Dynamics and features of mercury accumulation in coniferous trees of Tomsk region

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Abstract. This article performs an analysis of mercury concentration in uneven-aged needles of various wood species in peat bog ecosystems of Tomsk region. New data are given on mercury accumulation and distribution depending on the type of conifers, needle age, and landscape and climate conditions. The level of the mercury concentration data obtained in Tomsk region does not exceed the mercury concentration levels in the literature. In general, it lies within the range of average concentrations for Siberia and the total area of Russia.

1. Introduction

Mercury, an element of the first class of danger, has increased toxicity, migration ability, and specificity of the forms of transformation into environmental components [1]. It belongs to the group of thiol poison mutagenic, methylate with the formation of highly toxic compounds, and is recognized as one of the most dangerous pollutants of the natural environment [2]. With all the ways of mercury entering the environment from both anthropogenic and natural sources, the atmosphere contributes most to the migration of the pollutant. In this connection, the natural components that concentrate it are of particular importance and can be used as indicators of its atmospheric emission, for example, needles. Needles are a practical and informative bioindicator of the ecological state of atmospheric air. It contributes to the soil mantle formation. Besides, the accumulated chemical elements of needles form a composition of soil, surface, and ground waters [3]. A vitamin supplement made of needles is being actively used by farm enterprises of Siberian region for cattle food. Mercury is a heavy metal and an element of the first class of hazard. That is why study of the needles to determine the mercury concentration is important and necessary from the customers' point of view as well [4].

The purpose of present article is an investigation of the mercury concentration in uneven-aged needles in the territory of Tomsk region and identification of the special aspects of mercury accumulation in the needles depending on the tree age of the needles and climate and landscape references of the studied territories.

2. Methods and research objects

Investigation of the mercury concentration in the needles of trees growing in the peat bog ecosystems was conducted on the basis of the *Vasyuganie* Research Station (The Institute of Monitoring of Climatic and Ecological Systems SB RAS) located in Polynyanka village of Bakcharsky district in bog ecosystems of Tomsk region (Figure 1). All studied objects in Bakcharsky district are parts of the Big Vasyugan Swamp. Samples are collected on the typical plots of upland and lowland swamps.

Needle samples were collected from the trees growing in bog ecosystems of Bakcharsky district: Bakcharskoe and Samara peat bogs (hereinafter p.b.). Both plots belong to the native bog ecosystems. The territory is represented by the widest range of tree species: fir trees, pines, cedars, and junipers growing on two key plots of the bog ecosystems: Bakcharskoe and Samara bogs. These plots are part of the Big Vasyugan Swamp. This wetland is a native territory and is not under human impact. The trees on this territory vary according to the landscape, hydrological, botanical, and nutrition conditions.

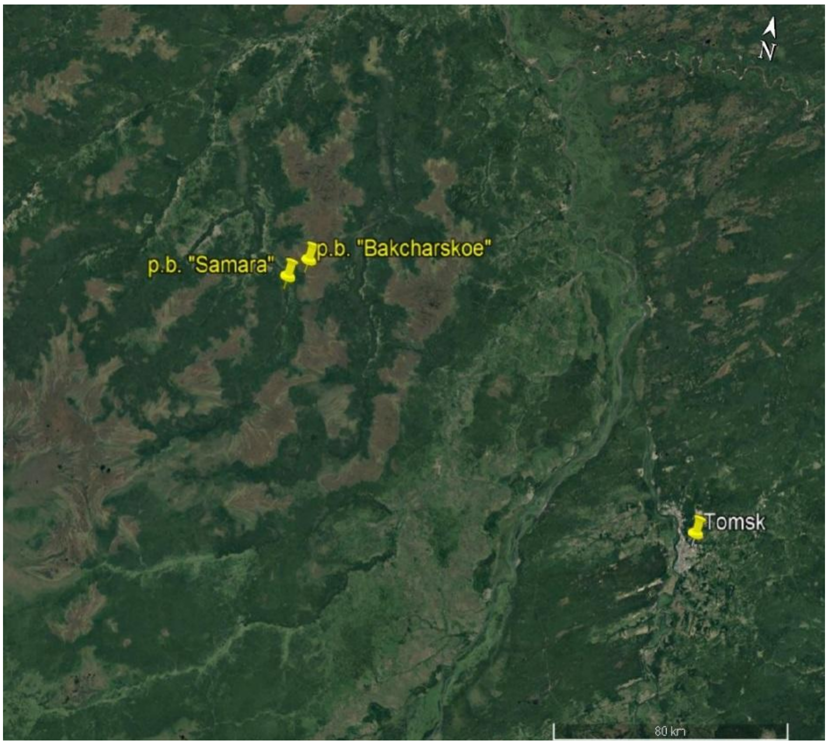

Figure 1. Tomsk region.

