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RESEARCH PAPER

Evaluation of Heavy Metal Pollution of Snow and Groundwater on the Territory of Suburban Community Garden Plots of the Arkhangelsk Agglomeration (Northwest Russia)

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Abstract
The article presents the results of a study of heavy metals in snow and groundwater within the industrially developed Arkhangelsk agglomeration, which is the largest among urban formations in the Arctic zone of Russia. This article describes the results of research on the territories of three suburban community garden plots used by residents of the cities of the Arkhangelsk, Severodvinsk and Novodvinsk agglomeration for recreation, growing fruits and vegetables, picking wild berries and mushrooms, and short-term residence. In groundwater samples taken from wells, the average concentrations of heavy metals decrease in the following order: Fe > Mn > Zn > Cr > Ni > Cu > Ti > V > Pb > U > As > Co > Mo > Sb > Cd. A comparison of metal concentrations in groundwater with WHO and SanPiN standards showed that only Fe and Mn exceeded the permissible limits, for the rest of the studied metals, the concentrations were significantly below the permissible limits. The study of heavy metals in the snow showed a similar order of decrease in concentrations to groundwater and total concentrations of soluble metal fractions. This fact indicates the migration of heavy metals into groundwater after the spring snowmelt and the fact the main source of groundwater pollution is the atmospheric channel. According to the values of the total areal pollution of the snow cover with heavy metals, the most polluted are suburban garden plots in the area of the Arkhangelsk city – 216.91 mg/m2. The results of the principal component analysis showed that the main sources of snow cover pollution with heavy metals in the suburban areas of the Arkhangelsk agglomeration were thermal power plants, machine-building and metallurgical plants, a solid waste landfill, and vehicles. The calculation of the heavy metal pollution index for water did not reveal a significant anthropogenic impact. However, the indices assessing the amount of metals (heavy metal evaluation index), toxicity (heavy metal toxicity load), non-carcinogenic risk (hazard index), and carcinogenic risk indicate a high level of heavy metal pollution of the studied waters, as well as the unsuitability of groundwater and melted snow as drinking water. Metals such as Fe, Mn, Ni, Cu, and Pb make the greatest contribution to the quality indices of the studied waters.

Keywords: heavy metal pollution, snow, groundwater, suburban garden plots, Arkhangelsk agglomeration.

INTRODUCTION

Various pollutants that fall on the surface of the earth with precipitation are of great importance for the functioning of many ecosystems and pose significant risks to biota and humans (Calvo et al., 2013; Shiraiwa et al., 2017; Luo et al., 2019; Xu et al., 2022). The most toxic pollutants are heavy metals due to their high degree of bioaccumulation and biomagnification in food chains (Hu et al., 2012a; Huang et al., 2016; Szynkowska et al., 2018; Truchet et al., 2020). Pollution of various

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ecosystems with heavy metals is a very common problem, mainly associated with atmospheric deposition from vehicles, exhaust emissions, and landfills, the operation of agricultural, mining, and other industrial enterprises (Wu et al., 2007; Hidemori et al., 2014; Oucher et al., 2015; Suvarapu & Baek, 2017; Ma et al., 2019; Gabrielli et al., 2020; Wang et al., 2020). Most of the heavy metals emitted into the atmosphere come to the surface with precipitation, forming heavy metal anomalies in the upper soil layer (Rosca et al., 2019; Zhou et., 2019, 2020; Chen et al., 2022). During the cold season, the transit zone for heavy metals is the snow cover, which is an effective absorber of pollutants from the atmosphere, especially in the northern regions, where the snow cover lasts 7–8 months a year (Veysseyre et al., 2001; Ceburnis et al., 2002; Westerlund et al., 2003; Osada et al., 2010; Dong et al., 2015; Opekunova et al., 2021; Palamodova, 2021). Therefore, snow cover is widely used as a reliable indicator to assess the type of air pollution and to track the relative contribution of various sources of air pollutants (Lei & Wania, 2004; Hu et al., 2012b; Gao et al., 2018; Rodland et al., 2022). Heavy metals accumulated over a long winter (their soluble forms) after snow melt migrate into groundwater and, spreading through aquifers, have a significant impact on the quality of drinking water, posing a significant risk to the population (Galfi et al., 2016; Zhang et al., 2020; Gavric et al., 2021; Taka et al., 2022). The economic development of territories and the growth in the number of industrial enterprises will obviously contribute to a further increase in the heavy metal emission into the atmosphere and pollution of ecosystems (Talovskaya et al., 2018). Thus, analysis of the content and distribution of heavy metals in precipitation, in particular in snow cover, can provide important information on the behavior and sources of atmospheric pollution (Moghadas et al., 2015; Chagina et al., 2016; Pozhitkov et al., 2018; Grinfelde et al., 2021). The study of soluble forms of heavy metals will make it possible to assess their bioavailability, trace their distribution in ecosystems, migration to groundwater and subsequent transfer to drinking water wells, and assess the toxicological quality of water when used by the population (Viklander, 1994; Siudek et al., 2015; Abiriga et al., 2020; Li et al., 2021; Zeng et al., 2021). Such studies are especially relevant near large cities and large industrial enterprises (Filippelli et al., 2012; Stepanova et al., 2018; Cherednichenko et al., 2021).

In this work, the research team carried out studies of heavy metals in snow cover and groundwater within the industrially developed Arkhangelsk agglomeration, which is the largest among urban formations in the Arctic zone of Russia with a population of more than 600 thousand people (Nefedova et al., 2001; Byzova et al., 2019). The three largest cities of the agglomeration (Arkhangelsk, Severodvinsk, and Novodvinsk) host a large number of industrial enterprises, such as engineering, metallurgy, and thermal power plants, which are potential polluters of ecosystems with heavy metals. There is also a large landfill for municipal solid waste (Perkhurova, 2021). In addition, the Arkhangelsk agglomeration cities, along with Norilsk, are leaders among the cities of the Russian Arctic zone in terms of the level of anthropogenic atmospheric pollution (Popova & Boos, 2020; Anufrieva et al., 2021). Nevertheless, there is no up-to-date data on the heavy metal concentrations in the snow cover of the Arkhangelsk agglomeration, there is no data on the sources of heavy metal emissions into the atmosphere, the quantitative contribution of each of them, there is no data on the toxicological hazard of heavy metals in snow for humans and biota. There is also no data on the concentrations of water-soluble forms of heavy metals, which, after snow melting, can migrate into groundwater and create significant environmental risks for the population when water is used for various purposes; accordingly, there is no data on heavy metals in groundwater in this area. Taking into account the importance of studying the entire territory of the Arkhangelsk agglomeration, at this stage, the research team set the task of assessing the degree of pollution of territories not within urban areas, residential areas, or industrial sites, but decided to concentrate on the most environmentally vulnerable areas. At this stage of the study, the sampling areas are suburban garden plots, which are small settlements with small summer houses located at some distance from cities in conditionally ecologically clean areas, used by citizens for growing fruits and vegetables, picking wild berries and mushrooms, short rest and living (Federal Law No. 217, 2020). According to the legislation of the Russian Federation, it is impossible to live within such areas for a long time and build large houses for permanent residence, baths, or garages on the foundation, but these rules are often violated. The ecological quality of water in wells or shallow wells located within summer cottages is not controlled by state authorities, since these sources are located in a territory where permanent residence is prohibited and, accordingly, there is no register of individual water supply sources. However, residents of such settlements actively use the water from these wells for watering plants, hygiene purposes, and drinking, often without any preparation or treatment. Currently, there is no data on the concentrations of heavy metals in the snow cover and groundwater of suburban areas. However, due to the presence of a large number of industrial enterprises in the Arkhangelsk agglomeration, there is a serious danger of pollution of both snow cover and subsequent pollution of groundwater with soluble forms of heavy metals, since the first aquifer from the surface is an open system and is not protected by a water-resistant layer from penetration of pollutants. In this regard, an urgent task is to assess the quality of groundwater used by the local population.

To achieve the goals set, samples of snow cover and groundwater were taken within the suburban areas of the Arkhangelsk agglomeration, located in the areas of Severodvinsk, Novodvins, and Arkhangelsk. The content of heavy metals in the samples of snow and groundwater was determined by inductively coupled plasma mass spectrometry (ICP-MS), the content of uranium and total alpha activity was performed by the method of alpha spectrometry and radiometry. The potential environmental hazard and toxicity of metals in snow and groundwater were assessed using the indices: heavy metal evaluation index (HMEI), heavy metal pollution index (HMPI), heavy metal toxicity load (HMTL), hazard index (HI), and carcinogenic risk (CR).

MATERIALS AND METHODS

Sampling of groundwater and snow cover was carried out in suburban garden plots located within three key areas – in the vicinity of the three cities of Arkhangelsk, Severodvinsk, and Novodvinsk, which form the Arkhangelsk agglomeration, the largest in the Russian Arctic zone. Sampling of snow and water from wells was carried out in March 2021 during the period of maximum snow accumulation, which coincides with the winter low water for groundwater. The sampling scheme is shown in Figure 1. As a result of the expedition, 5 groundwater samples and 9 snow samples were taken at suburban community garden plots in the Severodvinsk region, 5 groundwater samples and 7 snow samples in the Novodvinsk region, and 5 groundwater samples and 5 snow samples in the Arkhangelsk region. A total of 21 snow samples (code C) and 15 water samples from wells (code KW) were taken.

