Geochemical features of the elemental composition of meadowsweet (*Filipendula ulmaria (L).Maxim*) in Kemerovo Oblast

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Abstract. Biogeochemical sampling of the aboveground part of meadowsweet (*Fillipendula Ulmaria (L).Maxim*) allowed us to study ecological and geochemical features of 10 regions in Kemerovo Oblast, including both natural and man-made landscapes. The content of 55 elements in the plant is determined by ICP-MS. Statistical analysis of the results allowed us to establish the effect of the soil mineral composition and the mining region specificity on the elemental composition of meadowsweet, to reveal significant positive correlations of the elements and to establish a statistically significant difference in the studied areas on the basis of the content of some elements. Sample reference to one of the clusters, followed by an assessment of their geochemical features is determined by the K-average method.

1. Introduction

Biota is the most dynamic component of any landscape. Due to the numerous studies, the significant amount of both geo-botanical and chemical data has been accumulated, which pointed to close relationship between the plant and the environment. The application of biogeochemical methods in searching for deposits of nickel, cobalt, copper, chromium, lead, molybdenum, selenium, and other elements was described by A.E. Fersman, D.P. Malyuga, A.N. Perelman, H.L. Cannon [1-4 et al.]. On the other hand, the accumulation of information on the plants' elemental composition reflects clearly not only the natural component properties, but also man-made factors [5-8 et al.]. Thus, the goal of our research is to prove that the elemental composition of the widespread plants can be used to detect ecological and geochemical features of a region.

2. Materials and methods

Biogeochemical sampling was conducted for this purpose in 10 regions of Kemerovo Oblast in summer of 2015 in accordance with GOST 27262-87 and GOST 24027.0-80 standards. Meadowsweet (*Filipendula ulmaria (L). Maxim*) is characterized by high tolerance to the environment and occupies a dominant position in tall herbaceous layer of lowland meadows in Western Siberia. Samples of its overground parts were collected in blossom and early fruiting periods within the various natural and man-made landscapes. Air-dried raw material was crushed and sifted through 1 mm sieve. The total number of samples was 50.

The elemental composition study was carried out using mass spectrometry with inductively coupled plasma (ICP-MS) based on the standards in the accredited laboratory of the "Plasma" analytical center, Tomsk city (accreditation certificate ROSS RU.0001.516895).

3. Results and discussion

The content of 55 elements in the dry matter of meadowsweet aboveground parts was determined by ICP-MS. It was revealed that qualitative composition of the samples collected in different places was almost identical, while the quantitative content of the chemical elements differed significantly.

Concentrations of Sc, As, Cd, Eu, Er, Lu, Ta, Tl, Bi were below the sensitivity threshold of analysis in certain samples of plant material. Excess of Clarke concentrations in plant dry matter relative to the data obtained by B. Markert [9] was observed for Ca, As, Sc, Ba, Sb (table 1). High degree of concentration variabilities was established for Sm, Yb, Lu, Hf, Ta, Th, Rb, Eu, Sb.

Table 1. Clarke concentrations and variation coefficients in plant dry matter.

		Variation coefficient, %		
		Uniform (< 39)	Non-uniform (40 – 79)	Extremely non-uniform (> 80)
Clarke concentration	< 0.5	Cr	Na, Fe, Zn, Ag, Cs, La, Ce, Nd, Tb	Sm, Yb, Lu, Hf, Ta, Th, U
	0.5 – 1	Co	Sr	Rb, Eu
	1 – 2	Ca	As, Ba	Sb
	> 2		Sc	

Rank correlation assessment shows a large number of mainly positive significant correlations between the elements. The strongest of them ($R\alpha = 0.05 \geq 0.95$) are included in the lithophils group. It reflects the influence of the soil mineral composition and perhaps mining specialization of the region (figure 1). According to principal components analysis the same components, including Cs, are under the load of the first factor, constituting 32% from the general explained dispersion.

