Трансформация экосистем
Ecosystem Transformation

ISSN 2619-0931 Online
www.ecosysttrans.com

DOI: https://doi.org/10.23859/estr-251128
EDN: https://elibrary.ru/xhnjnv
UDC 504.75.05:504.064.2

Article

Mercury in hair of Irkutsk residents: accumulation levels and thermodesorption forms

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Abstract. This study presents the results of mercury (Hg) biomonitoring in hair samples from 217 residents of Irkutsk, obtained using direct thermal analysis and stepwise thermoscanning with a RA-915Lab analyzer. Hair Hg concentrations ranged from 0.010 to 1.873 μg/g, with a mean of 0.235 μg/g and a median of 0.165 μg/g. In 97.5% of participants, Hg levels did not exceed 1 μg/g, indicating a relatively low risk of chronic exposure for the majority of the population. Frequent fish consumption and hair dyeing were identified as the key factors associated with elevated Hg levels, whereas the effects of smoking, episodic household contact with mercury, and regular cosmetic use were not statistically significant. Thermodesorption analysis showed that 70–85% of total Hg is released within the 240–400 °C interval, which is predominantly associated with organic Hg species, including methylmercury. In samples with high Hg concentrations, a two-peak temperature profile was observed and interpreted as a redistribution of part of the Hg into more thermally stable complexes with the hair matrix. Overall, these results support the leading role of dietary intake in Hg exposure and suggest that stepwise thermoscanning can serve as a qualitative tool for assessing mercury forms in human hair.

Keywords: THg, MeHg, Hg exposure pathways, effects on the organism, biomonitoring, questionnaire survey, temperature profiles, Baikal region

Funding. This study was carried out within the framework of the state assignment of the Limnological Institute FWSR-2026-0017 "Investigation of the components of the carbon cycle, biogenic elements and other chemical substances in natural objects of the Baikal region under conditions of climate change and anthropogenic load".

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To cite this article: Lutskin, E.S., Savostyanova, E.O., 2026. Mercury in hair of Irkutsk residents: accumulation levels and thermodesorption forms. *Ecosystem Transformation* **9** (3), 46–63. https://doi.org/10.23859/estr-250819

Received: 28.11.2025
Accepted: 28.02.2026
Published online: 22.08.2026

DOI: https://doi.org/10.23859/estr-251128
EDN: https://elibrary.ru/xhnjnv
УДК 504.75.05:504.064.2

Научная статья

Ртуть в волосах жителей г. Иркутска: уровни накопления и термодесобционные формы

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Аннотация. Представлены результаты биомониторинга ртути (Hg) в волосах 217 жителей г. Иркутска, выполненного методом прямого термического анализа и ступенчатого термосканирования на приборе РА-915Лаб. Диапазон концентраций Hg составил 0.010–1.873 мкг/г при среднем значении 0.235 мкг/г и медиане 0.165 мкг/г. У 97.5% участников содержание Hg не превышало 1 мкг/г, что свидетельствует об относительно низком риске хронического воздействия для большинства населения. Показано, что ключевыми факторами повышения концентрации Hg являются частое потребление рыбы и окрашивание волос, тогда как вклад курения, эпизодического бытового контакта с ртутью и регулярного использования косметики статистически не значимы. С помощью термодесорбционного анализа определено, что 70–85% общего количества ртути приходится на диапазон 240–400 °C, соответствующий преимущественно органическим формам ртути, включая метилруть. В образцах с высокими концентрациями выявлена двухпиковая структура температурных профилей, интерпретируемая как перераспределение части Hg в более устойчивые комплексы с матрицей волоса. Полученные результаты подтверждают ведущую роль пищевого пути поступления Hg и указывают на возможность использования ступенчатого термосканирования как инструмента качественной оценки нахождения форм ртути в волосах человека.

Ключевые слова: THg, MeHg, пути поступления Hg, воздействие на организм, биомониторинг, анкетирование, температурные профили, Байкальский регион

Финансирование. Исследование выполнено в рамках государственного задания Лимнологического института FWSR-2026-0017 «Исследование составляющих углеродного цикла, биогенных элементов и других химических веществ в природных объектах Байкальского региона в условиях изменения климата и антропогенных нагрузок».

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Для цитирования: Луцкин, Е.С., Савостьянова, Е.О., 2026. Ртуть в волосах жителей г. Иркутска: уровни накопления и термодесобционные формы. *Трансформация экосистем* **9** (3), 46–63. https://doi.org/10.23859/estr-250819

Поступила в редакцию: 28.11.2025
Принята к печати: 28.02.2026
Опубликована онлайн: 22.08.2026

Introduction

Mercury (Hg) is a chemical element that is present in all components of the environment and possesses its own natural geochemical cycles, which still have not been studied completely (Driscoll et al., 2013; Pavithra et al., 2023). Mercury and its compounds, entering the atmosphere from anthropogenic or natural sources, are deposited both near pollution sources and at considerable distances from them (Pacyna et al., 2006; Pirrone et al., 2009). The most common form in atmospheric air is gaseous elemental mercury (Hg^0), which accounts for 90 to 98% of the total content; the atmospheric lifetime of Hg^0 has been estimated by various researchers to range from several months to 2 years (Horowitz et al., 2017; Lamborg et al., 2002). Once mercury enters aquatic ecosystems from the atmosphere, part of it is transformed by microorganisms into methylmercury (MeHg), which even in small doses is considerably more toxic than elemental mercury (Clarkson and Magos, 2006; Dietz et al., 2013). MeHg accumulates in aquatic organisms and is transferred along food chains, undergoing biomagnification, as a result of which the highest levels of this element are observed in organisms at the top trophic levels, including humans (Lehnherr, 2014). During pregnancy, MeHg crosses the placental barrier and is transferred from the mother to the developing fetus, where it accumulates and reaches high concentrations (Houston, 2011). Mercury is recognized as a global pollutant due to its toxicity, mobility, and capacity for accumulation in the environment[1].

