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Trace Element Distribution in the Snow Cover of Different Functional Zones in Berezniki-Solikamsk Industrial Hub, Russia

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ABSTRACT

The current study considered the distribution of trace elements in snow cover taking into account the functional zoning of the territory of Berezniki-Solikamsk industrial hub, Perm Region, Russia. The concentrations of 22 trace elements were determined in the dissolved phase of snowmelt using ICP-MS method. On the basis of on the background approach, it was found that Ni, Se, Cu, and Sn are actively accumulated in the snow cover. Snowmelt surface runoff during snow melting period significantly contributes to the total watershed discharge of rivers; therefore, the compliance with the Russian fishery quality standards was assessed. It was found that meltwater is the source of Cu, Mn, Se, Zn, V in surface waters. Significant concentrations of Pb, Cd, W, As, Se in snow are characteristic of conditionally background sites in comparison with average values of global concentrations of dissolved trace elements in river waters, and Se, W, Pb, Ni, As, Cd are characteristic of all functional zones. This study presented the possible sources of priority pollutants. The greatest technogenic impact was observed in the area of transport infrastructure development. Upon that, recreational and residential functional zones also experience significant anthropogenic impact. In order to create a comfortable and healthy urban environment it is necessary to implement the measures to restore these areas.

Keywords: trace elements, snowmelt, contamination, source identification, ecological risk assessment

INTRODUCTION

Nowadays, there are many approaches to assessing snow cover, depending on the objectives. For example, geochemical and mineralogical studies focused on studying the albedo parameters in snow cover and glaciers in order to model distributed energy balance of snow and predict snow melting [Pey et al., 2020; Schmale et al., 2017]. Estimating the contribution of meltwater runoff to total watershed discharge is conducted using various approaches such as direct discharge measurement, hydrological balance equations, hydrochemical tracers, and hydrological modeling [La Frenierre et al., 2014]. Changes in major ions and trace element composition of snow in both the dissolved and particulate phase were also studied [Moskovchenko et al., 2020; Vlasov et al., 2020]. Particulate matter found in the snow cover proves the relationship between air pollution and respiratory diseases in the population due to the intake of pollutants from different sources [Manisalidis et al., 2020; Jiang et al., 2016]. Concentrations of elements in the dissolved phase are indicative of anthropogenic sources with long-range transport of pollutants [Siudek et al., 2015]. The studies demonstrate impact of snow cover on the chemical composition of rivers and lakes [Shevchenko et al., 2017, Yuan et al., 2018].

Active global industrialization has led to the changes in trace elements in the dissolved phase of snow. Moreover, the concentrations of elements in snow in urban areas coming from local sources such as traffic and road maintenance can exceed the concentrations associated with deposition of pollutants from the atmosphere by two orders of magnitude. Thus, the concentrations of elements in roadside snow were higher in Trondheim (Norway) than in Luleå (Sweden), because of the higher traffic speed in Trondheim (by 20%

on average). In both cities, the distribution of elements in descending order is as follows: Zn > Cu > Cr > Ni > Cd [Moghadas et al., 2015]. High content of Pb, Ni, Zn and Cr in the snow cover of Poznań (Poland) is conditioned by the contribution of anthropogenic sources in the surrounding area (i.e. road traffic, fossil fuel combustion, industrial processes, soil/dust resuspension and interregional transport) [Siudek et al.,2015].

The studies conducted in Western Siberia [Shevchenko et al., 2015] demonstrate significant and previously underestimated impact of snowmelt that enters rivers during spring floods amid snowmelt. For example, in the permafrost zone, more than 50% of the river flow during the spring flood can be provided by snowmelt. In Beijing (China), high concentrations of elements in snow as a result of snowmelt pose a potential risk to the condition of water bodies in the city due to the entry of Cd, Cu, and PAHs [Yuan et al., 2018]. A comparative analysis of snow cover and soils in St. Petersburg revealed the relationship between a broad list of trace elements that form the following geochemical series according to the concentration factor for soils – Zn > Cu > Pb > Cr > Ni, for snow – Zn > Ni > Cu > Cr > Pb. For example, high positive correlation by Zn with the total pollution index Zc in the snow cover and soil was found [Lebedev and Agafonova, 2017].

Researchers indicated heavy metal pollution of snow cover in the following Russian cities: Tyumen, Irkutsk, Vorkuta, and Blagoveshchensk [Vasilevich et al., 2019; Moskovchenko et al., 2020; Grebenschikova, 2013; Radomskaya et al., 2018]. Only Moscow and St. Petersburg have a sufficient network of stationary and mobile snow melting facilities for urban snow disposal and subsequent management of melt water. In most regions, meltwater is a potential pollutant of water and soil systems within urban areas during snowmelt.

Over the last decades, little attention has been paid studying trace elements in the dissolved phase of snowmelt in the northern Prikamye (Russia) as well as their distribution and possible sources of input. The volume of pollutant emissions into the atmospheric air on the territory of Perm Region (Russia) increases every year. Thus, in 2020, the emissions from mobile and stationary sources amounted to 300.3 thousand tonnes per year and 308.9 thousand tonnes per year, respectively [Report, 2020].

