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ECOLOGICAL PROBLEMS IN PERMAFROST ZONE

SPATIAL DISTRIBUTION OF GEOCHEMICAL CHARACTERISTICS OF SNOW COVER WITHIN AND OUTSIDE TOMSK-SEVERSK INDUSTRIAL AGGLOMERATION

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The ability of snowpack to accumulate airborne substances allows analyzing spatiotemporal geochemical patterns and detecting polluted areas. Spatial features of geochemical regional distribution of dust deposited in the snow cover in areas remote from industrial centers are determined. The snowpack of Tomsk, Shegarka and Kozhevnikovo districts in the Tomsk Oblast was chosen to be the object of this research. The observations were carried out in the period from 1995 to 2000. The measurements of snow meltwater filtrate included: pH, concentrations of nitrate and ammonia nitrogen, phosphorus, potassium, calcium, magnesium, sodium, chlorine, while the solid residue was analyzed for heavy metal contents (Cu, Zn, Cd, Pb, Co, Mn, Cr, Ni) using atomic absorption spectrophotometry method. The average thickness of snowpack is evenly distributed within the study area and varies from year to year. Contents of dust, ammonia (NH_4^+), phosphorus (P_2O_5), Mg in snow on the forest floor significantly differ (an upward bias) from arable land areas. Ions NO_3^-, NH_4^+, alkaline and alkaline-earth elements show an increasing trend (relative to the background values) near the industrial zone. The levels of siderophilic and lithophilic elements, copper and zinc tend to be enhanced in proximity to the industrial zone of the Tomsk city agglomeration. Lead shows a mosaic distribution throughout the study area. In individual localities (Batkat village, Komarovo swamps), dust and heavy metals contents in snowpack were found to be higher relative to the background values.

Keywords: *solid aerosols, snow, heavy metals, dust, trace elements.*

INTRODUCTION

The seasonal phenomenon of the cryosphere of Western Siberia functions as a system-forming factor in many natural landscapes, which is controlled inter alia by horizontal fluxes of natural and anthropogenic substances [*Bordon, 1996*]. Although the formation of the chemical composition of snowpack in the West Siberian Plain is known to be affected by zonal peculiarities, the macro- and microelement transport (elementary fluxes) into rivers and lakes during the spring flood remains largely underestimated [*Ermolov et al., 2014; Shevchenko et al., 2017*]. The Northern Hemisphere climate warming trends [*AMAP, 2011*] in the Arctic geosystems dynamics marked by a reduction in snow and ice cover and longer ice-free periods of water bodies, have significantly changed major and trace element (TE) fluxes.

Three main approaches which are currently used for monitoring the geochemical properties of an object [*RD 52.04.186-89, 1991*] include: 1) impact estimation (e.g. gas flares), 2) TE pathway analysis, and 3) probabilistic-statistical methods. The impact estimation method is used to investigate objects expressly affecting the snow chemistry [*Chernyaeva et al., 1978; Ermilov et al., 2002; Filimonenko et al., 2013; Yanchenko et al., 2013; Onuchin et al., 2014; Talovskaya et al., 2014a,b; Krest'yannikova et al., 2015*]. The TE pathway method deals with external controls, e.g., natural local climate zones [*Ermolov et al., 2014; Shevchenko et al., 2017*]. The probabilistic-statistical approach is the most appropriate in the absence of visible boundaries of the impact zones and a priori geographic patterns and is therefore interpreted as unbiased in the study of natural ecosystems. In this case, the study area is divided into conditional squares, with one of them selected randomly for observation.

The relevance of this study is less concerned with the identification of ecologically unfavorable areas, with the emphasis placed instead on highly topical recognition of their redistribution patterns at a considerable distance from diverse sources of pollution [*Akba et al., 2013; Xue et al., 2020*] by analyzing the snowpack chemistry, as well as geographical distribution and formation of atmospheric precipitations laden with toxic substances and posing threats to human health.

This work aims to identify the spatial features of the region-scale geochemical distribution of dust aerosol particles deposited in the snowpack in areas located at varying distances from the industrial zone.