It is known that mercury compounds have adverse effects on various organs and systems of the human body (Dórea, 2020). Even relatively low doses of MeHg and inorganic Hg compounds can lead to impairment of brain functions – cognitive, motor, and neurological disorders (speech, attention, memory, coordination) (Rodier, 1995). Increasing evidence suggests that exposure to Hg and its compounds is associated with an elevated risk of cardiovascular diseases (Genchi et al., 2017; Hu et al., 2021), including arterial hypertension and diabetes mellitus, which are considered important cardiovascular risk factors (Hu et al., 2018). Because of its high affinity for sulfhydryl groups in proteins and enzymes (Roy et al., 2017), Hg can disturb their structure and function. One of the principal mechanisms of mercury toxicity is oxidative stress and the associated inflammation, which contributes to endothelial and renal dysfunction and also impairs the function of selenium-containing enzymes (Houston, 2011). According to experimental medical studies, these processes may play an important role in the development of cardiovascular pathologies, including atherosclerosis, coronary heart disease, myocardial infarction, and stroke (Yoshizawa et al., 2002). A detailed picture of mercury effects on humans is presented in Fig. 1.

The principal source of mercury intake into the human body is food (Mozaffarian and Rimm, 2006), with the most significant contribution coming from the consumption of fish and seafood, and – in some regions of Asia – also rice (Sheehan et al., 2014; Zhao et al., 2019). For the population of the Russian Federation, the main sources of Hg are fish and fish products. It is known that in the muscle tissue of fish more than 99% of total mercury occurs as MeHg (Bloom, 1992). About 95% of the methylmercury ingested with fish is absorbed in the human gastrointestinal tract, after which it is distributed among the organs and accumulates, among other tissues, in keratinized ones – hair and nails (Clarkson et al., 2007; Mergler et al., 2007). Hair analysis is therefore widely used for biomonitoring chronic mercury exposure (Basu et al., 2018).

[1] World Health Organization. Environmental Health Criteria 101: Methylmercury, 1990. World Health Organization, International Programme on Chemical Safety, Geneva, Switzerland, 144 p.

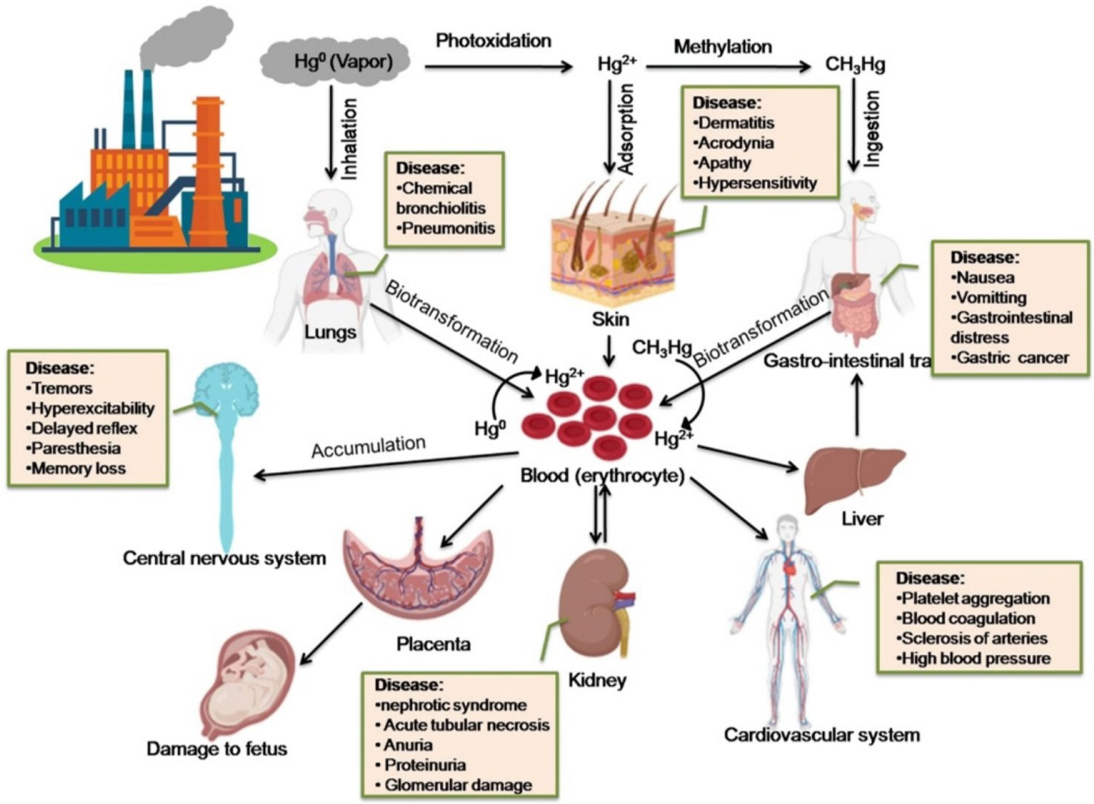

Fig. 1. Effects of mercury on the human body (Priyadarshanee et al., 2022).

