

## HUMAN ECOLOGY

## ЭКОЛОГИЯ ЧЕЛОВЕКА


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Mercury concentration in the snow cover  
of the city of KhabarovskOlga S. Khomchenko  , Alexandra G. Novorotskaya 

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**Abstract.** The research reveals results of studies of the total mercury content in the snow cover of Khabarovsk in winter period 2021–2022. Researchers highlight a connection between mercury and non-soluble residue, with minor transition into soluble phase. The total mercury content in the non-soluble residue ranged from 0.3 to 1.4 mg/kg. On the northern border of the Bolshekhlekhtsirsky Reserve, area with high content of quicksilver (3 mg/kg) was found, which exceeds the maximum permissible concentration by 1.4 times. Authors consider that high concentration of quicksilver may be a result of short-term local pollution and do not exclude cross-border origin of it. Content of mercury as a part of solid atmospheric precipitation on the Earth's surface in this area is 37.5  $\mu\text{g}/\text{m}^2$ , with average values of 10–18  $\mu\text{g}/\text{m}^2$ . The maximum content of mercury (73.9  $\mu\text{g}/\text{m}^2$ ) was found nearby CHP-3 area. The reason is a high concentration of combustion products in snow cover. The amount of solid atmospheric precipitation in the area of CHP-1 also significantly exceeded the average values, but this did not lead to an increase in the total amount of mercury that reached the surface. The minimum concentration of quicksilver was found in the embankment park area of the city – 3.2  $\mu\text{g}/\text{m}^2$ .

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**Keywords:** snow photography, mercury, snow cover, suspended substances, gorenje products


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## Ртуть в снежном покрове Хабаровска

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**Аннотация.** Представлены результаты исследований содержания общей ртути в снежном покрове г. Хабаровска, сформировавшемся в зимний период 2021–2022 годов. Отмечена связь ртути со взвешенными веществами, переход из которых в растворенную фазу незначителен. Содержание общей ртути в нерастворимом остатке находилось в диапазоне от 0,3 до 1,4 мг/кг. Выявлен участок на северной границе Большехехцирского заповедника с высоким содержанием Hg – 3 мг/кг, превышающим ПДК для почв в 1,4 раза, что, вероятно, явилось следствием кратковременного локального загрязнения, возможно, трансграничного происхождения. Осаждение Hg на земную поверхность в составе твердых атмосферных выпадений на данном участке составило 37,5 мкг/м<sup>2</sup>, при средних значениях 10–18 мкг/м<sup>2</sup>. Максимум – 73,9 мкг/м<sup>2</sup> был отмечен в районе ТЭЦ-3 и обусловлен наличием в снежном покрове большого количества продуктов горения. Количество твердых атмосферных выпадений в районе ТЭЦ-1 также значительно превышало средние значения, однако это не привело к увеличению общего количества ртути, поступившей на поверхность. Минимальное осаждение Hg отмечено в набережной парковой зоне города – 3,2 мкг/м<sup>2</sup>.

**Ключевые слова:** снегосъемка, ртуть, снежный покров, взвешенные вещества, продукты горения

**Вклад авторов:** О.С. Хомченко – определение концентрации ртути; А.Г. Новороцкая – проведение снегосъемки, определение взвешенных веществ.

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## Introduction

Snow cover is a universal research object that facilitates assessing the state of the atmosphere, to identify not only substances that are constantly present in the air, but also appearing occasionally as a result of periodic or catastrophic emissions, near or far atmospheric transport, the identification of which is possible only with constant monitoring, which is a very challenging and time-consuming task.

The study of the snow cover composition as part of the monitoring of atmospheric pollution is currently pervasive. The study of the snow cover of Khabarovsk has been carried out by the IWEP FEB RAS for a few years [1] However, the study of mercury content has been insufficiently researched. The volume and rate of mercury deposition from the atmosphere, in the form of wet precipitation and dry deposition alike, vary greatly depending on many factors [2], which necessitates monitoring studies, including local ones, in order to timely detect an increase in the mercury background, as well as the appearance of new sources of pollution.

