94
B	0.169	0.229	-0.033	-0.201	**0.820**	-0.259	0.025	0.011	-0.057	0.90
Ba	0.230	-0.058	0.031	*0.443*	0.406	0.033	-0.059	-0.119	**0.605**	0.81
Bi	0.158	-0.042	0.266	-0.057	0.155	0.204	0.056	**0.786**	0.101	0.78
Cd	**0.487**	-0.056	0.178	0.192	-0.081	**0.680**	0.211	0.147	-0.089	0.96
Co	**0.819**	0.138	0.021	0.348	-0.061	0.095	0.079	-0.091	-0.143	0.92

Cr	-0.109	-0.148	0.014	-0.014	-0.215	0.307	-0.086	**0.761**	0.119	0.87
Cu	0.281	-0.167	**0.751**	0.023	-0.120	0.232	0.170	0.268	0.085	0.92
F	**0.846**	-0.087	0.146	0.070	0.254	0.216	-0.029	0.130	-0.060	0.95
Ge	-0.004	0.302	*0.445*	0.141	**0.709**	0.135	0.089	-0.104	0.068	0.91
Li	-0.226	**0.782**	-0.150	0.257	0.128	-0.104	-0.244	-0.082	-0.125	0.92
Mn	0.175	**0.873**	0.048	0.149	0.136	-0.019	0.032	0.038	-0.028	0.95
Mo	0.078	-0.148	0.290	-0.259	0.095	**0.773**	0.133	0.264	0.197	0.97
Ni	**0.465**	-0.015	0.118	0.323	-0.130	-0.302	0.349	**0.490**	-0.131	0.80
Pb	-0.384	0.100	**0.576**	0.370	-0.123	0.124	0.056	0.095	**0.460**	0.94
Sb	-0.074	-0.052	0.187	-0.179	-0.151	-0.023	0.008	0.199	0.800	0.87
Sn	-0.027	-0.074	**0.847**	0.102	0.197	0.317	-0.012	0.029	-0.063	0.93
Sr	-0.053	-0.076	-0.101	0.225	0.192	0.101	**0.772**	0.124	0.024	0.77
Tl	0.122	-0.094	0.272	0.140	-0.090	**0.783**	0.128	0.006	*-0.411*	0.97
V	**0.712**	0.384	-0.117	0.140	0.012	-0.275	-0.161	-0.260	0.011	0.95
Zn	0.209	0.023	**0.699**	-0.049	0.145	-0.008	0.037	0.108	**0.466**	0.81

the lower coefficients of communality indicate an incomplete statistical model and necessity to consider more variables (chemical elements and compounds; e.g. organic matter concentrations and/or speciation of elements).

Significant positive loadings are observed in each factor for the following elements: F>Co>As>V>>Cd>Ni – PC-1; Mn>Mg>Fe>Li>Ti>>Al – PC-2; Sn>Cu>Zn>Pb>>Ag>Ge – PC-3; P>Ag>>Ba – PC-4; B>Ge>>Ba – PC-5; Tl>Mo>Cd>S – PC-6; Ca>Sr – PC-7; Bi>Cr>Ni – PC-8; Sb>Ba>>Zn>Pb – PC-9. Negative loadings are typical of only three factors: Si>K in PC-1; Ti>>K>Na>Al – PC-6; Sb>Ba>Zn≈Pb – PC-9. Some elements are simultaneously dominated in several factors accordingly to their loadings: K (negative loadings in PC-1 and PC-6); Cd (positive loadings in PC-1 and PC-6); Ni (positive loadings for PC-1 and PC-8); Al and Ti (positive loading in PC-2 and negative loading for PC-6); Ag (positive loadings for PC-3 and PC-4); Ge (positive loadings for PC-3 and PC-5); Pb and Zn (positive loadings for PC-3 and PC-9); Ba (positive loadings for PC-4, PC-5 and PC-9); Tl (positive loading for PC-6 and negative loading for PC-9). Thus, it implies that the above elements occur in several mineral phases of Ulaanbaatar soil samples. Fig. 3 demonstrates the spatial distributions of those factors.