Internationally, there is still no single, universal reference value for mercury content in human hair. However, leading organizations in the fields of medicine, public health, and environmental protection have developed indicative criteria for assessing the risk of chronic Hg exposure based on its accumulation in hair. These values differ depending on the target population group, the duration of exposure, and sensitivity (Table 1).

The threshold most frequently used in international practice is 1.0 μg/g; it was proposed by the United States Environmental Protection Agency as a reference level above which the probability of developing chronic toxic effects may increase. To compare the results of different studies it is often necessary to convert the mercury content in hair into an equivalent content in blood; for this purpose, a standard hair/blood ratio of 1:250 established by the WHO is used (Budtz-Jørgensen et al., 2004).

In most studies, total Hg is determined in hair, whereas its main fraction (80–95%) is usually represented by MeHg (George et al., 2010). However, a single total-Hg indicator is not always sufficient to interpret the pathways of mercury intake and the nature of its effects, because the ratio of organic to inorganic forms may differ depending on the exposure source. In this context, thermodesorption analysis is of additional interest, as it makes it possible to obtain a qualitative characterization of the forms in which Hg occurs in hair. For example, in people who do not consume fish but are chronically exposed to Hg vapor, the total Hg content in hair may be moderate, whereas the proportion of inorganic mercury is noticeably above average. The opposite situation is possible when exposure occurs only through food or through cosmetics: in that case almost all of the Hg is present as MeHg (Koenigsmark et al., 2021; Suárez-Criado et al., 2023). Therefore, the analysis of different mercury forms in hair allows refinement of the source and the nature of Hg exposure.

The aim of this study was to assess the mercury content in the hair of residents of Irkutsk and to provide a qualitative characterization of the thermodesorption forms of mercury. In addition to determining the total Hg concentration by direct thermal analysis, stepwise thermoscanning with registration of the desorption temperature profiles was carried out on a subset of samples.

Table 1. Indicative threshold values for mercury content in human hair according to international organizations and national agencies.

Country / organization	Indicator or status	Target group	Value, μg/g
USA / US EPA[2]	Reference level	General population	1.0
UN / FAO/WHO JECFA[3]	Recommended value	General population	2.3
		Women of reproductive age	0.58
Canada / Health Canada[4]	Tolerable level (blood equivalent)	Adults	5.0
	Threshold level for children and women of reproductive age (blood equivalent)	Children and women of reproductive age	2.0
Russia / Ministry of Natural Resources of the Russian Federation[5]	Indicative background level	Population without occupational exposure	0.5–1.0
	Tolerable biological level		5.0

Materials and methods

A total of 217 participants took part in the study: 155 women and 62 men aged from 14 to 76 years. The study was carried out in Irkutsk from November 2024 to September 2025. Each participant completed a questionnaire in which sex, age, place of residence, frequency of fish consumption, use of cosmetic products, and episodes of accidental (for example, a broken thermometer) and occupational contact with mercury were recorded.

Participants were divided into four age groups: < 18 years, 18–29 years, 30–44 years and ≥ 45 years. Fish consumption was classified by frequency as: less than once a month, 1–2 times a month, once a week, and several times a week. Three categories were distinguished for cosmetic use: non-users, rare use (less than 3 times a week) and frequent use (≥ 3 times a week). A similar classification was used for hair dyeing: "never dyed", "rarely" (episodic dyeing ≤ 1 time per year) and "frequently" (regular dyeing at least once every 2–3 months). Participants also answered a question about their current smoking status (smoker / non-smoker). The questionnaire did not include the presence or absence of amalgam dental fillings; questions on this topic are planned to be added to an updated version of the questionnaire in future studies.

For analysis, strands of hair several millimeters thick were taken from the occipital part of the head in accordance with WHO recommendations[6]. To determine the mercury content, a section of the strand

[2] U.S. Environmental Protection Agency. Methylmercury (MeHg) (CASRN 22967-92-6). Integrated Risk Information System (IRIS). Web page. URL: https://www.epa.gov/iris (accessed: 20.11.2025).

[3] Joint FAO/WHO Expert Committee on Food Additives (JECFA). Evaluation of certain food additives and contaminants. Sixty-seventh report of the Joint FAO/WHO Expert Committee on Food Additives, 2006. World Health Organization, Geneva, Switzerland.

[4] Evaluation of the effectiveness of risk management measures for mercury, 2020. Web-page. URL: https://www.canada.ca/en/environment-climate-change/services/management-toxic-substances/evaluation-effectiveness-risk-management-measures-mercury/mercury-human-health.html (accessed: 20.11.2025).

[5] Criteria for assessing the environmental situation of territories to identify zones of environmental emergency and zones of environmental disaster: methodology, 1992. Ministry of Natural Resources of Russia, Moscow, Russia, 189 p.

[6] United Nations Environment Programme; World Health Organization. Guidance for identifying populations at risk from mercury exposure, 2008. Web page. URL: https://www.who.int/foodsafety/publications/risk-mercury-exposure/en/ (accessed:20.11.2025).

approximately 2 cm long was cut from the root. Hair samples were packed in individual paper envelopes and stored in plastic bags at room temperature.

