Distinctive features of heavy metals’ accumulation in coniferous trees in Buryatia, Russia

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Abstract. Coniferous plants are very sensitive to atmospheric pollutants and frequently are used as environment pollution bioindicators. The purpose of this study was to define features of heavy metals (HM) accumulation by conifer needles from forest-forming tree species growing in Buryatia: Pinus sylvestris, Pinus pumila, Pinus sibirica, Picea obovata, Abies sibirica. The samples elements content was determined by ICP AES method after acid decomposition in microwave system MARS 6. HM accumulation rows showed similar trends for different tree species. The maximum content was determined for manganese in all needles samples, except Pinus sylvestris growing around Ulan-Ude. It is shown that there is a difference in HM accumulation between conifer species due to their biological features. The variation coefficient of heavy metals in conifer needles were calculated, Zn, Ni, Hg exposed highest level of variation. Industrial pollution caused the significant changes in the needles elemental composition – it is observed the growth of Fe, Zn and lowering of Mn content in Pinus sylvestris needles growing around Ulan-Ude. The accumulation of HM by conifer needles growing in Buryatia was higher than the average terrestrial vegetation element contents that might be related with the forest fires.

1. Introduction

The plants are the most important link of biological substances circulation. Study of plants element composition is necessary for more full description of chemical elements distribution in natural and anthropogenous landscapes. Ability of plants to accumulate chemical elements selectively is used in geology, ecology, medicine, etc. Makro- and microelements play an important role in the main processes of living organisms’ vital activity. Some of them belong to the heavy metals (HM) group, which are capable to be accumulated and, at excessive content, influence negatively on plants [1]. Chemical compound of air, soil, precipitation influence on plants element composition, so they can be used as environmental pollution indicators. In contrast to organic pollutants inorganic pollutants - heavy metals and metalloids (Cr, Ni, Cu, Zn, Cd, Pb, Hg, As, etc.) are not decomposable, could be accumulated and pass from one medium to another.

Coniferous plants are used as the bioindicators of aerogenic pollution more often than deciduous one due to their less steady to pollutants [2]. That’s why Pinus sylvestris [3-5] is mostly used for environment condition monitoring, Picea obovata [6,7], Abies sibirica [8] are used less. The coniferous trees assimilative apparatus (needles) is mainly used for bioindication. Due to the needles age of different species varies within 3-9 years it is possible to define dynamics of long-term technical pollution besides common HM content.
The purpose of present work was to define the main forest-forming conifers species growing in Buryatia: Scots pine (*Pinus sylvestris*), Siberian dwarf pine (*Pinus pumila*), Siberian pine (*Pinus sibirica*), spruce (*Picea obovata*), fir (*Abies sibirica*) heavy metals accumulation features.

2. Models and Methods

Needle samples of studied tree species were collected in natural growth conditions (Table 1).

Table 1. Samples collecting points (CP) in Buryatia.

| №  | Collecting points, geographical coordinates, altitude elevation (m) | Date of collection samples |
|----|---------------------------------------------------------------|----------------------------|
| 1  | Kabanskiy district, coast of Lake Baikal, nearby village Manturiha, N 51°46′40″ E 105°58′51″ h - 461 m | 18.07.15 | 18.07.15 | 18.07.15 | 18.07.15 | - |
| 2  | Kabanskiy district, north west foothill Khamar-Daban, nearby village Gornyj N 51°58′25″ E 106°24′21″, h - 666 m | 15.11.15 | 22.11.15 | 15.11.15 | 15.11.15 | - |
| 3  | Pribaikalskiy district, Lake Baikal coast, place Kotkovo, N 53°10’2″ E 108°25′39″, h - 468m | - | - | 19.05.15 | 30.09.15 | 19.05.15 |
|    | | | | 10.07.15 | 10.07.15 | 10.07.15 |
|    | | | | 30.09.15 | 30.09.15 | 02.03.16 |
| 4  | Ivolginsky district, mountain range Ulan-Burgasi, 30 km from Ulan-Ude, N 52°50′50″ E 109°03′40″, h - 1250 m | 14.05.15 | 10.07.15 | 30.09.15 | 14.05.15 | 14.05.15 |
|    | | | | 10.07.15 | 10.07.15 | 10.07.15 |
|    | | | | 30.09.15 | 30.09.15 | 16.03.16 |
|    | | | | 02.03.16 | 16.03.16 |
| 5  | Ulan-Ude, urban district Talltsy, N 51°84′61″ E 107°64′18″, h - 513 m | - | - | 20.12.15 | - | - |
| 6  | Ulan-Ude, urban district Gorkiy, N 51°79′34″ E 107°61′09″, h - 497 m | - | - | 20.12.15 | - | - |
| 7  | Ulan-ude, urban district Sotnikovo N 51°81′40″ E 107°55′10″, h - 495 m | - | - | 20.12.15 | - | - |
| 8  | Ulan-ude, urban district Verhnyaya Berezovka, N 51°84′61″ E 107°64′18″, h – 593m | - | - | 20.12.15 | - | - |

* « - » no samples were collected.