The territory of the Berezniki-Solikamsk industrial hub is one of the most technogenically affected in Perm Region, due to a large number of industrial and mining facilities located in the area. The results of the assessment of principal ions in the snow cover within the industrial agglomeration of Berezniki indicate transformation of the chemical composition of the snow cover in different functional zones. It was found that the distribution of principal ions in snowmelt of the industrial zone is as follows: K^+-Na^+-Cl^-; in the recreational zone – Ca^{2+}- HCO_3^-; in the residential zone – Ca^{2+}-NO_3^- HCO_3-; in the transport zone – Na^+- HCO_3^- [Khayrulina and Ushakova, 2020]. On the basis of the microelement assessment in Berezniki, it was found that recreational areas (recreational zone) are exposed to an increased technogenic impact relative to the industrial ones, where the total pollution index Zc was 33.6 and 30.1, respectively [Ushakova et al., 2020].

This research was aimed at assessing the spatial distribution of trace elements in the snow cover within the Berezniki-Solikamsk industrial hub, where significant urbanization of the territory is coupled with an increased industrial potential.

MATERIALS AND METHODS

The Berezniki-Solikamsk industrial hub is a large mining center, comprising chemical, pulp and paper, oil refining, logging and woodworking facilities located between 59°21′ and 59°45′ north latitudes and 56°39′ and 56°53′ east longitudes in Perm Region (Russia).

The snow samples were collected at the end of the season of stable snow cover before snowmelt (last ten days of March 2020). The snow was sampled taking into account the zones of functional purpose. There were 27 observation points: 8 points were located in the industrial zone, 5 points – in the zone of engineering and transport infrastructure, 7 points – in the recreational zone, and 7 points – in the residential zone (Figure 1). The average values of 7 samples taken in 2020 in the north-east of Solikamsk urban district at a considerable distance from the sources of anthropogenic impact were used as a conditional background.

The sampling sites were selected in the snow massif at a distance of 5 m at most from the roads with undisturbed initial snow cover, no traces of artificial snow dumping or clearing, no inclusions

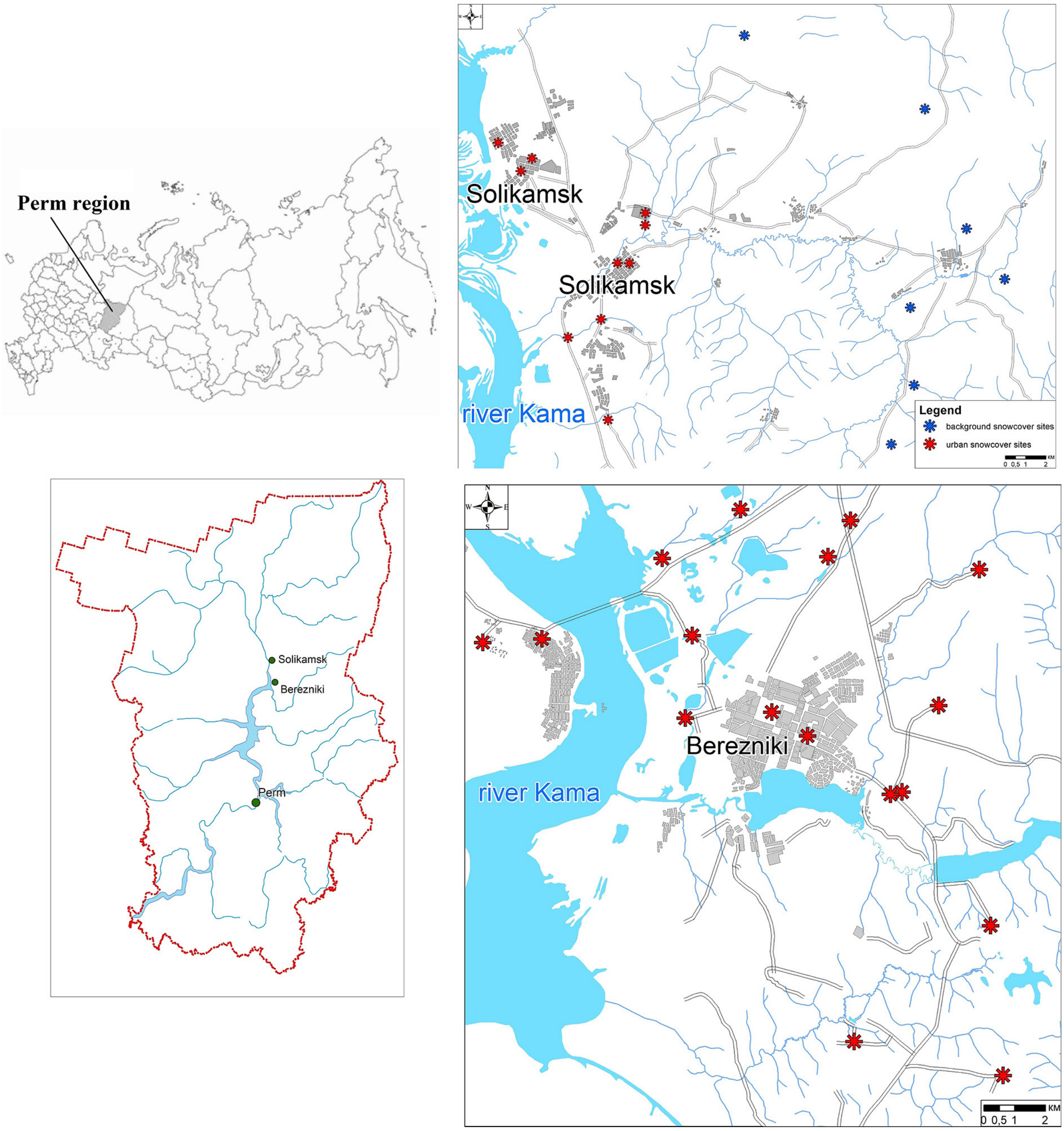

Fig. 1. Location map of the study area in the Berezniki-Solikamsk industrial hub of Perm Region (Russia)

