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# Ecological and Geochemical Assessment of Woody Vegetation in Tungsten-Molybdenum Mining Area (Buryat Republic, Russia)

N S Kasimov<sup>1,4</sup>, N E Kosheleva<sup>2</sup> and I V Timofeev<sup>3</sup>

<sup>1</sup> Head of the Dept., Faculty of Geography, Lomonosov Moscow State University, Moscow, Russia

<sup>2</sup> Leading researcher, Faculty of Geography, Lomonosov Moscow State University, Moscow, Russia

<sup>3</sup> Junior researcher, Faculty of Geography, Lomonosov Moscow State University, Moscow, Russia

E-mail: natalk@mail.ru

**Abstract.** Biogeochemical studies performed in the impact zone of the Dzhida tungsten–molybdenum mining and processing enterprise in Zakamensk (Buryat Republic, Russia) in 2013 showed that the needles and bark of *Lárix sibíríca Ledeb.* and the leaves and bark of *Bétula platyphýlla Sukacs* are characterized by certain changes in their trace element (TE) composition. The total index of the biogeochemical transformation  $Z_v$ , which sums all the positive and negative deviations of TE contents from the background values for larch and birch in the city averaged 95 and 46 for their assimilating organs and 30 and 25 for their perennial organs, respectively. This was caused by the increased uptake of W, Mo, V, Pb, Bi, Cd, and Co in the city. The close correlation between TE concentrations in soils and plants was observed for the elements of the strong and moderate biological capturing, including cationic Cu, Zn, Sr, Cd, and Ba and anions of the ore elements W and Mo and the associated Bi. The most intensive TE accumulation was found in the larch needles due to the wax layer which firmly fixes the dust enriched with TEs. Indication of the ecological state of urban woody plants revealed that their organs contain the increased concentrations of Pb and Fe and suffer from the Mn deficiency, which attests to disturbance of photosynthetic processes, most pronounced in the residential area. Birch leaves are characterized by a very low Cu/Zn ratio which detects the imbalance of these elements participating in the synthesis of enzymes.

## 1. Introduction

The development of nonferrous metal deposits exerts a significant impact on the environment and contributes to the emergence of cities and towns, mines, and factories that are exposed to high concentrations of pollutants. Being involved in the biogeochemical cycle, these pollutants enter through the soil, hydrosphere, and atmosphere into the plants. Getting trace elements (TEs) from the soil and the atmosphere, the plants are indicative of the degree of the environmental pollution. Therefore, the biogeochemical monitoring has become widely used in recent decades [1–4]. Woody assimilating organs (leaves and needles) are most rich in ash elements and are extremely sensitive to



changes in the environmental conditions [5-7]. TE concentrations in perennial organs (bark, root system) are insufficiently studied; there are few works devoted to the concentration of heavy metals and metalloids (HMMs) in these organs [6, 9, 10].

Our work was aimed at the study of the TE composition of assimilating (needles, leaves) and perennial (bark) organs of Asian white larch (*Lárix sibirica* Ledeb.) and Siberian birch (*Bétula platyphýlla* Sukacs) in the impact zone of the Dzhida tungsten–molybdenum factory (DTMF) in the Zakamensk city (the Buryat Republic, Russia), where the mining of nonferrous metals continued for more than 60 years. In 2001, the DTMF was closed. However, necessary environmental protection measures—elimination of mines, rehabilitation of disturbed lands, and purification of contaminated mine waters—were not realized. As a result, the zone of ecological disaster appeared in this area [10]. In our work, we attempted to (a) determine the degree of technogenic disturbances of the micro-elemental composition of tree organs, (b) specify the intensity of the uptake of TEs by the trees from soils, (c) evaluate the ecological state of larch and birch in mining landscapes, and (d) determine indicative potential of the considered tree organs for the geochemical monitoring of the environment.

## 2. Study objects

*Environmental conditions.* The city of Zakamensk occupies the area of 45 km<sup>2</sup> in 460 km to the southwest of the Ulan-Ude city in the Trans-Baikal region. It is allocated to the boundary between two regional geological structures represented by the Early Paleozoic calcareous–terrigenous deposits of the Dzhida synclinorium and granitoid intrusions of the Modonkul massive with a considerable (300–400 m) ruggedness of the local topography. The climate is sharply continental, with cold and low-snow winters and relatively short and warm summer seasons. Mean annual precipitation is about 250–300 mm; predominant winds blow from the west and southwest. Mountainous soddy taiga and soddy calcareous soils are developed in autonomous geomorphic positions and on steep slopes covered by forests. *Lárix sibirica* and *Bétula platyphýlla* are the major cenosis-forming tree species. In the intermontane depressions, on the footslopes, and in the valleys of the Modonkul and Dzhida rivers, soddy soils are developed under the anthropogenically disturbed meadow and meadow-bog vegetation, and meadow alluvial soils are formed under meadow vegetation with willow groves [11].

*Technogenic impacts.* From 1934 to 2001, the DTMF produced up to 80% of tungsten concentrate obtained in the USSR. The tungsten ore contains HMMs of the 1st–3rd hazard classes, such as Pb, Zn, F, Mo, W, Be, Bi, As [12]. Various reagents, including kerosene and sulfuric acid were applied for ore dressing. Waste products are stored in the Dzhida tailing (filled), the Barun-Naryn tailing (sludge pond), and the emergency tailing. In 2000, the first two tailings got the status of technogenic deposits because of high concentrations of W and Mo in them. In 2009, rehabilitation works begun, and some part of the stored wastes was removed toward the Barun-Naryn tailing, where in 2010, the Zakamensk JSC started to extract W concentrate. The new Zyn-Naryn tailing was formed for storage of wastes.

