Epiphytic lichens as indicators of air pollution in Tomsk Oblast (Russia)

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Abstract. This research presents the data on concentrations of 28 chemical elements in the ash of lichens growing in Tomsk Oblast where different industrial enterprises are located. In the sites of oil and gas exploration complex the lichens contain higher concentrations of Sc, Fe, Cr, Zn, As, Br, Rb, Ba, and Au in comparison with the background values. In the zone of Tomsk-Seversk industrial agglomeration the lichens accumulate Ca, Sr, Sb, Th, U, and lanthanides.

1. Introduction
Tomsk Oblast (Siberia, Russia) has such specific industries as nuclear and coal-fired power energy facilities, petroleum-chemical plant (Tomsk-Seversk industrial agglomeration) and oil and gas exploration complex (west and north-west of the region) which are the sources of various gaseous and particulate pollutants entering the atmosphere. These pollutants contain a wide range of chemical elements including rare and radioactive ones. These peculiarities of the area determine the necessity for control of air condition and analysis of atmospheric emissions.

The use of lichens for observation and investigation of chemical composition of atmospheric fallouts is a relevant trend for the assessment of environment quality because they allow obtaining the long-term averaged characteristics of ecosystems state during quite long life period of lichens. Lichens are found in almost all geographical regions because they are resistant to extreme nature conditions. Today in Russia the use of lichens as bioindicators for the study of the dynamics of atmosphere pollution has been proved in some researches [1,2,3]. As for Tomsk Oblast, the method of lichen-monitoring has not found wide application yet.

The use of lichens for the bio-geochemical research is also explained by wide abundance of forests in Tomsk Oblast (91% of the territory) [4] which are consequently characterized by the abundance of lichen flora. Because of the absence of root system lichens have atmospheric nutrition and their element composition reflect the integrated composition of chemical elements in the air present in gaseous, dissolved, or particulate forms.

Lichens are a symbiosis of mycobiont and photobiont. They have been proved to be excellent bio-monitors because of the particularity to accumulate chemical elements in concentrations exceeding their physiological needs and keep them in their thallus (body) for a long time. Since lichens have atmospheric nutrition, they get substances from wet and dry fallouts absorbing them by the whole thallus surface.
2. Data Sets
The samples of epiphytic lichens growing on trees were collected in August and September 2010-2012 in the territories of some oil fields of Tomsk Oblast (32 samples). Moreover, we used the lichen samples collected in 2006 [5] in the impact zone of Tomsk-Seversk industrial agglomeration (8 samples) and in the south and south-west of Tomsk region of Tomsk Oblast (10 samples) used as a regional background. In addition, for the assessment of global geochemical background the lichens from the Alpine region (Semmering, Austria) were sampled in 2012. The samples were collected from adult trees, mainly from warty birch or from coniferous trees at the height ranging from 1.5 to 1.8 m from the ground.

The samples were hermetically packed in plastic bags. In the laboratory we removed bark, needles and other impurities from the samples and dried them. For the analytical research we prepared lichens of the abundant background species: Evernia Mesomorpha, Usnea Subfloridana, Hypogymnia physodes, Parmelia Sulcata. In all cases the samples were mixed.

For the quantitative analysis of chemical element concentrations in lichens we used modern non-destructive high-sensitive nuclear-physical method of the neutron activation analysis (INAA) with the irradiation by thermal neutrons performed in the Nuclear-Geochemical Laboratory of the Geoecology and Geochemistry Department on the basis of the research nuclear reactor (Tomsk Polytechnic University). For the INAA the samples were reduced to powder and ashed in a muffle furnace at the temperature of 450-500°C. The sample ash allows decreasing errors in organic analysis and improves the reliability of results due to the element concentration in samples. The samples were weighted before and after ashing. The samples of 100 mg weight were prepared for the analysis. The lichen ash was analyzed by INAA for 28 chemical elements.

Concentrations of chemical elements in the samples were recalculated per a unit of dry mass using ashing coefficient for lichens samples.

The software used in the work included Microsoft Word, Microsoft Excel, STATISTIKA 6.0. The following statistical parameters of element distribution were calculated in terms of the obtained results: mean, standard error, standard deviation. The verification of normal element distribution was performed by the Kolmogorov-Smirnov test.

For the estimation of the ratio of anthropogenic and terrigenous sources of chemical elements we calculated the enrichment factor (EF) according to the formula [6]:

$$EF = \frac{(xi/Fe) \text{ in lichen tissues}}{(xi/Fe) \text{ in lithosphere}}$$

The essence of EF coefficient consists in the estimation of ratio of elements-pollutants and lithogenic elements (iron, aluminum, silicon). The EF calculation is a standard method for the estimation of potential sources of infused matter in plants [7].