of domestic and industrial waste, no pollution, no traces of skiing, etc., taking into account the functional use of the territory. The snow samples in the form of vertical columns with undisturbed structure (core samples), were cut out to the full thickness of the snow cover using a standard weighing snow gauge VS-43, which is widely used for snow surveys in Russia.

The snow samples were melted at a room temperature. The pH of snowmelt was determined by the potentiometric method. All samples were studied at the Centre for the Collective Use of Unique Scientific Equipment of Perm State National Research University. The content of trace elements (Li, V, Ti, Al, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Cd, Sn, Sb, Ba, W, Pb) was determined by mass spectrometry using Bruker Aurora M90 ICP-MS. The accuracy of the analysis was verified by analyzing blank samples and certified reference materials conducting the same procedure used for the samples. All samples were analyzed at least twice to assess measurement reproducibility. The samples were reanalyzed if the relative standard deviation of the measurements exceeded > 10%.

Taking into account the fact that meltwater is involved in recharging surface water bodies, the chemical composition of snowmelt was compared with the average global concentrations of dissolved trace elements in river waters and with the Russian fishery standards [Gordeev and Lisitzin, 2014]. The water quality standards for water bodies of fishery significance characterize the water suitability for aquatic biological resources and ensure the safety of products from it.

Assessment of trace elements contamination in the snowmelt was carried out using the contamination factor CF (ratio of chemical element concentration to its background content). The standard CF classification was used, where values as follows: CF <1 – low contamination, 1<CF<3 – moderate contamination, 3<CF<6 – considerable contamination and CF>6 – very high contamination [Custodio et al., 2021].

The total elemental pollution is given using the pollution load index (PLI) [Tomlinson, 1980]. The PLI is calculated as follows Equation (1):

$$PLI = \sqrt[n]{CF1 \times CF2 \times \ldots \times CFn} \qquad (1)$$

where: n is the number of trace elements, and
CF is a contamination factor determined for each element under study, which is one of the most recognized and effective tools for monitoring concentrations of these elements. On the basis of on PLI, melted snow can be divided into two classes: without contamination (PLI < 1) or with contamination (PLI≥1).

The method of assessing the potential ecological risk index (RI) of heavy metal pollution formulated by Hakanson (1980) is actively used by researchers in the assessment of bottom sediments, soils, dust, and dissolved phase in snowmelt [Yuan et al., 2014; Moskovchenko et al., 2020]. This method takes into account not only the content of heavy metals in soil, dust, etc., but also the possible negative ecotoxicological consequences of pollution [Yuan et al., 2018]. According to this method, the potential ecological risk factor is calculated using the coefficient E_r^i (2):

$$RI = \sum_{i=1}^{n} E_r^i = T_r^i \times CF \qquad (2)$$

where: CF is the contamination factor,
T_r^i is the toxicity response coefficient.

In this study, the response T_r^i values we used according to references [Yuan et al., 2014; Jiao et al., 2015; Nkansah et al., 2017], as follows: Ti, Zn, Mn, W, Sr, Ba = 1; V, Cr, Mo, Sn = 2; Pb, Cu, Co, Ni, Sb = 5; As = 10, Cd = 30. For risk assessments the following classification we adopted: E_r^i < 40 indicates low risk; 40 < E_r^i < < 80 indicates moderate risk; 80 < E_r^i < < 160 indicates considerable risk; 160 < E_r^i < < 320 indicates high risk; E_r^i < > 320 indicates extreme risk. RI was classified into four levels: RI < 150, low risk; 150 < RI < 300, moderate risk; 300 < RI < 600, considerable risk; RI > 600, high risk.

All calculations and figures were completed using Statistica 10.0 and Excel 2013. Pearson's correlation coefficients (r) were calculated to determine the relationships among different trace elements in the snowmelt. Cluster Analysis was used to group elements into meaningful groups (clusters) based on their concentrations at each sampling site snow for the whole study area (the method by Ward was used for data agglomeration).

RESULTS

Trace element concentrations in snow

Table 1 presents generalized data on the concentrations of trace elements in snow within the study area taking into account the functional use of the territory.

The acidity of background snow melt water is characterized by an alkaline environment at pH 7.46–8.91, with an average of 8.41. The snowmelt from the industrial hub is characterized by a hydrocarbonate-calcium composition with a wide pH range of 6.6–7.5, with an average of 6.88. In relation to background snow melt water, acidification of precipitation within the Berezniki-Solikamsk industrial hub is observed due to the emissions of sulfur compounds from enterprises and motor transport.

