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ARTICLE

Temporal variation of the pseudo total content of heavy metals in Ulaanbaatar soil

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Abstract: *This work shows some of the results of investigation into pseudo total content of heavy metals in the surface soil of Ulaanbaatar.*
The main objectives of this study are to (i) evaluate temporal variability of pseudo-total content of Pb, Cu, Zn, Cd, Cr, Ni, Co and Mn in surface soil of Ulaanbaatar collected from 2003 to 2018, (ii) identify the main discriminates - metals during the years 2003-2018 years and, (iii) investigate the interdependence of main discriminates on the soil reaction (pH) and soil organic matter.
Due to urbanization and negative human activities, surface soil in Ulaanbaatar losing their natural features, which are changing, while the spatial and temporal distribution of heavy metals in urban surface soil is becoming irregular. In Ulaanbaatar surface soil, the mean concentration of Cu, Zn and Pb much mois very high and the mean concentration of Co is lower than background soil. In some land use zones, it was found that the mean concentraion of Zn and Cr was considerably higher than the permissible level. The pollution condition of Mn, Zn, Cr, Ni and Cd was the same in 2010-2018 and the pollution conditions of Pb, Cu and Co are different. The main discriminants are Pb, Cu and Co. In Ulaanbaatar soil, a strikingly close correlationhip was established for Cu, Pb with the soil organic matter, and for Cd, Zn, Cr with the pH, respectively.

Keywords: *Ulaanbaatar; surface soil; temporal variation; heavy metal pollution; discrimination analysis; factor and cluster analysis;*

INTRODUCTION

Rapid urbanization, expansion of the industrial sector, and increasing vehicle emissions have largely led to heavy metal contamination of urban soils. Heavy metal contamination of urban soils, due to their toxicity and close relationship with the humans, continue to cause grave concern of the public, as well as international environmentalists. Two principal sources - anthropogenic and lithogenic, have been recognized for typical enrichment of heavy metals in urban soils [1-5].

In recent years, similarly like in any other major city, the state of ecological environment in Ulaanbaatar has been seriously compromised by urbanization and population growth.

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The soil cover has changed significantly and soil is polluted with heavy metals. Numerous studies have been carried out on heavy metal contamination of Ulaanbaatar soil. In our previous studies. we focused on spatial distribution pattern, source identification and the degree of pollution [6-14]. The toxicity of heavy metals depends on their forms or species in the soil and soil properties [3-4]. For the soils of Ulaanbaatar there are only few scientific works devoted to the study of their forms in soil [10, 15].

Pseudo-total concentration of heavy metals is expressed through the content of elements, which is measured in a soil sample after incomplete acid decomposition and is used for assessing potential risk and is also useful for assessing the direct intake of soil metals by young children or animals [4].

The main objectives of this study are to (i) evaluate temporal variability of pseudo-total content of Pb, Cu, Zn, Cd, Cr, Ni, Co and Mn in surface soil of Ulaanbaatar collected from 2003 to 2018, (ii) identify the main discriminates - metals during the years 2003-2018 years and, (iii) investigate the interdependence of main discriminates on the soil reaction (pH) and soil organic matter. And herein lies the novelty of our work.

MATERIALS AND METHODS

Object: Surface soil samples collected in 2003 (410), 2010 (57), 2014 (117) and 2018 (215) respectively are the main objects of this study. Urban soils were taken at a depth of 0-10 cm from the soil surface by "envelope" method on irregular network [16, 17]. Soil samples were dried at room temperature in air-dry condition and large inclusions, such as stones, glass, and plant roots were removed, sieved and ground in the Fritsch instrument.

Chemical analysis: The pseudo-total content of heavy metals in surface soil was exctacted in a mixture of HNO_3+$_2O_2$ acid [18]. All measurements were performed using the Perkin-Elmer Model 5000 and Shimadzu 6300 C atomic absorption spectrophotometer with flame atomization (FAAS). Air-acetylene flame and standard calibration methods were applied for atomization and determination of the pseudo-total content of heavy metals.

Quality control of the results was carried out using the analysis of certified standard reference samples SP-3, SP-2, SP-3. We determined the pH value of the soil water extracts using the potentiometric method and soil organic matter by ignition [19].

Statistical analysis: A Kruskal–Wallis rank ANOVA test and median test were used for the comparison of quantitative variables between 2003 and 2018. Discrimination analysis was used for the study of temporal variation of elements in soil and identification of respective discriminative variables for each years. Using CA and FA, elements with similar geochemical behavior and the dependence of the behavior of HM in soil on pH and SOM were identified.

