Assessment of mercury content in poplar leaves of Novokuznetsk agglomeration

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Abstract. In this paper, the content of mercury in poplar leaves in the Novokuznetsk industrial agglomeration and along the automobile route Novokuznetsk-Mezhdurechensk is assessed. The geoecological indicators are also calculated.

1. Introduction
Mercury is one of the most toxic metals polluting the environment. The total amount of mercury as a natural impurity connected with coal, oil and ore concentrates of non-ferrous metals. The main sources of atmospheric mercury emissions are coal and oil products combustion installations, as well as non-ferrous industry. Weighted average mercury content in Russian coal is estimated to be 0.08 mg / kg, and it largely depends on the average mercury concentration in coal from Kemerovo region, for which the half of mercury total amount from the extracted coal of Russia is accounted [4].

The goal of the study is assessment of mercury and its distribution in the territory of Novokuznetsk agglomeration according to the poplar leaves research data.

2. Methods and research objects
Novokuznetsk is one of the largest metallurgical and coal-mining centers of Russia. It is the second city in the number of inhabitants (more than 550 thousand of people) and the first one in the area (424 km²) in Kemerovo region [2]. The city is a center of Novokuznetsk (Kuzbass) agglomeration, which has population of over 1.3 million people (figure 1). This agglomeration is the 12th largest in Russian Federation. The industry of agglomeration has a strong specialization and represented by ferrous and nonferrous metallurgy; the coal industry (mines, open cuts), machine-building, construction and heat power industries.

The coal industry in the region amounts 56% of mineral coal production and 83% of coking coal of Russia. Mining and open cuts are situated in all city districts and municipal areas of the agglomeration. Russia's largest coal companies are Kuzbassrazrezugol, Yuzhkuzbassugol, and Raspadskaya.

The metallurgical industry is concentrated mainly in Novokuznetsk and presented by: Novokuznetsk and West-Siberian Metal Plants, ferroalloy and aluminum plants.

The largest enterprises producing construction materials are presented by: Kuznetsk cement plant, Baydaevsk brick factory, large house-building combines, enterprises manufacturing glass and soft roof, extracting non-metallic building materials for the needs of construction companies within Kemerovo region and outside of it.

The power plants are TPP of Kuznetsk Metallurgical Combine, Zapadno-Sibirskaya TPP, Kuznetsk TPP, South Kuzbass GRES, Tomusinsk GRES, Novokuznetsk GTPP.
Ecological situation in Novokuznetsk is assessed by state environmental agencies as hard [2]. In 2013-2014, Novokuznetsk was included in the list of Russian cities with the highest level of air pollution by such indicators as soot, suspended matters, nitrogen dioxide, hydrogen fluoride, carbon monoxide, formaldehyde and benzapyrene [1, 5].

In the 63 km eastwards of Novokuznetsk in sublatitudinal basin at the confluence of rivers Tom and Usa, Mezhdurechensk is located, its population is about 100 thousand of people. It is located in the south-eastern part of the Kuznetsk coal basin in the territory of Tomusinsk deposit. The mercury content in coal of this deposits is 0.8 mg / kg [4]. The coal industry is a city-forming industry. The main sources of air pollution are boiler houses, coal mines, open cuts, processing plants. They emit dust, carbon monoxide, nitrogen oxides, sulfur dioxide and heavy metals in the atmosphere.

The research object was the leaves of black poplar (Populus nigra L.). A black poplar reaches 30-35 m in height and 1-2 m in diameter of trunk. Poplar differs from other woody plants with rapid growth rate and more frequent use for landscaping of urban areas in the temperate zone. Poplar leaves are effective air filter. Due to the special structure of poplar surface, leaves are natural geochemical tablet to capture dust aerosols and reflect short-term seasonal (summer) cumulative effect.