Mercury content in hair was analyzed on a RA-915Lab instrument (Lumex, Russia) by atomic absorption spectrometry with Zeeman background correction. The method is based on measuring the absorption of resonance radiation by atomic mercury at a wavelength of 254 nm. The mass fraction of mercury in the samples was measured according to the measurement procedure PU 92-2024[7]. Calibration was established using a series of 7 aqueous calibration solutions of mercury with mass concentrations from 0.01 to 10 mg/dm^3. State standard samples of aqueous solutions of mercury ions, GSO 8004-93 and GSO 7879-2001, were used as primary standards. Matrix-matched standards containing methylmercury were not used in the work because they were not available. The acceptability of the calibration curve was verified using the PU 92-2024 criteria: $r \geq 0.99$ and relative deviations at calibration points ≤ 10%. Certified reference material SDPS-3 was used to verify the correctness of the measurements. Hair samples with a mass of 20–100 mg were used for the determination of total Hg. For stepwise thermoscanning, hair samples of 100 mg were used in order to provide a sufficient mass of Hg in the sample and to improve the accuracy of recording the distribution of mercury across temperature intervals. Replicate results were within the acceptable discrepancy of 15% for all samples.

Statistical processing of the data was carried out using a nonparametric approach. The normality of the distribution of Hg concentrations in hair was tested with the Shapiro–Wilk test; for the initial Hg values, normality was rejected ($W = 0.604$; $p = 2.43 \times 10^{-16}$). Accordingly, the Mann–Whitney U test was used to compare two independent groups, and the Kruskal–Wallis H test was used for three or more independent groups. The level of statistical significance was set at $p < 0.05$. The data are presented as box-and-whisker plots.

To quantify the total mercury content, a thermal decomposition mode at 850 °C was used. For thermoscanning, 15 hair samples were selected, representing three groups in terms of mercury concentration: below the mean, near the mean, and above the mean of the sample. In these samples, programmed stepwise heating was applied. The thermoscanning program included 10 stages with a gradual increase in temperature (Table 2).

The selected thermoscanning program provides stepwise heating of the sample from 125 to 850 °C with fixed time intervals and a constant carrier gas flow rate. This scheme makes it possible to differentiate a wide range of mercury forms by their thermal stability. In the present work, the temperature profiles were interpreted mainly in the range from 0 to 450 °C, since it was in this interval that the release of essentially all the Hg from the studied hair samples was recorded.

Table 2. Thermoscanning program for hair samples from Irkutsk residents; Q — carrier gas flow rate.

Stage	Interval duration, s	Atomizer temperature, °C	Q, L/min
Initial	0	0–125	1
1	120	125–150	1
2	120	150–200	1
3	120	200–250	1
4	120	250–300	1
5	120	300–350	1
6	120	350–400	1
7	120	400–500	1
8	120	500–600	1
9	120	600–700	1
10	120	700–850	1

[7] Practical recommendations for the determination of mercury content in biological materials using the RA-915Lab laboratory mercury analyzer (PU 92-2024), 2024. Lumex-Marketing, St. Petersburg, Russia, 18 p.

It should be emphasized that, in this work, thermoscanning is used as a tool for comparing the temperature profiles of Hg release from the hair matrix. A direct assignment of temperature maxima to specific Hg forms requires further research using hair samples with a known qualitative composition and dedicated control experiments modelling the incorporation of various Hg forms into the hair matrix. Such methodological verification is labour-intensive and is beyond the scope of the present study. To our knowledge, this approach of stepwise thermoscanning of hair with analysis of temperature profiles has been described only to a limited extent in the literature, and the data obtained provide a basis for further methodological verification and for discussion within the scientific community.

Results

The mercury concentration in the hair of Irkutsk residents ranged from 0.010 to 1.873 μg/g. The mean concentration was 0.235 μg/g, the median 0.165 μg/g, and the interquartile range Q_{25}–Q_{75} was 0.096–0.281 μg/g. In the majority of the population the hair mercury level was below 1 μg/g. A concentration exceeding 1 μg/g was recorded in 2.5% of the participants (Fig. 2).

Across all age groups, median Hg concentrations were below 0.30 μg/g; however, the shapes of the distributions differed substantially depending on age. The lowest levels were observed in persons under 18 years of age; subsequently, the median concentrations increased and reached their maximum in the 35–55-year group, in which the largest variability of values was also observed, including isolated cases above 1 μg/g. In participants older than 55 years the median level decreased somewhat, although the scatter of concentrations remained elevated compared with younger groups. Overall, the age-related profiles indicate increasing Hg accumulation up to the middle of the working age, followed by a decline in the median level while retaining a high variability in older participants.

A detailed picture of Hg content in hair based on the questionnaire survey of 217 people is presented below (Table 3). For each subgroup, the mean Hg concentration in hair and the proportion of participants with levels below 0.5 μg/g, in the range 0.5–1.0 μg/g, and above 1 μg/g are shown.