Statistical procedures were calculated and generalized with Microsoft Office Excel 2013 and Statistica 13.

RESULTS AND DISCUSSIONS

Soil properties: Soil pollution (especially high-level) with compounds of heavy metals leads to a change in the chemical, physical and biological properties of the soil. The results of the reaction (pH) and organic matter (OM) of the surface soil are presented in Table1. According to our result (Table 1.), it was found that the $pH_{(H2O)}$ in surface soil varies from slightly acidic (5.62) to alkaline (8.97), $pH_{(H2O)}$ average value is a neutral and slightly alkaline. As some authors have noted, urban soils are characterized by changes in pH values towards

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alkalization, which is also confirmed by our studies. Alkalization of soils shows that the soil cover of Ulaanbaatar is contaminated in some places due to various sources of pollution, since the soil reaction (pH) in the background soil was weakly acidic (6.61).

Table 1. Statistical results of soil organic matter (SOM, %) and pH

	BG	Max	Mean	Median	Min	σ	V, %
SOM	7.95	36.39	9.47	7.66	2.27	6.83	46.73
$pH_{(H2O)}$	6.61	8.97	7.45	7.52	5.62	0.47	0.22

Organic matter in surface soils ranges from 2.27-36.39%, averages 7.66% and is closer to the value of background soil (7.95). The high variability (46.73%) of soil organic matter indicates anthropogenic pollution of soils at some points.

Concentration and distribution of heavy metals in Ulaanbaatar soil between 2003 and 2018. The concentration of heavy metals in Ulaanbaatar soil in the years 2003-2018, regional background value (C_{BG}) for pseudo-total contents of elements in Ulaanbaatar surface soil [20] and the maximum permissible concentrations (MPC -**standard*), extracted in 1N HCl [21] are presented in Table 2. The distribution of elements in Ulaanbaatar soil during 2003-2018 were tested by the K-W ANOVA test and are also presented in the Table. Further figure 1 (example) shows the distribution of Co and Pb in Ulaanbaatar soil during the years from 2003 to 2018.

*Table 2. Concentration of heavy metals in Ulaanbaatar soil in the years betweem 2003 and 2018, regional background value (C_{BG}) for pseudo-total contents of elements in Ulaanbaatar surface soil and the maximum permissible concentrations (MPC -*Standard), extracted in 1N HCl*

groups	*n*	Concentration of heavy metals, mg/kg							
		Co	*Mn*	*Zn*	*Pb*	*Cu*	*Cr*	*Ni*	*Cd*
2003	*410*	*8.83*	*-*	*-*	*67.8*	*40.5*	*-*	*21.32*	*1.13*
2010	*57*	*7.25*	*159*	*70.7*	*64.8*	*47.9*	*18.32*	*15.59*	*0.3*
2014	*117*	*8.08*	*204*	*93.7*	*39.1*	*22.5*	*43.54*	*10.78*	*0.57*
2018	*215*	*7.43*	*164*	*56.6*	*33.4*	*24.1*	*31.85*	*16.69*	*1.03*
C_{BG}		*9.43*	*168*	*50.1*	*11.2*	*13.8*	*25.95*	*19.93*	*0.84*
*Standard		*12*	*600*	*60*	*60*	*50*	*15*	*36*	*1*
K-W	H	20.31	556.82	329.41	160.89	117.22	604.14	200.73	185.32
	p	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

The accumulation and leaching tendency for all investigated heavy metals are not identical during all the periods when the study was carried out. The distribution pattern of pseudo-total content of heavy elements in urban soil as well as the total content [6] are uniform. This is clearly shown by the K-W ANOVA test (K–W test; p=<0.01) as in Figure 1.