As regard to geochemical classification, out of 32 elements analyzed in the urban soil cover, the most widespread elements in the Earth's crust are present in five factors: PC-1 (Si, K), PC-2 (Al, Mg, Fe, Mn, Ti); PC-4 (P), PC-6 (Na, K, Ti, S) and PC-7 (Ca), while the lithogenic elements, which characterize the composition and structure of sedimentary rocks and soils, are included in factors of PC-1 and PC-2. These factors include both major and trace elements (Si, K, F, Co, As, V, Cd, Ni and Mn, Mg, Fe, Li, Ti, Al, correspondingly) thus providing the greatest contribution to the cumulative explained variance. The first factor reveals the siderophile elements, while the second one identifies major elements of soil clayey fraction.

Trace elements from PC-1 tend to be associated with manganese phases from PC-2 (Vodyanitskii 2008). Therefore, X-ray diffractometry, NIR-spectrometry or extraction methods are required for studying such relationships and mineral phases in soil samples. Additionally, the coefficients of communality for Al, Fe and Ni suggest some organic-biological processes, which were not taken into consideration in the present study, but influence the chemical composition of the clayey fraction. Geographical distribution of elements of PC-1 and PC-2 can be closely related to the landscape of the city area (Christensen et al. 2018: Steinnes and Lierhagen 2018). Positive loadings for F, As, V, Co, Ni; Mn and Li of PC-1 and PC-2 reflect their geochemical affinities and indicate their pedogenic and lithogenic origin in soils.

PC-3 (Sn-Cu-Zn-Pb-Ag-Ge) reflects the accumulation of heavy metals Cu, Pb, Sn and Zn in soils (Table 2) and indicates their spatial distribution along central transport highways and in the vicinity of bus terminal (Fig. 3). However, the soil pollution of these elements cannot be explained by motor transport emissions only, as lead and zinc were presented in PC-9, and silver and germanium – PC-4 and PC-5, correspondingly.

Elements (P-Ag-Ba) of PC-4 highlighted three zones of the city: along the Selbe River and in ger districts (Khailaast and Chingerltei) (Fig. 3). It should be noted that the maximum contributions of PC-4 are located in places of illegal dumping. The coefficients of communalities for phosphorus and barium are low and suggest the associations of these elements with the soil organic matter (Maurice 2009), which is beyond the scope of the present study.

Other two factors (PC-5 and PC-6, and correspondingly groups of (B-Ge-Ba) and (Tl-Mo-Cd-S-Na-K-Ti) elements) have similar spatial distributions in ger districts. It indicates that the soils contain minerals formed by coal combustion. During rains, garbage and ash migrate from ger districts located on elevated sites to low-lying areas where the element-contaminants are accumulated. Note, that sulfur from PC-6 can create complexes with toxic elements, that have high coefficient of biological absorption (over 70%) and any their speciation are highly toxic for organisms occurring in soils with poor organic matter abundance (Chou 2012). These features could be weaker if the concentrations of potassium, sodium, aluminum and titanium increase.

PC-7 and PC-8 characterize the relationships between (Ca-Sr) and (Bi-Cr-Ni) elements with lower communality coefficients, which can be possibly related to the formation of compounds with the soil organic matter. Amongst 5 key elements of PC-7 and PC-8 only nickel occurs in another factor (PC-1). Calcium, strontium and bismuth tend to accumulate in the soil cover (Table 2). PC-7 is distributed in two big areas occupied by unplanned ger districts: Bayankhushuu (north-west district) and Shark-Khad (north-east district). An increase level of soil contamination is only observed at the sale sites of firewood and coal from various deposits (Baga-nuur, Nalaikh, Shivee-Ovoo, etc.). Elements of PC-8 are distributed in the industrial area with thermal power stations # 2, 3, 4 as well as close to old inoperative station. Small plants of wool and leather processing which use reagents with bismuth, chromium and nickel, are located close the thermal power stations under operation.

The PC-9, correspondingly Sb-Ba-Zn-Pb-Tl elements, is difficult to relate to any natural or technogenic phenomena. However, based on its spatial distribution (closeness to wholesale markets), accumulation of specific wastes containing these elements could be suggested.