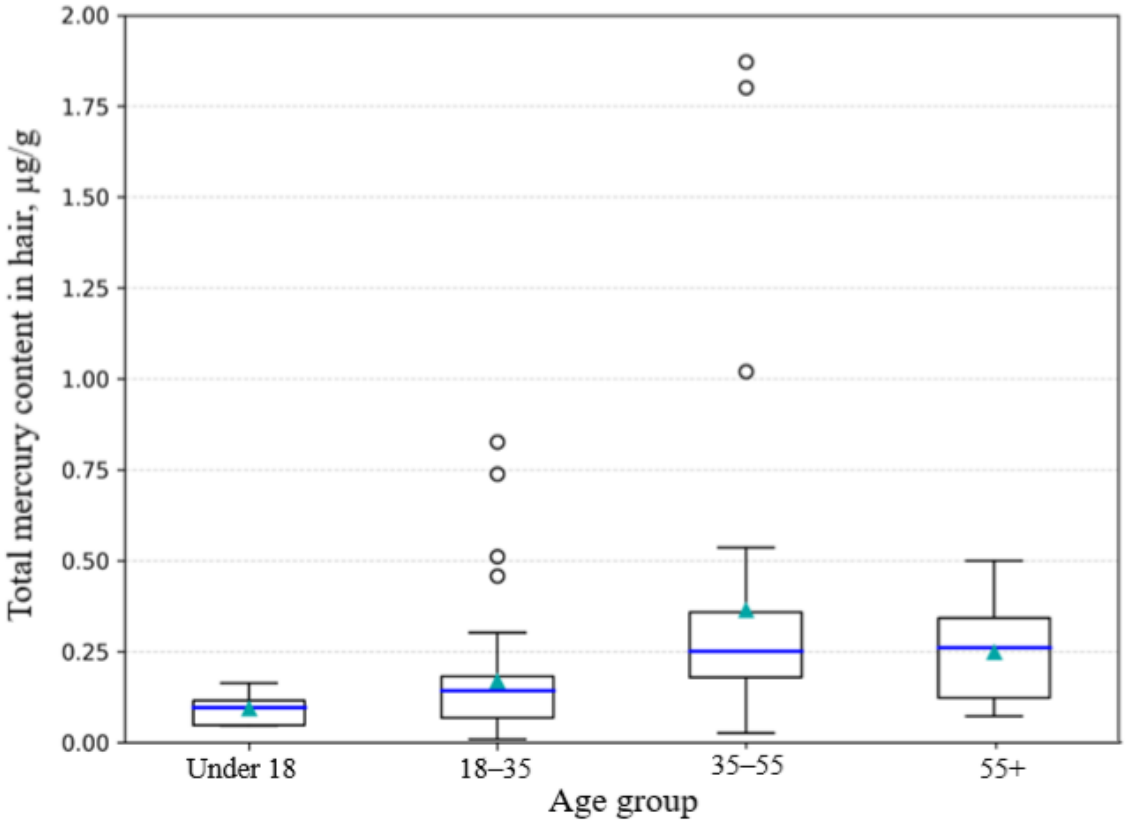

Fig. 2. Box-and-whisker plot of mercury content in the hair of Irkutsk residents by age. The horizontal line inside the box is the median, the box edges are the 25th and 75th percentiles (Q1–Q3), the whiskers are values within 1.5 interquartile ranges (IQR), and individual circles are outliers. Triangles indicate the arithmetic mean.

Mean mercury concentrations in the hair of men and women are similar; at the same time, values below 0.5 μg/g occur somewhat more frequently in men, whereas women show a higher proportion of background levels of 0.5–1.0 μg/g. The share of high values > 1 μg/g remains comparable in both groups.

The most pronounced differences are associated with fish consumption. In the group with rare or absent consumption the mean concentration is minimal; no participant in this group showed values > 1 μg/g. With an increase in frequency to 1–2 times per month and ≥ 1 time per week, the mean Hg level increases 2.7- and 3.4-fold, respectively. The frequency of fish consumption was statistically associated with hair Hg level ($H = 19.33$, $p = 6.34 \times 10^{-5}$).

Table 3. Mean mercury concentration in hair of Irkutsk residents and assessment of health-risk categories.

Factor (N – sample size)	Mean Hg concentration in hair, μg/g	Share of participants with different Hg content in hair, %		
		< 0.5 μg/g (below background, minimal risk)	0.5–1.0 μg/g (below background, minimal risk)	> 1.0 μg/g (exceeds US EPA reference level)
Men (62)	0.197	92.3	3.8	3.8
Women (155)	0.233	86.0	10.5	3.5
Fish consumption				
< 1 time per month (149)	0.117	92.6	7.4	0
1–2 times per month (29)	0.316	93.8	0	6.2
> 1 time per week (39)	0.396	85.7	4.8	9.5
Smoking				
Non-smokers (204)	0.235	91.9	5.4	2.7
Smokers (13)	0.227	85.7	14.3	0
Household contact with mercury				
Had contact (90)	0.216	93.9	6.1	0
No contact (127)	0.247	90.0	5.0	5.0
Cosmetic use				
Do not use (101)	0.217	89.1	9.1	1.8
Rarely (59)	0.221	93.8	6.2	0
Frequently (57)	0.255	93.5	0.0	6.5
Hair dyeing				
Never dyed (88)	0.226	91.7	8.3	0.0
Rarely (53)	0.183	94.3	1.9	3.8
Frequently (17)	0.278	82.4	11.8	5.9

No substantial differences were observed for smoking. The share of values > 1 μg/g in non-smokers was low, and among smokers in this sample no such cases were recorded (it should be noted that the sample of smokers included only 13 persons). Likewise, a history of household contact with mercury (broken mercury thermometers) was not associated with a noticeable increase in the mean concentrations and was not accompanied by cases above 1 μg/g in this subgroup. According to the questionnaire data, no cases of occupational contact with mercury were recorded. For the factors "smoking" ($U = 365.0$, $p = 0.695$) and "household contact with mercury" ($U = 1034.5$, $p = 0.801$), no statistically significant differences were revealed.

For the factor of cosmetic use, differences between groups were weakly expressed: with rare use the mean Hg level remained virtually unchanged, and with frequent use it increased only by approximately 1.2-fold compared with the group of non-users. The share of participants with Hg > 1 μg/g at frequent use of cosmetic products also increased 3.6-fold. However, no statistically significant differences were revealed for this factor ($H = 0.004$, $p = 0.950$).