The snowpack geochemical monitoring commenced in the Tomsk Oblast in the 1980s included the elemental and chemical composition of snow [*Boyarkina et al., 1993*]. In the 1990s, many Russian regions were exposed to atmospheric air pollution by nitrogen and sulfur oxides (SO_x and NO_x) and heavy metals [*Walker et al., 2003*]. Also worth noting is that, previously, snowpack research was undertaken by scientists from the National Research Tomsk Polytechnic University (TPU), under the guidance of E.G. Yazikov [*Filimonenko et al., 2013; Talovskaya et al., 2014a,b, 2018a*]. This work draws heavily on the data obtained from the snowpack monitoring in the 1990s at the Soil Science Laboratory (headed by L.A. Izerskaya) of the Research Institute of Biology and Biophysics at Tomsk State University.

RESEARCH OBJECTS AND METHODS

The object of the study is the snowpack of background sites in the Tomsk Oblast (Fig. 1). The observation (sampling) points were scattered around the Tomsk-Seversk industrial agglomeration.

The background conditions for substances transport to snowpack, as this is defined by [*RD 52.04.186-*

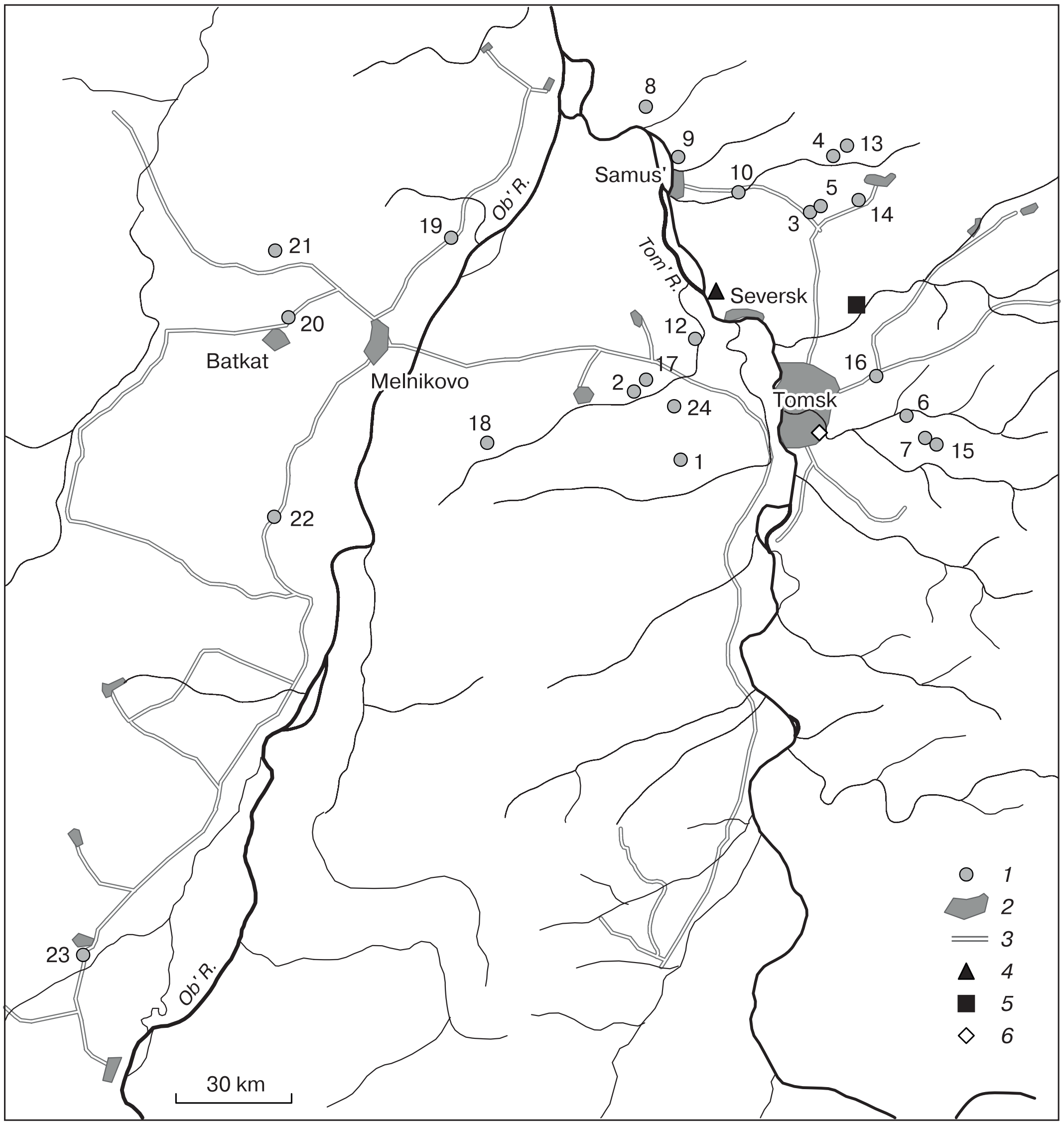

Fig. 1. Sampling points location with indications of the site number and position of air pollution sources.

1 – sampling points (SPs); *2* – settlements; *3* – roads; *4* – Siberian Chemical Combine (SCC); *5* – Tomsk Petrochemical Plant (Tomskneftekhim); *6* – Hydropower plant HPP-2.

89, 1991], were investigated to reveal interregional and transboundary transmission of solid aerosols in the winter season. Their input from Kazakhstan and subsequent transfer from the Novosibirsk Region and Altai Territory were anticipated.

While setting up the regional background monitoring network in the Tomsk Oblast, locations of sampling sites within the area were determined based on the probabilistic-statistical approach. The works commenced in 1994. Snow samples were systematically taken within a five-year period (1995–2000). The chemical composition of snow was analyzed at the monitoring sites located at different distances from pollution sources. The monitoring site selection met the following criteria: area 0.5 ha [*GOST 17.4.3.01-83, 2004*]; car accessibility.