The results of epiphytic lichens are presented in table 1.

| No. | Elements | Area of oil and gas exploration complex, Tomsk Oblast (32 samples) | Area of Tomsk-Seversk industrial agglomeration (8 samples) | Background of Tomsk Oblast (10 samples) | Mean in the lichens of Tomsk region (50 samples) | The Alps, (Semmering, Austria) (1 sample) |
|-----|----------|--------------------------------------------------|--------------------------------------------------|-----------------------------------|-----------------------------------------------|----------------------------------------|
| 1   | Na       | 289±116                                          | 305±84                                          | 235±92                            | 276                                           | 88                                     |
| 2   | Ca       | 1700±617                                         | 3041±1299                                       | 3650±1464                         | 2797                                          | 1719                                   |
### 3. Discussion

The results of lichen element concentration analysis (Table 1) show that this biological species from the area of the oil and gas exploration complex is more enriched with Na, Sc, Fe, Cr, Zn, As, Br, Rb, Ba, Au (in 1.3 to 9 times) than the lichens from the background territory of Tomsk region. From the analysis of Table 1 we can also see the peculiarity of the geochemical lichen spectrum taken in the impact zone of Tomsk-Seversk industrial agglomeration generally formed by the enterprises of nuclear-fuel cycle, petroleum-chemical combine, and coal-fired power stations. This peculiarity is determined by the concentrations of lanthanides, actinides (U, Th), Sr, and Sb. Elevated Ca concentration in the background samples can be referred to as a local feature.

Besides, the EF coefficient as an indirect indicator confirms geochemical differences in the lichen composition of the different areas. Comparison of the EF values shows that main elements-pollutants for the area of oil and gas exploration complex are Zn, As, Br, Rb, Ba, and Au; for Tomsk-Seversk

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| No. | Elements | Area of oil and gas exploration complex, Tomsk Oblast (32 samples) $X_{mean} \pm \delta$ | Area of Tomsk-Seversk industrial agglomeration (8 samples) $X_{mean} \pm \delta$ | Background of Tomsk Oblast (10 samples) $X_{mean} \pm \delta$ | Mean in the lichens of Tomsk region (50 samples) $X_{mean} \pm \delta$ | The Alps, (Semmering, Austria) (1 sample) $X_{mean} \pm \delta$ |
|-----|---------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 3   | Sc      | 0.29±0.1                                        | 0.36±0.13                                        | 0.22±0.04                                        | 0.29                                             | 0.06                                             |
| 4   | Cr      | 4.14±1.6                                        | 2.14±0.5                                        | 1.72±0.3                                        | 2.7                                              | 3.7                                              |
| 5   | Fe      | 785±263                                         | 913±245                                         | 606±120                                         | 768                                              | 401                                              |
| 6   | Co      | 0.43±0.1                                        | 0.50±0.13                                       | 0.29±0.05                                       | 0.4                                              | 0.16                                             |
| 7   | Zn      | 45±14                                           | 34±0                                            | no data                                         | 40                                               | 31                                               |
| 8   | As      | 0.19±0.04                                       | 0.08±0                                          | 0.07±0                                          | 0.11                                             | 0.003                                            |
| 9   | Br      | 5.6±1.8                                         | 0.89±0.3                                        | 0.60±0.2                                        | 2.4                                              | 5.4                                              |
| 10  | Rb      | 7.2±2                                           | 3.12±1.1                                        | 2.93±0.7                                        | 4.4                                              | 1.5                                              |
| 11  | Sr      | 11.4±4                                          | 32.3±12                                         | 1.8±0                                           | 15.2                                             | 4.8                                              |
| 12  | Ag      | 0.011±0.007                                     | 0.019±0.003                                     | 0.018±0                                         | 0.016                                            | 0.011                                            |
| 13  | Sb      | 0.046±0.02                                      | 0.133±0.04                                      | 0.063±0.02                                      | 0.081                                            | 0.113                                            |
| 14  | Cs      | 0.14±0.04                                       | 0.13±0.02                                       | 0.08±0.02                                       | 0.12                                             | 0.05                                             |
| 15  | Ba      | 30±8                                            | 27±6.6                                          | 18±5                                            | 25.0                                             | 7                                                |
| 19  | La      | 0.9±0.3                                         | 1.32±0.5                                        | 0.79±0.15                                       | 1.0                                              | 0.009                                            |
| 20  | Ce      | 1.56±0.6                                        | 2.15±0.7                                        | 1.30±1.1                                        | 1.67                                             | 0.004                                            |
| 21  | Nd      | 0.51±0.2                                        | 1.19±0                                          | no data                                         | 0.85                                             | 0.011                                            |
| 22  | Sm      | 0.14±0.06                                       | 0.18±0.06                                       | 0.10±0.03                                       | 0.14                                             | 0.002                                            |
| 23  | Eu      | 0.036±0.01                                      | 0.040±0.01                                      | 0.026±0.007                                     | 0.03                                             | 0.02                                             |
| 24  | Tb      | 0.022±0.009                                     | 0.028±0.01                                      | 0.017±0.002                                     | 0.02                                             | 0.002                                            |
| 25  | Yb      | 0.064±0.03                                      | 0.106±0.03                                      | 0.065±0.01                                      | 0.08                                             | 0.001                                            |
| 26  | Lu      | 0.012±0.008                                     | 0.014±0.005                                     | 0.009±0.003                                     | 0.01                                             | 0.002                                            |
| 26  | Hf      | 0.16±0.07                                       | 0.19±0.06                                       | 0.10±0.02                                       | 0.15                                             | 0.019                                            |
| 17  | Ta      | 0.028±0.01                                      | 0.042±0.01                                      | 0.024±0.007                                     | 0.03                                             | 0.002                                            |
| 18  | Au      | 0.0012±0.0007                                   | 0.0002±0                                        | 0.0002±0                                        | 0.0005                                           | 0.0008                                           |
| 27  | Th      | 0.18±0.07                                       | 0.26±0.09                                       | 0.14±0.03                                       | 0.19                                             | 0.05                                             |
| 28  | U       | 0.07±0.03                                       | 0.20±0.05                                       | 0.06±0.02                                       | 0.11                                             | <0.01                                            |
| 29  | Th/U    | 2.5                                              | 1.3                                             | 2.4                                             | 2.1                                              | >5                                               |
| 30  | La/Yb   | 14.1                                             | 12.4                                            | 12.1                                            | 12.9                                             | 19.5                                             |
| 31  | Ash yield, % | 3.6                                      | 4.1                                             | 4.1                                             | 3.9                                              | 1.3                                              |
industrial agglomeration – La, Ce, Sr, Sb, and U; and background territory is characterized by elevated Ca and Ag concentrations.