The average mercury content in coals, both stone and brown, is about 0.1 g/t, with the exception of abnormal mercury-bearing coals found in some areas of Russia, Ukraine, the USA and China [3], in the coals of the Khabarovsk Territory it is higher – 0.4 g/t. The existing rates of its consumption supply from 10 to 13 tons of mercury to the atmosphere of the Russian Federation annually [4]. The share of coal in the energy component of Khabarovsk and domestic heating systems of the city and suburbs is high. In addition, mercury is characterized by the presence of long-range atmospheric transport, which, given the proximity of the borders with China, one of the countries with the largest mercury emissions [5], may be an additional source of mercury pollution of the atmosphere.

## Characteristics of the research area

Khabarovsk is a regional center with a population of 617 thousand people, located in an area of increased potential for atmospheric pollution with unfavorable conditions for the dispersion of impurities. The climate is temperate, monsoon. The longest season of the year is winter. A stable snow cover is established in mid-November. The coldest month is January with an average temperature of  $-21.6$  °C. The average wind speed in winter (November – March) is 4.7 m/s. The prevailing wind directions are south-west and west [6]. Winter 2021–2022 was observed within the usual timeframe, the amount of precipitation exceeded that for the

previous five-year period by 1.5 times, and the average temperature was  $-13.4\text{ }^{\circ}\text{C}$ , against  $-11.7\text{ }^{\circ}\text{C}$ <sup>1</sup>.

The intake of pollutants into the atmosphere of Khabarovsk only from stationary sources in 2021 amounted to 38,414 thousand tons<sup>2</sup>. The main ones are thermal power facilities – structural divisions of JSC FEGC branch “Khabarovsk generation”: Khabarovsk CHP-1, Khabarovsk CHP-3, as well as an oil refinery – JSC ORP-Khabarovsk Refinery. Some contribution is made by low-power autonomous boiler houses and, located on the outskirts of the city and in the nearest suburbs, low-rise houses with autonomous coal and wood heating.

CHP-3 is the largest and youngest power plant in the Khabarovsk region and the second largest thermal power plant in the Russian Far East. The main fuel is coal, natural gas, fuel oil. Three of the four power units of CHP-3 are coal-fired. The coals of the Neryungri deposit are mainly used, in recent years they have begun to use the coals of the Urgal deposit and occasionally coals from China from the fields of Heilunjiang province. The planned transfer to gas should be completed in three years [7].

CHP-1 uses natural gas from Sakhalin deposits as fuel, as well as coal and brown coal from various deposits (most often Urgalsky and Pereyaslavsky). As a result of the gradual conversion to natural gas, coal consumption has tripled from 2006 to 2018. Currently, the structures and equipment of Khabarovsk CHP-1 are outdated and have reached a high degree of wear. Modernization of the station is considered impractical, in the 2020s it is planned to decommission it with the construction of a replacement Khabarovsk CHP-4 on the same site.<sup>3</sup>

At the surveyed thermal power plants, coal combustion occurs at a temperature of  $1100\text{--}1600\text{ }^{\circ}\text{C}$ . At CHP-1, ash collection is wet on scrubbers with Venturi pipes, at CHP-3 – dry on electric filters. The amount of fly ash, depending on the type of boilers, the type of fuel and its combustion mode, can be 70–85% of the mass of the mixture, slag – 10–20% [7].

## Materials and methodology

Samples of snow cover (SC) were taken on March 2–3, 2022 during the maximum moisture reserve using the VS-43 snow weight meter according to RD 52.04.186-89 from sites with different intensity of anthropogenic load. Conditionally, they can be divided into the following zones.

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<sup>1</sup> Weather and climate. Reference and information portal. Available from: [http://www.pogodaiklimat.ru/history/31735\\_2.htm](http://www.pogodaiklimat.ru/history/31735_2.htm) (accessed: 29.12.2022).