The transport and industrial functional zones are characterized by the presence of alkaline waters at an average pH of 7.06 and 6.90, respectively. In general, these zones have the highest concentrations of elements in snowmelt relative to other zones. In the transport functional zone, the maximum concentrations of Ni, Zn, Se, Rb, Sr and Ba are noted, whereas in the industrial zone – Al, Ti, Mn, and Cu. The main source of the high concentrations in the transport zone involves the emissions from motor transport and operation as well as treatment of roads with de-icing agents in

Table 1. Concentrations of trace elements in snowmelt in different functional zones (μg L^{-1})

TE	Transport (n=4)			Industrial (n=9)			Recreational (n=7)			Residential (n=7)			Background	MPC
	Min.	Max	Mean	Min.	Max	Mean	Min.	Max	Mean	Min.	Max	Mean		
Li	0.02	0.12	0.07	0.06	0.18	0.11	0.11	0.19	0.15	0.12	0.19	0.17	0.24	80
Al	1.21	10.38	6.53	3.06	22.74	8.57	2.75	9.03	7.11	6.51	9.36	8.07	–	40
Ti	0.23	3.73	1.37	0.07	11.83	1.70	0.09	1.00	0.33	0.001	0.33	0.19	4.96	60
V	0.02	0.27	0.14	0.04	0.28	0.14	0.01	1.35	0.22	0.003	0.13	0.06	0.73	1
Cr	0.15	0.73	0.45	0.12	0.57	0.35	0.07	0.21	0.15	0.02	0.26	0.10	1.33	20
Mn	2.15	31.74	10.89	1.43	68.34	15.43	1.27	9.43	3.60	0.78	11.18	4.03	10.13	10
Co	0.02	0.17	0.07	0.05	0.88	0.11	0.003	0.16	0.03	0.005	0.19	0.04	0.17	10
Ni	0.84	1.48	1.28	0.84	1.46	1.04	0.78	1.00	0.91	0.78	0.97	0.86	0.13	10
Cu	0.65	3.36	1.83	0.76	4.75	1.81	0.53	2.82	1.35	0.35	1.94	1.09	0.42	1
Zn	0.19	15.02	2.29	1.02	9.97	6.21	0.76	5.64	3.54	0.59	9.33	4.94	2.29	10
Ga	0.04	0.16	0.11	0.03	0.22	0.09	0.05	0.10	0.08	0.05	0.12	0.08	0.11	-
As	2.08	5.00	3.67	2.43	5.93	3.82	2.24	5.87	3.62	2.01	5.92	4.19	8.22	50
Se	1.82	6.17	3.72	3.26	5.53	4.32	2.54	6.08	3.68	2.34	5.11	4.02	0.61	2
Rb	0.22	1.23	0.61	0.17	1.08	0.47	0.20	0.60	0.32	0.15	0.52	0.30	0.57	100
Sr	12.27	21.34	17.48	4.03	16.70	10.38	5.18	11.68	8.87	4.86	9.95	6.96	50.72	400
Mo	0.002	0.039	0.019	0.004	0.15	0.04	0.002	0.06	0.02	0.003	0.03	0.02	0.03	1
Cd	0.01	0.05	0.02	0.01	0.03	0.02	0.01	0.04	0.02	0.009	0.02	0.02	0.14	5
Sn	0.03	0.08	0.06	0.03	0.09	0.06	0.03	0.09	0.06	0.05	0.08	0.06	0.03	112
Sb	0.05	0.10	0.08	0.01	0.23	0.09	0.004	0.08	0.04	0.004	0.08	0.03	0.04	-
Ba	3.86	26.11	11.75	3.01	18.46	9.70	4.67	16.40	11.20	2.19	22.42	9.15	6.69	740
W	0.08	0.29	0.15	0.004	0.16	0.12	0.03	0.17	0.12	0.11	0.19	0.15	0.19	0,08
Pb	0.23	0.70	0.41	0.24	1.12	0.39	0.23	0.53	0.29	0.20	0.37	0.26	0.76	6

winter whereas the main source, in the industrial zone corresponds to industrial enterprises. For example, the sampling point with the maximum Al and Mn content is located near the facility for mining and processing of potassium-magnesium salts, the maximum concentration of Ti is associated with the facility producing ingots and mill products in titanium alloys, the maximum concentration of Cu is associated with a thermal power plant.

Alkaline snowmelt at an average pH of 6.85 and 6.79 were noted in the recreational and residential zones, respectively. In the residential zone, the maximum content of As was noted; in fact, the average content is also higher relative to other zones. The average content of Al, Zn and Se in the residential zone is higher than in the transport and recreational zones. Maximum concentrations only for V are noted in the recreational zone, and the average content of Ba stands at the level of the transport zone.

Due to the low population density, considerable remoteness from other industrial centers, and smaller volume of pollutant emissions into the atmosphere compared to Irkutsk and Blagoveshchensk, there is no significant acidification of precipitation in the study area as opposed to the regional pH background for Irkutsk (5.75) and fo Vorkuta (5.02). It is worth mentioning that alkalization of atmospheric precipitation depends on carbonate dust, the ingress of which is associated with both the underlying surface and, accordingly, the geological structure of the area, as well as with the building structures. Taking into account the alkaline environment of snowmelt, the migration activity of the elements will be different.