Groundwater sampling was carried out from shallow wells (3–5 meters), revealing the first aquifer from the surface (GOST 17.1.5.05–85, 1985). In water samples, unstable physical and chemical parameters, such as pH, Eh, TDS-EC (electrical conductivity and content of water-soluble salts), and temperature, were measured directly during sampling. Analysis of pH and Eh was carried out using an HI 9126 pH/ORP meter (Hanna Instruments, USA) with a replaceable electrode; TDS-EC measurements of water temperature were performed using a Five Go Cond meter F3 (Mettler-Toledo GmbH, Switzerland). Groundwater samples for the determination of trace elements were taken into 50 ml polymer test tubes, filtered through a membrane filter with a pore size of 0.45 μm, and acidified with HNO_3 to pH < 2.

Snow sampling was carried out from sites ($S=0.125\ m^2$) into plastic buckets with a volume of 11 liter using a plastic sampler for the entire depth of the snow cover (except for the lower 5 cm layer contaminated with underlying soils). After delivery to the laboratory, the snow samples were melted at room temperature in closed buckets. Immediately after melting, pH was

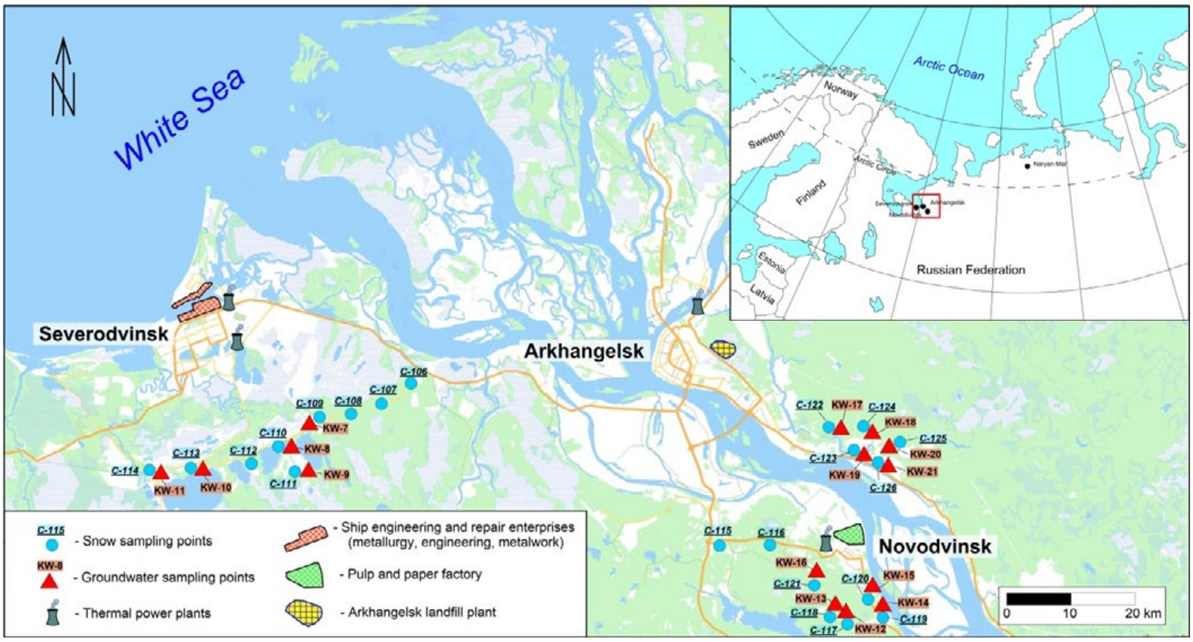

Fig. 1. Sampling points for snow and groundwater in suburban community garden plots of the Arkhangelsk agglomeration.

measured in melted snow samples using an HI 9126 pH/ORP meter (Hanna Instruments, USA) and TDS-EC with a Five Go Cond meter F3 (Mettler-Toledo GmbH, Switzerland). Next, the samples were passed through cellulose nitrate filters with a diameter of 47 mm and a pore size of 0.45 μm by vacuum filtration to separate dissolved fractions and solid particles. Samples for analysis of dissolved metal fractions were preserved by adding concentrated nitric acid. Filters containing insoluble (solid) fractions were treated by acid extraction by dissolving in 2 ml of nitric acid and 1 ml of hydrogen peroxide in closed Teflon cups at 95 °C.

Analysis of heavy metals in groundwater, soluble and insoluble fractions of snow was carried out by ICP-MS on an Aurora Elite instrument (Bruker Daltonics, Inc.). The concentrations of metals in the fraction of suspended (undissolved) snow particles were related to the filtered volume of the water equivalent. Analysis of the U content in groundwater was performed by the alpha spectrometric method with preliminary radiochemical preparation on an MKS-01A Multirad instrument (NPP Doza, Russia) (Methods for measuring the volumetric activity of uranium isotopes…, 2013). The total alpha activity of groundwater was determined in the dry residue after evaporation of 1 liter of water using an RKS-01A Abeliya radiometer (Amplitude, Russia) (GOST 31864-2012, 2012).

Calculation of water quality parameters
Heavy metal evaluation index (HMEI)

The HMEI index is determined by the formula (1):

$$HMEI = \sum_{i=1}^{n} \frac{HM_{Conc}}{HM_{MPC}} \tag{1}$$

where HM_{Conc} is the specified metal concentration and HM_{MPC} is the maximum allowable metal concentration in water (Zakir et al., 2020). For this index HMEI <1.0 is "fit", HMEI >1.0 is "unfit" for usage (Zakir et al., 2020). An extended classification of pollution: <0.3 is "very pure";

0.3-1.0 is "pure"; 1.0-2.0 is "slightly affected"; 2.0-4.0 is "moderately affected"; 4.0-6.0 is "strongly affected"; and >6.0 is "seriously affected" (Haque et al., 2019).

Heavy metal pollution index (HMPI)

The HMPI index is calculated using the formula (2):

$$HMPI = \frac{\sum_{i=1}^{n}(Q_i \times W_i)}{\sum_{i=1}^{n} W_i} \quad (2)$$

where, Q_i is the sub-index of the *i*-th metal parameter, W_i is the unit weight of the *i*-th parameter reflecting its relative importance, and n is the number of parameters considered (Qu et al., 2018). The sub-index (Qi) is calculated with Eq. (3):

$$Q_i = \frac{C_i}{S_i} \times 100 \quad (3)$$

where C_i is the concentration of the *i*-th trace metal (μg/L), and S_i is the maximum standard allowable concentration of the *i*-th trace metal (WHO, 2017, Table 1).

The unit weight (W_i) is calculated using Eq. (4):

$$W_i = \frac{k}{S_i} \quad (4)$$

where k is a proportionality constant equal to 1(Wanda et al., 2012). The critical value of the HMPI index for drinking water is 100 (Prasad & Bose, 2001). However, a modified scale with three levels is used: <15 is "low", 15-30 is "medium", and >30 is "high" (Edet & Offiong, 2002).

Heavy metal toxicity load (HMTL)

The HTML index evaluates the metal contents that cause toxic effects on the population (Saha & Paul, 2018; Zakir et al., 2020); it is calculated using Eq. (5):

$$HMTL = \sum_{i=1}^{n} C_i \times HIS_i \quad (5)$$

where C_i , mg/kg is the content of trace metals in the test water and HIS_i is the general hazard level of individual metals (Table 1). The hazard ratings for each metal are found in the toxicology profiles of the Priority Hazardous Substances List (ATSDR, 2019). A modified classification of waters was introduced depending on the level of HMEI values: 0-100 is "low toxicity"; 100-300 is "moderate toxicity"; 300-500 is "high toxicity"; 500-1000 is "very high toxicity"; above 1000 is "extremely high toxicity".

Non-carcinogenic health risk (HI_{ing}, HI_{derm})

The absorbed human dose is calculated as the average daily dose (ADD) (USEPA, 2004; Kumar et al., 2019). ADD values were calculated using Eqs. (6) and (7):

$$ADD_{ing} = \frac{C_i \times IR \times EF \times ED}{BW \times AT} \quad (6)$$

Table 1. Values of the parameters of metals required for calculating water pollution indices and human health risks.

Metal	C_i, µg/L	HIS$_i$	K$_p$	RfD$_{ing}$	RfD$_{derm}$	SF, mg/L
Mo	70	442	$1{\cdot}10^{-3}$	5	1.9	-
Fe	300	0	$1{\cdot}10^{-3}$	700	140	-
Sb	5	600	$1{\cdot}10^{-3}$	0.4	0.008	-
Ti	-	482	$1{\cdot}10^{-3}$	-	-	-
Mn	500	797	$1{\cdot}10^{-3}$	24	0.96	-
Zn	3000	913	$6{\cdot}10^{-4}$	300	60	-
V	-	648	$1{\cdot}10^{-3}$	1	0.01	-
Cr	50	895	$2{\cdot}10^{-3}$	3	0.08	0.5
Ni	20	993	$2{\cdot}10^{-4}$	20	0.8	1.7
As	10	1676	$1{\cdot}10^{-3}$	0.3	0.12	1.5
Cu	2000	805	$1{\cdot}10^{-3}$	40	8	-
Co	100	1011	$4{\cdot}10^{-4}$	0.3	0.06	-
Cd	3	1318	$1{\cdot}10^{-3}$	0.5	0.03	15
Pb	10	1531	$1{\cdot}10^{-4}$	1.4	0.42	0.0085

$$ADD_{derm} = \frac{C_i \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \tag{7}$$

where ADD_{ing} (µg/kg day) and ADD_{derm} (µg/kg day) are the average daily doses through ingestion and dermal absorption of water, respectively (Kumar et al., 2019; Saha & Paul, 2018). In Eqs. (6) and (7) C_i is the concentration of the HMs (µg/L), IR is the ingestion rate (2.0 L/day), EF is the exposure frequency (350 days), ED is the exposure duration (30 years), BW is the body weight (70 kg), AT is the average time (10,950 days), SA is the exposed skin area (18,000 cm^2), Kp is the skin adherence factor (Table 1), ET is the exposure time (0.58 h/day), and CF is the conversion factor (0.001).