<sup>2</sup> State report “On the state and environmental protection of the Khabarovsk Territory in 2021”. Available from: <http://mpr.khabkrai.ru/Deyatelnost/Ekologiya/Gosudarstvennyj-doklad-ostoyanii-i-ob-ohrane-okruzhayushej-sredy-Habarovskogo-kрая> (accessed: 29.12.2022).

<sup>3</sup> Decree of the Government of the Russian Federation No. 1544-r dated 15.07.2019. Available from: <http://publication.pravo.gov.ru/Document/View/0001201907170007?index=1&rangeSize=1> (accessed: 29.12.2022).

Zone of industrial technogenic impact. Spot No. 1 (CHP-3 area, 48.571715° N, 135.143285° E) is located 400 m west of CHP-3, characterized by heavy contamination of the snow cover with soot particles, due to which the profile of the joint venture has a layered color. The average height of the SC is 42 cm, the density is 0.17 g/cm<sup>3</sup>.

Spot No. 2 (CHP-1 area, 48.410403° N, 135.118544° E) is located 200 m south of CHP-1, characterized by moderate contamination of snow cover with a weakly pronounced layering profile. The average height of the SC is 49 cm, the density is 0.22 g/cm<sup>3</sup>.

Spot No. 3 (refinery area, 48.493285° N, 135.040061° E) is located 350 m southwest of the refinery and 150 m northeast of the Amur coast. The average height of the SC is 40 cm, the density is 0.24 g/cm<sup>3</sup>.

Residential development zone. Spot No. 4 (48.488518° N, 135.080751° E) is located in the courtyard of a residential building, shielded from busy streets by 5-storey buildings, there are no industrial enterprises nearby. The average height of the SC is 50 cm, the density is 0.24 g/cm<sup>3</sup>.

Park area. Spot No. 5 (children's health camp, 48.529152° N, 135.029209° E) is located 600 m northeast of the Amur coast, from which it is shielded by a forest park zone. There is a motorway nearby. There are no industrial enterprises in the premises. The average height of the SC is 41 cm, the density is 0.22 g/cm<sup>3</sup>.

Spot No. 6 (Dynamo Park area, 48.483493° N, 135.076957° E) is located 70 m south-east of Muravyov-Amursky Street (the main street of the city), from which it is not shielded. The average height of the SC is 45 cm, the density is 0.22 g/cm<sup>3</sup>.

Spot No. 7 (the area of the park “CPKO”, 48.471992° N, 135.054385° E) is located 170 m northeast of the Amur coast. The average height of the SC is 50 cm, the density is 0.19 g/cm<sup>3</sup>.

Coastal zone. Spot No. 8 (48.546253° N, 135.016174° E) is located 100 m east of the Amur coast, 850 m north of the automobile-railway bridge. The average height of the SC is 31 cm, the density is 0.19 g/cm<sup>3</sup>.

Spot No. 9 (Amur River, ice 48.546508° N, 135.013296° E) is located 200 m west of spot No. 8. The average height of the SC is 32 cm, the density is 0.22 g/cm<sup>3</sup>.

The SC samples were melted at room temperature and filtered through a “blue ribbon” paper filter. Determination of the dissolved mercury content was carried out according to FER 14.1:2:4.271-2012 (M 01-52-2012), suspended solids – according to RD 52.24.468-2019, mercury content in suspended matter – according to M 03-09-2013. The studies were carried out on the mercury analyzer RA-915+ at the Environmental Monitoring Center of the IWEP FEB RAS.

## Results and discussion

The content of dissolved forms of mercury at spot No. 1 (CHP-3) was 11.4+2.3 ng/dm<sup>3</sup>, which slightly exceeded the MPC for water of fishery reservoirs,

amounting to 0.00001 mg/dm<sup>3</sup>, and significantly lower than the MPC for other waters – 0.0005 mg/l. In other areas studied, the concentration of dissolved mercury did not exceed the limit of quantitative determination of the method – 10 ng/dm<sup>3</sup>. In the area of Tomsk SDPP-2, the average mercury content in thawed snow water was also very low – 8.4 ng/dm<sup>3</sup> [8]. In Heilongjiang Province (China), in the area closest to Khabarovsk and having similar climatic conditions, the content of dissolved mercury in the snow cover in 2018 was in the range of 75-95 ng/l, which is higher than in western China. The authors attribute this to the peculiarities of the local industry, a large share of which is coal-fired power plants and boiler houses [9].