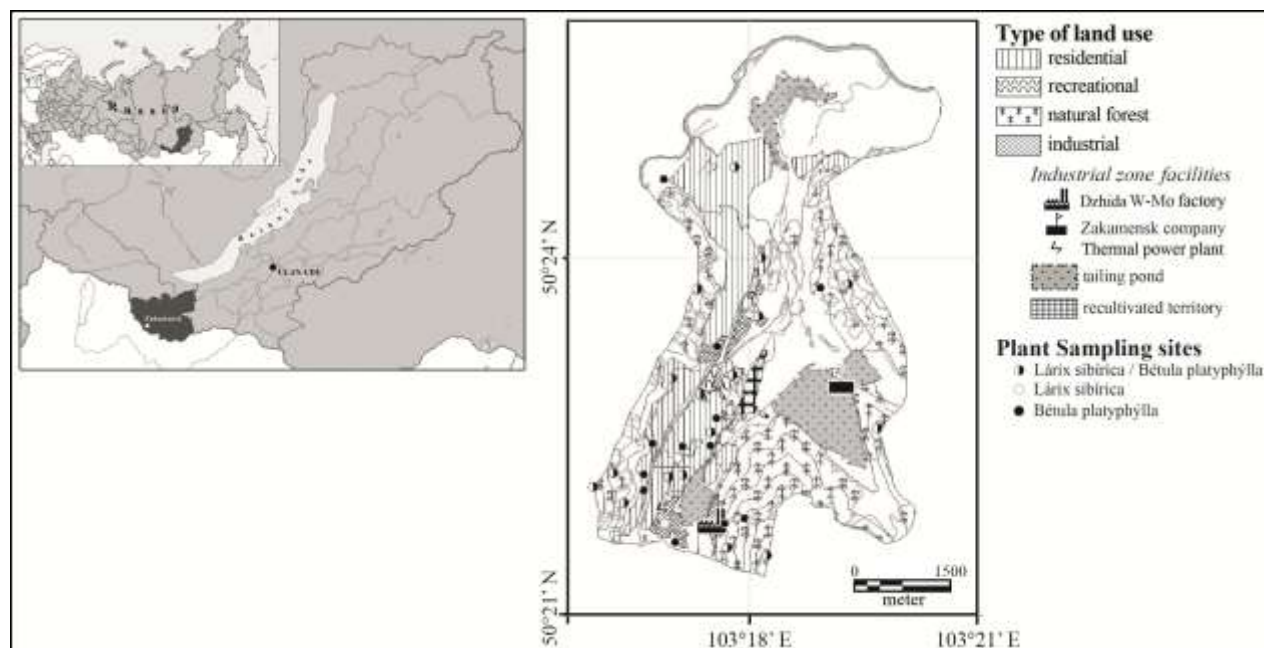
*Land-use structure of the city.* Three land-use zones—residential, industrial, and natural recreation—can be distinguished in Zakamensk. The industrial zone includes the DTMF, the "Foundry" Smelter, the thermal power plant to the south of the residential zone and the Barun-Naryn, Zun-Naryn, and Dzhida tailings to the west of the residential zone on the right bank of the Modonkul River. On the left bank, in place where the river channel turns from the meridional direction to the sublatitudinal one, the Modonkul deposit of technogenic sands was shaped. The tops and gentle slopes of the hills in the Modonkul and Zimka river valleys were considered as background natural territories.

## 3. Materials and methods

Assimilating (needles and leaves) and perennial (bark) organs of Asian white birch and Siberian larch were sampled in the middle of the summer of 2013 in different land-use zones of the city. The mixed samples were taken from three or more trees of the same age after the flowering stage and after the five-day long rainless period. Needle and leaf samples were dried for 6 hours at 70–80°C. In contrast to larch needles, birch leaves were initially washed by distilled water in order to remove elements

precipitated on the leave surface and not participating in plant metabolism [12, 13]. Overall, we collected 32 samples for birch leaves and bark and 21 samples for larch needles and bark (Figure 1).

Bulk contents of 54 HMMs in the dry samples of plant material were determined by mass and atomic emission spectrometry with inductively coupled plasma methods in the All-Russian Institute of Mineral Ores on Elan-6100 and Optima-4300 devices (Perkin Elmer, USA). For a detailed analysis, 16 priority pollutants typical of Mo–W deposits [14] and characterized by the high toxicity for living organisms were selected. They belong to the first (Zn, As, Pb, Cd), second (Cr, Co, Ni, Cu, Mo, Sb), and third (V, Sr, Ba, W) hazard classes; in addition, data on Sn and Bi were analyzed.



**Figure 1.** Map of sampling points and land-use zoning of Zakamensk.

The intensity of biological uptake of elements was judged from the coefficient of biological accumulation  $CBA = I_x/C_s$ , where  $I_x$  is an element concentration in plant ash;  $C_s$  is its concentration in the soil [15]. The changes in the TE composition of plant materials were evaluated with the help of the

total index of biogeochemical transformation:  $Z_v = \sum_{l=1}^{n_1} EF_l + \sum_{l=1}^{n_2} DF_l - (n_1 + n_2 - 1)$ , where  $EF_l = C_l/C_b$

and  $DF_l = C_b/C_i$  are local enrichment and dispersion factors, respectively;  $C_i$  and  $C_b$  are the concentrations of TEs in the urban and background samples, respectively; and  $n_1$  and  $n_2$  are the numbers of TEs with  $EF_l > 1$  and  $DF_l > 1$ , respectively [16]. The  $Z_v$  index reflects the disturbance of normal proportions of TEs in plant organs typical of their phylogenetic and ontogenetic specialization. It is a quantitative measure of the imbalance of elements in plants which appears under the impact of anthropogenic loads. The  $Z_v$  index has five grades corresponding to minimal (10–20), moderate (20–30), strong (30–40), very strong (40–60), and extremely strong (>60) disturbance. The ecological state of the plants was specified from the Fe/Mn, Pb/Mn, and Cu/Zn ratios [17–19].