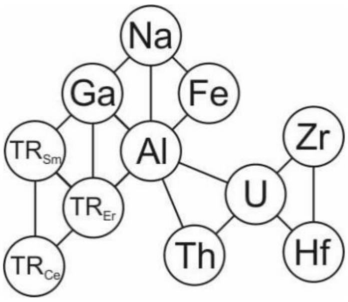

Figure 1. Graph of associations in plant dry matter.

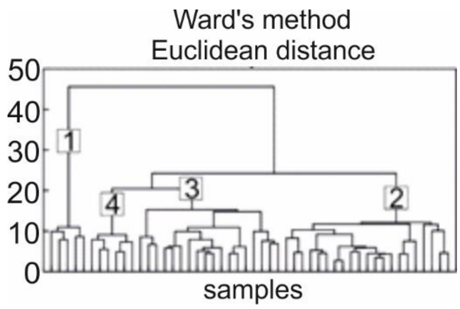

Figure 2. Dendrogram of plant dry matter correlation matrix: 1, 2, 3, 4 - number of clusters.

According to the results of nonparametric Kruskal–Wallis one-way analysis of variance, statistically significant difference between the studied areas is found by the content of some elements (table 2). Concentration coefficients presented in the tables are calculated using the average values.

Cluster analysis using standardized values of the component concentrations reveals a significant effect of local factors on the generalized biogeochemical characteristics of the area. Four clusters, including samples with close element distributions are allocated based on the dendrogram structure features (figure 2). Sample reference to one of the clusters, followed by an assessment of their geochemical features, is determined by the K-average method (table 3, figure 3).

Samples of the second and third clusters are likely to present "near background" element concentrations with some geochemical specificity of the regions and plant sample points. Samples from Tisul region are the most number-representative in the second cluster. The third cluster, where samples of Kemerovo Oblast dominate, is characterized by the relative concentration (CC ≥ 1.5) of rare and rare-earth lithophilic elements.

Table 2. Concentration coefficients of elements in *Filipendula ulmaria* (underground pert) with statistically significant biogeochemical difference in the regions of Kemerovo Oblast.

Region (number of samples)	Coefficient of concentration (CC)															
	Sc	Ti	V	Co	Ni	As	Ag	Hf	Ga	Pb	Bi	Th	U	TR(Ce)	TR(Sm)	TR(Er)
Ch (6)	1.2	1.3	0.9	1.0	0.8	0.9	1.2	0.9	0.7	1.0	1.4	1.0	1.0	0.9	0.9	0.9
G (7)	**0.1**	0.6	0.7	1.2	**0.5**	**0.5**	**0.2**	1.0	**1.5**	**1.8**	0.9	1.0	1.0	0.8	0.7	0.9
I (5)	1.1	**3.2**	**1.6**	1.2	**1.7**	**1.9**	1.0	1.0	**1.8**	1.0	1.0	1.3	1.3	1.4	1.3	1.4
K (5)	**0.4**	0.7	0.9	1.2	**1.8**	0.9	0.6	**1.7**	1.4	**1.6**	0.9	1.3	1.2	**2.1**	**1.8**	**2.4**
L (4)	0.6	0.7	**1.7**	1.3	**0.4**	1.0	**1.5**	**2.1**	**3.0**	1.4	**2.3**	**1.7**	**2.0**	1.2	1.2	1.3
M (7)	1.4	1.4	1.4	0.8	1.4	**1.5**	1.1	0.8	0.7	0.6	0.9	0.7	1.0	1.2	1.2	1.2
T (12)	1.1	1.2	1.0	0.8	0.7	1.3	1.0	0.7	0.6	0.7	1.0	**0.5**	0.8	0.6	0.6	0.6
Ya (1)	1.1	**4.7**	0.7	**0.5**	**1.5**	1.2	1.0	**0.5**	0.6	1.4	1.1	**0.4**	0.6	0.7	0.6	**0.3**
B (2)	**0.5**	1.0	1.1	1.1	0.9	0.9	**0.4**	**3.8**	**1.8**	**2.0**	1.1	**3.1**	**3.2**	**2.1**	**2.2**	**2.5**
P (1)	**0.2**	0.6	1.4	1.2	1.0	**0.2**	**0.5**	**4.2**	**2.2**	1.2	**1.5**	**3.8**	**2.7**	**2.4**	**2.6**	**3.3**

Note: regions: Ch - Chebula, G – Gurevsk, I – Izhmorsky, K – Kemerovo, L – Leninsk-Kuznetsk, M – Mariinsk, T – Tisul, Ya – Yaya, B – Belovo, P – Promyishlennovsky; 0.5 ≤ CC ≥ 1.5

Table 3. Geochemical characterization of meadowsweet (*Fillipendula Ulmaria*) in different clusters.