The calculation of non-carcinogenic risks was carried out by calculating the hazard coefficient (HQ) using the USEPA (2004) method following Eq. (8):

$$HQ_{ing/derm} = \frac{ADD_{ing/derm}}{RfD_{ing/derm}} \tag{8}$$

where RfD_{ing} and RfD_{derm} are the ingestion and dermal reference doses (µg kg^{-1} day^{-1}), respectively (Table 1), HQ_{ing} is the hazard quotient through ingestion, and HQ_{derm} is the hazard quotient through dermal absorption (Kumar et al., 2019; Naveedullah et al., 2014; Iqbal & Shah, 2013; Wu et al., 2009).

The HI is the non-carcinogenic risk to human health caused by the presence of metals in water (Zakir et al., 2020); it was calculated using Eq. (9):

$$HI_{ing/derm} = \sum_{i=0}^{n} HQ_{ing/derm} \tag{9}$$

The threshold was set at 1.0. and at HI 1.0, there may be non-carcinogenic health risks to human health (Mohammadi et al., 2019).

Carcinogenic health risk

The incremental lifetime cancer risk ($CR_{ing/derm}$) was calculated due to exposure to potentially carcinogenic metals such as Cr, Ni, Cd, As, and Pb. Potential CR possibilities were calculated by multiplying together the ADD and slope factor (SF, mg/kg day, Table 1) (USEPA, 2004, Kumar et al., 2019) using the following equation (Eq. 10):

$$CR_{ing/derm} = ADD_{ing/derm} \times SF \tag{10}$$

The SF values for carcinogenic metals were taken from the California Office of Environmental Health Hazard Assessment (OEHHA, 2020). The acceptable range for ΣCR is 1.0×10^{-6} to 1.0×10^{-4}, and values $>10^{-4}$ indicate a high likelihood of human cancer (USEPA, 2004; Mohammadi et al., 2019).

RESULTS AND DISCUSSION

Physical and chemical parameters of groundwater

The results of determining the physical and chemical parameters of groundwater are presented in Table 2. For groundwater sampled in the area of the Severodvinsk city, pH values varied within 5.95–6.80; the average value was 6.30. For the Novodvinsk region, pH values varied from 6.80 to 8.38, with an average value of 7.60. Groundwater in the vicinity of Arkhangelsk was characterised by minimal variations in pH values from 7.48 to 7.69, with an average value of 7.63. It should be noted that, in general, the average groundwater pH values for all areas were within the range recommended by WHO (WHO, 2017).

Mineralisation of groundwater in the area of Severodvinsk varied from 50.5 to 790.3 mg/l; the average value was 246.2 mg/l. Groundwater in the vicinity of Novodvinsk had salinity values ranging from 27.5 to 685.3 mg/l with an average value of 206.8 mg/l. Groundwater mineralisation values for the vicinity of Arkhangelsk varied from 424 to 1202 mg/l; the average value was 739.6 mg/l, which was more than 2 times higher than the average mineralisation characteristic for Severodvinsk and Novodvinsk. In one sample of KW-17, mineralisation exceeded the TDS values for drinking water according to Russian requirements of 1000 mg/l. Elevated TDS values in groundwater in the Arkhangelsk area were likely related to the lower proportion of atmospheric recharge from the aquifer from which the samples were taken.

The value of the redox potential in groundwater in the area of Severodvinsk ranged from -134 to 205 mV; the average value was 205 mV. In the vicinity of Novodvinsk, the Eh values fluctuated in a fairly narrow range from 134 to 165 mV, with an average value of 147.2 mV. Positive average values of Eh, typical for the groundwaters of Severodvinsk and Novodvinsk, indicate the presence of free oxygen in the water, which is more typical for surface waters (Dvinskikh, 2020). An excellent picture was observed for groundwater in the Arkhangelsk region, where negative Eh values were typical for all samples (from -92 mV to -17.2 mV, average -48.8 mV), which was defined as a recovery mode due to the presence of hydrogen sulfide and low-valent metals in the water (Fe^{2+}, Mn^{2+}, Mo^{4+}, V^{4+}, U^{4+}) (Dvinskikh, 2020).

Physical and chemical parameters of the snow cover

The results of determining the physical and chemical parameters of the snow cover are presented in Table 3. The values of the pH value in the melted snow waters sampled in the vicinity of Severodvinsk varied in the range of 6.25–8.81, with an average value of 7.15. The pH value varied from 6.37 to 8.85 (the average value was 7.14) for melted snow in the Novodvinsk region. The pH value varied within 6.54–6.80, with an average value of 6.67, in melted snow sampled in the vicinity of Arkhangelsk. The pH of pure atmospheric precipitation is in the range of 5.5–6.5 for the territory of Russia (Pershina et al., 2021), while at the same time, for all the areas studied by the authors, the average pH values were above the background range, which

Table 2. Physicochemical parameters and heavy metal concentrations in groundwater from Arkhangelsk agglomeration .

Areas	Sample ID	Physical and chemical parameters				Concentration of metals in groundwater, µg/L															Total alpha activity, Bq/L
		EC, µCm/cm	TDS, mg/L	pH	Eh	Ti	Cr	Mn	Co	Ni	Cu	Zn	Cd	Mo	Pb	V	As	Sb	Fe	U	
Severodvinsk	KW-6	1586	790.3	6.8	-134	1.57	14	522	0.42	17.1	2.68	39	<0.001	0.33	0.15	0.84	1.77	<0.05	4292	0.134	0.006
	KW-7	259	123.1	6.05	205	7	16.3	38	0.26	10	6.92	11	<0.001	0.16	0.91	2.26	0.75	0.07	873	0.096	0.004
	KW-8	135	50.5	6.37	180	4.8	15.2	42	0.22	10.2	2.5	8.9	<0.001	0.14	1.5	1.72	0.25	0.05	1133	0.045	0.002
	KW-9	119	64.4	6.47	170	4.5	15.3	51	0.26	10.6	2.3	14	<0.001	0.14	2.68	1.43	0.59	0.07	1046	0.023	0.001
	KW-10	128	59.6	6.18	188	4.8	17.9	33	0.25	12.1	2	11	<0.001	0.4	1.69	1.61	0.48	0.05	1079	0.09	0.003
	KW-11	186	389	5.95	198	1.63	16.1	147	0.43	11.3	3.29	13	0.004	0.32	2.32	1.21	0.31	0.18	300	0.123	0.005
	Mean	402	246.2	6.30	134.5	4.05	15.80	138.8	0.31	11.88	3.28	16.15	0.004	0.25	1.54	1.51	0.69	0.08	1454	0.09	0.00
Novodvinsk	KW-12	337	169.4	7.19	134	1.24	15.7	3.1	0.25	12.2	2.44	14	0.004	0.21	0.31	1.65	0.73	<0.05	311	0.13	0.005
	KW-13	60	27.5	8.18	165	0.9	15.3	5.6	0.18	10.9	1.13	6.7	<0.001	0.13	0.2	0.59	<0.01	<0.05	145	0.144	0.006
	KW-14	57	27.6	8.38	156	0.91	14.8	73	0.22	9.5	1.74	26	0.045	0.23	0.46	0.28	0.19	<0.05	124	0.079	0.002
	KW-15	261	124	7.43	142	1.1	15.6	220	0.43	10.8	6.22	51	<0.001	0.2	0.24	0.19	<0.01	0.07	262	0.061	0.002
	KW-16	1382	685.3	6.8	139	1.49	16.2	242	0.58	18.4	3.2	118	0.165	0.47	2.28	1.24	0.28	0.12	816	3.338	0.089
	Mean	419	206.8	7.60	147.2	1.13	15.52	108.7	0.33	12.36	2.95	43.14	0.07	0.25	0.70	0.79	0.40	0.10	332	0.75	0.02
Arkhangelsk	KW-16-1	761	424	7.69	-92	2.38	17.4	260	0.89	14.9	3.69	34	<0.001	0.34	0.96	1.64	0.74	0.2	2935	0.189	0.006
	KW-17	2389	1202	7.64	-17.2	1.79	19.6	355	0.86	16.4	2.86	11	<0.001	0.78	0.18	3.21	0.31	0.09	556	0.19	0.005
	KW-18	1415	691	7.66	-74	1.64	15.7	1499	1.3	14.4	2.4	13	<0.001	0.68	0.25	2.31	0.96	0.07	664	7.83	0.209
	KW-19	1190	605	7.67	-26	1.22	14	959	0.56	13.5	1.61	13	<0.001	0.31	0.16	1.32	<0.01	0.04	521	1.011	0.034
	KW-20	1561	776	7.48	-35	1.73	16.1	2468	2.02	16.2	2.59	19	<0.001	0.36	0.43	1.83	0.28	0.12	1258	0.428	0.012
	Mean	1463	739.6	7.63	-48.8	1.75	16.56	1108.2	1.13	15.08	2.63	18.00	-	0.49	0.40	2.06	0.57	0.10	1187	1.93	0.05
Mean for all areas		739.13	388.04	7.12	81.18	2.42	15.95	432.36	0.57	13.03	2.97	25.16	0.05	0.33	0.92	1.46	0.59	0.09	1020	0.87	0.02
	WHO	-	1000	9	-	-	50	500	100	20	2000	3000	3	70	10	-	10	5	300	30	0.5
	SanPiN	-	2000	9	-	-	50	100	100	100	1000	5000	1	250	30	100	50	50	300	15	0.2

Table 3. Heavy metal concentrations in the dissolved fractions for each of the snow samples from Arkhangelsk agglomeration. Physicochemical parameters measured in melted snow samples before separation of dissolved and particulate fractions.