Collecting points 1 and 2 are located on the southern and south-eastern coast of Lake Baikal in Kabansky district. The forests consist from pine, larch, birch, fir, and spruce. CP 1 is located on the north of the Manturiha river mouth, along the Trans-Siberian Railway. The long distances of this area from industrial pollution sources allow to consider this area as background territory. CP 2 is located on the north-western foothill Khamar-Daban, in 13 km from Kamensk. To the south-west of CP 2 is situated the Tarakanovsky limestone quarry - the main source of raw materials for Timlujskij cement plant. This CP is located near two industrial centers - Selenginsky and Kamensk, on the territory where the enterprises are located (Selenginsky Pulp and Carton Mill, Timlujskij Asbestos-Cement Products Plant, etc.). CP 3 is located on the eastern coast of Lake Baikal on the border of the Pribaikalsky and Barguzinsky districts in the place Kotkovo. This area is characterized by a peculiar climate due to the influence of the lake. The absence of sources of industrial pollution nearby allows characterize this place as background territory. CP 4 is located in the Ivolginsky district on the top of Ulan-Burgasy mountain.
range in 30 km on the north from Ulan-Ude at an altitude of 1,250 m. The forest belt prevails in most part of the mountain range. The climate is sharply continental with large amplitude fluctuations in annual and daily temperatures. The mountainous terrain of this area reduces the influence of industrial pollution intensity from the nearest source – the city of Ulan-Ude which is located in intermountain depressions and hollows. CP 5-8 are located around Ulan-Ude, where the largest industrial hub in Buryatia is situated. The thermal power plants, industry and transport are the main sources of pollutants into the atmosphere in Ulan-Ude. The location of Ulan-Ude in intermountain basins causes weak dispersion of emissions and the formation of high air pollution indices, especially near emission sources.

In 2015, in Buryatia, according to Rosgidromet, winter, spring and summer were warmer than usual (anomalies up to 3.5°C), there was a deficit of precipitation in summer and autumn (summer precipitation was 76% of normal, especially dry it was in July - 58%), which led to extensive forest fires in Buryatia [8]. Needle samples were taken from 10-20 trees of different ages from different sides of the crown at a height up to 2-2.5 m, then the sample was averaged by the quartering method. Indoors, the needles were dried at room temperature to air-dry condition. Determination of the samples elements quantitative content was carried out with atomic emission spectroscopy conducted with inductively coupled plasma (ICP) after preliminary decomposition of dry ground needles with concentrated nitric acid in the microwave system MARS 6.

3. Results and Discussion

The HM content analysis results of the studied trees needles are presented in Table 2.

| Tree species          | Mn   | Cu   | Zn   | Pb   | Ni   | Fe   | Hg   |
|-----------------------|------|------|------|------|------|------|------|
| *Picea obovata*       | 132-591 | 6.4-9.2 | 15-56 | 1.99-2.62 | 1.6-6.4 | 89-161 | 0.102-0.384 |
| *Abies sibirica*      | 470-733 | 8.7-12.3 | 32-74 | 2.51-5.47 | 0.9-3.6 | 158-219 | 0.021-0.112 |
| *Pinus sylvestris*    | 198-435 | 8.3-10.3 | 22-57 | 2.58-3.05 | 2.9-8.1 | 68-118 | 0.065-0.239 |
| *Pinus sylvestris* (Ulan-Ude) | 29-103 | 8.6-11.1 | 140-389 | 2.48-3.07 | 1.6-8.0 | 365-586 | 0.021-0.117 |
| *Pinus sibirica*      | 184-523 | 7.9-17.6 | 27-70 | 1.82-3.25 | 0.7-5.8 | 100-200 | 0.071-0.249 |
| *Pinus pumila*        | 285-566 | 6.7-9.9 | 26-59 | 1.85-3.65 | 0.4-5.6 | 73-231 | 0.014-0.454 |
| Average terrestrial vegetation element contents [1] | 240 | 8.0 | 30 | 1.25 | 2.0 | 200 | 0.012 |

The analysis of the samples HM content data showed a significant variability in the HM concentration in the needles. The lowest values of HM content were noted for Siberian pine and Siberian dwarf pine samples which was collected at the vegetation season beginning. Taking into account the calculated coefficient of variation, the elements can be divided into four groups: with normal 0-40%, significant 40-70%, high 70-90%, and abnormal > 90% levels of variation (Figure 1). The elements Cu, Pb are characterized by a low variation level; Fe and Mn have a normal variation level; Zn, Ni – significant, Hg – high variation levels. Also, a high variation level is found for Mn in the spruce needles.
Figure 1. The variability of the content of elements in the needles VL - element content variation levels:
N - normal (0-40%),
S - significant (40-70%),
H - high (70-90%),
A - abnormal (> 90%).

Based on the obtained needles HM content data, the following accumulation rows were constructed:

- **Picea obovata**: Mn > Fe > Zn > Cu > Ni > Pb > Hg;
- **Abies sibirica**: Mn > Fe > Zn > Cu > Pb > Ni > Hg;
- **Pinus sylvestris**: Mn > Fe > Zn > Cu > Ni > Pb > Hg;
- **Pinus sylvestris (Ulan-Ude)**: Fe > Mn > Zn > Cu > Ni > Pb > Hg;
- **Pinus sibirica**: Mn > Fe > Zn > Cu > Ni > Pb > Hg;
- **Pinus pumila**: Mn > Fe > Zn > Cu > Ni > Pb > Hg.