In September 2015 in Novokuznetsk in the regular network of 2 × 2 km along the route Novokuznetsk-Mezhdurechensk with a grid of 3-5 km, black poplar leaves were sampled (figure 2). Totally, 45 samples were selected. Leaves were sampled by the average sample method with approximately the same age of the trees at a height of 1.5-2 meters above the ground, according to methodological guidelines [3]. Sample preparation for analysis includes drying by the environmental temperature, mechanical grinding and stirring to achieve the highest homogeneity of the material, sample taking for analysis.
The sample analysis was conducted in the laboratories of International innovative academic center «Uranium Geology», Geocology and Geochemistry Department, Tomsk Polytechnic University. Mercury content in the poplar leaves samples was detected on the Atomic Absorption Spectrometer RA-915+ with pyrolyzer PYRO-915 (pyrolysis reaction, mercury detection limit – 5 mkg/kg). For the control of mercury measurements in dry mass of poplar leaves in this devise, a standard sample "birch leaf" was used (GSO 8923-2007, COOMET CRM 0067-2008-RU).

3. Results and discussion
The results are statistically processed and presented in Tables 1 and 2. The analysis of these tables allows us to distinguish features of mercury distribution in the territory of Novokuznetsk industrial agglomeration. The average mercury content in dry mass of poplar leaves in the territory of Novokuznetsk agglomeration (26.7 ng / g), which is comparable with the content of mercury in the standard sample composition of poplar leaves (GSV-3) registered abroad (Institute of Geophysical and Geochemical Exploration (China)) - 26.0 ng / g. The maximum mercury content in the sample 1.9 times exceeds the value. By the value of variation coefficient, the homogeneous sample is typical for mercury (<50%), for Novokuznetsk, as well as along the route Novokuznetsk-Mezhdurechensk.

Average mercury content in the territory of Novokuznetsk, as well as along the route Mezhdurechensk-Novokuznetsk is approximately the same and do not differ significantly. The maximum contents in the investigated areas are within the measurement error. However, the minimum concentration in the territory of Novokuznetsk is 2 times higher in comparison with the data for the route Novokuznetsk-Mezhdurechensk.

**Table 1. Statistical parameter of mercury content (ng/g) in dry mass of poplar leaves in the territory of Novokuznetsk (N=33).**

| Index                  | Value   | Index                | Value   |
|------------------------|---------|----------------------|---------|
| Average                | 23.6±1.5| Standard deviation   | 7.9     |
| Minimum                | 7.9     | Excess               | 0.5     |
| Maximum                | 46.7    | Asymmetry            | 0.7     |
| Median                 | 22.4    | Variation coefficient, % | 35     |
Table 2. Statistical parameter of mercury content (ng/g) in dry mass of poplar leaves along the route Novokuznetsk-Mezhdurechensk (N=12).

| Index              | Value    | Index            | Value  |
|--------------------|----------|------------------|--------|
| Average            | 26.4±2   | Standard deviation| 8.3    |
| Minimum            | 14.3     | Excess           | 0.93   |
| Maximum            | 43.9     | Asymmetry        | 0.90   |
| Median             | 25.3     | Variation coefficient, % | 31     |

Schematic map of the spatial distribution of the concentrations of mercury in Novokuznetsk, built using the programs SURFER and COREL DRAW 10 and 16, is shown in Fig. Four significant halos of gross mercury 1.5-2 times exceeding the average value were discovered. The largest in area and high-contrast halo (38-48 ng / g) is located in the central part of the city and connected with industrial zones of the Central TPP and Metallurgical Combine (site of rail WSMC). Two other local halos (38-44 ng / g) are concentrated in the Zavodskoy district (in the north-eastern part of the city), and refer to the industrial zone of WSMC, including the West Siberian TPP. The fourth, less contrast halo is in the Kuznetsk district (in the eastern part of the city) within the impacted areas of the Kuznetsk thermal power station, aluminum and ferroalloy plants. The prevailing south-western wind direction influences the halos configuration (figure 1).

It has been established that detected halos of mercury are located in industrial areas of the city. Mercury contained in the leaves of poplar is one of the geochemical indicators of industrial specialization of Novokuznetsk. The question of mercury emission sources within the industrial areas of the city is not completely clear. What is the separate contribution of TPP, plants of ferrous and non-ferrous metallurgy in the total emissions of mercury into the environment of Novokuznetsk?

Figure 3. Isoconcentrations of mercury in the territory of Novokuznetsk according to poplar leaves sampling. Upper left inset – summer wind rose.

Figure 4 represents a graph showing mercury distribution in dry mass of poplar leaves along the route Novokuznetsk-Mezhdurechensk. Increased mercury concentrations in poplar leaves refer to the
western and eastern sections of the route Novokuznetsk - Mezhdurechensk. Western section joins to Novokuznetsk - vil. Atamanovo (sample At-1), the eastern section is located in Mezhdurechensk area(sample Mk-2, 3, 4).