The amount of suspended substances (SS) in the SC was similar between most control spots of the city and varied between 166-281 mg/dm<sup>3</sup>. Only the central park zone, where the suspended substances content was 71 mg/dm<sup>3</sup>, and the areas of CHP-1 and CHP-3 with a content of 625 and 1935 mg/dm<sup>3</sup>, respectively, differed significantly (Table).

Suspended substance and mercury concentration in snow cover

Study area	Sampling point	Concentration			Solid atmospheric fallout, g/m <sup>2</sup>	Hg arrival on surface, µg/m <sup>2</sup>
		SS in SC, mg/dm <sup>3</sup>	Hg in SS SP, µg/kg	Total Hg, ng/dm <sup>3</sup>		
Industrial area	№ 1	1935	687±172	1329	107,6	73,9
	№ 2	625	344±86	215	51,3	17,6
	№ 3	236	1029±257	243	17,6	18,1
Residential area	№ 4	200	629±157	126	19,1	12,0
Park area	№ 5	253	825±206	210	18,3	15,1
	№ 6	166	885±221	147	12,2	10,8
	№ 7	71	605±151	43	5,4	3,2
Coastal area	№ 8	227	1396±349	279	11,4	15,9
	№ 9	281	992±248	317	11,6	11,5
Suburban area	№ 10	82	1065±266	87	6,0	6,4
	№ 11	138	3036±759	419	12,4	37,5

SS – suspended substance in snow cover, mg/dm<sup>3</sup>, SC – snow cover, Hg in suspended substance in snow cover, µg/kg

The high content of suspended substances in the SC in the area of CHP-3 indicates a significant intake of solid combustion products into the atmosphere. The total amount of solid atmospheric precipitation in the winter period of 2021–2022 in the area of CHP-3 was the highest among all the studied sites and amounted to 107.6 g/m<sup>2</sup>, which is 7.8 times more than the average for the city and 2.1 times more than in the area of CHP-1. The latter is probably due to the use of different types of fuel. The estimated gross amount of mercury in the SC ranged from 43 to 1329 ng/dm<sup>3</sup>.

Studies of the Khabarovsk snow cover conducted in the winter of 2018–2019 showed an even higher content of total mercury in the area of CHP-3 – 3.44 micrograms/dm<sup>3</sup>.<sup>4</sup>

The Hg content in the suspended matter of the snow cover was quite high, even in park and residential areas – 605–885 micrograms/kg, and exceeded that in the industrial zone of Usolye-Sibirsky (0.6 mg/kg)<sup>5</sup> and Tomsk (0.21 mg/kg)<sup>6</sup>.

A comparable concentration was also detected in the area of CHP-3 – 687 micrograms/kg. The minimum amount (344 micrograms/kg) was determined in the area of CHP-1. Earlier, initial concentrations were noted for the vicinity of Tomsk SDPP-2 [8] and for Blagoveshchensk, where the average mercury content in the insoluble fraction of snow was 0.136 mg/kg. Depending on the direction and distance from the CHP, concentrations increased up to 20 times compared to background concentrations – from 0.021 mg/kg to 0.410 mg/kg [9]. In 2018–2019, the mercury content in the solid residue of the Khabarovsk snow cover was much lower: CHP-1 – 0.12 mg/kg, CHP-3 – 0.06 mg/kg, refinery – 0.02 mg/kg [10].