Number of cluster	Ordered by the value of the concentration coefficient series of chemical elements: chemical element (coefficient of concentration)	Region (number of samples)
1.	U (5.0), TR(Er) (4.6), Hf (4.3), TR(Sm) (4.3), Zr (4.1), Th (4.1), Cs (3.9), Nb (3.7), Ta (3.6), Al (3.5), Y (3.4), TR(Ce) (3.3), Na (2.9), Fe (2.7), Ga (2.5), V (2.1), Tl (1.8), Sb (1.7), Pb (1.6), Si (1.6), Bi (1.5), Sn (1.5), Ti (1.5), Mo (1.4), Cd (1.3), Co (1.3), Rb (1.3), Li (1.2), Ba (1.2), Zn (1.1), Ni (1.1), Cr (1.1), Mn (1.1), P (1.1), Sc (1.1), Cu (1.0), W (1.0), Ag (1.0), Ca (1.0), Sr (1.0), K (0.9), As (0.8), Mg (0.8), B (0.7)	I (2), B (1), L (1), P (1)
2.	Sb (1.0); K (1.0). W (1,0), Bi (1.0), Rb (1.0), Cd (1.0), Mg (1.0), As (1.0), Sr (1.0), P (1.0), Ag (1.0), Cu (1.0), Cr (0.9), Ca (0.9), Co (0.9), Ba (0.9), Mo (0.9), B (0.9), Fe (0.9), Sn (0.9), V (0.8), Pb (0.8), Cs (0.8), Ta (0.8), Ti (0.8), U (0.8), Mn (0.8), Na (0.8), Zr (0.7), Si (0.7), Zn (0.7), Ga (0.7), Al (0.7), Sc (0.7), Tl (0.7), Nb (0.7), Ni (0.7), Hf (0.6), Li (0.6), TR(Sm) (0.6), TR(Er) (0.6), TR(Ce) (0.6), Y (0.5), Th (0.5)	I (1), M (1), Ch (3), T (7), B (1), G (4), L (1)
3.	W (2.2), TR(Er) (1.7), Ta (1.7), Y (1.6), Hf (1.6), Cs (1.5), TR(Ce) (1.4), Al (1.4), TR(Sm) (1.4), Zr (1.4), Bi (1.4), Nb (1.4), Fe (1.3), Ga (1.3), U (1.3), Th (1.3), Mn (1.3), V (1.2), Na (1.2), Co (1.2), Sb (1.2), Ti (1.2), Li (1.1), Sn (1.1), B (1.1), Si (1.1), Pb (1.1), Ca (1.1), Mo (1.1), Cr (1.1), Tl (1.0), Sr (1.0), Mg (1.0), Zn (1.0), Cd (1.0), Cu (1.0), P (1.0), As (1.0), Ba (0.9), Ag (0.9), K (0.9), Ni (0.9), Sc (0.9), Rb (0.8)	I (1), M (3), Ch (3), T (3), K (5), G (2), L (2)
4.	Ni (2.9), Ba (1.8), Cd (1.8), Ti (1.8), Zn (1.6), Cu (1.4), As (1.4), Mn (1.3), Rb (1.3), Sc (1.1), P (1.1), K (1.1), Cr (1.1), Ag (1.0), Bi (1.0), Mg (1.0), Li (0.9), Ca (0.9), Sr (0.9), B (0.9), Si (0.9), V (0.9), W (0.8), Sn (0.8), Mo (0.8), Y (0.8), Fe (0.8), Ga (0.7), Hf (0.7), Zr (0.7), Cs (0.7), TR(Ce) (0.7), TR(Sm) (0.7), Co (0.6), Na (0.6), U (0.6), Al (0.6), Pb (0.6), Nb (0.5), Tl (0.5), TR(Er) (0.5), Th (0.5), Ta (0.4), Sb (0.4)	Ya (1), I (1), M (3), T (2), G (1)