The conditional background concentrations of most of the studied elements in the snowmelt from the urbanized area (Table 1) are significantly lower than the average global concentrations of dissolved trace elements in river water. The exception is the content of Pb, Cd, W, As, Se, which was exceeded 3–7 times, the values of Cr, Mn, Ga were at the level of the average global concentrations. Such a comparison for the samples of snowmelt from urban areas demonstrates a significant excess of Se, W, Pb, Ni, As, Cd that are typical for all functional zones (Figure 2).

In snowmelt, excesses in terms of the fishery standards were recorded for Mn up to 6.8 times, Cu up to 4.7 times, W up to 3.6 times, Se up to 3.1 times, Zn up to 1.5 times, V up to 1.3 times.

It should be noted that melting water is one of the main sources of ground and surface water supply in the region. The result of pollutants entering the local river systems during snowmelt will be the accumulation of elements in fish organs and tissues [Moiseenko and Gashkina, 2016].

Ecological risk of the trace elements in snowmelt

The calculated PLI values of metals in snowmelt are summarized in Table 2. According to the PLI classification, all functional zones are classified as polluted (PLI>1) with very high contamination as per CF by the following elements: Ni, Se and Cu. The highest values of the contamination factor by Ni (CF>10) are seen only in the transport functional zone. In addition, this zone is characterized by the largest list of trace elements Ni, Cu, Se, Zn, Sn, Sb, Mn, and Ba, the content of which exceeds the background values.

High industrial potential in the studied urbanized area in the residential and recreational zone indicated by the results of CF calculation showed very high contamination by Ni and Se, with the smallest list of elements exceeding the background concentrations. It should be noted that the concentration of Ni is 2–4 times lesser and concentration of Cu is 3 to 4.6 times lower than those in Irkutsk, Tyumen, Blagoveshchensk [Vasilevich et al., 2020; Grebenschikova, 2013; Radomskaya et al., 2018].

The distribution of trace elements (Table 2) shows that the developed transport infrastructure and proximity of industrial enterprises to the residential and recreational zones in the study area negatively affect the snow cover due to the input of Ni, Cu, Se, Zn, Sn, Sb, Mn, and Ba. The studies conducted in 2018 in Berezniki, showed the highest Zc in the recreational zone, which corresponded with high level of pollution [Ushakova et al., 2020]. High anthropogenic impact is characteristic of the recreational zones of many industrial centers. For example, in Yekaterinburg, Kolchugino, the priority pollutants in soils are Pb, Cu, Ni, Cr, and Zn [Trifonofa et al., 2018; Baitimirova et al., 2020]. All of this sets an objective to control the ecological state of these areas with the subsequent implementation of measures for their restoration.

The values of the ecological risk factor (E_r^i) by element varies from 0.1 to 49.3, which corresponds with ecological risk categories from low to moderate. Only in the transport functional zone, a moderate category of ecological risk by Ni is noted. In other functional zones, the values (E_r^i) indicate low category of ecological risk. The index of potential ecological risk (RI) in all functional zones corresponds with low ecological risk: transport zone – RI (108.5); industrial zone – RI (101.6), recreational zone – RI (78.8), residential zone – RI (72.6).

Statistical analysis

A correlation matrix, showing the relationships between trace elements at the significance level $p < 0.05$ and $p < 0.01$, is shown in Table 3. A significant positive relationship ($r = 0.70$ to 0.86; $p < 0.01$) was identified between Pb – Ti, Ti – Ga and Mo, As – Se; Cu – Rb. A weaker correlation was found between the contents of the following elements: Pb-Ga (r=0.68), Ti-Sn (r=0.65), Ti-Cr (r=0.66), Mn-Al (r=0.62), Cr-Sb (r=0.61), Ni-Zn (r=0.58), Ni-Sr (r=0.58), Pb-Ga (r=0.57), Sb-Cu (r=0.56), Cr-Ni (r=0.53), Ni-Cu (r=0.52), Ni-Co (r=0.52), Ti-Sb (r=0.51),

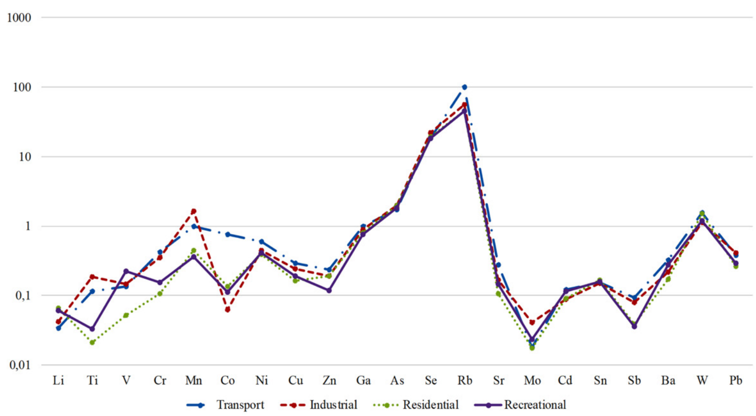

Fig. 2. Geochemical specificity of snowmelt in view of comparison with the average global concentrations of dissolved trace elements in river waters (μg L^{-1})