When comparing the data from Tomsk region with the background area from the Alps (Austria) we can observe a more considerable difference in the accumulation levels of chemical elements (figure 1). The lichen sample from the Alps contains minimal concentrations of most studied chemical elements. The exceptions are Cr, Br, Sb, and Au. Presumably, elevated Cr, Br and Sb concentrations, which are close to those from the areas of oil and gas exploration complex of Tomsk Oblast, reflect the impact of oil-processing plants or other industrial facilities in Vienna suburbs.

![Figure 1. Comparison of chemical elements concentrations in the lichen ash from Tomsk Oblast and Alps (Simmering, Austria), mg kg⁻¹, recalculated for the dry matter.](image)

4. Conclusion

The comparative analysis of lichens growing in Tomsk Oblast allows for conclusion that lichens form the areas of oil and gas exploration complex and Tomsk-Seversk industrial agglomeration have geochemical peculiarities. The geochemical peculiarity of the first area is determined by intense accumulation of such elements as Cr, Zn, As, Br, Rb, Ba, and Au. Elevated concentrations of As, Zn, and Cr were likely to be caused by combustion processes of oil-dissolved gas in flares, oil heaters, diesel power stations and transport, or drilling operations. These elements are known to be accumulated by lichens due to their high biophylity. Oil-field and high mineralized water of oil fields contains elevated concentrations of Br and Au [8] that can explain high concentrations of these elements in lichen ash. Previous investigations of dust aerosols [9] and upland peat [10] in this area showed that Rb, Ba, and Br are indicative elements for the areas of oil and gas exploration complex. Thus, the current research has revealed the fact of atmosphere pollution in the areas of oil and gas exploration complex of Tomsk region.

The peculiarity of the geochemical spectrum of the lichens from the impact zone of Tomsk-Seversk industrial agglomeration formed by the facilities of nuclear-fuel cycle, petroleum-chemical combine, and power stations, is determined by the concentrations of Sr, Sb, lanthanides, and actinides (Th, U).
The study of the space distribution of these elements in the Tomsk-Seversk industrial zone testifies that their sources are mainly Siberian Chemical Combine facilities.

The results of this study support the concept of good bio-monitoring properties of the epiphytic lichens and allow us to recommend them for using in assessing anthropogenic transformation of natural environment as a main component.

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