Differentiation between the amounts of dust particles deposited in snowpack in agricultural land areas and in forests is of particular interest. To estimate the dust capture and retention capacity of tree species, the snow sampling points were in most cases paired: in the forest and in a nearby agricultural field [*Glazovskii, 2006*]. Snow samples were taken in March within one week. In Tomsk Oblast, the period with snow cover lasts 175–180 days, and the duration of snow cover averages T = 178 days [*Filimonenko et al., 2013*]. The number of prepared monitoring sites was initially 11 (0.5 ha) which increased to 18 in the first year, and to 23 in the next year; the duration of observations at the sites was 3–6 years in the period from 1995 to 2000.

Snow meltwater was sampled for the chemical analysis which was performed in compliance with generally accepted procedures [*Vasilenko et al., 1985; RD 52.04.186-89, 1991*]. Snow samples were taken by using a snow gauge (a widely used instrument for meteorological observations) through the full depth of the snowpack. In order to exclude contamination of samples by soil particles and litter admixtures, the lower 5 cm of snow was removed. After that, snow density was determined. Dust content was estimated from the cumulative sample composed of 3–5 samples depending on the snow depth.

The snowpack samples were melted in the laboratory at room temperature, and water volume was measured. The meltwater was filtered using a vacuum pump: the partitioning was achieved by passing the melted samples through the “blue ribbon” filter. The filters were dried in a desiccator at 105 °C. The filtrate analysis included determinations of: pH [*PND F 14.1-2-3-4.121-97, 1997*], concentrations of nitrates and NH_4^+ [*PND F 14.1-2.1-95, 1995*], contents of phosphates [*GOST 26204-91, 1992*] expressed as P_2O_5, potassium [*RD 52.24.391-95, 1995*] expressed as K_2O, calcium (Ca^{2+}) and magnesium (Mg^{2+}) [*GOST 26487-85, 1985*], sodium [*RD 52.24.391-95, 1995*], chlorides [*GOST 4245-72, 2010*]. The solids (dust) trapped on filters were dried at 105–110 °C and decomposed by hydrofluoric acid digestion. Total concentrations of nickel, cobalt, lead, copper, zinc, manganese, chromium, and cadmium in the resulting solution were determined by atomic absorption spectrophotometry (factorial design with eight runs). The atomic absorption analysis of trace elements yielded relative accuracy (%): 3.8 for Zn, 3.5 for Cu, 1.2 for Mn, 3.7 for Co, 4.2 for Pb, 14.3 for Cd.