CONCLUSIONS

Therefore, the relationships between major (Si, Al, Mg, Fe, Ca, Na, K, S, P and Ti) and potentially toxic trace elements (Ag, As, B, Ba, Bi, Co, Cd, Cr, Cu, F, Ge, Mo,

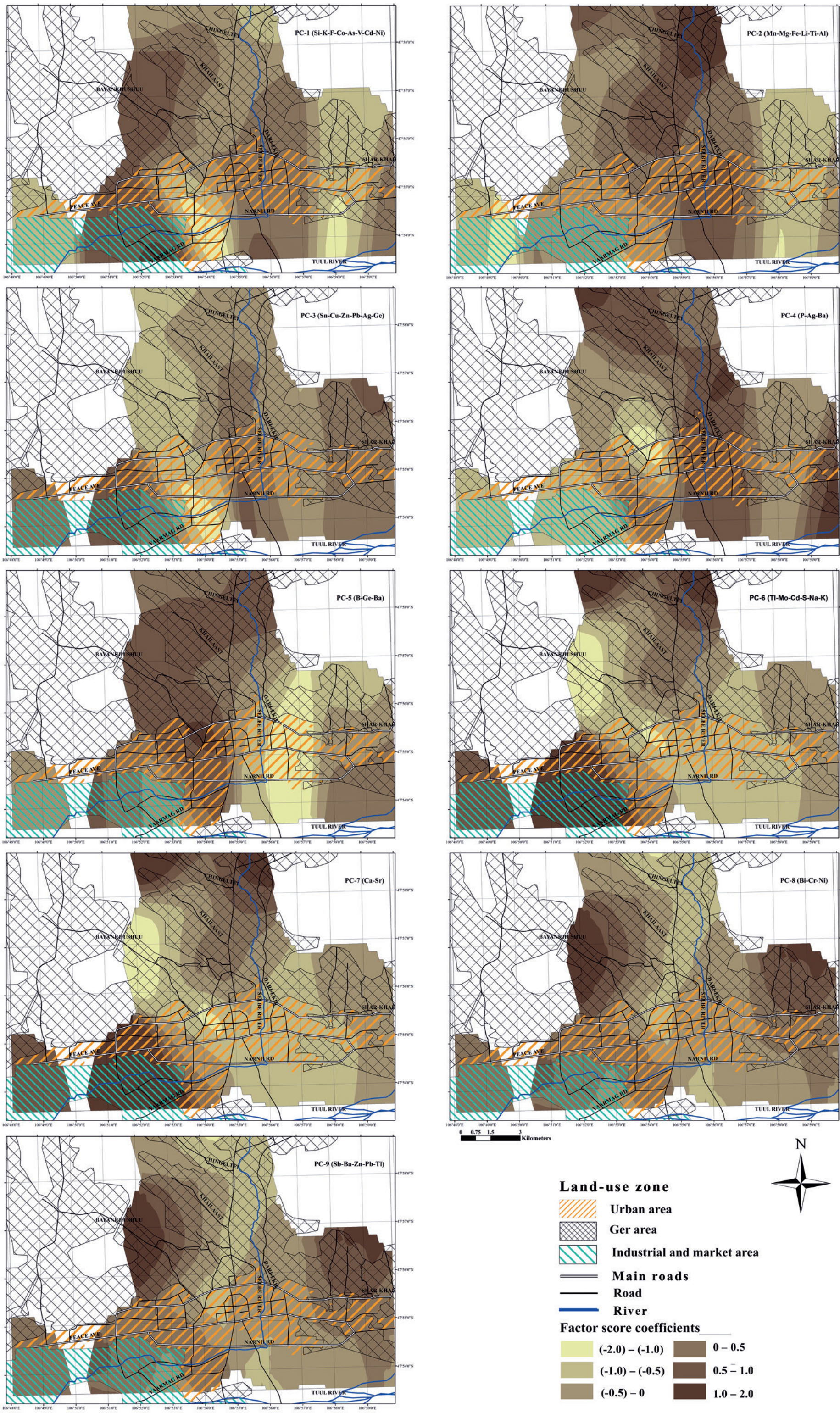

Fig. 3. Geographical distributions of the distinguished principal components

Mn, Li, Ni, Pb, Sb, Sn, Sr, Tl, V and Zn) were studied in 325 Ulaanbaatar soil samples. Results of exploratory data analysis show accumulation of Ca, S, B, Bi, Cu, Mo, Pb, Sb, Sn, Sr and Zn in urban soils (Kasimov et al. 2011; Vasilyeva et al. 2013; Amgalan 2016; Byambasuren et al. 2018). The cluster analysis distinguished associations of major elements which characterize main soil fractions: sandy P-(K-Na-Si), clayey (Mg-Ti-Fe-Al) and silty (S-Ca). The factor analysis shows that silty fraction is enriched in major elements of both natural and anthropogenic origin. From 32 variables the principal component analysis extracted nine PCs with 82.49% of the cumulative explained variance. The obtained principal components describe the most elements well, except of Al, Ba, Bi, Ca, Cr, Fe, Ni, P, Sb, Sr and Zn. The results of cluster and principal component analyses well agree with data (Kasimov et al. 2011; Vasilyeva et al. 2013; Amgalan 2016; Byambasuren et al. 2018) and reaffirm that the enrichment causes of potentially toxic elements are coal combustion at thermal power stations (B, Bi, Ca, Mo, S and Sr) and traffic emissions (Cu, Pb, Sn and Zn). Spatial distributions of trace elements were obtained by ordinary kriging. This method also helped to identify the districts of Ulaanbaatar city being the most vulnerable to antropogenic impact (ger districts, central transport highways, areas close to bus terminal and factories of wool and leather processing). Some elements occur in the different factors thus implying various origin and pattern of accumulation of these elements in soils. The supplementation of data set by the concentration of organic carbon and the speciation could help to identify the sources of elements such as P, Ni, Al, Fe, Ca, Ba, Bi, Cr, Zn, Sr and Sb in urban soils more completely. Besides, toxic elements contamination of Ulaanbaatar soils requires a continuous monitoring, planning and conducting practical measures to improve soil fertility.

ACKNOWLEDGMENTS

The study was fulfilled within the framework of the Agreement on scientific cooperation between the A.P. Vinogradov Institute of Geochemistry of Siberian branch of the Russian Academy of Sciences and Institute of Physics and Technology of the Mongolia Academy of Sciences.

REFERENCES