## 4. Results and discussion

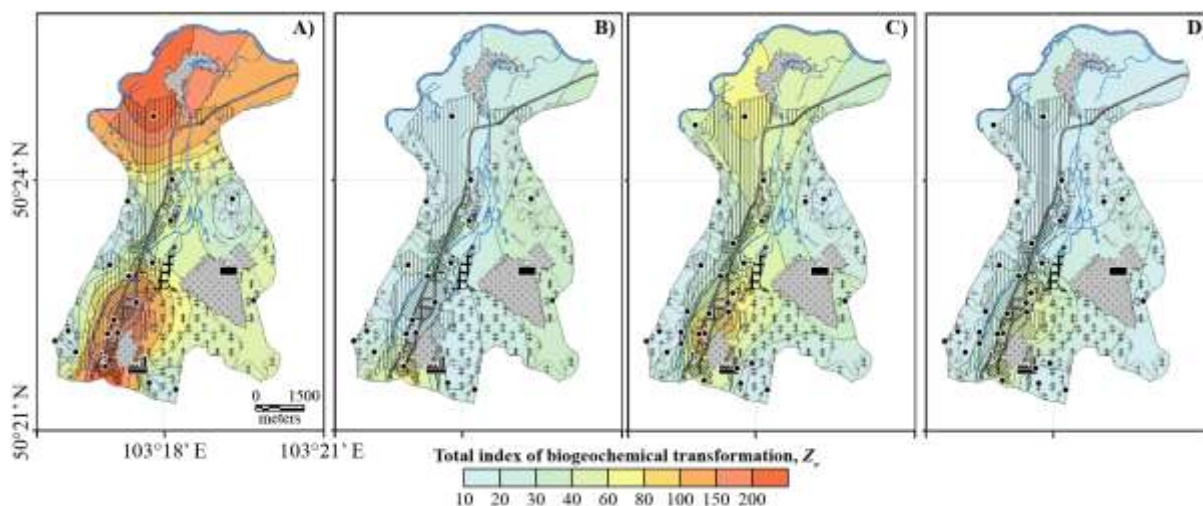
### 4.1.1. Assessment of the technogenic geochemical transformation of plants

The response of the tree species to technogenic pollution was judged from the total  $Z_v$  index. As the woody vegetation and, hence, sampling points in the city had an uneven distribution pattern, the compiled maps (Figure 2) can only present the most general spatial trends of the multielemental

contamination of the trees. Coniferous and small-leaved deciduous species differ greatly in geochemical transformation. Larch needles are characterized by higher values of the  $Z_v$  index: its average value in the city reaches 95, i.e., it corresponds to the extremely strong technogenic transformation of the TE composition of larch needles. For birch leaves, the average  $Z_v$  index is 46. The major contribution to the  $Z_v$  value for larch needles is paid by the following element association:  $Cr_{19}W_{16}V_{14}Pb_{12}Bi_9Mo_8Sb_7Ni_{6.5}Cd_{4.3}Co_{3.3}Sn_{2.5}$ ; for birch leaves, this association is somewhat different:  $W_8V_7Mo_7Bi_{5.9}Pb_{5.4}Sb_{4.5}Cd_{2.1}Co_{2.0}$  (subscripts denote  $EF_i$  values averaged for the city).

There are two stable biogeochemical anomalies in the center and north of the city (Figs. 2A and 2C). The first anomaly is formed in the industrial and residential zones, where  $Z_v$  values reach 320 and 205 for larch needles and 100 and 71 for birch leaves, respectively. This anomaly accumulates pollutants from several sources: the Dzhida tailing, the material of which is subjected to erosion and deflation; the thermal power plant which utilizing black oil, and the "Foundry" Smelter producing foundry iron, steel, and bronze and reworking scrap metal and old cars. The pollutants emitted into the atmosphere and discharged with waste water are taken up by the trees from the soils and absorbed from the air.

The northern anomaly with  $Z_v$  values reaching 260 in larch needles and 72 in birch leaves is allocated to the residential zone, to the southwest from the Modonkul deposit of technogenic sands. Its origin is mainly related to the aerial pollution with TEs. Local weather conditions are characterized by frequent and relatively strong (up to 20 m/s) winds, and the narrow valley of the Modonkul River with high banks, on which the city is found, creates the wind corridor, along which fine dust particles are transferred from the places of waste storage. Thus, the major factor of the biogenic accumulation of the pollutants is the precipitation of dust particles enriched in W, Mo, Pb, Bi, Cd, Sb, and V on the surface of assimilating plant organs; the higher accumulation of the pollutants by larch needles is explained by the presence of the wax film favoring firm fixation of the dust on their surface [20–26].



**Figure 2.** The degree of geochemical transformation of the (A) needles and (B) bark of *Larix sibirica* and (C) leaves and (D) bark of *Bétula platyphýlla* in Zakamensk.

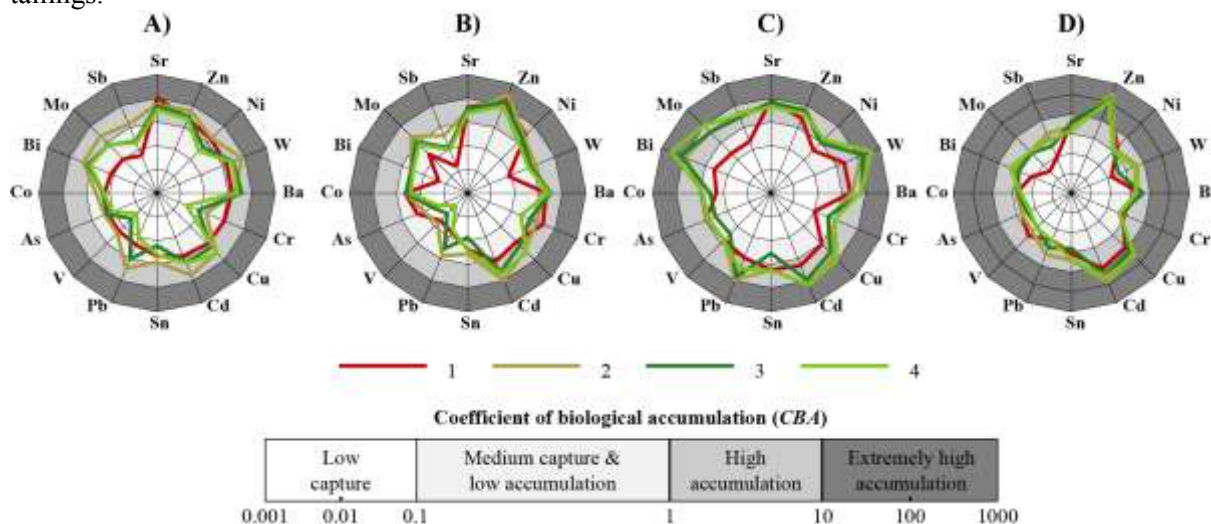
The accumulation of the pollutants in perennial organs of the trees is much weaker; the corresponding  $Z_v$  values are smaller than those of the assimilating organs (Figure 2). Thus,  $Z_v$  averages 30 for the bark of larch and 25 for the bark of birch, which corresponds to the strong and moderate biogeochemical transformation, respectively. The major contribution is due to the W–Pb–Bi ( $EF_i=3-7.5$ ) and Cd–Mo–Zn (1.7–3) element associations, respectively. Maximum  $Z_v$  values—85 for larch bark and 55 for birch bark—were determined in the biogeochemical anomaly in the south of the city, near the "Foundry" Smelter and the thermal power plant.