Table 2. Quantitative distribution of trace elements in the composition of snow cover on the territory of the Berezniki-Solikamsk industrial hub

Functional zone	Contamination factor			PLI
	CF>6	6>CF>3	3>CF> 1	
Industrial	Ni_8, Se_7	Cu_5, Mn_4	Sn, Zn, Sb,	1.19
Transport	Ni_{10}, Cu_6	Se_5, Zn_3	Sn, Sb, Mn, Ba	1.20
Recreational	Ni_7, Se_6	Cu_4, Sn_3	Zn, Sb,	1.18
Residential	Ni_7, Se_6	Cu_4, Sn_3	Ba, Zn	1.18

Cr-Ga (r=0.51), and Sb-Ga (r=0.49). There was a strong negative relationship (r>0.70; $p < 0.01$) between Sn-Pb and Sn-Ga.

The dendrogram of the hierarchical cluster analysis for the trace elements contents in the studied snowmelt shown in Figure 3. In general, the results of cluster analysis agree very well with correlation analysis in that the grouped elements come from another sources of pollution. The dendrogram shows two clusters with subclusters. Cluster I contained Ti, Ni, Cu and Rb, Pb, Cr, V, Co, Sn, Cd, Mo, Sb, Ga, W, and Li. The Ni and Cu elements show high mean concentrations, compared with the background values in the studied area. Moreover, an excess of Cu relative to the MPC of for fishery water bodies was found. The presence of two subclusters can be explained by mixed of sources pollution. Cluster II consisted of Al, Zn, As, Se, Sr, and Ba. However, was observed, that this group of elements joins with Mn.

Trace metals in the snow cover – comparison with other locations

The analysis of background concentrations of trace elements in snow melt water of the study area (Figure 4) has considerable variation relative to other background areas of Russia [Vasilevich et al., 2020; Grebenschikova, 2013; Radomskaya et al., 2018]. The background concentrations in this study are characterized by significant excesses of V, As. Rb, Sr, W and, to a lesser extent, Cd and Pb relative to other areas, which is probably a regional specific feature of the territory.

Table 3. Pearson correlation coefficients for the measured trace elements (n = 27)

TE	Li	Al	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	As	Se	Rb	Sr	Mo	Cd	Sn	Sb	Ba	W	Pb
L	1.00																					
Al	0.03	1.00																				
Ti	-0.35	-0.01	1.00																			
V	-0.01	-0.08	0.10	1.00																		
Cr	-0.63**	-0.17	0.66**	0.18	1.00																	
Mn	-0.42*	0.62**	0.03	-0.10	0.05	1.00																
Co	-0.05	-0.17	-0.08	-0.06	0.14	-0.01	1.00															
Ni	-0.47*	-0.22	0.09	-0.06	0.53**	0.30	0.52**	1.00														
Cu	0.00	-0.29	-0.07	-0.04	0.30	-0.05	0.33	0.52**	1.00													
Zn	-0.17	-0.07	0.17	0.03	0.14	0.50*	0.28	0.58**	0.25	1.00												
Ga	-0.23	0.02	0.77**	-0.05	0.51**	-0.05	-0.02	-0.02	-0.04	-0.04	1.00											
As	0.00	0.23	-0.08	-0.30	-0.24	0.20	-0.27	-0.33	-0.15	-0.20	0.37	1.00										
Se	-0.19	0.08	0.37	-0.16	0.23	0.12	-0.15	-0.12	0.03	-0.07	0.65**	0.78**	1.00									
Rb	-0.08	-0.05	-0.08	-0.04	0.30	-0.13	0.54**	0.46*	0.72**	-0.03	0.03	-0.21	-0.08	1.00								
Sr	-0.55**	-0.10	-0.10	-0.07	0.41*	0.14	0.22	0.58**	0.33	-0.03	0.01	-0.17	-0.23	0.54**	1.00							
Mo	0.04	-0.06	0.73**	0.02	0.36	-0.11	-0.10	-0.05	-0.06	0.08	0.41*	-0.12	0.17	-0.17	-0.31	1.00						
Cd	0.19	-0.17	-0.08	0.12	0.20	-0.23	0.31	0.37	0.65**	0.13	-0.14	-0.47*	-0.37	0.64**	0.31	-0.06	1.00					
Sn	0.09	-0.04	-0.65**	0.13	-0.38*	0.06	-0.03	-0.07	-0.14	-0.03	-0.71**	-0.28	-0.55**	-0.10	0.14	-0.35	0.01	1.00	-			
Sb	-0.26	-0.32	0.51**	0.13	0.61**	-0.09	0.31	0.37	0.56**	0.23	0.49**	-0.21	0.17	0.48*	0.24	0.33	0.31	-0.30	1.00			
Ba	0.12	0.02	-0.30	-0.07	0.12	-0.13	0.34	0.27	0.31	-0.36	-0.16	-0.19	-0.27	0.48*	0.53**	-0.24	0.44*	0.08	0.05	1.00		
W	-0.03	-0.49*	0.16	0.20	0.27	-0.52*	0.13	0.07	0.01	0.01	0.25	-0.13	0.07	0.07	-0.13	-0.10	0.04	-0.29	0.15	-0.09	1.00	
Pb	-0.30	-0.02	0.86**	0.08	0.73**	-0.11	-0.06	0.16	0.09	0.05	0.68**	-0.10	0.34	0.10	-0.04	0.57**	0.09	-0.76**	0.47*	-0.12	0.31	1.00

Note: * $p < 0.05$. ** $p < 0.01$.