Amgalan N., Narantsetseg T. and Shagjjamva D. (2016). Valuations of elemental concentrations of particle matter in Ulaanbaatar, Mongolia. Open Journal of Air Pollution, 5(4), pp. 160-169. doi: 10.4236/ojap.2016.54012

Armstrong M. (1998). Basic Linear Geostatistics. Springer-Verlag Berlin Heidelberg GmbH.

Batkhishig O. (1999). Extended Abstract of Candidate's Dissertation in Geography. Ulaanbaatar (in Russian).

Byambasuren Ts., Shabanova E.V., Korolkov A.T., Vasilyeva I.E., Ochirbat G. and Khuukhenkhuu B. (2018). Distribution of Trace Elements in Soils of Ulaanbaatar. The Bulletin of Irkutsk State University. Series Earth Sciences, 26, pp. 31-45. (in Russian with English summary)

Capital statistics. (2018). Official Website. [online] Available at: http://www.ubstat.mn/ [Accessed 01 Oct. 2018] (in Mongolian).

Chai Y., Guo J., Chai Sh., Cai J., Xue L.and Zhang Q. (2015). Source identification of eight heavy metals in grassland soils by multivariate analysis from the Baicheng-Songyuan area, Jilin Province, Northeast China. Chemosphere, 134, pp. 67-75. doi: 10.1016/j.chemosphere.2015.04.008

Chen T., Liu X.M., Zhu M.Z., Zhao K.L., Wu J.J., Xu J.M. and Huang P. (2008). Identification of trace element sources and associated risk assessment in vegetable soils of the urban-rural transitional area of Hangzhou, China. Environmental Pollution, 151(1), pp. 67-78. doi: 10.1016/j.envpol.2007.03.004

Chou C.-L. (2012). Sulfur in coals: A review of geochemistry and origins. International Journal of Coal Geology, 100, pp. 1-13. doi: 10.1016/j.coal.2012.05.009

Christensen E.R., Steinnes E. and Eggen O.A. (2018). Anthropogenic and geogenic mass input of trace elements to moss and natural surface soil in Norway. Science of the Total Environment, 613-614, pp. 371-378. doi: 10.1016/j.scitotenv.2017.09.094

Erdenetsogt B.-O., Lee I., Bat-Erdene D. and Jargal L. (2009). Mongolian coal-bearing basins: Geological settings, coal characteristics, distribution, and resources. International Journal of Coal Geology, 80, pp. 87-104. doi: 10.1016/j.coal.2009.08.002

Facchinelli A., Sacchi E. and Mallen L. (2001). Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. Environmental Pollution, 114, pp. 313-324. doi: 10.1016/S0269-7491(00)00243-8

Gunicheva T. (2012). Application of nondestructive X-Ray fluorescence method (XRF) in soils, friable and marine sediments and ecological materials. In: Panagiotaras D., ed., Geochemistry – Earth's System Processes. InTech, pp. 371-388. Available from: http://www.intechopen.com/books/geochemistry-earth-s-system-processes/application-of-nondestructive-wavelength-dispersive-x-ray-fluorescence-wd-xrf-method-in-soils-friabl [Accessed 09 Feb. 2019].