#### 4.2. Relationships between TE composition of soils and plants

The trees can selectively absorb some elements from the environment and accumulate them in their organs. The geochemical specialization of the particular tree species is reflected in the coefficients of the biogenic accumulation of elements (CBA). To calculate the CBA, soil profiles were examined in the sites of tree sampling, and soil samples were taken for the determination of TEs with the ICP-MS method. For each soil profile, the mean weighted (according to the thickness of various soil horizons) concentrations of elements were calculated, because the tree roots take up mineral and organic substances from various depths. Then, the averaging of these mean weighted concentrations was performed for each land-use zone of the city.

In all the land-use zones, larch needles actively accumulate mainly cation-forming elements (Cu, Zn, Sr, Cd, Ba), which is typical of the Trans-Baikal region with acid soils [27]. This group also includes the anion-forming elements: major ore element W and his associate Bi (Figure 3A). Their high concentrations in soils and plants are explained by the natural lithochemical anomaly. The group of elements with weak biological uptake in the background and natural recreation zones of the city includes anion-forming V and Cr. The maximum number of elements (11) is accumulated in the larch needles in the residential zone, where TEs enter by lateral migration from the crumbling nearby tailings.



**Figure 3.** Diagrams of the accumulation of TEs in the (A) needles and (B) bark of *Larix sibirica* and (C) leaves and (D) bark of *Bétula platyphýlla* in Zakamensk. Land-use zones: (1) industrial, (2) residential, (3) natural recreation, and (4) background territories.

The geochemical specialization of larch bark is analogous to that of larch needles (Figure 3B) and is characterized by the accumulation of cation-forming (Cd, Ni, Cu, Zn, Sr, Sn, Ba, Pb), ore (W, Mo), and accompanying (Bi) elements. However, if we analyze CBA values calculated with respect to the soils of the same land-use zones, where plant samples were taken, we shall not see the intense biological accumulation of TEs in the industrial zone, where the soils have very high bulk element concentrations, so that element abundance in the plants relative to the soils (CBA value) becomes relatively low. For example, the concentrations of Mo, W, and Bi in the soils reach 127, 199, and 21 mg/kg, i.e., they are 30 to 120 times higher than their clarkes in the lithosphere. Under such high soil content of TEs, no significant bioconcentration of these elements takes place.

The accumulation of elements by assimilating and perennial organs of Asian white birch displays some common features with that of larch; at the same time, the differences between these two species are significant (Figure 3C, 3D). Both tree species absorb mainly cation-forming (Cu, Zn, Sr, Cd, Ba), ore (W, Mo), and accompanying (Bi) elements. In the industrial zone, ore elements belong to the groups of the moderate and strong element "capturing" by the plants.

A specific feature of birch leaves and bark (as compared with larch needles and bark growing in the same urban ecosystem) is a more intense accumulation of Cd and Zn which are typical pollutants of urban environments. Our results are in agreement with the earlier obtained data [28, 29].

#### 4.3. Ecological state of the plants

The *Fe/Mn ratio* is the most informative indicator of photosynthesis with the optimum range of 1.5–2.5 necessary for the normal development of plants [30]. The *Fe/Mn ratio* in assimilating organs of the trees in Zakamensk depends on the level of anthropogenic load (Table 1). In larch needles, this ratio changes from 0.11 on the background plots to 4.7 in the residential area. Maximum values (12.4) in the latter zone attest to a sharp deficit of Mn and biological accumulation of active ferrous oxide inducing plant chlorosis [31] and the stress state of the plants [32]. The optimum ratio (1.75) was found only in the industrial zone. A reverse situation—the high Mn concentration—leads to the decreased concentrations of ferrous oxides that are mobilized in plant cells in the form of iron organophosphates, which also induces chlorosis related to the deficit of iron [31]. This situation is typical of the background and natural recreation areas, where the *Fe/Mn* in larch needles is about 0.11–0.22. Birch leaves in all the land-use zones suffer from the deficit of iron and excess of Mn (*Fe/Mn* = 0.11–0.63), only the maximum values of this ratio (2.4) are within the optimum range.

The distribution of *Fe/Mn ratios* in the perennial organs of the trees has much in common with that in the assimilating organs. Thus, minimum values are observed in the bark of larch trees growing on the natural recreation and background territories (0.97 and 1.99 respectively); with an increase in the anthropogenic load, the *Fe/Mn ratio* sharply increases up to 4.5 in the residential zone and 5.7 in the industrial zone, i.e., it becomes 1.8 and 2.3 times higher than the upper limit of the optimum range, respectively. The bark of birch trees is characterized by the even more pronounced deficit of iron and excess of manganese than that in the birch leaves. The *Fe/Mn ratio* in the birch bark is 0.02 in the natural recreation zone. In the other land-use zones, it varies from 0.04 to 0.21.