Areas	Sample ID	Physical and chemical parameters			Concentration of dissolved forms of metals, µg/L													
		EC, µCm/cm	TDS, mg/L^{-1}	pH	Ti	Cr	Mn	Co	Ni	Cu	Zn	Cd	Mo	Pb	V	As	Sb	Fe
Severodvinsk	C-106	11.89	5.5	7.02	0.88	15.7	3.7	0.15	9.9	0.95	10	0.044	0.15	1.36	1.7	<0.01	<0.05	118
	C-107	15.48	7.1	8.81	0.92	15.5	4.7	0.16	10.1	0.99	14	<0.001	0.12	0.4	2.53	0.12	<0.05	103
	C-108	10.12	4.68	6.25	0.84	15.3	3.6	0.15	10.6	1.16	15	<0.001	0.08	0.29	2.25	0.03	<0.05	98
	C-109	12.17	5.6	6.52	1.08	14.9	7.3	0.15	9.9	0.97	8.5	<0.001	0.67	0.35	4.65	0.03	<0.05	97
	C-110	16.85	7.8	8.15	0.74	14.7	5.2	0.13	9.3	0.91	14	0.003	0.12	0.34	1.42	<0.01	<0.05	91
	C-111	13.36	6.3	8.25	0.82	14.2	2.3	0.14	9.1	0.88	31	<0.001	0.53	0.36	0.32	<0.01	<0.05	80
	C-112	14.04	6.54	6.42	1.04	14.4	7.4	0.15	9.1	1.14	19	0.014	0.32	0.25	0.58	0.05	<0.05	79
	C-113	9.87	4.58	6.37	0.93	14.7	9.8	0.16	9.5	0.85	18	<0.001	0.06	0.31	0.55	<0.01	<0.05	94
	C-114	22.83	10.6	6.29	0.92	14.9	18	0.14	9.7	0.8	18	<0.001	0.14	0.24	0.52	<0.01	0.05	93
	C-115	11.43	5.4	7.5	0.87	14.7	7.2	0.15	9.4	0.86	12	<0.001	0.08	0.28	0.63	0.04	<0.05	93
	Mean	13.804	6.41	7.15	0.904	14.9	6.92	0.15	9.66	0.951	15.95	0.02	0.227	0.42	1.515	0.054	0.05	94.6
Novodvinsk	C-116	14.79	6.85	6.62	0.84	14.6	13	0.22	10.3	0.75	9.7	0.003	0.11	0.2	3.71	0.04	<0.05	89
	C-117	28.79	13.45	6.37	0.95	12.9	636	0.24	10.2	1.53	14	0.015	0.17	0.27	2.25	0.25	0.07	57
	C-118	14.06	6.5	6.91	0.79	13	26	0.17	9.8	0.95	12	<0.001	0.14	0.23	1.01	0.15	<0.05	51
	C-119	16.56	7.6	7.43	0.73	12.8	16	0.15	9.7	0.78	17	0.057	0.11	0.24	1.05	0.57	<0.05	50
	C-120	39.41	18.2	8.85	0.83	14.5	23	0.16	10.3	2.36	28	0.042	0.34	0.23	1.21	0.65	0.06	89
	C-121	17.18	7.95	6.66	1.19	14.7	23	0.17	9.6	0.74	14	0.011	0.15	0.21	1.21	0.34	<0.05	87
	Mean	21.8	10.1	7.14	0.9	13.8	122.8	0.20	10.0	1.2	15.8	0.0	0.2	0.2	1.7	0.3	0.1	70.5
Arkhangelsk	C-122	19.15	8.88	6.67	1.05	15	3.4	0.16	9.9	1.51	13	<0.001	0.15	0.34	1.74	0.75	0.07	92
	C-123	14.26	6.67	6.68	0.86	15.1	15	0.17	10.1	0.97	21	0.053	0.12	0.24	1.55	0.48	<0.05	87
	C-124	13.66	6.2	6.8	0.83	14.1	135	0.15	9.9	1.07	15	0.008	0.12	0.31	1.05	0.2	<0.05	87
	C-125	16.18	7.55	6.54	0.84	14.6	32	0.14	9.8	0.81	33	<0.001	0.14	0.2	1.87	0.29	<0.05	82
	C-126	13.91	6.45	6.65	0.84	14.6	17	0.17	10.2	1.11	23	0.018	0.1	0.24	0.7	0.29	<0.05	83
	Mean	15.43	7.15	6.67	0.88	14.68	40.48	0.16	9.98	1.09	21.00	0.03	0.13	0.27	1.38	0.40	0.07	86.20
Mean for all areas		16.48	7.64	7.04	0.89	14.52	48.03	0.16	9.83	1.05	17.10	0.024	0.19	0.33	1.55	0.27	0.063	86
	WHO	-	1000	9	-	50	500	100	20	2000	3000	3	70	10	-	10	5	300
	SanPiN	-	2000	9	-	50	100	100	100	1000	5000	1	250	30	100	50	50	300

indicates a significant level of snow alkalisation, probably associated with the fallout of carbonate dust particles (Moskovchenko et al. 2021).

The values of mineralisation of melted snow in the Severodvinsk area ranged from 9.87 to 22.83 mg/l, with an average value of 13.80 mg/l. The mineralisation of melted snow varied from 14.06 to 39.41 mg/l, the average value was 21.80 mg/l, for the Novodvinsk vicinity. The mineralisation value varied from 13.66 to 19.15 mg/l; the average value was 15.43 mg/l, in melted snow, taken in the Arkhangelsk vicinity. The weighted average values of sediment mineralisation do not exceed 10–15 mg/l for the Russian background territories (Anufrieva et al., 2021). The authors' data on snow mineralisation in the Arkhangelsk agglomeration were on average higher than the background values typical for Russia, which may be due to the influence of anthropogenic activity.

Heavy metal content in ground water

The results of determining the heavy metal content in groundwater are presented in Table 2. The heavy metal values were compared with the recommended values of WHO (2017) and SanPiN 2.1.4.1074-01 (2001) for the purpose of determining the quality of drinking water. The average heavy metal concentrations in the groundwater of the Arkhangelsk agglomeration were in the following order: Fe (1020 μg/L) > Mn (432.36 μg/L) > Zn (25.16 μg/L) > Cr (15.95 μg/L) > Ni (13.03 μg/L) > Cu (2.97 μg/L) > Ti (2.42 μg/L) > V (1.46 μg/L) > Pb (0.92 μg/L) > U (0.87 μg/L) > As (0.59 μg/L) > Co (0.57 μg/L) > Mo (0.33 μg/L) > Sb (0.09 μg/L) > Cd (0.05 μg/L).

The concentration of Fe in the groundwater of the Arkhangelsk agglomeration ranged from 124 to 4292 μg/l, on average 1020 μg/l, and the allowable limit is 300 μg/l recommended by WHO and SanPiN. Considering the distribution of iron in key areas, it can be seen that in all samples taken in the vicinity of Severodvinsk and Arkhangelsk, the concentration of Fe was higher than the values recommended by WHO and SanPiN, while the average concentrations of Fe for the regions of Severodvinsk and Arkhangelsk exceed 1600 and 1100 μg/l, respectively. In the Novodvinsk area, only two out of five samples slightly exceed the standards for iron, and the average value was ~ 330 μg/l. A probable source of extremely high concentrations of iron in groundwater at the Severodvinsk and Arkhangelsk sites are metallurgical enterprises located in these cities. High iron content, in addition to imparting an unpleasant taste, turbidity, and coloration, can have a negative impact on human health. The concentration of Mn in the groundwater of the study area varied from 3.1 to 2468 μg/l, with an average value of 432.4 μg/l. The permissible limit of Mn is 500 μg/l and 100 μg/l according to WHO and SanPiN, respectively. The spatial distribution of Mn to key areas was also extremely heterogeneous. In the Severodvinsk region, out of six samples studied, only in two samples, Mn concentrations exceed the SanPiN limit (100 μg/L) and in one sample the WHO limit (500 μg/L). In the Novodvinsk region, out of five samples studied, two exceed the SanPiN limit, while none of the samples exceeded the permissible WHO value. The maximum average concentrations of Mn (<1100 μg/l) were found in groundwater from the Arkhangelsk vicinity, exceeding the allowable SanPiN limit in all samples and the WHO limit in three out of five. High concentrations of manganese in water have proven toxic to the central nervous system, causing a variety of neurological effects, including a cognitive decline in adults and children after drinking manganese-contaminated water (WHO, 2017). As a rule, high concentrations of manganese in groundwater are characteristic of the humid zone and are associated with natural causes (Beshentsev, 2021).

