Trace element concentrations in needles and bark of *Larix sibirica* within the Mo-W ore field (Buryat Republic, Russia)

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Introduction

The aim of this study is to assess the changes in the trace element composition of *Lárix sibírica* species growing in the impact area of Dzhida tungsten and molybdenum company (DTMC) in the Zakamensk city where from 1934 to 2001 one of the largest non-feric deposits has been exploited. As a result of 67-year mine operation more than 44,5 million tons of tailing has been formed in the valley of Barun-Narin and Modonkul rivers and within the city.

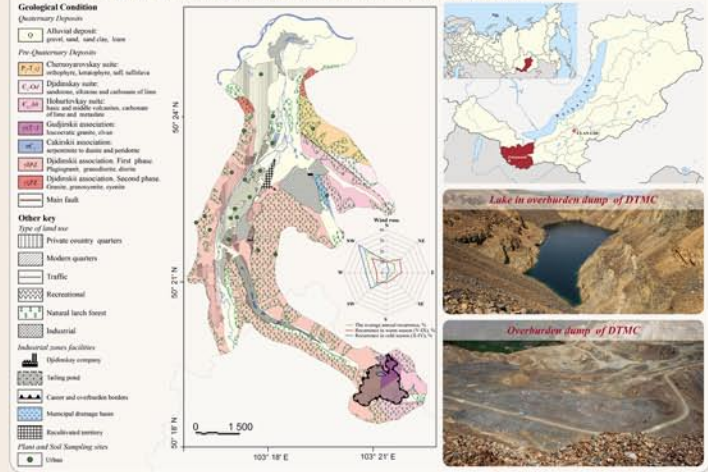
The objectives of the present study:

- to determine trace element levels in organs of background and urban plants and to assess geochemical transformation of the city's plants;
- to identify the rates of trace element translocation in soil-plant system;
- to assess the ecological state of larch plantation in different land use zones of the city.

Methods and materials

Biogeochemical survey was conducted by the authors in summer, 2013. Assimilate (needles) and perennial (bark) organs of Siberian larch (*Lárix sibírica*) were collected from the trees about the same age in the growing phase after flowering and after five days without rainfall. Composite samples were formed by mixing individual samples from three or more trees. All 42 samples of needles and bark were dried within 12 hours at a temperature 70-80°C.

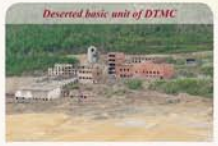
Bulk contents of trace elements in plant samples were analyzed by mass-spectral method with inductively coupled plasma (ICP-MS) at the Research Institute of mineral raw materials (Moscow) using Elan-6100 and Optima-4300 devices (Perkin Elmer, USA). The method allows to determine the content of 54 elements. Data on 17 priority pollutants belonging to I (Zn, As, Pb, Cd), II (Cr, Co, Ni, Cu, Mo, Sb), III (V, Sr, Ba, W) hazard classes, as well as Sn, Bi and Mn were used for detailed analysis.



Sources of pollution

The Dzhida tungsten and molybdenum company produced from 73 to 80% of total tungsten concentrate in the USSR. The was carried out by flotation, which was used toxic chemicals: kerosene, sulfuric acid, xanthogenate, pine oil, soluble glass and other. Processed rocks formed in three tailings: Djidinskoe (bulk cargo), Bsrun-Narinskoe (hydraulic fill) and emergency. In 2011 the emergency tailing was mechanically recultivated and 3,5 million tons of tailings was moved to upper part of hydraulic fill.

Since 2010 "Zakamensk" company retreat technogenic sands (tailing) and formed new tailing area in the valley of the Zun-Narin river. In addition to mining operations the full-tree system and milling, casting iron, steel, bronze, construction are engaged in the town in.



Biogeochemical indices

Coefficient of biogeochemical transformation

$$Z_v = \sum_{l=1}^{n} EF_l + \sum_{l=1}^{n} DF_l - (n_1 + n_2 - 1)$$

where $EF_l = C_l / C_b$ and $DF_l = C_b / C_l$ – local enrichment and depletion factors. C_l, C_b – element content in urban and background plants, n1, n2 – number of elements with $EF_l > 1$ and $DF_l > 1$. Coefficient of biogeochemical transformation has five gradations: minimum (Z_v = 10–20), medium (Z_v = 20–30), high (Z_v = 30–40), very high (Z_v = 40–60), and extremely high (Z_v = 60–80 and higher).