Needle samples were collected in the summer of 2013 from approximately even-aged trees using the mixed samples method. According to the standard methodology guidelines [5], samples were taken from the lower part of the tree crown (at a height of 1.5-2 m above the ground) and packed into ziplock bags. In total, 62 needle samples were taken from different kinds of trees: Siberian stone pine (*Pinus sibirica Du Tour*), common pine (*Pinus silvestris L.*), Siberian fir (*Abies sibirica Ledeb.*), Siberian spruce (*Picea obovata Ledeb.*), and common juniper (*Juniperus communis L.*). The samples were brought to the air-dried state at room temperature up to a constant mass of the sample and milled. The needles were not rinsed. In the course of the work, the mercury concentration for 2009 - 2013 was determined.

The mercury concentration in the needle samples was determined by the atomic absorption spectrometry method using an RA-915+ [6] mercury analyzer with a PYRO-915 [7] attachment (the pyrolysis method) [8]. The detection limit of mercury is 5 ng/g. The mercury concentration was calculated per 1 gram of the dry basis mass. The technique for processing of the results included the calculation of ecological-geochemical indexes: the concentration coefficient and the temporarily allowable concentration. For the calculation of the interrelation between the mercury concentration and the meteorological characteristics, information on the air temperature and humidity was taken at the meteorological station of Bakchar Village (Tomsk region).

3. Results and discussion

Needles sample of Tomsk Region are collected from a wide range of conifers: fir, pine, spruce, and cedar. The maximum needle age is 5 years. The trees growing in the territory being studied vary in landscape. The hydrological, botanical, and nutritional conditions of Bakcharskoe peat bog (p.b.) provided 4 sampling points, and Samara p.b., 3 sampling points.

The average mercury concentration in the needles in the studied territory ranges from 14 to 21 ng/g regardless of the wood species (Figure 2). The average mercury concentration for both peat bogs is the same (20 ng/g). In the territory of Bakcharskoe p.b., the maximum average mercury concentration is found in the fir needles, its amount is 24 ng/g, whereas the minimum average concentration is in the pine needles (14 ng/g). The average concentrations in cedar and spruce needles have no significant difference (21 and 20 ng/g, respectively). In the territory of Samara p.b., the maximum average mercury concentration is also found in the fir needles, its amount is 23 ng/g, whereas the minimum average concentration is in the pine needles (16 ng/g). The average concentrations in stone pine and spruce needles are the same (21 ng/g).

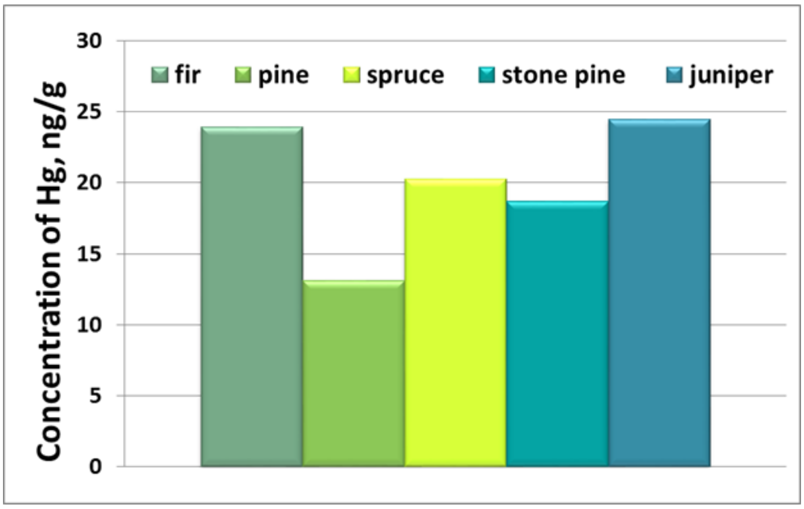

Figure 2. Mercury concentration depending on the type of needles.

The maximum time interval which allows evaluating mercury accumulation in the studied samples is 5 years. According to other researchers [9], the older the needles, the more mercury they contain. In the present study, this tendency is traced in the cedar and spruce needle samples as well. However, our studies reveal that the maximum concentration is settled when the needles become 3-4 years old (Figure 3). Moreover, in this case no further significant differences in the mercury accumulation were registered. Such regularity is identified for the pine and fir needles.