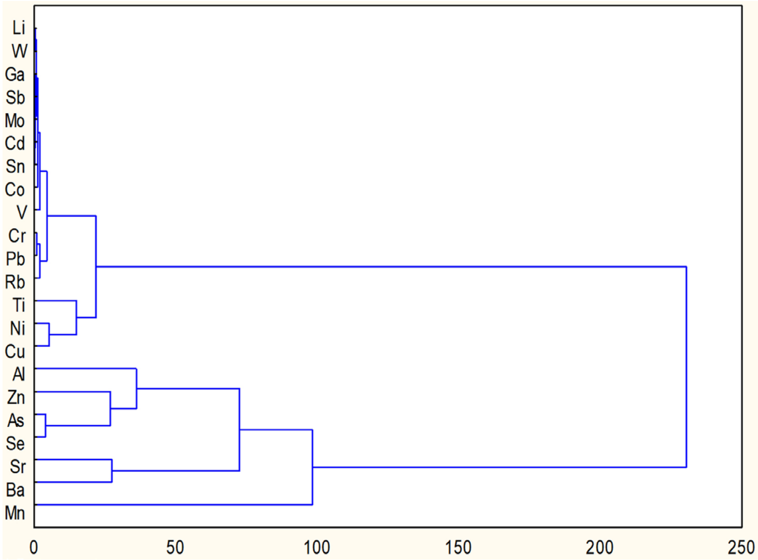

Fig. 3. Cluster analysis of the trace element distribution patterns using Ward's method with the squared Euclidean distance

The generalization of trace elements in the dissolved phase of snowmelt in the conducted study is reduced to a comparison of a small list of elements in other urbanized territories with an increased industrial potential (Table 4).

The results of the annual report in the environment showed that from 2015 to 2019 on the territory of Berezniki there was a tendency of air pollution with the following heavy metals: Fe, Cd, Mn, Cu, Ni, Cr and Zn. However, a comparison of elements concentrations with other territories indicates insignificant pollution of atmospheric air within the study area.

The data from the Voeikov Main Geophysical Observatory indicates the highest level of atmospheric air pollution in Irkutsk and Blagoveshchensk. Therefore, all concentrations in snowmelt in these cities are higher than the values in the Berezniki-Solikamsk industrial hub, Tyumen, and Vorkuta. At the same time, the average content of Mn, Zn, and Cr in the study area is 2.7; 1.4; and 1.3 times higher than in Vorkuta, respectively. However, the As content in the study area is 4.7 times higher than in Irkutsk and 3 times higher than in Blagoveshchensk, which is conditioned by the increased geochemical background. The concentrations of other elements are at intermediate levels and fit into the range of variations found in Tyumen. However, the concentrations of Ni, Cu, Zn, Sr and Ba in Tyumen are higher relative to the study area due to the emissions from the metallurgical enterprises and oil production and processing facilities located in that region.

Sources of elements in the snow cover

The application of the background approach in assessing the pollution of the snow cover in the urban area, using such indicators as the contamination factor (CF) and potential ecological risk factor (E_r^i), revealed the priority pollutants with the highest Ni, Se, and Cu pollution only in the transport functional zone. The results of cluster analysis also showed Ni and Cu, Se and As in the same cluster, which is confirmed by their positive correlation with each other. The absence of As in the geochemical association in the urban area is explained by high concentrations within the background area. Thus, these elements came from different sources. The main pollution sources of Ni and Cu in snow roadside were attributed to vehicular transportation (vehicle operation, including exhaust emissions, motor fluid leaks, and wear and tear) [Meland et al., 2010; Müller et al., 2020].

In the study area, crude oil production and refining facilities can be considered as the possible sources of the As and Se input in the atmospheric air. It is believed that wet deposition of selenium brings 5610 tonnes per year to land. For example, in the UK, wet deposition (rain, snow, etc.) accounts for 76–93% of total deposition, with 70% of selenium in a soluble form [Fordyce, 2013].

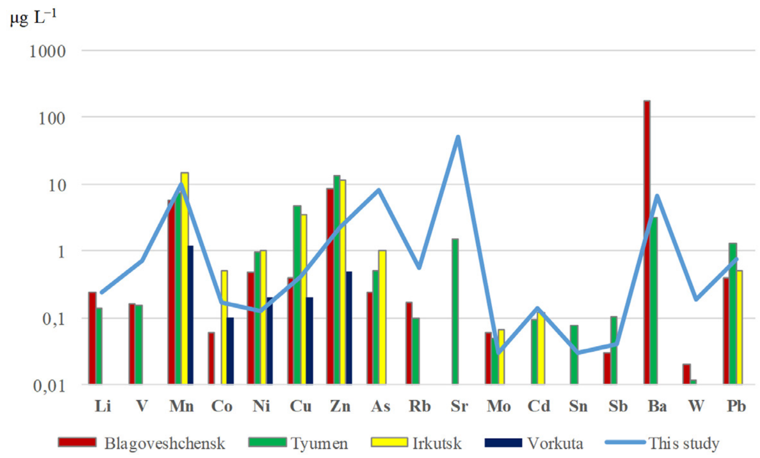

Fig. 4. Comparison of background concentrations in this study with other areas

The increased Se content is also fixed in such sediments as limestones, sands, and mudstones which are present in the study area, which suggesting a possible influence of the underlying surface on the composition of the snow cover.