ISO 10381-2008: Soil quality, Sampling, Part 1-5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination.

Kabata-Pendias A. (2011). Trace elements in soils and plants. 4th ed. CRC Press, Boca Raton, FL, 2011.

Kasimov N.S., Kosheleva N.E., Sorokina O.I., Bazha S.N., Gunin P.D. and Enkh-Amgalan S. (2011). Ecological-geochemical state of soils in Ulaanbaatar (Mongolia). Eurasian Soil Science, 44(7), pp. 709-721. doi: 10.1134/S106422931107009X

Kosheleva N.E., Kasimov N.S. and Vlasov D.V. (2015). Factors of the Accumulation of Heavy Metals and Metalloids at Geochemical Barriers in Urban Soils. Eurasian Soil Science, 48(5), pp. 476-492. doi: 10.1134/S1064229315050038

Lee C.S., Li X., Shi W., Cheung S.C. and Thornton I. (2006). Metal contamination in urban, suburban and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Science of The Total Environment, 356(1-3), pp. 45-61. doi: 10.1016/j.scitotenv.2005.03.024

Luo X.-S., Xue Y., Wang Y.-L., Cang L., Xu B. and Ding J. (2015). Source identification and apportionment of heavy metals in urban soil profiles. Chemosphere. 127, pp. 152-157. doi: 10.1016/j.chemosphere.2015.01.048

Maurice P.A. (2009). Environmental surfaces and interfaces from the nanoscale to the global scale. John Wiley & Sons, Inc.

Norra S., Lanka-Panditha M., Kramar U. and Stüben D. (2006). Mineralogical and geochemical patterns of urban surface soils, the example of Pforzheim, Germany. Applied Geochemistry, 21, pp. 2064-2081. doi: 10.1016/j.apgeochem.2006.06.014

Soil cover and soils of Mongolia. (1984). In: I.P. Gerasimov, N.A. Nogina, Dorjgotov D., ed. Moscow: Science. (in Russian).

Steinnes E. and Lierhagen S. (2018). Geographical distribution of trace elements in natural surface soils: Atmospheric influence from natural and anthropogenic sources. Applied Geochemistry, 88, pp. 2-9. doi: 10.1016/j.apgeochem.2017.03.013

Vasil'eva I.E. and Shabanova E.V. (2012). Arc atomic-emission analysis in geochemical research. Industrial laboratory. Diagnostics of materials, 78(1-II), pp. 14-24. (in Russian with English summary).

Vasilyeva I.E., Shabanova E.V., Doroshkov A.A., Proydakova O.A., Otgontuul Ts., Khuukhtnkhuu B., Byambasuren Ts. (2013) Distribution of toxic and essential elements in soils of Ulaanbaatar city. Environment and sustainable development in Mongolian plateau and surrounding regions, vol. 1, pp. 67-71. Available at: https://docs.google.com/viewer?a=v&pid=sites&srcid=ZGVmYXVsdGRvbWFpbnxtb25wbGF0ZWF1MjAxM3xneDoyMzJjMWJlNjRmNTU3NmM [Accessed 09 Feb. 2019].

Vodyanitskii Yu.N. (2008). Heavy metals and metalloids in soils. Moscow: V.V. Dokuchaev Soil science Institute. (in Russian).

Wei B.G. and Yang L.S. (2010). A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchemical Journal, 94(2), pp. 99-107. doi: 10.1016/j.microc.2009.09.014

Wong C.S.C., Li X. and Thornton I. (2006). Urban environmental geochemistry of trace metals. Environmental Pollution, 142(1), pp. 1-16. doi: 10.1016/j.envpol.2005.09.004

Zinkutė R., Taraškevičius R. and Želvys T. (2011). Major elements as possible factors of trace element urban pedochemical anomalies. Central European Journal of Chemistry, 94(2), pp. 337-347. doi: 10.2478/s11532-011-0012-z

Received on February 13th, 2019 Accepted on August 8th, 2019