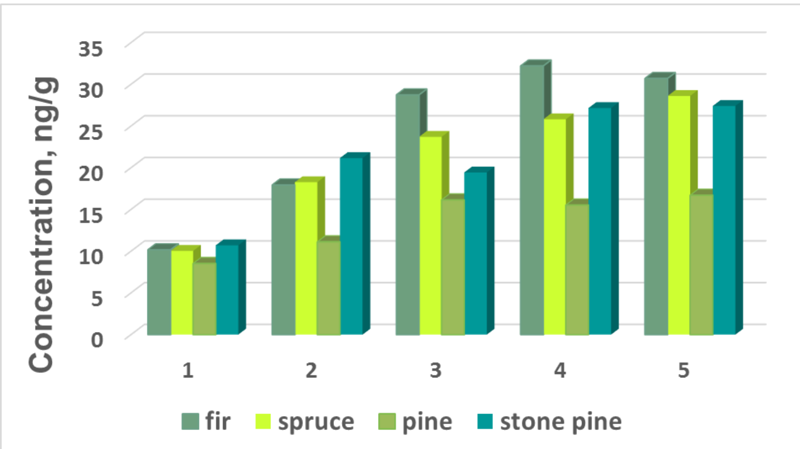

Figure 3. Concentration of mercury depending on the age of needles.

Among all samples of 1-year-old needles the maximum mercury concentration is found in the samples of cedar needles (14 ng/g), and the minimum concentration, in the spruce needles (8 ng/g) taken from Samara p.b. On average, the mercury concentration in 1-year-old needles is equal to 11 ng/g.

If 2-year-old needles are considered, the maximum mercury concentration is found in the cedar needles from Samara p.b. (29 ng/g) and the minimum concentration, in the pine needles from Bakcharskoe p.b. On average, the mercury concentration in the 2-year-old needles is 18 ng/g.

In the studied 3-year-old needles, the maximum mercury concentration is registered in the fir needles from Samara p.b. (29 ng/g) and the minimum concentration, in the pine needles from Bakcharskoe p.b. (14 ng/g). On average, the mercury concentration in the 3-year-old needles is 23 ng/g.

In the 4-year-old needle samples, the maximum mercury concentration is registered in the fir needles (38 ng/g) and the minimum concentration, in the pine needles from Bakcharskoe p.b. (15 ng/g). On average, the mercury concentration in 4-year-old needles is 25 ng/g.

After analysis of 5-year-old needle samples, the maximum concentration of mercury is registered in the fir needles (37 ng/g), while the minimum concentration is found in the pine needles from Bakcharskoe p.b. (17 ng/g). On average, the mercury concentration in the 5-year-old needles is 25 ng/g.

It should be noted that, on average, the highest mercury concentration is present in the 5-year-old needles and the lowest one, in the 1-year-old needles.

It is known that the younger a tree, the more intensive its nutrition, development and growth and, thus, it captures chemical elements from the atmosphere faster. As the needles grow and get older, the biochemical processes in them slow down [9]. During the first year of the needle growth over the territory of Tomsk region, the mercury ingress is almost the same among the different tree species, except for the juniper needles (18 ng/g). The minimum mercury concentration is registered in the pine needles (9 ng/g).

During the study performed in the territory of Tomsk region, the following was revealed: there is a mild correlation between the mercury accumulation and the habitat of a tree.

After the processing of the research findings, the ecological-geochemical indexes of the mercury load in the territory of Tomsk region were calculated (Table 1).

Table 1. Ecological-geochemical characteristics of mercury load in the territory of Tomsk region.

Type of needles	**Concentration. ng/g**	**Kc**	**VDK**
Fir	24/112*	6/28	3/14
Pine	13/115	3.3/28.8	1.6/14.4
Spruce	20/165	5/41.3	2.5/20.6
Stone pine	19/99	4.8/24.8	2.4/12.4
Juniper	25/79	6.3/19.8	3.1/9.9

Note: * - 2013/2003; Kc= C/C_{Bg} - is the concentration factor, where C is the concentration of mercury, ng/g. C_{Bg} is the background content of mercury (4 ng/g. Ivanov V., 1997 [10]); VDK=$C/2C_{Bg}$ is the temporarily allowable concentration, where C is the concentration of mercury, ng/g. C_{Bg} is the background content of mercury (4 ng/g. Ivanov V., 199**7** [10]).

It exceeds the background concentration up to six times. The coefficient of temporarily allowable concentration in the territory of Tomsk region is 2.5.

To define the dependence between the mercury accumulaetion and climate characteristics, the correlation coefficient is calculated. It considers the interrelations between the mercury concentration in the needles, air temperature, and the amount of precipitation during the year, as well as over the period of vegetation. The correlation between the mercury concentration and the annual cycle of precipitation is calculated only for the 5-year-old needles. The calculations include only average data on the mercury concentration depending on the tree species around the studied territory. The calculation results reveal no uniformity of the correlation between the mercury concentration and air temperature and between the mercury concentration and amount of precipitation. For instance, for all studied needle samples no interrelations between the mercury concentration and air temperature are detected. However, the interrelation with the precipitation is negative and quite stable for all studied needle samples, both during the year and over the vegetation period (Table 2).

Table 2. Content of mercury depending on meteorological parameters.