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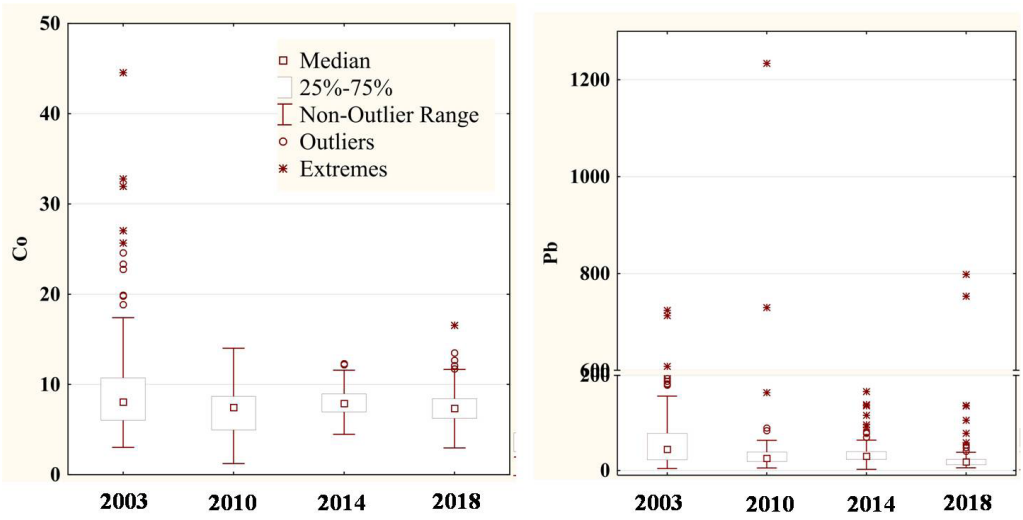

Figure 1. Distribution of pseudo-total concentration of Co and Pb

As can be seen from Table 1, from 2003 to 2018, excluding only 2014, the concentration for Pb, Cu, Zn decreases, which may indicate the positive outcome of the government's efforts to curb environmental pollution on the territory of Ulaanbaatar, such as restriction of number of vehicles on the road. On the other hand, the concentration for Mn, Co, Ni, Cd increases, the biogeochemical feature of urban soil cover in Ulaanbaatar, since these pedogenic and lithogenic elements [20, 21] are leached by human exposure. On the contrary, Cr showed different results.

In Mongolia, MPC standard for total contents of heavy metals have been approved and adopted, while the standards for pseudo-total concentration or acid-soluble concentration of HM have not been adopted. In order to assess the ecological state of soils by pseudo-total concentration or acid-soluble concentration of HM, we was the value of heavy metal concentration, extracted in 1N HCl, as in Russia. When comparing with value extracted in 1N HCl, the pseudo-total concentration of only the Cr content in the background soil and Zn and Cr contents in urban soil are higher.

The results of this study were compared with the other findings of studies that werecarried out in 2008-2012 [15, 23-26]. Although the conditions and times, when the studies were carried out are different, the distribution feature and pollution status were the same and a high content was noted in the industrial and ger districts of the city.

Temporal variation

Temporal variation of heavy metals in Ulaanbaatar soil was estimated using multiple stepwise discriminate analyses to distinguish the main elements, which were being increasingly accumulated in the tears 2003-2018 and which were polluting the surface soil in Ulaanbaatar and the results of the study are summarized in Table 3. According to our analysis, the state of contamination is clearly distinguished with Co (Wilks' ƛ-0,194) in the standard and forward stepwise mode Cu (Wilks' ƛ-0.192). In the backward stepwise mode, Mn, Zn, Cr, Ni, and Cd are included in the models and are the main elements indicating the geochemical features of the city's soils. This indicates that during 2010-2018, the ecological state of Ulaanbaatar soil was different in terms of the concentration of Mn, Zn, Cr, Ni, and Cd due to the biogeochemical feature of soil cover in the city.

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Table 3. Stepwise discrimination analysis result

Metal	Standard mode				Forward stepwise mode				Backward stepwise mode			
	Wilks' λ: 0.19; F (16,758)=60.72; p<0.0000				Wilks' λ: 0.19; F (14,760)=69.52; p<0.0000				Wilks' λ: 0.19; F (10,764)=94.62; p<0.0000			
	Wilks' λ	F	p	R^2	Wilks' λ	F	p	R^2	Wilks' λ	F	p	R^2
Co	**0.194**	**2.157**	**0.117**	**0.751**	**0.194**	**2.135**	**0.120**	**0.754**				
Mn	0.242	48.806	0.000	0.713	0.242	48.778	0.000	0.715	0.270	67.493	0.000	0.787
Zn	0.252	58.755	0.000	0.767	0.253	59.651	0.000	0.772	0.271	68.850	0.000	0.806
Pb	0.196	4.001	0.019	0.577	0.197	5.030	0.007	0.905				
Cu	**0.192**	**0.162**	**0.851**	**0.583**								
Cr	0.203	11.214	0.000	0.975	0.204	11.322	0.000	0.976	0.210	10.230	0.000	0.985
Ni	0.273	80.317	0.000	0.663	0.276	83.003	0.000	0.689	0.285	81.999	0.000	0.722
Cd	0.389	194.340	0.000	0.800	0.391	196.279	0.000	0.805	0.399	190.834	0.000	0.823