Coefficient of biological accumulation

$$CBA = l_x / C_s$$

where l_x – element content in ash of urban and background plants; C_s – weighted by horizon thicknesses mean element conten in soil profile

Geochemical features of background plants

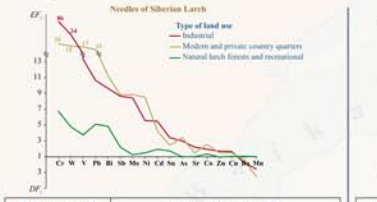
Organs	V	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Mo	Cd	Sn	Sb	Ba	W	Pb	Bi
Needles	0.07 2.13	0.04 0.04	603 18682	0.09 2.89	0.38 11.74	3.3 101.5	11.5 356.5	0.04 0.04	51 1602	0.07 2.1	0.02 0.52	0.03 0.89	0.01 0.2	66 2059	0.37 11.5	0.23 7.2	0.012 0.36
Bark	1.5 84.79	0.82 45.8	180 11411	0.20 11.4	1 57.4	3.7 228.9	10.4 626	0.16 9	35 2087	0.49 27.8	0.08 4.9	0.07 4	0.07 3.9	78 4830	0.18 13.6	3.3 183.8	0.015 1.13
World-wide average	1.5 30	1.8 35	205 4100	0.5 10	2 40	8 160	30 600	0.12 3	35 700	0.5 10	0.04 0.7	0.25 5	0.10 -	23 450	0.20 -	1.25 25	0.01 -

Note: in the numerator - dry matter; denominator - in ash

Biogeochemical specialization of local background was detected by comparing the average trace element content in the studied tree organs with a concentrations of trace elements in the vegetation annual gain.

Geochemical spectra of urban plants

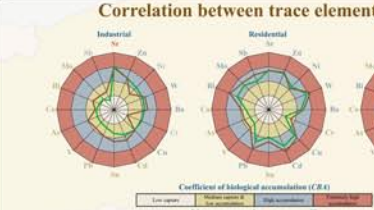
Priority pollutants in Zakamensk plants were determined by geochemical spectra analysis for different types of land use. Elements were ranged in accordance with EF_l values for needles in *Lárix sibírica* in the most polluted mining zone of Zakamensk.



Type of land use	Elements with EF_l > 1.2
Industrial	$Cr_{86}W_{34}V_{15}Pb_{10}Bi_{9}Sb_{8}Mo_{7}Ni_{7}Cd_{6.5}Sn_{5.4}As_{5.0}Sr_{3.5}Co_{3}Cu_{2}Zn_{1.7}$
Modern and private country quarters	$Cr_{20}W_{10}V_{9}Pb_{10}Bi_{7.5}Mo_{6}Sb_{5}Ni_{4.5}Cd_{4.1}As_{3}Cu_{2.5}Sn_{2.3}Co_{2}Zn_{1.5}Sr_{1.3}$
Natural larch forests and recreational	$Cr_{6.8}Pb_{3.3}Bi_{3}W_{2.8}V_{1.8}Sb_{2.5}Cd_{1.8}Sn_{1.7}Ni_{1.5}Co_{1.3}Mo_{1.3}$

Type of land use	Elements with EF_l > 1.2
Industrial	$W_{108}Bi_{27}Sn_{2.5}Sb_{2}Pb_{1.4}As_{1.4}Mo_{1.2}Cd_{1.1}V_{1.1}$
Modern and private country quarters	$W_{27}Bi_{7}Sb_{2}Pb_{2.2}Cd_{1.1}Cu_{1.1}Zn_{1.1}Mo_{1.2}Sn_{1.1}Sr_{1.1}V_{1.1}Ni_{1.1}$
Natural larch forests and recreational	$W_{35}Bi_{12}Sb_{1.8}Pb_{1.8}Cd_{1.5}Sr_{1.3}$

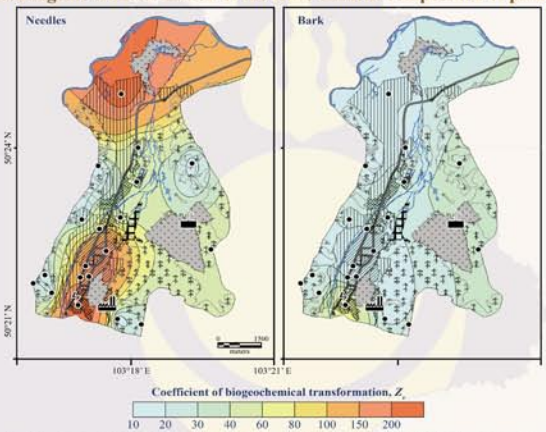
Correlation between trace element content in plants and soils



In all land use zones of Zakamensk a vigorous and pronounced accumulation of mainly cationogenic elements (Cu, Zn, Sr, Cd, Ba) occurs in the larch needles. It is typical for areas of the Baikal region, where acidic soils are widespread. This group also includes the anionic elements: ore W and its accessory Bi.