The maximum permissible concentration of Fe in plants is 240 mg/kg of dry phytomass [33]. In the assimilating organs of the trees it is exceeded in the industrial and residential zones; in the bark of larch, virtually in all the samples; and in the bark of birch, only in the samples from the industrial zone. The critically high concentration of 750 mg/kg dry phytomass [33] is exceeded in the organs of larch in some local anomalies: in the industrial zone Fe concentration in the bark of larch is up to 1800 mg/kg of dry phytomass, in the residential zone, the critical concentration is exceeded in the needles.

The phytotoxic concentration of Mn for the trees reaches 500 mg/kg of dry phytomass [34]. It is exceeded in the bark and leaves of the birch in all the land-use zones. For larch, it is only exceeded in the needles in the background and natural recreation zones. It is known that Siberian larch has a "ferrallitic" composition of ash and is a concentrator of Mn [35]. The concentration of Mn by birch even under minimal anthropogenic loads is probably related to the fact that in the acid medium (at pH <5.7), this element is transformed into the mobile and available form  $Mn^{2+}$  [36]. In the leaves of birch growing in the city, the concentration of Fe decreases simultaneously with an increase in the concentration of Mn. Change of the natural ratios of these elements—antagonists in assimilating organs of the trees subjected to the contamination was also observed by other authors [30, 37–40].

**Table 1.** Indicators of the ecological state of assimilating and perennial organs of the trees in various land-use zones of the Zakamensk city

| Land-use zone | Indicator                        |           |         |               |         |           |
|---------------|----------------------------------|-----------|---------|---------------|---------|-----------|
|               | Fe/Mn                            |           | Pb/Mn   |               | Cu/Zn   |           |
|               | average                          | min-max   | average | min-max       | average | min-max   |
|               | Needles of <i>Larix sibirica</i> |           |         |               |         |           |
| B             | 0.11                             | 0.06-0.17 | 0.0005  | 0.0002-0.0008 | 0.29    | 0.28-0.31 |
| R             | 0.22                             | 0.06-0.56 | 0.002   | 0.0004-0.005  | 0.31    | 0.28-0.34 |
| S             | 4.68                             | 0.41-12.4 | 0.042   | 0.003-0.125   | 0.29    | 0.2-0.36  |
| I             | 1.75                             | 0.68-2.82 | 0.011   | 0.006-0.34    | 0.28    | 0.23-0.34 |

| Leaves of <i>Bétula platyphýlla</i> |      |           |        |                |      |           |
|-------------------------------------|------|-----------|--------|----------------|------|-----------|
| B                                   | 0.11 | 0.08-0.16 | 0.0004 | 0.0003-0.0004  | 0.07 | 0.05-0.1  |
| R                                   | 0.14 | 0.07-0.4  | 0.001  | 0.0002-0.002   | 0.07 | 0.03-0.11 |
| S                                   | 0.56 | 0.09-1.62 | 0.006  | 0.0006-0.032   | 0.05 | 0.03-0.1  |
| I                                   | 0.63 | 0.08-2.39 | 0.002  | 0.0004-0.003   | 0.03 | 0.03-0.05 |
| Bark of <i>Larix sibirica</i>       |      |           |        |                |      |           |
| B                                   | 1.99 | 0.25-3.4  | 0.02   | 0.002-0.031    | 0.37 | 0.3-0.44  |
| R                                   | 0.97 | 0.25-1.7  | 0.02   | 0.002-0.05     | 0.37 | 0.26-0.56 |
| S                                   | 4.49 | 1.5-10.8  | 0.05   | 0.005-0.12     | 0.42 | 0.21-0.99 |
| I                                   | 5.68 | 0.8-10.6  | 0.06   | 0.008-0.11     | 0.62 | 0.58-0.67 |
| Bark of <i>Bétula platyphýlla</i>   |      |           |        |                |      |           |
| B                                   | 0.04 | 0.02-0.06 | 0.0004 | 0.0003-0.0004  | 0.06 | 0.04-0.07 |
| R                                   | 0.02 | 0.01-0.06 | 0.0004 | 0.00004-0.0008 | 0.07 | 0.04-0.1  |
| S                                   | 0.21 | 0.01-1.6  | 0.002  | 0.0001-0.006   | 0.05 | 0.03-0.1  |
| I                                   | 0.13 | 0.01-0.5  | 0.001  | 0.0003-0.004   | 0.05 | 0.04-0.06 |

Note: B—background areas. Land-use zones of the city: R—natural recreation, S—settlement (residential), and I—industrial.

The Pb/Mn ratio characterizes the relationship between the technogenic and biophilous elements, i.e., the level of anthropogenic load. An optimum value of this ratio for undisturbed terrestrial vegetation was taken equal to the ratio of the clarkes (natural abundances of Pb and Mn) [41]. It is equal to 0.006, which attests to the low portion of technogenic elements in the TE composition of the plants which are not involved in the physiological processes. The excess of Pb in plants inhibits respiration and suppresses photosynthesis because of the disturbance in electron transport [30].

The assimilating organs of birch in all the land-use zones of Zakamensk are not subjected to technogenic pressure, because average values of the Pb/Mn ratio are low (0.0004–0.006). A local anomaly with the maximum of 0.032 was found in the residential zone near the Lenin street, the major highway in the city, which is the source of Pb. Minimum Pb/Mn values in the needles of larch were found in the background (0.0005) and natural recreation (0.002) zones, and maximum values were found in the residential zone with the average Pb/Mn ratio of 0.04 and the local maximum of 0.339; these values exceed those in the unpolluted terrestrial vegetation by 7 and 56 times, respectively [42].

Perennial organs usually accumulate higher amounts of pollutants [5]. The Pb/Mn ratio indicates that an increase in technogenic loads is accompanied by the rise in the concentration of Pb. However, in the bark of birch in all the land-use zones, the Pb/Mn ratio is no higher than that in the unpolluted vegetation and ranges from 0.0004 to 0.002. In contrast, in the bark of larch, the average Pb/Mn ratio is minimal (0.02) on the background plots and increases in the industrial zone up to 0.06 with local peaks of up to 0.119, which is 20 times higher than the normal value.