It can be noted for the studied conifers species regardless of the gathering place similar HM accumulation trends are observed, with some differences. In the fir needles HM accumulation row the lead content exceeds the nickel content, unlike other samples. For all needles samples, except Scots pine, collected nearby Ulan-Ude, the maximum element content is measured for manganese. It is known that the availability of an element from soil for different plant species depends on their biochemical processes specifics, which allow to regulate its quantity even at the same concentration in the soil [9].

The highest content of manganese is determined for the fir needles growing on CP 4, the smallest - for all samples of Scots pine needles, growing nearby Ulan-Ude. In comparison with another CP, the manganese content in the needles of trees growing on CP 4 is higher (421-664 mg/kg) than in other CP (220-315 mg/kg). Manganese belongs to HM, but manganese pollution is very rare and local. There is a part of metalloenzymes in plants, under which action an oxidants inactivation and protection of cell membranes from their damaging effects occurs. It is also necessary for photosynthesis, as it participates in the water molecule photochemical decomposition [10]. High manganese content indicates the absence of technogenic load [11] that is confirmed with our data, where the manganese content is minimal in the needles growing nearby industrial center (Ulan-Ude).

The highest iron content is determined in the Scots pine needles, which grows nearby Ulan-Ude, that is 5-10 times higher than in other samples. As established earlier [12], an iron content growth and manganese content lowering in Scots pine needles in industrial pollution conditions is characteristic that is in agreement with our data. The most common reason is the enhancement of oxidation processes in plant cells and its displacement from the soil-absorbing complex by protons and ions of other HM. Similar trends were shown for spruce needles growing on the territory of Krasnoyarsk, where the iron contents also exceeds the manganese content [7].

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The zinc content in the needles was also the highest in the Scots pine needles growing nearby Ulan-Ude. Under industrial pollution conditions zinc accumulation in herb is often noted, motor transport has a significant contribution to the zinc emission [11].

The maximum copper content is determined in the Siberian pine needles growing in CP 1 and 2, the minimum - in the needles of spruce growing in CP 1, that could be connected to the biological specificity of Siberian pine. Similar data were obtained for Siberian pine needles growing nearby the city of Baikalsk, where the copper content was higher than in the needles of other trees [13]. In general, the
copper content in the investigated samples was comparable to average elements content in terrestrial vegetation; the maximum excess was no more than 2 times.

The obtained data on the needles nickel content are comparable with the data for Scots pine and spruce needles in the background territories of the Kola Peninsula (6-11 mg/kg), Murmansk Region (3 mg/kg) [14]. Earlier an increase in the nickel content in Scots pine needles near industrial pollution sources was noted [15, 16]. In general, the nickel content is higher for Scots pine compared to the other conifers. In comparison with the average nickel content in terrestrial vegetation, the highest values obtained exceed it in 3-4 times.

The lead content in the samples varied in 1.82-3.65 mg/kg. The highest lead content is determined in needles samples in CP 2 and 5-8 which located in the industrial influence zone (Timljujskij cement plant and Ulan-Ude). Lead is one of the widespread HM environmental pollutants. Excessive lead in plants inhibits respiration, suppresses photosynthesis and generally reduces their productivity. The toxic effect occurs at concentrations above 6 mg/kg [17].

The needles mercury content in comparison with its terrestrial vegetation average content showed elevated values in most of the samples, reaching 10-30 times, which requires further research to clarify the data.

In comparison with the data on the average content of elements in land vegetation [1], almost all elements show an excess above background values in 2-4, sometimes 10-30 times (for mercury). In addition to regional features and biological specificity, this excess may be associated with extensive and prolonged forest fires that occurred during the period of needles samples gathering. According to the behavior nature during forest fires, heavy metals are active air migrants and depending on atmospheric conditions, can enrich the components of the biogeocenosis in new areas [18].

4. Conclusion

The main forest-forming species growing in Buryatia needles HM accumulation levels are determined. According to the obtained data, rows of HM accumulation were constructed, that shows similar trends in HM accumulation, regardless of the conifers species. In technogenic pollution conditions, iron and manganese change places in HM accumulation row. For all needles samples, except Scots pine growing nearby Ulan-Ude, the maximum content element is determined for manganese. It is shown that for different conifers growing in the same conditions, selective HM accumulation is specific, due to their biological features. In the Siberian pine needles copper is accumulated more than in other conifers. The HM content variation levels are calculated. It is noted that zinc, nickel and mercury are more variable. Significant changes in the elemental composition of the needles occur with atmospheric industrial pollution. A high content of iron, zinc, and decrease in the manganese content in Scots pine needles growing nearby Ulan-Ude was determined. It has been established that for the application of the studied conifers for environmental monitoring, it is necessary to take into account the peculiarities of the growing areas, the vegetation stage and the features of used species.

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