For persons with different frequencies of hair dyeing, the differences were more pronounced. With rare dyeing the mean Hg level was lower, and with frequent dyeing it was higher. Compared with the rare-dyeing group, the mean Hg concentration increased approximately 1.5-fold, and the share of values > 1 μg/g increased approximately 1.6-fold. A tendency toward differences between groups was observed for the frequency of hair dyeing ($H = 4.36$, $p = 0.113$).

Discussion

The results obtained demonstrate that the level of mercury accumulation in the hair of Irkutsk residents (mean 0.235 μg/g, median 0.165 μg/g) lies below the reference values recommended by international organizations (1.0 μg/g according to the US EPA and 2.3 μg/g according to JECFA), and also below the indicative range of 0.5–1.0 μg/g given in Russian guidance documents for populations without occupational exposure to mercury. This indicates a relatively low risk of chronic Hg exposure for the majority of the city's population. However, in 2.5% of participants the concentration exceeded 1 μg/g, which warrants attention, especially in the context of age-related and behavioural factors.

A comparison of the obtained results with other regions of the Russian Federation shows that hair mercury levels in Irkutsk are comparable to or lower than those elsewhere. For example, in the Trans-Ural zone of Bashkortostan the median was 0.072 μg/g for men and 0.122 μg/g for women, with elevated risk in 13.2% of adults, which is lower than in Irkutsk (Rafikova et al., 2019). In the Vologda region, the mean concentration is higher – 0.445 μg/g (median 0.220 μg/g) – with variation by area: lower in industrial cities (0.297 μg/g in Cherepovets) and higher in rural western districts (up to 0.884 μg/g), where fish consumption predominates (Rumiantseva et al., 2022). For a group of pregnant women from the northwestern part of the Russian Federation, an association of increased hair Hg levels with the frequency and amount of fish consumption was also reported: the mean hair concentration was 0.428 μg/g (range 0.018–3.1 μg/g), and 22% of the women had mercury values exceeding 0.58 mg/kg, which is considered hazardous for the fetus (Rumiantseva et al., 2024). In Crimea, levels vary by geographical zone: they are low in the central agricultural territories (min = 0.033 μg/g, max = 0.072 μg/g), higher in the eastern (min = 0.178 μg/g, max = 0.312 μg/g) and southern (min = 0.134 μg/g, max = 0.505 μg/g) regions, which is comparable to Irkutsk (Evstafieva et al., 2017).

At the global level, Irkutsk values are lower than those in regions with high fish consumption or in areas polluted with mercury. For instance, in coastal regions of India the mean hair mercury concentration is 0.49–0.80 μg/g, which is associated with elevated fish consumption (Gibb et al., 2016). In Italy this indicator reaches 0.638 μg/g in the urban population with regular fish consumption (Diez et al., 2008). In developing countries with artisanal gold mining, such as Colombia (Olivero-Verbel et al., 2016), hair mercury levels in residents of gold-mining areas reach 1.56 μg/g. In Iran, concentrations are 1.56–5.12 μg/g depending on the city and the frequency of seafood consumption (Okati and Esmaili-Sari, 2018).

Moving from general patterns to the analysis of specific cases of exceedance, we consider the possibilities offered by thermoscanning as a tool for refining the nature of exposure. In our study, additional thermodesorption analysis was performed on samples with low, medium and elevated total Hg content.

For the group with low hair Hg concentration, no clearly expressed regularities in the temperature profiles could be identified. In cases where the total signal was pronounced, the maximum fell within the 280–360 °C interval (Fig. 3). The low-temperature region 100–240 °C yielded no more than 3–8% of the signal. In the 240–280 °C interval, 9–14% of the signal appeared and formed the ascending shoulder of the main peak. The maximum of the total signal was located in the 280–360 °C range, accounting for about 45%. The temperature zone 360–400 °C contributed about 20–27%, and the zone 400–450 °C another 13–16% of the signal, corresponding to the final decay (reduction of the main peak without the appearance of additional pronounced maxima); thus, no additional contribution from new Hg forms was observed.

For the group with low mercury concentration, the total share of Hg released within the 240–400 °C interval was about 80% of the total Hg content. As an order of magnitude, this is comparable with literature data on the predominance of organic Hg forms, including methylmercury, in hair (Berglund et al., 2005; George et al., 2010). Therefore, this temperature range can be tentatively interpreted as the region of preferential release of the organic (MeHg-associated) fraction of Hg.

Characteristic temperature profiles for the group with Hg concentrations close to the mean value of the study are presented in Fig. 4. In the 100–240 °C zone, 5–23% of the total Hg is released in total (on average 17%). In the 240–280 °C interval, 5–20% of Hg is released (on average 14%), corresponding to the beginning of the main peak. The main fraction of Hg is released in the 280–360 °C interval (about 45–50% of total Hg); the contribution of this zone, however, varies noticeably between samples and, in individual cases, reaches 75–80% (0.268 μg/g), corresponding to a narrower and higher maximum of the temperature profile. In the 360–400 °C interval an additional 10–20% of Hg is released (on average ~14%). In the 400–450 °C range, typically no more than 5–10% of Hg is released (in one profile the contribution was close to zero). The curves decrease monotonically toward zero without the formation of additional local maxima, so this segment is regarded as the final stage of the main thermodesorption process rather than as a manifestation of a separate temperature fraction of Hg.