A comparison of data on Pb concentrations in the trees growing in different land-use zones of Zakamensk with the maximum permissible Pb concentration shows that the bark of larch is subjected to the highest technogenic Pb load: average Pb concentrations in it vary from 5.8 to 9.9 mg/kg rising up to 25 and 19 mg/kg in local anomalies within the residential and industrial zones, respectively. The first anomaly is found in the center of the city, near the Modonkul River, where a ford operates in the summer. The source of Pb is probably related to motor oil, gasoline, and car exhausts. In the second anomaly, the accumulation of Pb is related to the emissions from the "Foundry" Smelter and thermal power plant. Active accumulation of Pb in the bark of larch is favored by dust precipitation and retention on the rough surface of the bark. In the needles of larch, the highest concentrations of Pb (3.3 mg/kg with local peaks up to 9.1 mg/kg) are observed in the residential zone. The organs of birch are characterized by generally low concentrations of Pb in all the zones, except for the residential zone, where Pb concentration in the leaves averages 1.5 mg/kg.

Thus, coniferous trees accumulate Pb more actively than small-leaved (birch) trees. This can be explained by the morphological specificity of the assimilating organs, i.e., by the presence of waxy



cuticle firmly fixing TEs on larch needles [20–21]; and also by the pretreatment of the samples—the washing of birch leaves with distilled water to remove dust particles—can also be the reason for the lower concentration of Pb in the birch leaves.

The *Cu/Zn ratio* characterizes the supply of these biogenic metals participating in the synthesis of enzymes. The optimum ratio in the nonpolluted terrestrial vegetation is 0.27 [17]. In the assimilating and perennial organs of birch trees from different land-use zones of Zakamensk, the average Cu/Zn ratio varies from 0.03 to 0.07 attesting to the high concentrations of Zn (Table 1). This ratio in larch needles is close to the optimum (0.28–0.31). The most significant imbalance of Zn and Cu ( $Cu/Zn = 0.36$ ) is observed in larch needles in the residential zone. In the bark of larch, minimum values of the Cu/Zn ratio (0.37) are disclosed in the background and natural recreation landscapes; they exceed the optimum by 1.4 times. Maximum values (0.62) are typical of the residential zone. In the local maximum in the industrial zone, this ratio increases up to 0.99.

A significant positive correlation between Cu and Zn concentrations in the assimilating organs of larch and birch trees was discovered (correlation coefficients  $r = 0.65$ , and  $r = 0.88$ , respectively). This fact contradicts previously published data about antagonism of Cu and Zn, as their uptake by the roots is controlled by the same mechanism, and one element can inhibit the uptake of the other [30, 43]. Such a discrepancy can be explained by the fact that, in our study, the Cu/Zn values are close to the optimum for nonpolluted terrestrial vegetation and that the uptake of these elements by the leaves and needles from the atmosphere plays a significant role in their total absorption. For perennial organs of birch and larch, such a correlation is weak ( $r = 0.56$ , and  $r = 0.57$ ).

Copper belongs to biophilous elements; it is always present in soils, plants, and animal tissues and participates in various metabolic processes. It enters the composition of plastocyanin that is involved in electron-transfer processes between photosystem II and photosystem I; it is also present in Cu-containing proteins and enzymes that catalyze oxidation of ascorbic acid and biphenols, and hydroxylation of monophenols [36]. The critical phytotoxic concentration of Cu reaches 20 mg/kg of dry phytomass [34]. In the studied tree species of Zakamensk, such a concentration has not been exceeded. The concentration of Cu in the assimilating and perennial organs varies from 3.2 to 9.4 mg/kg; the local maximum (15 mg/kg) was determined in larch needles in the industrial zone.

Zinc participates in redox processes in plant tissues; it stabilizes air-exchange processes and affects photosynthesis; it is included in the composition of tryptophan (an amino acid) [36]. The phytotoxic concentration of Zn is 300 mg/kg of dry phytomass. With an increase in the anthropogenic load, the concentration of Zn in the organs of the trees increases. Minimum values were found in the background and natural recreation areas, and maximum values – in the industrial zone. Birch is a more active concentrator of Zn in comparison with larch: average Zn concentrations in the leaves and bark of birch were within 78.5–182 and 99–132 mg/kg of dry phytomass, respectively; in the needles and bark of larch, they were within 11.5–19.5 and 7.2–15.8 mg/kg of dry phytomass, respectively. Taking into account the fact that birch leaves were preliminary washed with distilled water, it can be supposed that the main input of Zn into the leaves was from the Zn-contaminated soils. Similar results were obtained in other studies of the TE composition of tree species in Europe [44–47].

## 5. Conclusions

Biogeochemical studies performed in Zakamensk (Buryat Republic) showed that the trees of this city are subjected to high anthropogenic loads. The resulting imbalance of elements in the trees is characterized by the total index of the biogeochemical transformation  $Z_v$ , calculated for the assimilating and perennial organs. The changes in the TE composition of larch needles are specified by intense accumulation of Cr, W, V, Pb, Bi, Mo, Sb, Ni, Cd, Co, and Sn; birch leaves concentrate W, V, Mo, Bi, Pb, Sb, Cd, and Co. The highest values of  $Z_v$  index are typical of larch needles, which are explained by the fixation of precipitating dust particles containing TEs by the wax film on needle surfaces. The accumulation of TEs in the assimilating organs of larch and birch is more intense than that in the perennial organs.

Two stable biogeochemical anomalies were revealed in the center and in the north of the city. In

the central anomaly,  $Z_v$  values for larch needles and birch leaves reach 205–320 and 71–100, respectively. HMMs enter the plants from tailings, thermal power plant, and the "Foundry" Smelter. In the northern anomaly,  $Z_v$  is up to 260 for larch needles and 72 for birch leaves. This anomaly is located in the residential zone; it is contaminated with HMMs blown out from the Modonkul technogenic sand deposit.