When assessing the level of contamination of urban snow elements V, As, Rb, Sr, W are absent in the geochemical association in a series of elements accumulated due to increased natural background which confirms the comparative analysis with the data from other areas. Elevated concentrations of As and Sr within the Berezniki-Solikamsk industrial hub are also observed in soils, surface waters, groundwater and bottom sediments [Voronchikhina and Zhdakaev, 2019; Belkin, 2018; Karfidova and Sizov, 2020; Khayrulina, 2014]. For example, the V emissions in Western Europe are associated with port activity and oil refinery operation. Vanadium is present in both crude oil and coal, and is also used mainly in the steel industry to produce high-strength and low alloys. Due to the effect of submicron particles of vanadium in the atmospheric air, long-range transport is possible, which implies transboundary transfer of the pollutant [Visschedijk, 2013].

The Rb input into the atmospheric air is associated with the marine origin, as there is a clear pattern of the element concentration decrease when moving deep into Antarctica from the coastline [Thamban and Thakur, 2013]. The study area is located at a considerable distance from the sea coast, but the possible source of the input of this element in the atmospheric air is the potassium industry enterprises, namely the emissions from enrichment plants, ventilation shafts of mines and dusting of salt tailings piles. One-time exceedances of Rb in the transport functional zone are associated with the treatment of roads with de-icing agents. The results of trace elements assessment of snowmelt showed the association, to a large extent with the sources of entry, which should be studied in more detail, since snowmelt has a high potential for the spread of these pollutants. In order to minimize the entry of pollutants into urban rivers as well as into soils, the implementation of stationary or mobile snow-melting facilities in the study area is necessary.

CONCLUSION

Within this research, a spatial analysis of trace elements from the dissolved phase in snowmelt samples collected from four different functional zones of the urban area was conducted. The concentrations of 21 elements were measured in snow samples collected in the urban area of Berezniki (Perm Region, Russia). The concentrations of Mn, Cu, W, Se, Zn, and V exceeded the norms of water quality of fishery water bodies, which characterize its living suitability for aquatic biological resources and ensure product safety. Some of the maximum element concentrations (μg L^{-1}) were ranked as follows: Mn (68.34) > Ba (26.11) > Al (22.74) > Sr (21.34) > Zn (15.02) > Ti (11.83). In general, the CF values for Ni, Se, and Cu were greater than 6. The highest technogenic impact was recorded in the transport and industrial zones with PLI of 1.20 and 1.19, respectively.

The (E_r^i) value of all trace elements except Ni was below 40, indicating low risk. The RI value for all functional zones ranged from 72.6 to 108.5, indicating low ecological risk. Taking into account

Table 4. A comparison of trace element concentrations in snow from different locations μg L^{-1}

TE	This study	Vorkuta, Russia Vasilevich et al., 2019	Irkutsk, Russia Grebenschikova 2013	Blagoveshchensk, Russia Radomskaya et al., 2018	Tyumen, Russia Moskovchenko et al., 2020
Li	0.131	–	2.33	1.7	0.88
Al	7.76	36.0	83.0	490	14
Ti	0.906	–	–	–	-
V	0.142	10.0	2.44	3.4	0.16
Cr	0.247	0.19	0.4	–	-
Mn	8.733	3.2	36.0	92	1.8
Co	0.066	0.035	0.77	0.7	-
Ni	0.994	2.2	2.0	2.5	4.3
Cu	1.508	0.72	7.0	4.7	4.9
Zn	5.224	1.6	40.0	9.8	10.0
Ga	0.086	–	–	–	-
As	3.841	–	0.8	1.7	0.44
Se	3.986	–	–	2.1	-
Rb	0.408	–	0.61	3.1	0.37
Sr	10.153	–	27.0	–	30.0
Mo	0.026	–	0.7	2.5	0.24
Cd	0.020	<0.20	0.1	0.02	0.05
Sn	0.062	–	–	–	0.079
Sb	0.059	–	–	0.92	0.35
Ba	10.252	–	40.0	160	59.3
W	0.130	–	–	1.2	0.11
Pb	0.334	–	0.5	0.34	0.34

the industrial characteristics of the study area and a small number of recreation areas (squares, parks) within the city, the existing recreational areas experience a technogenic impact due to the inflow of Ni, Cu, Se, Zn, Sn, Sb, Mn, and Ba into the snow cover. During snowmelt, increased concentrations of Cu, Mn, and Se will enter the local river systems with snowmelt surface runoff, which may affect the trace element composition of river water and bottom sediments. When compared with the findings of studies from other locations, it was determined that anthropogenic activities have greater effect on the quality of snowmelt in Irkutsk and Blagoveshchensk than in the present study.

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