In total, the 240–400 °C interval provides ~75–80% of the total Hg for this group (min – 66%, max – 94%), and the 240–450 °C interval ~80–85% (up to ~95% for the sample with an Hg concentration of 0.268 μg/g).

Characteristic temperature profiles for the group with Hg concentrations above the mean value of the study are presented in Fig. 5. The low-temperature region 100–240 °C accounts for 10–30% of the total Hg. The temperature interval 240–280 °C contributes another ~10–20% of Hg. The main maximum of total Hg release is still localized in the 280–340 °C range, accounting for about 40–55% of Hg. In

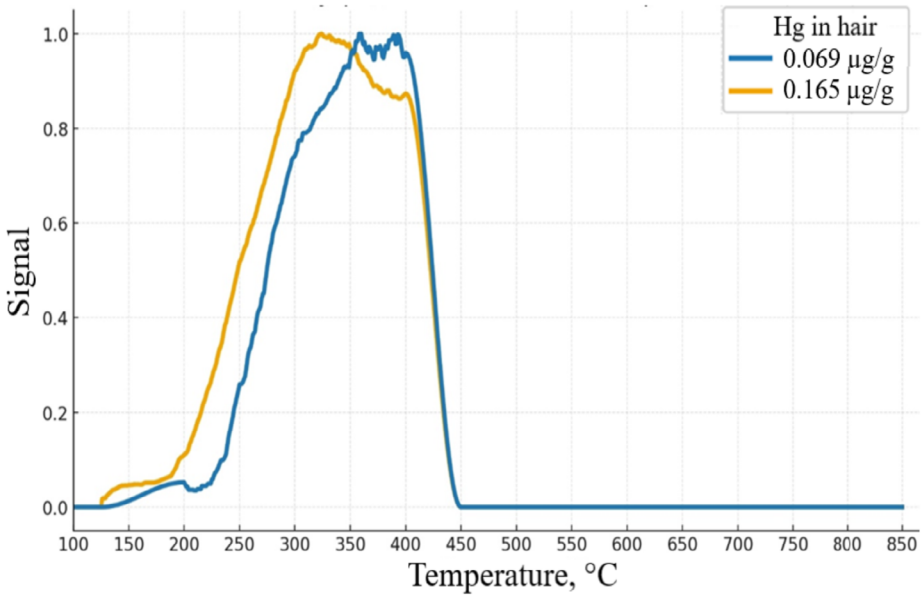

Fig. 3. Temperature profiles of Hg in hair samples with concentrations below the mean value of the study.

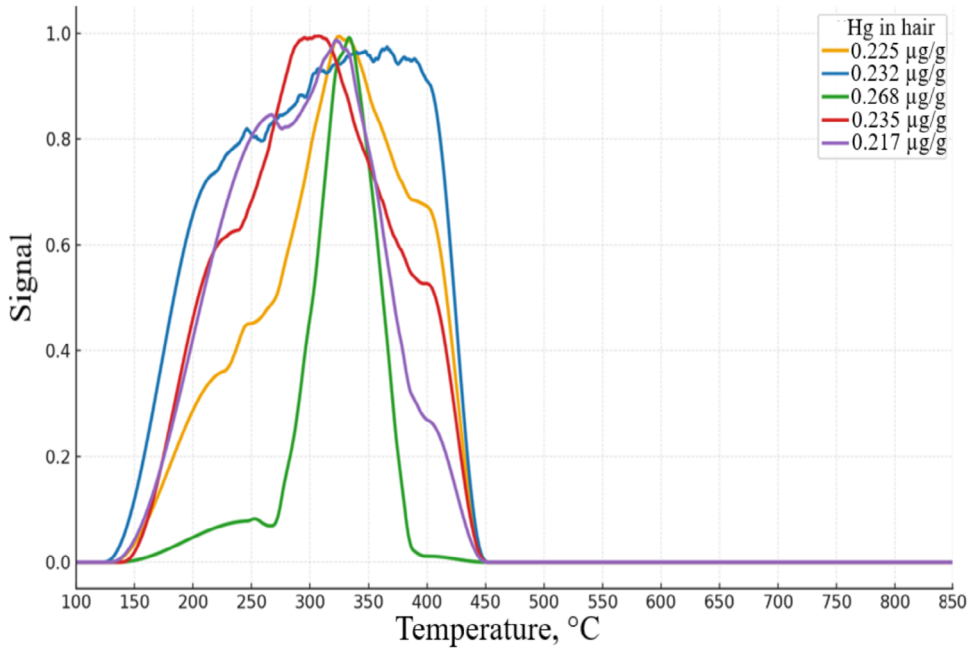

Fig. 4. Temperature profiles of Hg in hair samples with concentrations close to the mean value of the study.

the participant with the maximum concentration (1.801 µg/g), the contribution reaches 63%, which is consistent with a narrow and high peak. In the 340–400 °C interval another 15–25% of Hg appears, and in some participants a pronounced second maximum is formed here. The high-temperature range 400–450 °C provides no more than 5–10% of Hg. In total, the 240–400 °C interval accounts for about 70–85% of the total Hg in this group, and the extended interval 240–450 °C for about 80–90% of Hg.