The values of element concentrations in filtrates were converted to their concentration per liter of meltwater (μg/L), trace elements (TEs) inventory per unit area of snow (μg/m^2), and trace element flux (μg/(m^2·day)). Concentration coefficients were calculated as the ratio between TE content (Kc) and the background value (Kb):

$$K = \frac{\mathrm{Kc}}{\mathrm{Kb}}$$

and the total pollution index as

$$\mathrm{Zc} = \sum K - (n-1),$$

where K is concentration coefficient; n is amount of elements with $K > 1$.

Dust content was calculated using the formula

$$C = \frac{P_c}{V_w},$$

where C is dust mass concentration, g/L; P_c is dust weight in meltwater, g; V_w is the volume of water, L. The total dust input (P) was calculated as the mass of dust per unit area per unit of time. The area value was derived from the sampler diameter multiplied by the number of samples taken at one point. Sampling points (except points 20 and 21) which are located significantly away (30 km or more) from the Tomsk-Seversk agglomeration were referred to as the background values.

The dust flux emitted onto the snowpack surface was determined by the formula

$$P = \frac{P_c}{ST},$$

where P is TE flux per surface unit per time unit; P_c is the mass of trapped dust; S is the total sampling area; T is the time interval between the moment of sampling and the date of the onset of stable snow cover, days.

Geographic coordinates of the observation points were defined with GPS, and spatial distribution of trace element concentrations was analyzed using QGIS. This allowed mapping of the cluster analysis results. The distances from each observation point to the Siberian Chemical Combine (SCC) and Hydro Power Plant (HPP)-2 (i.e. potential impact factors) were measured.

The Orange software suit and appropriate Python packages were used for statistical analysis of the data. Clustering analysis with multiple variables using the algorithm K-means enabled the identification of the groups of representative points for contamination levels and pollutants inventory within the snowpack. Similar analytical procedures were used previously [*Shevchenko et al., 2017*]. The Statistica for Windows software package allowed us to assess the factors controlling pollutants intake into the snowpack.

RESULTS AND DISCUSSION

Snowpack characteristics inferred from measurement results at 24 monitoring sites are: snow depth averaging (56.4 ± 2.7) cm (Table 1); uniform distribution of snowpack within the studied area (coefficient of variation is 25.9 %). The variability of some indicators is interpreted as moderate (snow depth, pH) or high (>100) for others (contents of dust, P_2O_5, Mg^{2+}, NO_3^-).

The average snow depth values are greater for the forest versus agricultural land areas, which is corroborated by the Mann-Whitney test (at a significance level of $p < 0.05$). The dust load is shown to be on average (8.5 ± 3.6) mg/(m^2·day), approximating the background values for the Tomsk Oblast (7 mg/(m^2·day)) [*Talovskaya et al., 2014a,b*].

The average snow density is generally (0.19 ± 0.01) g/cm^3, although it tends to be higher within the agricultural land area than in the forest. This differentiation proved to have low credibility, though. The amounts of solid insoluble particles in snow meltwater average (6.8 ± 1.2) mg/L. Elevated dust concentrations were reported both at sampling points near the urban agglomeration (points 5, 6, 10, 12, 16) and away from dust emission sources (points 4, 21, 22, see Fig. 1). Average amounts of dust particles in the surface layer of snowpack are known to be about 2.74–2.91 mg/L within the background sites located in the Arctic [*Shevchenko et al., 2002, 2007*]. Our results have shown that in the territory of Tomsk Oblast, total solid impurities in snow mass are 2.5 times higher as compared to levels reported for remote Arctic regions.

Both spatial and temporal variability of this parameter is shown to be significant. The year 1997 stands out in terms of maximal snow cover depth (78.2 ± 4.7 cm) and minimal total dust content in snow (0.40 ± 0.13 mg/L) (Fig. 2).

The snowpack thickening translated to lower dust concentrations as a result of dilution by a larger snow volume. The next year, 1998, saw a remarkably enhanced flux of dust aerosol particles settled on snowpack. A comparison of the two samples – from the forest and agricultural field – of snow meltwater using the Mann-Whitney test ($p < 0.05$) showed a greater amount of dust particles in the snowpack sampled in the forest. The snow meltwater yielded a pH value varying from 5.6 to 6.6 (on average, 6.04 ± 0.13), which suggests weak alkalinity, as compared to the data obtained by other authors: pH of 5.89 for snow within the 30-km zone around the SCC [*Artamonova, 2011*], pH of 5.4 for snow in the Khanty-Mansi Autonomous Okrug (KhMAO) [*Moskovchenko, Babushkin, 2012*].