In background and natural recreational areas group of low capture includes V and Cr anions, these is typical for these land-geochemical conditions. The wide range of of elements is accumulated in the Siberian larch needles within a residential zone, this is caused by the intensive element input in the soils as a result of their lateral migration from tailing ponds.

Technogenic transformation of the trace element composition of plants



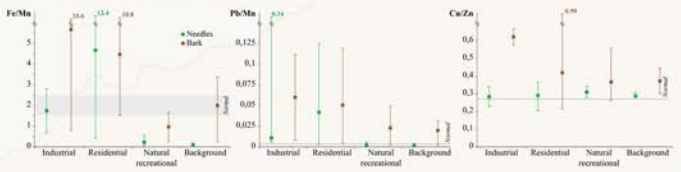
Needles of larch is characterized by the highest values – the average of Z_v across the city is 95. It indicates the extremely high level of geochemical transformation of urban plants. $Cr_{29}W_{16}V_{14}Pb_{12}Bi_{9}Mo_{8}Sb_{7}Ni_{6.3}Cd_{4.3}Co_{3.3}Sn_{2.5}$ make the main contribution to the Z_c value for larch needles.

Two stable biogeochemical anomalies were determined in the center and on the north of the city. The first was formed in industrial and residential zones where Z_c values for needles reach 320 and 205. Needle accumulate pollutants from different sources: Djida tailings, which material is undergone active erosion and deflation; TPP, working on heating oil; "Liteschik" plant, where cast iron, steel, bronze and recycling of scrap metal are made; motor vehicles. Heavy metals and metalloids incoming to soils and air from emissions and sewage waters are absorbed by trees by roots and leaves.

The second anomaly, were Z_c values reach 260, is re-vealed within the residential zone in the northern part of the city, south-west from technogenic Modoncul stale sands deposit. This anomaly was formed mainly because of trace element input from the atmosphere. Local weather conditions are characterized by frequent and strong winds (up to 20 m/s), and the narrow river valley with high sides stimulates a "canyon" effect and causes migration of fine particles from "Djidinskii tungsten and molybdenum company" tailings.

Assessment of ecological state of urban plants

The ecological state of the urban plants was diagnosed from the Fe/Mn, Pb/Mn, and Cu/Zn ratios. The first ratio is one of the most informative parameters of photosynthetic processes; the second ratio characterizes the relationship between technogenic and biophilic elements, and the third ratio determines the proportion in the supplies of these biogenic metals for enzyme synthesis.



Conclusions

1. Regional biogeochemical features of siberian larch in natural landscapes are determined by a high content of only one cationogenic siderophile element – Ba, due to its mobilization in acid soils. The concentration of all the other trace elements in longstanding and assimilative organs is usually lower than the global clarks.

2. In non-feric mining landscapes active accumulation of trace elements was found, despite of the close of mining complex 20 years ago. Assimilative and longstanding organs of coniferous species in all land use zones of the Zakamensk city are cationofilic and actively accumulate elements of moderate and low capture – Cu, Zn, Sr, Cd, Ba, as well as specific ore manifestations anions – W and Mo. The biological accumulation coefficients of these trace elements are higher than 1, indicating woody plants as biogeochemical barrier.

3. Trace element bioaccumulation within Zakamensk is maximum in two anomaly zones in the center and northern part of the city. The assimilative larch organs more strongly absorb trace elements as estimated in the dry matter, than longstanding, indicating bazipetal type of distribution. The main contribution to the total contamination of the larch needles is given by Cr, W, V, Pb, Bi, Mo, Sb, Ni, Cd, Co, Sn.

4. Indication of woody plant ecological state according to the relationships Fe/Mn and Pb/Mn in the larch needles found violations in the photosynthesis processes. The highest values of Fe/Mn (4.7) and Pb/Mn (0.042) were recorded in the residential area. First ratio indicates a sharp deficiency of Mn and bioaccumulation of the excess active ferrous Fe, which can cause chlorosis and plant stress. Second ratio shows Pb excess which inhibits respiration and photosynthesis. Cu/Zn ratio values equal 0.28-0.31 in needles and bark of Siberian larch slightly deviate from optimal for uncontaminated land plants.

5. The experience of geochemical assessment of woody plant state in mining centers demonstrates the need in geochemical sampling both larch needles and bark. Needles sampling allows to evaluate seasonal and barck's – long-term impact. Results show high sensitivity of studied plant species to the technogenic load, indicating weak resistance of conifers to heavy metals. So they are good indicators of environmental pollution.