In all the groups studied, the temperature profiles have a similar shape and differ mainly in the relative contributions of individual temperature intervals. In the low-temperature zone 100–240 °C, a relatively small fraction of Hg is released, which presumably reflects the contribution of weakly bound and adsorbed forms localized on the hair surface and in the outer layers of the matrix. The 240–280 °C interval accounts for another ~10–20% of Hg; this segment corresponds to the initial stage of the main temperature maximum and apparently reflects the transition from surface forms to more firmly bound complexes within the hair structure. The main fraction of Hg is released in the 280–360 °C region, which forms the main thermodesorption peak. The appearance of two maxima in the temperature profiles of samples with elevated concentrations may indicate a distribution of Hg between at least two fractions differing in the thermal stability of their binding to the hair matrix. By analogy with literature data (Berglund et al., 2005; George et al., 2010), the maximum in the 280–320 °C zone can be attributed to the release of organic Hg forms, including MeHg. The maximum in the 320–380 °C zone, the share of which grows with increasing total Hg concentration, in our opinion corresponds to the thermal release of Hg from more thermally stable binding forms, which may include both strong organic compounds and inorganic mercury complexes (e.g., compounds with S or Cl) formed at high levels of metal accumulation (Klöfer, 2021; Shuvaeva et al., 2008). The high-temperature range 400–450 °C provides no more than 5–10% of Hg; in this interval, the curves decrease monotonically to zero without the appearance of additional maxima, so it can be regarded as the terminal stage of thermodesorption. Our approach to interpreting multi-peak temperature profiles is consistent with thermoscanning practice in solid matrices, where several "fractions" are distinguished by differences in temperature maxima (Mashyanov et al., 2017).

Thus, in the group with elevated mercury concentration, the temperature curves reflect not simply an increase in the amount of the presumed organic Hg form, but also a redistribution of part of the Hg into more stable, more slowly decomposing complexes, which manifests itself as the two-peak structure of the profile.

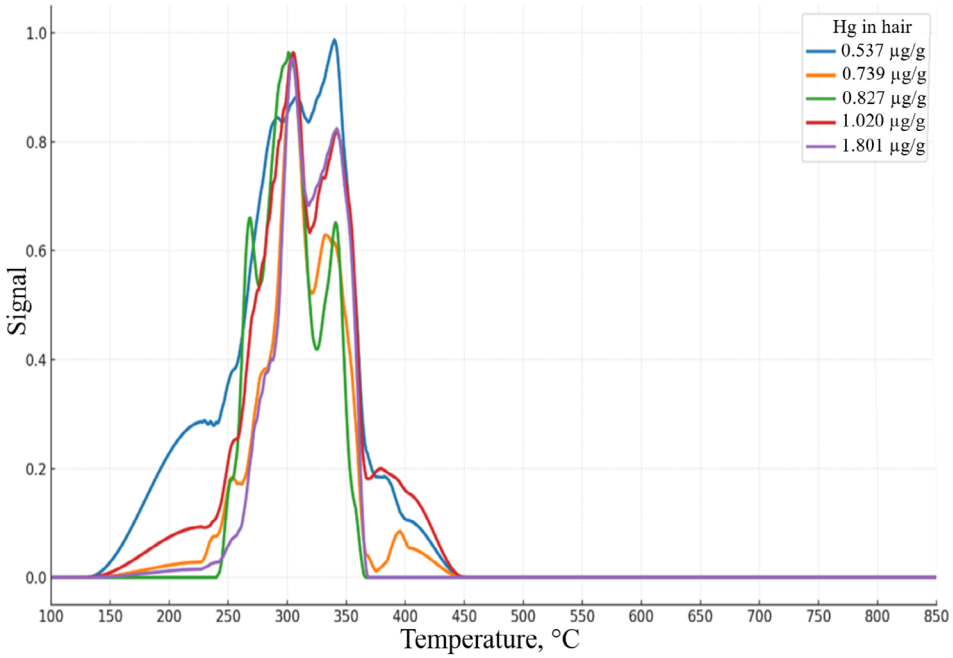

Fig. 5. Temperature profiles of Hg in hair samples with concentrations above the mean value of the study.

Conclusions

The mean Hg concentration in the hair of Irkutsk residents was 0.235 µg/g, and the median was 0.165 µg/g. Comparison of Hg concentrations in hair with the reference values of international organizations and with the range of tolerable exposure given in Russian guidance documents for populations without occupational exposure to mercury showed that in the majority of those examined the Hg values were below the specified levels. Thus, the risk of chronic Hg exposure in the group studied is relatively low. However, in 2.5% of participants the Hg concentration in hair exceeded 1 µg/g, which indicates an elevated intake of Hg into the body and allows these participants to be classified as a group at potential risk of chronic exposure. The minimum mercury concentrations are typical of persons younger than 18 years, whereas the maximum levels are recorded in the 35–55-year age group. The mean Hg concentrations in the hair of men and women are close – 0.197 and 0.233 µg/g, respectively.

Comparison with other regions of the Russian Federation and of the world shows that hair mercury levels in the population of Irkutsk are comparable to or lower than those in regions with high fish consumption or with mercury pollution associated with gold mining. According to the questionnaire data, the main risk factors are frequent fish consumption and hair dyeing, whereas for smoking, episodic household contact with mercury, and regular use of cosmetics, no statistically significant effect was revealed in our study, which may be related to the small sub-sample sizes.

Thermodesorption analysis showed a predominance of organic Hg forms: 70–85% of the total mercury release falls within the 240–400 °C interval, which, according to the literature, corresponds to organic forms of mercury, including MeHg. For the group with Hg concentrations in hair above the mean value of the study, the temperature profiles acquire a two-peak structure, indicating a distribution of Hg between organic forms (temperature range 280–320 °C) and more thermally stable complexes (temperature range 320–380 °C).

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