Despite the high anthropogenic load, the organs of the trees preserve their capacity to take up cationic elements (Cu, Zn, Sr, Cd, Ba) from the soil, which is generally typical of humid environments with acid soils, in which these elements are mobile. Anion-forming ore elements W and Mo and Bi as the major accessory are also actively absorbed from the soils. Tailings serve as the main sources of soil and plant pollution with TEs. The surface of tailings remains barren, and they are characterized by good aeration and increased water permeability. As a result, the material of tailings is subjected to wind and water erosion and to chemical weathering under the impact of sulfuric acid. These processes enhance the lateral migration of TEs in the soil cover and their accumulation by the tree species.

The ecological state of the trees in the urban environment was judged from the Fe/Mn and Pb/Mn ratios. Their values attest to the disturbance of photosynthetic processes in the trees, especially in the residential zone of the city. The highest values of the Fe/Mn (4.7) and Pb/Mn (0.042) ratios were found in larch needles. The high Fe/Mn ratio is explained by the deficit of Mn in the environment and the active bioconcentration of ferrous oxides that may induce chlorosis and the stress state of the trees. The high Pb/Mn ratio is due to the excessive content of Pb resulting in the inhibition of respiration and suppression of photosynthesis. The Cu/Zn ratio in the needles and bark of *Larix sibirica* in the city is within 0.28–0.31, i.e., it is close to the optimum for the unpolluted terrestrial vegetation. In the leaves and bark of *Bétula platyphýlla*, the Cu/Zn ratio is 0.03–0.07, which attests to an imbalance in the concentrations of these elements.

A comparative analysis of different organs of the trees showed that the needles and bark of *Larix sibirica* can be used as sensitive indicators of the environmental pollution with HMMs during the growing season and long-term periods. This is favored by the presence of a wax film on the needle surface ensuring fixation of dust particles with the pollutants precipitating from the atmosphere and by the rougher surface of the larch bark, which ensures more active biological uptake of TEs from the atmosphere.

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### References

- [1] Markert B 1993 Instrumental analysis of plants *Plants as Biomonitors. Indicators for Heavy Metals in Terrestrial Environment* ed B Markert (Weinheim: VCH Verlagsgesellschaft) pp 65–103
- [2] Bargagli R 1998 Trace Elements in Terrestrial Plants: An Ecophysiological Approach to Biomonitoring and Biorecovery (Berlin: Springer-Verlag) p 324
- [3] Weiss P, Offenthaler I, Öhlinger R and Wimmer J 2003 Higher plants as accumulative bioindicators *Bioindicators & Biomonitors, Principles, Concepts and Applications* vol 6, ed B Markert, et al. (Amsterdam: Elsevier) pp 465–500
- [4] Fujiwara F G, Gómez D R, Dawidowski L, Perelman P and Faggi A 2011 Metals associated with airborne particulate matter in road dust and tree bark collected in a megacity (Buenos Aires, Argentina) *Ecol. Indic.* **11** 240–7
- [5] Shcherbenko T A, Koptsik G N, Groenenberg B-J, Lukina N V and Livantsova S Y 2008 Uptake of nutrients and heavy metals by pine trees under atmospheric pollution *Moscow Univ. Soil Sci. Bull.* **63** 51–9
- [6] Koptsik G N, Koptsik S V, and Omlid D 1999 Transformation of the elemental composition of plants in forest biogeocenoses of the northern taiga under the impact of aerial pollution *Vestn.*

- Mosk. Univ., Ser. 17: Pochvovedenie* **1** 37–49.
- [7] Nieminen T M, Derome J and Saarsalmi A 2004 The applicability of needle chemistry for diagnosing heavy metal toxicity to trees *Water, Air, Soil Pollut.* **157** 269–79
- [8] Lindeberg J 2004 X-ray Based Tree Ring Analyses *Acta Univ. Agric. Sueciae Sivistria* 1–25
- [9] Anon 2011 *Explanatory note on realization of the target republican program "Environmental safety in the Buryat Republic in 2009–2011 and up to 2017"* (Ulan-Ude)
- [10] Smirnova O K and Plyusnin A M 2013 *Dzhida Ore Region (Environmental Problems)* (Ulan-Ude: Izd. Buryat. Nauchn. Ts. SO RAN) p 181
- [11] Nogina N A 1964 *Transbaikal Soils* (Moscow: Science Publ.) p 312
- [12] Jones J B J and Case V W 1990 Sampling, handling, and analyzing plant tissue samples *Soil testing and plant analysis* (Madison, Wisconsin: SSSA book series) pp 389–247
- [13] Kosheleva N E, Makarova M G and Novikova O V 2005 Heavy metals in the leaves of tree species in urban landscapes *Vestn. Mosk. Univ., Ser. 5: Geografiya* **3** 74–81
- [14] Saet Yu E, Revich B A, Yanin E P, Smirnova R S, Basharkevich I L, Onishchenko T L, Pavolva L N, Trefilova N Ya, Achkasov A I, and Sarkisyan S Sh 1990 *Environmental Geochemistry* (Moscow: Nedra) p 335
- [15] Ufimtseva M D and Terekhina N V 2005 *Phytoindication of the state of urban geosystems in Saint Petersburg* (St. Petersburg: Nauka) p 339
- [16] Kasimov N S, Bityulova V R, Kislov A V, Kosheleva N E, Nikiforova E M, Malkhazova D M and Shartova N V 2012 Problems of the ecogeochemistry of large cities *Okhrana i razvedka nedr* **7** 8–13
- [17] Elpat'evskii P V and Arzhanova V S 1990 *Geochemistry of Landscapes and Technogenesis* (Moscow: Nauka) p 196
- [18] Novikova O V and Kosheleva N E 2007 Ecogeochemical assessment of the state of arboreal vegetation in Quito (Ecuador) *Vestn. Mosk. Univ. Ser. 5: Geografiya* **1** 43–8
- [19] Kosheleva N E, Timofeev I V, Kasimov N S, Kisselyova T M, Alekseenko A V and Sorokina O I 2016 Trace Element Composition of Poplar in Mongolian Cities *Biogenic-Abiogenic Interactions in Natural and Anthropogenic Systems* Lecture Notes in Earth System Sciences ed V. Frank-Kamenetskaya, et al. (Switzerland: Springer International Publishing) pp 165–78
- [20] Aznar J C, Richer-Lafleche M, Bégin C and Bégin Y 2009 Lead Exclusion and Copper Translocation in Black Spruce Needles *Water, Air, Soil Pollut.* **203** 139–45
- [21] Gandois L and Probst A 2012 Localisation and mobility of trace metal in silver fir needles *Chemosphere* **87** 204–10
- [22] Lin Z Q, Schuepp P H, Schemenauer R S and Kennedy G G 1995 Trace metal contamination in and on Balsam fir (*Abies balsamea* (L) Mill.) Foliage in southern Quebec, Canada *Water, Air, Soil Pollut.* **81** 175–91
- [23] Müller C and Riederer M 2005 Plant Surface Properties in Chemical Ecology *J. Chem. Ecol.* **31** 2621–51
- [24] Raitio H, Tuovinen J P and Anttila P 1995 Relation between sulphur concentrations in the Scots pine needles and the air in northernmost Europe *Water, Air, Soil Pollut.* **85** 1361–6
- [25] Rautio P and Huttunen S 2003 Total vs. internal element concentrations in Scots pine needles along a sulphur and metal pollution gradient *Environ. Pollut.* **122** 273–89
- [26] Trimbacher C and Weiss P 2004 Norway Spruce: A Novel Method using Surface Characteristics and Heavy Metal Concentrations of Needles for a Large-Scale Monitoring Survey in Austria *Water, Air, Soil Pollut.* **152** 363–86
- [27] Perel'man A I 1989 *Geochemistry* (Moscow: Vysshaya Shkola) p 528
- [28] Esenzholova A Zh and Panin M S 2012 Bioindication potential of the leaves of trees and shrubs in Temirtau *Vestn. Tomsk. Gos. Univ. Biologiya* **3(19)** 160–8
- [29] Opekunova M G 2013 *Diagnostics of the Technogenic Transformation of Landscapes on the Basis of Bioindication: Author's abstract of doctoral (Geogr.) dissertation* (St. Petersburg: St.