The concentration of Zn in groundwater ranged from 6.7 to 118 μg/l, with an average value of 25.16 μg/l. In general, in all the studied samples of the Arkhangelsk agglomeration, rather low concentrations of Zn were observed, the distribution over key areas was relatively uniform, and the maximum zinc concentrations were significantly below the permissible limits according to WHO (3000 μg/l) and SanPiN (5000 μg/l). The concentration of Cr in groundwater varied in the range of 14.0–19.6 μg/l, the average value was 15.95 μg/l. Variations in chromium concentrations in different areas of the Arkhangelsk agglomeration were insignificant and did not exceed the permissible limits according to WHO (50 μg/l) and SanPiN (50 μg/l). The content of nickel (Ni) in the groundwater of the Arkhangelsk agglomeration ranged from 9.5 to 18.4 μg/l, with an average value of 13.03 μg/l, which was below the acceptable Ni limits according to WHO (100 μg/l) and SanPiN (20 μg/l). The maximum concentrations of the remaining metals Cu, V, Pb, U, As, Co, Mo, Sb, and Cd were well below the acceptable WHO and SanPiN limits (see Table 2). For Ti, limiting concentrations have not been established either by WHO or by SanPiN. At the same time, in terms of total alpha activity in one sample taken in the Arkhangelsk region (KW-18, 0.209 Bq/l), there was a slight excess according to SanPiN (0.2 Bq/l), which makes it necessary to pay close attention to this water source in terms of radiation safety.

Heavy metal content in the snow cover

The results of determining the heavy metal content in the snow cover of the Arkhangelsk agglomeration are presented in Table 3. The authors have considered water-soluble forms of heavy metals in snow, in connection with their ability to further migrate into groundwater. Since the content of water-soluble forms of heavy metals in snow obviously affects the quality of drinking groundwater, the values of water-soluble forms of heavy metals were also compared with the recommended values of WHO (2017) and SanPiN 2.1.4.1074-01 (2001) for drinking water. The average concentrations of water-soluble forms of heavy metals in the snow of the Arkhangelsk agglomeration were in the following order: Fe (85.71 μg/L) > Mn (48.03 μg/L) > Zn (17.10 μg/L) > Cr (14.52 μg/L) > Ni (9.83 μg/L) > V (1.55 μg/L) > Cu (1.05 μg/L) > Ti (0.89 μg/L) > Pb (0.33 μg/L) > As (0.27 μg/L) > Mo (0.19 μg/L) > Co (0.16 μg/L) > Sb (0.06 μg/L) > Cd (0.02 μg/L).

A distinctive feature is that the descending order of metal concentrations in snow was similar to groundwater, which probably indicates a relationship between metal concentrations in melted snow and groundwater. Exceeding the permissible limits according to WHO and SanPiN for none of the metals in the snow was noted, with the exception of Mn, the concentration of which in one sample of C-117 (636 μg/l) exceeded WHO (500 μg/l) and SanPiN (100 μg/l). Comparing the average concentrations of metals in groundwater and melted snow, it can be seen that significant differences in the concentrations of metals in groundwater and snow were observed only for Fe and Mn – the concentration of iron and manganese in groundwater was about 10 times higher than in snow. At the same time, the concentrations of other metals in the snow of Zn, Cr, Ni, Cu, Ti, V, Pb, As, Co, Mo, Sb, and Cd were generally comparable with the concentrations in groundwater, which may indicate that melted snow is the main source of heavy metals in groundwater. In terms of the spatial distribution of heavy metals in snow within various key areas of the Arkhangelsk agglomeration (Severodvinsk, Novodvinsk, and Arkhangelsk), some features can be distinguished for individual metals. Thus, the maximum average concentration of Mn in snow (122.8 μg/l) was typical for the Novodvinsk region. In the areas of Arkhangelsk and Severodvinsk, the average concentration of Mn was 40.48 μg/l and 6.92 μg/l, respectively. Elevated average As concentrations were observed in snow samples in the Arkhangelsk and Novodvinsk regions and were 0.40 μg/l and 0.33 μg/l, respectively, while the average As concentration was 0.05 μg in the Severodvinsk region. Significant differences in key areas were also observed for Pb and Mo, the maximum average concentrations of which 0.42 μg/l and 0.23 μg/l were observed in the Severodvinsk area, in the areas of Arkhangelsk and Novodvinsk the average concentrations of Pb were 0.27 and 0.23 μg/l and 0.17 and 0.13 μg/l, respectively. For other metals, Co, Cu, Zn, Cs, V, Sb, and Fe, the variations in average concentrations from region to region were insignificant and ranged from 19 to 25%. For metals Ti, Cr, and Ni, the variations in the average concentrations were even more insignificant and amount to 1.7%, 7.7%, and 3.2%, respectively.

To estimate the distribution of heavy metals between the suspended and dissolved forms of snow, the method of calculating the distribution coefficient (C_p) was used according to the following formula $C_p = C_{part}/C_{total}$, where $C_{total} = C_{part} + C_{dis}$, C_{part} is the concentration of the metal in the suspended fraction, C_{dis} is the concentration of the metal in the dissolved fraction (Bacardit & Camarero, 2010). Values for the distribution coefficient (C_p) range from 0 (the presence of the metal in the snow only in dissolved form) to 1 (the metal is in the snow only in the form of solid particles).

According to the calculation of the distribution coefficient (C_p) for the heavy metal concentration in the snow of the Arkhangelsk agglomeration, such metals as Ti, Fe, Cu, Pb, and Sb were found mainly in the particulate fraction with C_p values of 0.94–1.0 (Table 4). Metals such as Cr and Mo were found mainly in dissolved forms with C_p values of 0.42 and 0.30, respectively. The remaining metals Ni, Cd, Zn, As, Mn, V, and Co were in an intermediate position (C_p varies in the range of 0.56–0.88).

Thus, according to the ratio of soluble forms, the studied elements can be divided into three groups: high- (Cr and Mo), medium- (Ni, Cd, Zn, As, Mn, V, and Co), and insoluble (Ti, Fe, Cu, Pb, and Sb). As a rule, the solubility of various elements is related to the origin and mechanisms of aerosol formation, which affect the particle size and chemical properties (Azimi, 2004; Vlasov, 2020). Thus, high contents of insoluble components are associated with large particles of terrigenous origin, while soluble elements are mainly associated with adsorption on small aerosol particles. Accordingly, the proportion of soluble forms is higher in smaller particles due to their higher surface/volume ratio (Bacardit & Camarero, 2010). The predominance of insoluble forms of Ti, Fe, Cu, Pb, and Sb is probably due to their predominant terrigenous origin, or also to large silty particles of anthropogenic origin (for example, ash from coal-fired power plants) (Slukovsky et al., 2020). It can be assumed that the presence of the main part of Cr and Mo and a significant proportion of Ni, Cd, Zn, As, Mn, V, and Co in soluble form is associated with anthropogenic aerosol pollution, and not with insoluble terrigenous minerals. The increased solubility of these metals determines their fate during the spring snowmelt, during which there will be a high migration of metals into groundwater and predominant absorption by biota (Borgmann, 2000; Navas & Lindhorfer, 2005).

To quantify the precipitation of heavy metals per unit area, the index of areal pollution of snow cover in key areas of the Arkhangelsk agglomeration was calculated according to the formula $X=C_{total}\times V\times S$, where C_{total} is the total concentration of the metal of the dissolved and insoluble fraction in 1 liter of melted snow, V is the volume of melted snow water at the sampling point, l, S is the area of the pit, m^2, X is the amount of heavy metal that fell per 1 m^2, mg/m^2.

Table 5 presents data on the areal pollution of snow cover with heavy metals in mg/m^2. So, if one analyses the total areal pollution of all studied metals per 1 m^2, then it can be noted that the least polluted snow cover in the Severodvinsk region is ~ 77 mg/m^2, while the total indicator of snow pollution in the Novodvinsk and Arkhangelsk regions was almost three times higher and was 210.51 and 216.91 mg/m^2, respectively. The snow cover in the areas of Arkhangelsk and Novodvinsk for most metals had similar indicators of areal pollution for almost all metals, while the Severodvinsk area was characterised by several times lower values for most metals. Metals Cr, Ni, Cu, and Zn were characterised by close indicators of areal pollution in all three key areas. Differences in the heavy metal concentrations deposited per 1 m^2 between the studied key areas are associated with different sources of pollution, the distance of sampling points from heavy metal emission sources, differences in the direction of air mass movement, and a number of other factors. Possible sources of pollution of the snow cover of the Arkhangelsk agglomeration will be discussed below in the section "Analysis of heavy metal sources".

Analysis of heavy metal sources (Severodvinsk)

To identify the sources of heavy metals in the snow cover of the Arkhangelsk agglomeration, data analysis was performed using the principal component analysis (PCA), which made it

Table 4. Heavy metal concentrations in the particulate fractions for each of the snow samples from Arkhangelsk agglomeration . The last row shows partition coefficients (CP) between dissolved and particulate concentrations.