The relationship between heavy metals and basic soil properties

Many researchers have found that the accumulation and migration of elements in the soil is determined by the physicochemical properties of soils (physical clay, absorbed substrates, soil reaction and organic matter). Accumulation and migration dependence of heavy metals in the soil was investigated applying the factor and cluster analysis. The results are presented in Figure 2 and Table 4.

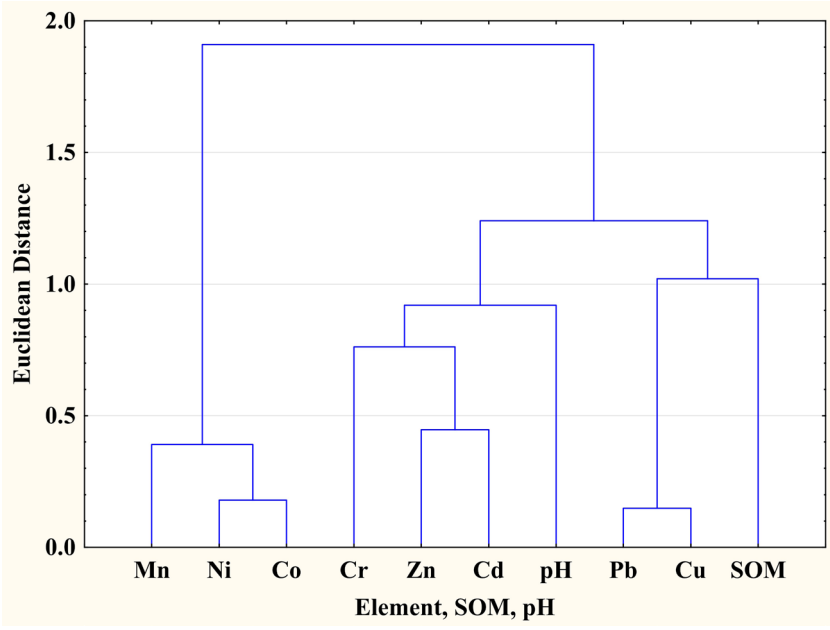

Figure 2. Dendogram of relationship between metals and SOM and pH in urban soils

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Table 4. Results of factor analysis showing relative loading of pseudo total concentration metals (The loadings over 0.45 are marked in bold).

Statistic	*PC-1*	*PC -2*	*PC -3*
Eigenvalue	*3.70*	*1.95*	*1.51*
Variance, *%*	*36.96*	*19.51*	*15.06*
Cumulative explained variance, *%*	*36.96*	*56.46*	*71.53*
Element	Loading		
Pb	***0.918***	*-0.163*	*0.107*
Cu	***0.893***	*0.231*	*0.124*
Cd	***0.683***	*0.403*	*-0.092*
Zn	***0.549***	*0.409*	*-0.203*
Ni	*0.069*	***0.943***	*0.102*
Co	*0.006*	***0.840***	*0.279*
Mn	*0.306*	***0.725***	*0.205*
Cr	*0.159*	*0.493*	*-0.207*
SOM	*0.222*	*0.012*	***0.846***
pH	*0.172*	*-0.187*	***-0.877***

In our present study, heavy metals show the following groups: [Co-Ni-Mn] - [(Cu-Pb-SOM) - (Cd-Zn-Cr-pH)]. Cu and Pb accumulate in soil as in organic compounds, while Cd, Zn and Cr accumulate due to soil neutralization [27].

CONCLUSIONS

In this work are shown some investigation results of pseudo total content of heavy metals in Ulaanbaatar surface soil.

Soil in Ulaanbaatar, especially in the central part of the city is highly distributed and itheir properties have changed due to urbanization and human activities.

The distribution pattern of pseudo-total content of heavy elements in the urban soil is uniform. Not showing the accumulation tendency for all investigated heavy metals.

The accumulation of heavy metals in Ulaanbaatar surface soil depends on the soil biogeochemical feature: organic matter for Cu and Pb, alkaline for Cd, Zn and Cr and soil parent material for Co, Ni and Mn.

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