Emissions of NO_3^- into the atmosphere account for air pollution as a result of liquid fuel combustion, with sulfur and nitrogen compounds unevenly spreading within snowpack in the northern Russia [*Vetrov et al., 2014*]. The levels of NO_3^- in snowpack of the Tomsk Oblast are on average (1.4 ± 0.03) mg/L, and (0.54 ± 0.33) mg/L at sampling points located away from pollution sources. The NO_3^- concentration values amount to 0.45 mg/L for KhMAO, which is higher than the background values [*Moskovchenko, Babushkin, 2012*], while the 0.01–0.37 mg/L interval is indicative of the natural gas fields area in the Yamal Peninsula [*Ermilov et al., 2002*]. Contents of NH_4^+ in snowpack of the study objects are in the range (0.41 ± 0.04) mg/L, which is in good agreement with the available data for both the Tyumen Oblast and KhMAO. The background level was determined as (0.36 ± 0.04) mg/L. Concentrations of NO_3^-, NH_4^+ are enhanced relative to the background values in proximity to the industrial zone. Comparison of NH_4^+

Table 1. **Statistical characteristics of snow depth and pH, chemical composition of snow meltwater at the monitoring sites**

Characteristics	Snow depth, cm	pH	Concentration, mg/L								
			Dust	N_NO_3	NH_4	P_2O_5	K_2O	Ca	Mg	Na	Cl
Mean	56.44	6.05	7.08	0.14	0.42	0.08	1.06	7.34	2.48	1.03	7.46
Confidence interval*	2.69	0.13	1.31	0.03	0.05	0.02	0.17	1.13	0.75	0.13	1.09
Median value	54.95	6.10	4.90	0.05	0.35	0.06	1.00	5.41	1.22	1.00	7.00
Standard deviation	14.63	0.73	7.14	0.18	0.23	0.09	0.90	6.18	4.07	0.62	5.15
Variation coefficient	25.93	12.07	100.86	132.23	56.16	106.70	84.75	84.15	164.00	60.45	69.03
Mean value for background points	55	6	4.1	0.12	0.38	0.06	1.02	6.75	2.01	1.09	7.17
No. of background site	114	114	114	114	103	103	114	114	114	86	86

* At a significance level $p < 0.05$.

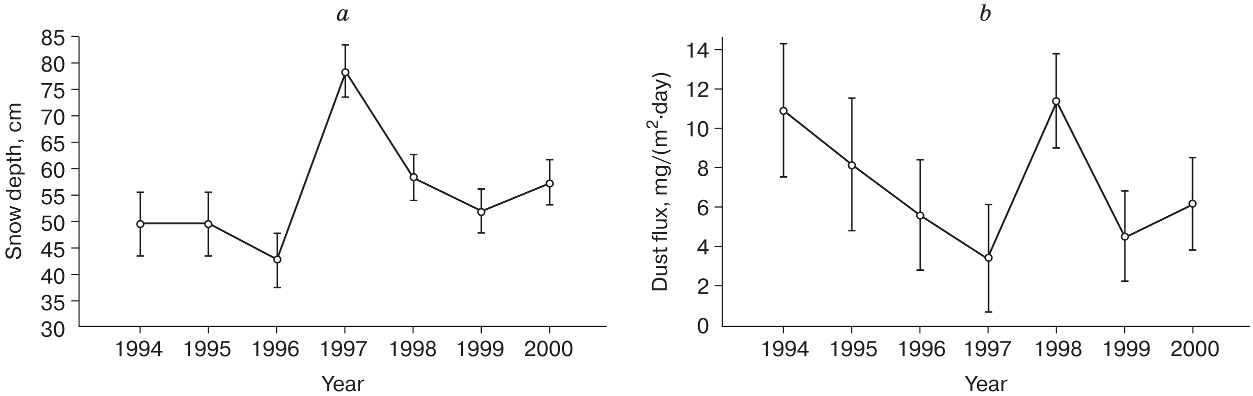

Fig. 2. Average annual snow depth (*a*) and dust aerosol flux (*b*).

contents in the forest and agricultural areas has revealed a reliable differentiation, indicating its higher levels in the forest.