Areas	Sample ID	Concentration of particulate forms of metals, µg/L													
		Ti	Cr	Mn	Co	Ni	Cu	Zn	Cd	Mo	Pb	V	As	Sb	Fe
Severodvinsk	C-106	49.11	10.98	68.75	0.61	10.54	15.36	72.32	0.04	0.16	7.46	9.82	0.56	1.10	1335.71
	C-107	27.71	4.68	19.05	0.42	6.75	10.30	49.35	<0.001	0.03	3.58	4.77	0.30	0.68	676.19
	C-108	53.06	8.98	57.14	0.82	23.67	41.63	126.53	0.33	<0.01	11.63	21.18	0.24	2.86	1791.84
	C-109	71.74	8.04	41.30	0.85	13.04	21.54	54.35	<0.001	<0.01	6.24	11.78	0.46	1.89	1530.43
	C-110	44.92	5.34	37.29	0.56	7.29	12.54	46.61	0.00	0.03	8.19	7.44	0.41	0.80	1013.56
	C-111	11.46	2.71	18.75	0.20	4.79	7.99	41.67	0.03	<0.01	1.93	1.29	0.11	0.59	487.50
	C-112	7.07	2.40	81.33	0.60	4.53	9.43	32.00	0.14	<0.01	1.52	0.55	<0.01	0.68	384.00
	C-113	112.12	5.76	35.35	0.93	7.58	10.40	28.28	<0.001	0.10	5.04	6.79	0.21	0.77	1973.74
	C-114	108.70	34.78	239.13	2.35	60.43	58.26	426.09	0.58	0.09	15.61	6.30	<0.01	2.83	2921.74
	C-115	77.92	5.97	36.36	0.84	5.71	17.01	35.06	0.02	0.04	5.00	4.18	0.06	1.10	1515.58
	Mean	56.38	8.96	63.45	0.82	14.43	20.45	91.23	0.16	0.08	6.62	7.41	0.30	1.33	1363.03
Novodvinsk	C-116	160.98	10.98	47.56	2.52	14.02	14.76	29.27	<0.001	0.26	14.63	19.51	1.54	1.27	2412.20
	C-117	475.68	52.70	378.38	6.46	41.62	41.62	121.62	<0.001	0.38	20.73	27.03	3.81	2.95	8748.65
	C-118	170.21	11.28	129.79	2.34	12.98	28.09	59.57	0.02	0.13	12.30	14.38	2.77	2.13	2702.13
	C-119	86.67	9.33	86.67	1.22	8.00	21.71	55.56	0.09	0.04	8.96	8.96	1.36	2.27	1524.44
	C-120	321.74	17.61	506.52	3.67	19.35	32.83	147.83	0.30	0.30	30.43	23.91	7.63	3.65	5021.74
	Mean	243.05	20.38	229.78	3.24	19.19	27.80	82.77	0.14	0.22	17.41	18.76	3.42	2.45	4081.83
Arkhangelsk	C-121	263.54	14.17	171.88	3.33	12.29	12.71	59.38	<0.001	0.22	23.96	9.90	2.94	1.61	3236.46
	C-122	228.00	14.00	172.00	2.76	22.40	35.32	144.00	<0.001	<0.01	25.84	18.72	2.72	4.08	3656.00
	C-123	265.22	17.39	647.83	3.43	23.04	36.43	182.61	0.16	<0.01	28.74	26.78	2.17	5.13	4156.52
	C-124	210.00	10.20	136.00	2.46	14.40	20.40	56.00	<0.001	0.04	16.16	18.20	0.90	2.34	3020.00
	C-125	264.18	19.10	840.30	4.13	18.21	16.42	207.46	<0.001	0.13	19.40	28.36	4.10	1.88	7786.57
	C-126	122.97	8.11	193.24	1.66	9.46	9.46	63.51	<0.001	<0.01	7.00	10.45	1.04	1.32	2625.68
	Mean	225.65	13.83	360.21	2.96	16.63	21.79	118.83	0.16	0.13	20.18	18.73	2.31	2.73	4080.20
Mean for all areas		149.19	13.07	187.84	2.01	16.20	22.58	97.10	0.16	0.14	13.06	13.35	1.75	2.00	2786.70
Partition coefficients (*Cp*)		0.98	0.42	0.85	0.88	0.56	0.94	0.80	0.57	0.30	0.95	0.86	0.83	1.00	0.95

Table 5. Data on the areal pollution of snow cover with heavy metals.

Metal	Areal heavy metal contamination of key areas, mg/m^2		
	Severodvinsk	Novodvinsk	Arkhangelsk
Ti	2.500	10.757	9.134
Cr	1.017	1.409	1.196
Mn	2.976	15.205	17.722
Co	0.041	0.148	0.127
Ni	1.034	1.201	1.159
Cu	0.929	1.151	1.041
Zn	4.615	4.253	6.259
Cd	0.005	0.005	0.002
Mo	0.011	0.017	0.007
Pb	0.306	0.830	0.821
V	0.388	0.832	0.906
As	0.011	0.169	0.107
Sb	0.058	0.103	0.125
Fe	63.372	174.426	178.306
Σ	77.26	210.51	216.91

possible to reveal the structure of relationships between the studied snow components. The datasets for the three key areas – Severodvinsk, Novodvinsk, and Arkhangelsk were considered separately, since each area is characterised by its own specific sources of heavy metal emissions into the atmosphere, and it was important to identify the dominant source for each area. The results of PCA analysis for the Severodvinsk region are presented in Table 6. Quantitatively, the data set was divided into four main components explaining 94.31% of the cumulative dispersion in the distribution of the chemical composition of snow in the Severodvinsk region. In the first principal component PC1 with a dispersion of 60.74% for high loads, the parameters of snow mineralisation TDS-EC and most of the studied metals Ti, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Sb, and Fe stand out. A likely source of such a wide range of metals in the snow were emissions from industrial enterprises in Severodvinsk associated with metallurgical production, mechanical engineering, and metalworking (Korobitsina et al., 2013; Boykova & Belozerova, 2016).

The second principal component PC2 accounts for 16.92% of the total variance, which has a high positive load on V and As. Their sources are probably the city's thermal power plants, which still use hard coal as fuel, since V and As are the main heavy metals of the ash emitted into the atmosphere (Zhuravleva et al., 2013; Vasilevich et al., 2019). The third PC3 component accounts for 9.26% of the total dispersion with a high load on Mo. The segregation of molybdenum in the PC3 component probably points to a separate dominant source of Mo. The main technogenic source of Mo supply is metallurgy and mechanical engineering since the process of processing and enrichment of Mo-containing ores is actively used for the production of heat-resistant steels. Additional sources may be road dust from the use of molybdenum additives in automobile engines and the abrasion of Mo-containing asphalt by moving vehicles (Rybakov & Krutskikh, 2021). In the fourth component of PC4, with a load of 7.39%, As is released, which was also released in the second component of PC2. Arsenic is also a by-product of metallurgical production (Mikhalina, 2003); therefore, the metallurgical enterprises of Severodvinsk can probably act as an additional source of As in snow.

Table 6. Total variance explained and component matrix of heavy metals in snow of the Severodvinsk city.

Element	Principal Component Number			
	PC 1	PC 2	PC 3	PC 4
pH	-0.54	-0.50	0.14	0.48
TDS	0.63	-0.71	0.08	0.26
EC	0.63	-0.70	0.09	0.27
Ti	0.63	0.39	0.43	-0.31
Cr	0.97	-0.12	0.17	0.06
Mn	0.93	-0.26	0.05	-0.09
Co	0.96	-0.05	0.12	-0.19
Ni	0.99	-0.08	-0.06	0.06
Cu	0.95	0.14	-0.25	0.09
Zn	0.97	-0.20	-0.01	0.07
Cd	0.91	-0.10	-0.31	-0.05
Mo	0.30	0.18	0.85	-0.02
Pb	0.90	0.25	0.00	0.29
V	0.29	0.83	-0.28	0.38
As	-0.28	0.50	0.38	0.67
Sb	0.83	0.38	-0.37	0.13
Fe	0.87	0.36	0.22	-0.15
Eigenvalue	10.33	2.88	1.57	1.26
Percentage of Variance	60.74%	16.92%	9.26%	7.39%
Cumulative	60.74%	77.67%	86.92%	94.31%

Analysis of heavy metal sources (Novodvinsk)

Quantitative parameters of PCA analysis for snow sampled in the Novodvinsk area (eigenvalue, PC principal components, variable loads, explained variance) are presented in Table 7. Thus, PCA analysis shows that the three main components explain 96.41% of the total sample variance. The first principal component PC1 with a high load (> 0.49) explains 66.64% of the total variance and combines all heavy metals and TDS snow mineralisation indices. As can be seen from the presented data, all metals have one dominant source of origin in the snow of the Novodvinsk city. According to (Perkhurova, 2021), two sources of atmospheric air pollution predominate in the Novodvinsk city – these are the Arkhangelsk Pulp and Paper Mill and motor vehicles.

Most likely, it is the activity of the pulp and paper mill, both due to direct industrial emissions and due to the operation of a coal-fired thermal power plant on its territory, that is the supplier of the main share of heavy metals in the snow cover of the city. The second PC2 and third PC3 principal components account for 23.09% and 6.68% of the total variance with a high load on pH, Cd, and As (0.92, 0.84, and 0.51, respectively) in the second component and on Pb (0.55) in the third component. Given that As, Cd, and Pb were also in the first principal component, it is likely that Cd, As, and Pb have some additional sources of entry into the snow, which may be associated with the activity of vehicles.

Analysis of heavy metal sources (Arkhangelsk)

Results of PCA for the snow cover dataset in the Arkhangelsk region are presented in Table 8. In Table 8, according to the quantitative parameters of component loads, four groups of principal components are distinguished with eigenvalues of 9.71, 4.14, 2.35, and 0.79, which explain all

Table 7. Total variance explained and component matrix of heavy metals in snow of the Novodvinsk city.