Note: regions: Ch - Chebula, G – Gurevsk, I – Izhmorsky, K – Kemerovo, L – Leninsk-Kuznetsk, M – Mariinsk, T – Tisul, Ya – Yaya, B – Belovo, P – Promyishlennovsky

Samples of the first cluster are distinguished by quite contrast relative accumulation of mainly lithophilic elements. At the same time, a clear indication to natural radioactive, rare earth and rare elements is of particular interest in this cluster.

The fourth cluster samples are distinguished by a mixed chalco-sidero-lithophilic association of concentrating elements.

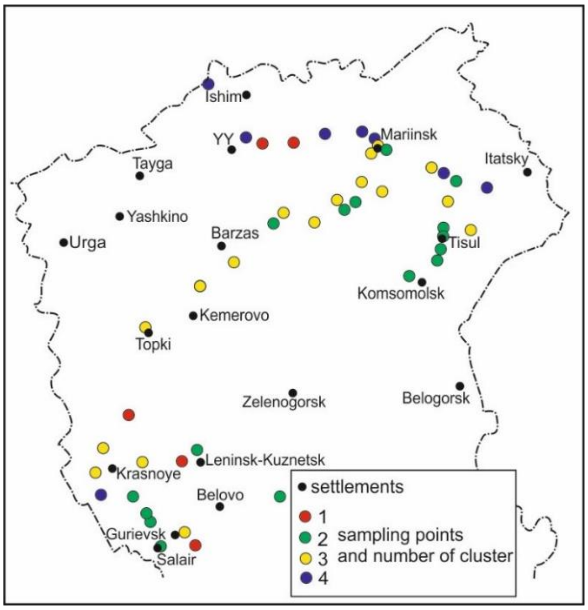

Figure 3. Geochemical features of meadowsweet (*Fillipendula Ulmaria L.*) in different clusters of Kemerovo Oblast.

4. Conclusions

Thus, the regional biogeochemical differentiation of the study areas of Kemerovo Oblast should be carried out taking into account the natural and man-made features of the sampling sites. The dependent number of samples with abnormal deviation at the accumulation levels of element series introduces a significant distortion in the generalized biogeochemical characteristics of the territories.

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References

[1] Fersman A E 1937 *Geochemistry* Leningrad: ONTI-Himteoret.
[2] Malyuga D P 1963 *Moscow: SA USSR Press.* Biogeochemical methods of ore deposit prospecting.
[3] Perelman A I 1975 *Moscow: High School.* Landscape geochemistry.
[4] Cannon H L 1960 *Science.* Botanical prospecting for ore deposits. Vol. **132** pp. 591–598.
[5] Hegland S J, Dunne J and Nielsen A 2010 *Biol. Cons.* How to monitor ecological communities cost-efficiently: The example of plant–pollinator networks. Vol. **143** pp 2092–101.
[6] Reimann C, Englmaier P and Fabian K 2015 *Sci. Total Environ.* Biogeochemical plant–soil interaction: Variable element composition in leaves of four plant species collected along a south–north transect at the southern tip of Norway. Vol. **506–507** pp. 480–95.
[7] Favas P J C, Pratas J and Mitra S 2016 *Sci. Total Environ.* Biogeochemistry of uranium in the soil-plant and water-plant systems in an old uranium mine. Vol. **568** pp. 350–68.
[8] Favas P J C, Pratas J and Prasad M N V 2012 *Sci. Total Environ.* Accumulation of arsenic by aquatic plants in large-scale field conditions: Opportunities for phytoremediation and bioindication. Vol. **433** pp. 390–7.
[9] Markert B 1991 *Water Soil Air Poll.* Establishing of “Reference plant” for inorganic characterization of different plant species by chemical fingerprinting. Vol. **64** pp. 533–8.