**Figure 4.** Mercury content distribution in dry mass of poplar leaves along the route Novokuznetsk-Mezhdurechensk.

Legend: At-1 (vil. Atamanovo), Br-1 (vil. Borovkovo), Ts-1 (Tom-Usinsk GRES), Pd-1 (vil. Podobas), Ms-1–4 (Myski), Mk-1, 2, 3, 4 (Mezhdurechensk). Upper left inset – summer wind rose.

So, determined areas with the highest mercury content in poplar leaves refer to the territories, which have the greatest technogenic impact in the summer season and reflect the influence of the industrial areas of Novokuznetsk, as well as the impact of coal open cuts near Mezhdurechensk. It is worth paying attention to the fact that the influence of Tom-Usinsk GRES (sample T-1) as a potential source of mercury emissions into the environment is not evident in the chart.

The calculated geoecological indicators of mercury load in the territory of Novokuznetsk industrial agglomeration in the summer have shown the up to 4 times excess of mercury content in poplar leaves in comparison with the mercury Clarke for terrestrial plants (Table 3). The excess over the temporary acceptable concentration is 2 times.

By comparison of the obtained data on the mercury concentration in poplar leaves in the studied areas with the results given in the literature, a significant excess compared to the mercury content in Europe vegetation (Aboal, 2001) and medium for terrestrial plants (according Yanina, 1992) should be mentioned. However, in general, the obtained in this research data are comparable with the background for terrestrial plants (Yanina, 1992) (Table 4).

**Table 3.** Geoecological characteristics of mercury load on the territory of Novokuznetsk agglomeration according to poplar leaves research data.

| Location                           | C, ng/g | Ce | TAC |
|------------------------------------|---------|----|-----|
| Novokuznetsk                       | 8-49/26 | 0.7-4.1/2.2 | 0.1-0.2/0.1 |
| Route Novokuznetsk-Mezhdurechensk. | 14-44/25 | 1.2-3.7/2.1 | 0.6-1.8/1.1 |

a C - mercury content;

b Ce - concentration coefficient (regarding to Clarke for terrestrial plants after Dobrovolsky, 2003 – 12 ng/g)

c TAC - temporarily admissible concentration
Table 4. Indicative levels of mercury content in flora of parts of the world.

| Region                           | Average content, ng/g | Literature source |
|----------------------------------|-----------------------|-------------------|
| Background value in terrestrial plants | 30-700                | Yanin, 1992       |
| Average value in terrestrial plants | 15                   | Aboal, 2001       |
| Europe                           | 8                     | Steinnes, 2001    |
| Norway                           | 47-116                |                   |

4. Conclusions
Mercury containing in poplar is a sensitive indicator of industrial specialization of Novokuznetsk agglomeration area. The results of this research can be used for biogeochemical monitoring in industrialized, and in particular, in coal mining areas. The obtained data are comparable with those mentioned in the literature and do not exceed them. The calculated geoecological indicators of mercury load on the investigated areas in the summer have shown the increased mercury concentration by poplar leaves (up to 4 times), and as a result, the up to 2 times excess of the estimated amount of temporary acceptable concentrations.

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References
[1] 2011 State Report on Environment and Environmental Protection in the Russian Federation in 2014 (Moscow: Ministry of Natural Resources of the Russian Federation)
[2] 2015 Report on Environment in Novokuznetsk in 2014 (Novokuznetsk: Committee of Environmental Protection and Natural Resources of Novokuznetsk Sity Administration)
[3] 1981 Guidelines for Conducting of Field and Laboratory Researches of Soil and Plants by the Control of Metal Pollution of Environment (Moscow: Hydrometeoizdat)
[4] 2005 Assessment of Mercury Input to Environment from the Territory of the Russian Federation (Moscow: Federal Service for Ecological, Technological and Nuclear Supervision Service/Copenhagen: Danish Agency for Environmental Protection)
[5] 2014 Report on Environment and Environmental Protection in the Kemerovo Region in 2013 (Kemerovo: Department of Natural Resources and Environmental Protection of the Kemerovo Region)