Type of needles	Vegetation period (May-September)		Year	
	T^0C	Precipitation, mm	T^0C	Precipitation, mm
	r	r	r	r
Pine	-0.26	-0.35	-0.69	0.33
Stone pine	-0.09	-0.70	-0.93	-0.22

Study of the mercury concentration in conifers allows monitoring of the dynamics of mercury accumulation in the needles of these conifers. If compared to a similar study performed in 2003 in the territory of Tomsk region [11], this study shows that the mercury concentration has descended during the period from 2008 to 2013.

Studies of the content of mercury in coniferous Tomsk region in 1999-2003 showed that the average concentration of mercury in the needles, regardless of the age of species and location of a tree is 114 ng/g. The maximum content of Hg is typical for pine needles (Samara p.b.): 315 ng / g. The minimum content for pine needles (Bakcharskoye p.b.) is 60 ng / g. In the studied tree species growing in oligotrophic conditions, there is a weakly expressed pattern of accumulation of mercury in the needles depending on the place of growth. It is more pronounced in pine needles. The maximum amount of mercury accumulates in the four-year-old needles of pine and cedar, the five-year-old needles of fir. For fir and spruce, the content of mercury in needles decreased with age. Based on the results of the correlation analysis, a weak relationship between the mercury content in needles and the climatic indices was revealed.

However, it should be noted that the average mercury content (20 ng/g) in the needles decreased in 2009-2013 more than 5 times (Table 3). This feature is explained by a decrease in the technophilicity of mercury more than 5 times, the only element of all those studied [5]. This parameter (technophilicity) makes it possible to understand the main trends in the intensity of extraction of an element from the interior and use in technogenesis. A sharp reduction in the technophilicity of mercury is justified by the awareness of the ecological danger of this element, the degree of its negative impact on the living organisms at elevated concentrations of Hg in the components of the environment [12].

Table 3. Average concentrations of mercury in needle gymnosperms in 2003-2013

Type of needles	Medium concentration of Hg in needles, ng/g		Frequency of concentration decrease
	2003 (Lyapina, 2009)	2013	
Stone pine	99	19	5
Pine	115	13	9
Fir	112	25	5
Spruce	165	21	8
Juniper	79	25	3

The mercury concentrations in Siberia in needle samples do not exceed the concentrations introduced in the studies of other researchers, and fall within the range of average mercury concentrations in the needle samples from Canada and Spain. However, the obtained concentrations are significantly lower than the average concentrations in Russia (Table 4).

Table 4. Typical mercury concentration levels in plants from different parts of the world.

Region	Medium, ng/g	Source
Background in terrestrial plants	30-700	Yanin, 1992 [1]
Medium in terrestrial plants	15	
Europe	8	Aboal, 2001 [13]
Norway	47-116	Steinnes, 2005 [14]
	Needles	
Canada	4-48	Laperdina, 2000 [15]
Poland	100-500	Chernenkova, 2002 [16]
Spain	6-32	Aboal, 2001 [136]
Russia	132	Anoshin, 1995 [9]
West Baikal region	6-12	Afanasieva, 2004 [17]
The Republic of Buryatia	9-13.4	Afanasieva, 2010 [18]
Mountain and ore Altai region	300	Gusev 2012, [19]
Baikal region	5.8-13	Michailova, 2010 [20]
Leaves and needles of trees	8-26	Yermakov, 2010 [3]
Tomsk region	79-165	Lyapina, 2015 [11]
Purovsky District (YaNAO)	20/(10-22)	Strakhovenko *et al*, 2012 [21]
Altai region	22/(10-72)	Strakhovenko *et al*, 2012 [21]
Altai Republic	22/(0-43)	Strakhovenko *et al*, 2012 [21]
Novosibirsk region	29/(10-40)	Strakhovenko *et al*, 2012[21]
Irkutsk region (WAAO)	60/(10-44)	Strakhovenko *et al*, 2012 [21]
Chita region (ABAO)	35/(10-130)	Strakhovenko *et al*, 2012 [21]
Sakha Republic	270/(10-440)	Strakhovenko *et al*, 2012 [21]
Arkhangelsk region	34	Nadein *et al*, 2002 [22]
Altai-Sayan ecoregion	30-50	Shurkina, 2013 [23]

4. Conclusions

This study was devoted to an analysis of mercury concentrations and geoecological characteristics of its accumulation in the tree needles of Tomsk region. The study showed that the above obtained data agree well with data collected by other researchers, both in Siberia and the total area of Russia [11]. The highest mercury concentrations have been found in fir needles and the lowest ones in pine needles. The mercury concentration grows over years and reaches its maximum when the needles are 3-4 year old ones with no further significant changes. Calculations of the interrelation between mercury accumulation and climate characteristics have revealed the presence of a feedback with the amount of precipitation for the needles of all tree species studied. Geoecological calculations demonstrated a low level of mercury accumulation in the conifers of Tomsk Region.

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