Petersburg State University)

- [30] Kabata P A 2011 *Trace Elements in Soils and Plants. Fourth Edition* (Boca Raton: CRC Press) p 548
- [31] Kopylova L V 2010 Accumulation of iron and manganese in the leaves of trees in technogenic areas of Trans-Baikal region *Izvest. Samarskogo Nauchn. Ts. RAN* **12** 709–12
- [32] Lyanguzova I V 2010 *Tolerance of the Components of Forest Ecosystems in the Russian North towards Aerotechnogenic Pollution: Author's abstract of doctoral (Biol.) dissertation* (St. Petersburg: V L Komarov Botanical Institute)
- [33] Kopylova L V 2011 Specific features of the uptake of heavy metals by tree species in the urban environment *Vestn. Irkutsk. Gos. Univ.* **44(3)** 91–9
- [34] Kazantsev I V 2008 *Ecological assessment of the impact of the rail transport on the contents of heavy metals in soils and plants of the right-of-way: Author's abstract of Cand. Sci. (Biol.) dissertation* (Samara)
- [35] Bashkin V N and Kasimov N S 2004 *Biogeochemistry* (Moscow: Nauchnyi mir) p 648
- [36] Kulagin A and Shagieva Yu A 2005 *Arboreal plants and the Biological Conservation of Industrial Pollutants* (Moscow: Nauka) p 190
- [37] Giniyatullin R Kh, Kulagin A Yu, Batalov A A, and Salikhova R N 1997 *Concentrations of Some Metals in the Aboveground Organs of Betula pendula under Conditions of Industrial Contamination*
- [38] Kopylova L V 2002 Assessment of the level of soil contamination with heavy metals and the intensity of their uptake by arboreal plants *Uchenye zap. Zabaikal'skogo Gos. Univ.* **1(42)** 70–5
- [39] Kopylova L V and Yakimova E P 2013 Specificity of the accumulation of metals by arboreal plants in the urban environment *Uchenye zap. Zabaikal'skogo Gos. Univ. Ser. Estestven. nauki* **1(48)** 74–81
- [40] Alvarez T M C, Leal A and Martínez L R 1980 Iron-manganese interaction and its relation to boron levels in tomato plants *Plant Soil* **55** 377–88
- [41] Dobrovolskii V V 2003 *Fundamentals of Biogeochemistry* (Moscow: Izd. Ts. "Akademiya")
- [42] Vega F A, Covelo E F, Vazquez J J and Andrade L 2007 Influence of mineral and organic components on copper, lead, and zinc sorption by acid soils *J. Environ. Sci. Heal. Part A* **42** 2167–73
- [43] Graham R D 1981 Absorption of copper by plant roots, in *Copper in Soils and Plants* ed J F Loneragan, A D Robson and R D Graham (New York: Academic Press) p 141
- [44] Brekken A and Steinnes E 2004 Seasonal concentrations of cadmium and zinc in native pasture plants: consequences for grazing animals *Sci. Total Environ.* **326** 181–95
- [45] Kopponen P, Utriainen M, Lukkari K, Suntioinen S, Kärenlampi L and Kärenlampi S 2001 Clonal differences in copper and zinc tolerance of birch in metal-supplemented soils *Environ. Pollut.* **112** 89–97
- [46] Marguí E, Queralt I, Carvalho M L and Hidalgo M 2007 Assessment of metal availability to vegetation (*Betula pendula*) in Pb-Zn ore concentrate residues with different features *Environ. Pollut.* **145** 179–84
- [47] Steinnes E, Lukina N, Nikonov V, Aamlid D and Røyset O 2000 A Gradient Study of 34 Elements in the Vicinity of a Copper-Nickel Smelter in the Kola Peninsula *Environ. Monit. Assess.* **60** 71–88