The detected concentrations of Hg exceeded them in the area of CHP-1 and CHP-3 – by 5.7 times, in the area of the refinery – by 51 times. One of the reasons for such a significant discrepancy in data may be differences in the conditions of formation of the SC. The winter of 2018–2019 was warm and snowless. Under such conditions, the contribution of soil particles carried by the wind from areas uncovered by snow to the formation of the composition of insoluble sediment of the SC increases. The mercury content in the soils of Khabarovsk and the nearest suburb is in the range of 0.012–0.112 mg/kg, with an average value of 0.03–0.04 mg/kg [11]. Winter 2021–2022 on the contrary, it was snowy and cold, in connection with which, the insoluble precipitate of the SC was almost completely formed from atmospheric precipitation with a high content of combustion products.

For comparison, the content of total mercury in the suspended matter of the SC was studied, selected in the same period at two spots located along the northern border of the Bolshekhekhtsirsky Reserve, the territory of which some researchers used as a control one [10, 15]. Spot No. 10 (48.281528° N, 134.755951° E) is located at the mouth of Sosninsky Creek. The average height of the SC is 25 cm, the density is 0.34 g/cm<sup>3</sup>. Spot No. 11 (48.295736° N, 134.808365° E) is the Bykova River, near the village of Velvatnoye. The average height of the SC

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<sup>4</sup> Decree of the Government of the Russian Federation No. 1544-r dated 15.07.2019. Available from: <http://publication.pravo.gov.ru/Document/View/0001201907170007?index=1&rangeSize=1> (accessed: 29.12.2022).

<sup>5</sup> Order of the Ministry of Agriculture of the Russian Federation No. 552 dated December 13, 2016 “On approval of water quality standards for water bodies of fishery significance, including standards for maximum permissible concentrations of harmful substances in the waters of water bodies of fishery significance”. Available from: <https://docs.cntd.ru/document/420389120> (accessed: 29.12.2022).

<sup>6</sup> Sanitary rules and norms of SanPiN 1.2.3685-21 “Hygienic standards and requirements for ensuring safety and (or) safety of environmental factors for humans”. Available from: <https://docs.cntd.ru/document/573500115> (accessed: 29.12.2022).

is 45 cm, the density is 0.26 g/cm<sup>3</sup>. The distance between the selected spots is 4 km. The sites are located northeast of China, 5.5 and 8.5 km from the Russian-Chinese border passing through the Bolshoy Ussuriysky Island. Both sites are affected by air masses coming from the territory of the People's Republic of China during prevailing south-westerly winds. The content of suspended solids in the SC at spot No. 11 was higher than at spot No. 10 and amounted to 138 mg/dm<sup>3</sup> versus 82 mg/dm<sup>3</sup>. The mercury content in the suspended matter of the SC exceeded that at spot No. 10 by almost 3 times and amounted to 3.03 mg/kg, which is 1.4 times higher than the MPC for soils. It is likely that there is a local source of permanent mercury pollution in this area, or there has been a significant single release.

The latter is supported by data on a low mercury content in the solid sediment of the snow cover in the winter of 2018-2019 – 0.06 mg/kg [10].

In the winter of 2021-2022, the intake of mercury to the earth's surface as part of solid atmospheric precipitation in most of the studied sites did not exceed 20 micrograms/m<sup>2</sup>. The maximum amount of mercury (73.9 micrograms/m<sup>2</sup>) was received in the area of CHP-3, which is due to a significant amount of suspended solids. In addition, a higher indicator (37.5 micrograms/m<sup>2</sup>) was noted for the area of the Bykov river, but here this is due to the increased content of the element in the suspended matter of the SC.

## Conclusion

Mercury in the snow cover of Khabarovsk is associated with suspended substances, the transition from which to the dissolved phase is insignificant. The content of dissolved mercury in the snow cover did not exceed 10 ng/dm<sup>3</sup>, with the exception of the area in the zone of influence of CHP-3, where it was 11.4 ng/dm<sup>3</sup>. The mercury content in the suspended matter of the snow cover within Khabarovsk varied in the range from 0.3 to 1.4 mg/kg. A site was identified on the northern border of the Bolshekhekhtsirsky Reserve with a mercury content of 3 mg/kg, which is 1.4 times higher than the MPC for the soil.

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