Element	Principal Component Number		
	PC 1	PC 2	PC 3
pH	0,23	0,92	0,25
TDS	0,92	0,33	-0,10
EC	0,93	0,36	-0,02
Ti	0,90	-0,35	0,20
Cr	0,75	-0,63	-0,09
Mn	0,96	0,26	0,00
Co	0,83	-0,51	0,18
Ni	0,81	-0,59	-0,07
Cu	0,81	-0,19	-0,54
Zn	0,95	0,25	-0,14
Cd	0,49	0,84	-0,17
Mo	0,80	-0,34	0,43
Pb	0,76	0,34	0,55
V	0,84	-0,26	-0,02
As	0,83	0,51	0,10
Sb	0,84	0,35	-0,40
Fe	0,89	-0,44	0,01
Eigenvalue	11,33	3,93	1,14
Percentage of Variance	66.64%	23.09%	6.68%
Cumulative	66.64%	89.73%	96.41%

100% of the total sample variance. The first principal component PC1 with a high load (> 0.46) on TDS-EC, Ti, Cr, Mn, Co, Ni, Cu, Zn, Mo, Pb, V, As, Sb, and Fe accounts for 57.13% of the total variance. This indicates that one powerful source is the supplier of heavy metals in the snow in the Arkhangelsk vicinity. Such a source is probably the Arkhangelsk CHPP, which, according to (Perkhurova, 2021), supplies the bulk of air pollution in the Arkhangelsk city. The second principal component PC2 explains 24.36% of the total variance with a high load on pH, Ni, Cu, Cd, Pb, and Sb. Apparently, these metals come from a common source. A possible source of these metals in the snow cover of the study area may be a solid domestic waste landfill located just a few kilometres from the snow sampling points. The main pollutants at landfills formed during the decomposition and combustion of waste are seepage water, combustion and dust products, the content of a huge amount of toxic components, including heavy metals (Zamotaev et al., 2018). An increase in the content of heavy metals in seepage waters, combustion and dusting products is facilitated by the ingress of waste to landfills, which must be disposed of in a special way – accumulators, dry batteries, metal products, paint and varnish products, mercury thermometers, etc (Vladimirov & Karchevsky, 2005; Sharova & Barmin, 2013). Earlier, high concentrations of heavy metals such as mercury, zinc, bismuth, iron, manganese, etc. were found in groundwater samples taken along the perimeter of the Arkhangelsk solid waste landfill (Chizhevskaya et al., 2017). It is likely that the input of metals Ni, Cu, Cd, Pb, and Sb into the snow is also associated with the existing landfill due to the release of waste combustion products and dusting, which, among other things, increase the alkalinity of snow, as indicated by the high load (0.62) on the pH parameter in the PC2 component. According to (Perkhurova, 2021), the Arkhangelsk solid waste landfill is the second emitter of harmful substances into the atmosphere

Table 8. Total variance explained and component matrix of heavy metals in the snow of the Arkhangelsk city.

Element	Principal Component Number			
	PC 1	PC 2	PC 3	PC 4
pH	-0,54	0,62	-0,21	0,53
TDS	0,51	0,12	0,85	-0,05
EC	0,48	0,13	0,87	0,00
Ti	0,93	0,14	-0,16	0,31
Cr	0,99	-0,09	-0,11	-0,03
Mn	0,80	-0,39	-0,40	-0,21
Co	0,95	-0,22	-0,17	0,15
Ni	0,84	0,52	0,12	0,05
Cu	0,56	0,82	0,10	0,06
Zn	0,97	-0,10	-0,01	-0,21
Cd	0,41	0,56	-0,63	-0,34
Mo	0,46	-0,81	-0,08	0,36
Pb	0,80	0,59	0,02	0,10
V	0,93	-0,07	-0,31	0,17
As	0,88	-0,38	0,28	-0,07
Sb	0,54	0,84	-0,07	-0,09
Fe	0,78	-0,62	-0,03	0,06
Eigenvalue	9,71	4,14	2,35	0,79
Percentage of Variance	57.13%	24.36%	13.85%	4.67%
Cumulative	57.13%	81.49%	95.33%	100.00%

of Arkhangelsk after the thermal power plant, which is also confirmed by the authors' data. In the third principal component PC3, the parameters of the total snow mineralisation TDS-EC (> 0.85) were isolated with a total dispersion of 13.85%. Despite the fact that the TDS-EC parameters were also included in the first principal component, there is probably some additional source of mineral components in the snow in the Arkhangelsk vicinity. Salt mixtures used by road services in winter can be such a source (Chagina et al., 2016). In the fourth component PC4 with a load of 4.67%, the pH parameter stands out.

Water and snow quality indices

The assessment of the quality of the water used is very important for human health and can be used to determine the sources of toxic pollutants released into the environment as a result of anthropogenic activities (industrial processes, housing and communal and agricultural effluents, etc.) in the study area (Adelagun et al. 2021). This is essential to minimise potential public health risks. The assessment of the degree of pollution of the studied snow melt water (soluble form) and well water was carried out by calculating the indices of water quality and the risk to public health during its consumption. In general, it can be noted that the index values for well water were higher than for filtered melted snow, which is associated with stagnation of well water and the accumulation of metals, as well as with the infusion of groundwater.

The HMEI index takes into account the maximum allowable limit of each heavy metal. The HMEI values varied from 1.0 to 2.3 for melt water and from 1.5 to 15.4 for well water (Figure 2a). In a narrow classification, with a value of HMEI>1.0, the water is unsuitable for drinking, and, therefore, all the waters and melted snow studied in general were unsuitable as drinking water.

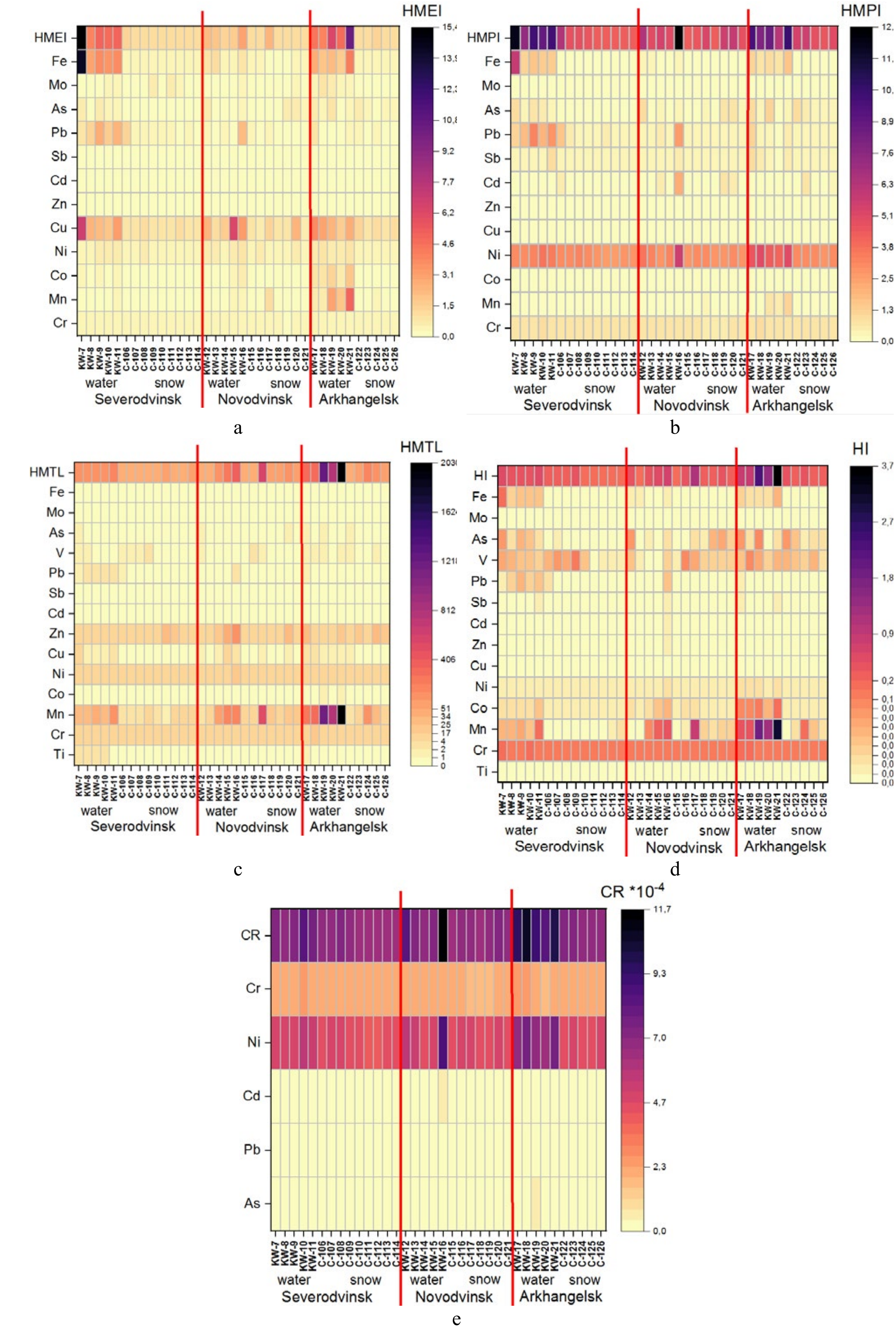

Fig. 2. Values of water quality indices and risk for public health in the territories of country areas of the Arkhangelsk agglomeration:a) heavy metal evaluation index; b) heavy metal pollution index; c) heavy metal toxicity load; d) non-carcinogenic health risk; e) carcinogenic health risk.