The Mann-Whitney test at $p < 0.05$ confirmed the contents of phosphates in melted snow samples taken in the forest to be greater than in the field. P_2O_5 contents averaging (0.08 ± 0.2 mg/L) in snow meltwater differ only slightly from the mean value for the background sites (0.07 ± 0.02 mg/L).

Measured concentrations of potassium (K_2O) and sodium (Na^+) are on average (1.06 ± 0.16) mg/L and (1.03 ± 0.13) mg/L, respectively, and vary only slightly over the sampling points.

Results of this study has revealed that chloride-ion contents along with alkali metals represent snow contamination with readily soluble salts, which on average is (7.46 ± 1.1) mg/L. Cl^- concentrations vary only slightly at the observation points. For KhMAO, the average chloride levels within snowpack are significantly lower (3.4 mg/L) [*Moskovchenko, Babushkin, 2012*] increasing in the direction from west to east.

Abnormally high chloride-ion contents reported for the period 1997–1998 decreased dramatically later to (1.3 ± 0.5) mg/L (Fig. 2). Given that the sea influence on the coastal zone is known to spread within 200–250 km [*Zverev, Rubeikin, 1973*], this effect can be ruled out for chloride content in the analyzed samples.

With calcium contents averaging (7.3 ± 1.1) mg/L within snowpack, there is a logarithmic dependence between Ca^+ and Cl^-:

$$Cl = 3.3 \ln (Ca) + 3.2 \ (R^2 = 0.5 \text{ at } p < 0.05).$$

The presence of calcium in the snowpack is mainly associated with soil erosion [*Kutsenogii, 2006*], which suggests continental origins of the chloride ion. The study on the dissolution behavior of calcium in the eastern Tien Shan glaciers has demonstrated that calcium has the highest DFP (dissolved fraction percentage (%) calculated as the dissolved fraction divided by the sum of the dissolved and insoluble fraction) which is logarithmically regressed for the samples with SO_4^{2-} [*Wu et al., 2018*]. From a range of major mineral dust cations, Ca^{2+} has the highest solubility with chloride ion.

The content of magnesium in snow meltwater is (2.5 ± 0.7) mg/L. Spearman correlation coefficient between calcium and magnesium, magnesium and chlorine content is shown to be less than 0.3, which indicates of a weak link between them. The Mann-Whitney test at $p < 0.05$ showed that Mg content in the snowpack is higher for the forest than agricultural land area.

The distribution of trace element contents within the snowpack varies significantly between the observation points (Table 2).

The average content of nickel within the snowpack is (2.68 ± 0.33) µg/L, with its lowest levels (1.38 µg/L) reported from background site (BS) 18 (Verkh-Sechenovo village). The sampling points (SPs) which reported Ni concentrations within a confidence interval ($p < 0.05$) below the mean are: SP19 (Trubochevo v.), SPs 7 and 8 (Orlovka v.), and SP1 (Timiryazevo v.). The sampling points showing remarkably higher Ni contents at $p < 0.05$ are numbered 4, 5, 12, 14, 16, 20, and 21. Comparison of the obtained results with the data from the background sites provided a compelling evidence of enhanced Ni content in snowmelt waters sampled from within the Tomsk-Seversk industrial agglomeration. Thus, nickel concentrations range from 0.2 to 0.8 µg/L in the Ural industrial region [*Chernyaeva et al., 1978*], and equal to 0.7 µg/L within natural gas fields area in the Yamal Peninsula [*Ermilov et al., 2002*]. The average content of zinc in snow meltwaters is (26.7 ± 9.9) µg/L. Its content in the snowpack of the Tyumen Oblast reaches 81 µg/L in settlements. In the KhMAO, the most probable value for Zn concentrations is in the range of 10–27 µg/L [*Moskovchenko, Babushkin, 2012*]. The reported values for zinc concentrations range from maximal (81.7 µg/L) at

Table 2. **Averages concentrations (μg/L) of trace elements in solid residue of snow meltwater**