Snowmelt waters were generally characterised as “slightly affected”, with the exception of sample C-117 (HMEI=2.3) in Novodvinsk, which was classified as “moderately affected”. Copper had the greatest influence on the HMEI index for melt water, and to a lesser extent Mn and As. Water from wells was classified from “slightly affected” to “seriously affected”; the maximum value of the index was observed for sample KW-7 (HMEI=15.4) in Severodvinsk. In the case of well water, the largest contribution to the index value was made by Fe, Cu, Mn, Pb, and to a lesser extent Co. The contributions of metals to the index depend on the study area and surrounding industrial facilities. Thus, based on the values of the HMEI index, one can note increased values of Fe, Cu, and Pb for Severodvinsk, Cu for Novodvinsk, and Fe, Cu, Mn for Arkhangelsk. For other regions of Russia, the prevalence of Fe, as well as other metals, was noted. Thus, in the industrial areas of the Kola Peninsula, the HMEI index of natural surface waters was influenced by Fe, Ni, and Al (Yakovlev et al. 2021).

The HMPI index is useful for identifying and quantifying trends in water pollution by heavy metals (Singh et al., 2017). In the study areas, the HMPI index was in the ranges of 4.2-6.4 and 4.9-12.6 for snowmelt water and well water, respectively (Figure 2b). For snow samples, the highest index value was noted for sample C-106 in Severodvinsk, and for well water, for KW-16 in Novodvinsk. It should be noted that the values of the HMPI index for all the studied waters were below the critical level (HMPI<100) for drinking water, and were also at a low level (HMPI <15) according to the extended classification. It should be noted that Ni had a significant effect on the index for snow and water in all the studied areas. There was also a significant contribution of Fe, Pb, and As in Severodvinsk, Pb, Cd, and As in Novodvinsk, Fe, As, and Mn in Arkhangelsk.

The HMTL toxicity index ranged from 41–546 for melted snow and 47–2022 for well water (Figure 2c). The maximum toxicity for snow was observed for sample C-117 in Novodvinsk, and for well water – KW-21 in Arkhangelsk. Given the classification used, only two samples of melted snow had toxicity levels of “moderate toxicity” (Arkhangelsk) and “very high toxicity” (Novodvinsk); the rest of the samples were characterised by the level of “low toxicity”. High toxicity was observed for water from wells; two samples in Arkhangelsk had the highest level of “extremely high toxicity”. It should be noted that according to the method of calculating the HMTL index, the toxicity of Fe is 0; therefore, high concentrations of this metal do not affect the index. For the studied samples, high toxicity was mainly associated with a high concentration of Mn both in water and in melted snow. Thus, the extremely high toxicity index for water in Arkhangelsk was due to high concentrations of Mn. A significant contribution to the index of toxicity of water and snow was also made by Zn, Ni, and Cr for all the studied areas. In the other northern territory of Russia, for the polluted waters of the Kola Peninsula, where minerals are mined and processed, Ba, Ni, Al, Mn, Cu, and Co had the greatest impact on the toxicity index (Yakovlev et al. 2021).

The overall non-carcinogenic risk index HI ranged from 0.19–1.08 for meltwater and 0.22–3.70 for well water (Figure 2d). The highest value of the probability of non-carcinogenic risk was found for the snow sample C-117 in Novodvinsk, and for well water – KW-21 in Arkhangelsk. It is worth noting that only 1 melted snow sample (Novodvinsk) and 3 well water samples (Arkhangelsk) had index values above the threshold (HI>1), which means an increased risk of non-cancer-related effects. Moreover, according to the values of this index, the studied water and melted snow were safe when absorbed through the skin ($HI_{derm}<1$). Figure 2d shows that the index of all samples was strongly influenced by Cr, but this was related to the detection limit of this metal. All areas of the study were characterised by a significant contribution of Mn, V, As, Fe, and Co to the HI index; moreover, Mn and Co to a greater extent determine the risk for the population of Arkhangelsk. It is also worth noting that there was a contribution of V and As to the HI index of snow cover and water.

The CR index was in the intervals $(6.1\text{-}7.3)\cdot 10^{-4}$ and $(6.7\text{-}11.6)\cdot 10^{-4}$ for melt and well water, respectively (Figure 2e). The maximum carcinogenic risk was noted for samples of snow C-120 and water KW-16 in Novodvinsk. The obtained values of CR mean that the risk of developing cancer diseases is high ($CR>1 \cdot 10^{-4}$) during the consumption of each studied water source during a lifetime, i.e. there is a possibility of developing cancer in 6–12 residents out of every 10,000 people as a result of oral and dermal exposure to toxic metals from melted snow and well water in the study area (Zakir et al. 2020). It should be noted that with only skin exposure, the studied waters do not carry high carcinogenic risk ($CR_{derm}<1 \cdot 10^{-4}$). In general, well waters with a large CR index were located in Arkhangelsk, with a lower index value – in Severodvinsk, while for snow the indices were at the same level for all study areas. For all samples, the main metal that has a predominant effect on the CR index was Ni, and to a lesser extent Cr. Sometimes Cr acts as the main source of risk. So, for example, in the Alidadi study (Alidadi et al. 2019), when analysing 140 drinking water samples in Mashhad (Iran), Cr made the largest contribution to the HI and CR indices (up to 71.2% and up to 63.2%, respectively).

As a result of applying various approaches to identifying the degree of contamination of melted snow and well water with metals in the territories of suburban areas of the Arkhangelsk agglomeration, it can be noted that the HMPI index did not reveal a significant anthropogenic impact, while the values of the HI, HMEI, HTML and CR indices indicate a high level of contamination of the studied waters with metals, as well as the unsuitability of water as drinking water. The greatest impact occurred at sampling sites for well water KW-7, KW-16, and KW-21 and snow C-107, C-117 and C-120. Well water was most polluted in the Arkhangelsk region. The quality indices for melted snow were lower than for well water, and were generally similar to each other; however, the regions of Novodvinsk and Arkhangelsk experience the greatest impact from industry. Based on the calculated indices, attempts should be made to minimise the exposure to Ni, Cu, Fe, Mn, and Pb in order to reduce the adverse health effects for the inhabitants of the study area.

CONCLUSION

The analytical results presented in this article allow drawing the following conclusions:

In groundwater samples taken from wells in suburban community garden plots of the Arkhangelsk agglomeration, the average concentrations of heavy metals decrease in the following order: Fe (1020 μg L^{-1}) > Mn (432.36 μg L^{-1}) > Zn (25.16 μg L^{-1}) > Cr (15.95 μg L^{-1}) > Ni (13.03 μg L^{-1}) > Cu (2.97 μg L^{-1}) > Ti (2.42 μg L^{-1}) > V (1.46 μg L^{-1}) > Pb (0.92 μg L^{-1}) > U (0.87 μg L^{-1}) > As (0.59 μg L^{-1}) > Co (0.57 μg L^{-1}) > Mo (0.33 μg L^{-1}) > Sb (0.09 μg L^{-1}) > Cd (0.05 μg L^{-1}). The values of heavy metals were compared with the recommended values of WHO (2022) and SanPiN 2.1.4.1074-01 (2001) to determine the quality of drinking water. The results of the comparison showed that the allowable limits for Fe and Mn were exceeded; for the other studied metals, the concentrations were significantly below the allowable limits. In some cases, increased mineralisation and general alpha activity were observed in groundwater.

The study of heavy metals in snow showed a similar order of decrease in the concentrations of soluble fractions of metals to groundwater, which indicates the migration of heavy metals into groundwater after the spring snowmelt. A comparison of the average metal concentrations in groundwater and melted snow showed that significant differences in the metal concentrations in groundwater and snow were observed only for Fe and Mn – the concentration of iron and manganese in groundwater was about 10 times higher than in snow. At the same time, the concentrations of other metals in the snow – Zn, Cr, Ni, Cu, Ti, V, Pb, As, Co, Mo, Sb, and Cd were generally comparable with the concentrations in groundwater, which may indicate that melted snow was the main source of heavy metals in groundwater. According to the values of the total areal pollution of the snow cover with all the studied heavy metals, the most polluted were suburban community garden plots in the area of the Arkhangelsk city – 216.91 mg/m^2.

According to the ratio of soluble and insoluble forms of heavy metals in the snow of the

Arkhangelsk agglomeration, the studied elements were divided into three groups: high (Cr and Mo), medium (Ni, Cd, Zn, As, Mn, V, and Co) and insoluble (Ti, Fe, Cu, Pb, and Sb).

The PCA results showed that the main sources of snow cover pollution with heavy metals in the suburban areas of the Arkhangelsk agglomeration were thermal power plants, machine-building and metallurgical plants, the solid waste landfill, and vehicles.

The values of the HMPI water quality indicator were at a low level of pollution, which indicates a weak anthropogenic impact on the study areas. However, the indices for assessing the amount of metals HMEI, toxicity HTML, non-carcinogenic risk HI, and carcinogenic risk CR indicated a high degree of contamination of some of the studied waters with heavy metals. Most of the studied waters and melted snow were not suitable for use as drinking water. The greatest contribution to the quality indices of the studied waters was made by such metals as Fe, Mn, Ni, Cu, and Pb; therefore, it is necessary to take measures to reduce the concentrations of these metals in atmospheric fallout.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practices in the research.

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