Sampling points*	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb	Zc
1	3.61	15.80	0.26	1.89	7.25	8.09	0.047	1.10	4.8
2	5.08	23.61	0.30	2.43	6.39	15.01	0.084	1.22	9.3
3	4.59	22.63	0.27	2.70	6.62	10.66	0.035	1.01	7.0
4	5.96	50.88	0.69	3.52	7.19	15.46	0.042	1.51	11.2
5	4.67	55.06	0.89	3.84	8.79	24.52	0.035	1.62	9.8
6	4.69	25.40	0.32	2.37	8.91	19.12	0.045	1.04	5.9
7	14.51	14.88	0.26	1.67	5.24	18.79	0.051	1.10	7.6
8	4.40	17.28	0.22	1.62	6.05	22.08	0.041	1.13	6.7
9	5.28	25.96	0.33	2.25	8.32	37.92	0.068	1.51	7.7
10	6.19	77.23	0.62	2.90	7.34	26.31	0.051	1.49	11.0
12	6.11	55.42	0.36	3.08	6.54	81.68	0.065	0.87	12.9
13	6.24	33.80	0.31	1.76	7.98	20.51	0.040	1.32	6.4
14	7.48	65.17	0.75	3.93	11.38	74.57	0.053	1.43	16.9
15	4.87	21.77	0.44	3.78	7.86	30.33	0.066	1.43	7.8
16	12.24	72.75	0.59	4.09	10.50	13.71	0.101	1.64	18.4
17	3.81	24.01	0.35	2.99	7.32	15.21	0.037	0.76	6.8
18	2.00	7.71	0.14	1.38	4.62	22.68	0.026	1.14	3.1
19	2.85	9.26	0.11	1.57	4.36	13.17	0.065	1.49	3.8
20	5.57	58.76	0.72	3.28	8.19	40.99	0.049	2.62	9.9
21	4.00	29.62	0.54	3.65	6.36	26.09	0.043	2.50	7.4
22	4.45	18.52	0.32	2.63	7.16	32.89	0.049	4.61	7.1
23	2.80	13.78	0.29	1.71	6.06	15.71	0.057	1.68	3.5
24	1.37	14.54	0.25	1.73	3.55	9.78	0.036	0.99	2.7
Mean	5.60	34.16	0.42	2.68	7.30	26.7	0.052	1.42	8.5
Background value	3.64	18.42	0.25	1.97	6.27	15.70	0.04	1.17	5.07

* Numbering of the sampling points is given in Fig. 1.

SP 12 in Kolomino village to slightly lower (74.6 μg/L) at Naumovka village. At this, high levels (within a confidence interval ($p < 0.05$) above the mean) was observed at sampling points 9 (Samus v.) and 20 (Batkat v.). While Samus village is located within the SCC impact zone [*Artamonova, 2011*], there are no industrial enterprises in the vicinities of Batkat village. Emissions of pollutants may be released by gas flares, the snowpack near which shows Zn concentrations reaching 52 μg/L [*Moskovchenko, Babushkin, 2012*]. However, Batkat village is located hundreds of kilometers away from oil fields, and the distance from the impact zone responsible for translocation of pollutants measures 5–15 km, depending on the wind rose [*Lezhenin et al., 2016*]. Coarse dust aerosol particles are dominantly (90 %) deposited within a radius of 7 km from the pollution source, and spread within a radius of 40 km [*Onuchin et al., 2014*], with snowfalls assisting both in dry and wet washout of atmospheric pollutants [*Talovskaya et al., 2014a*].

Among different types of boilers, the coal-fired boiler house in Batkat village contributes its share into the environmental impact from coal combustion which is confirmed by the reported enhanced concentration coefficients for zinc along with other trace elements [*Talovskaya et al., 2018a,b*].

The contents cobalt in snowpack have received little consideration so far [*Kutsenogii, 2006*]; within the observation sites, Co levels are reported to be higher than the average value at SPs located northeast and east of the Tomsk city agglomeration and at SP 20 (Batkat village). Dust emissions from the coal-fired boiler house are featured by elevated Co contents and greater Na and Ca concentration coefficients. Contents of metals in the snow-captured dust at least twice as higher than the background values.

The contents of lead within snowpack averages 7.6 μg/L against the background value of 6.3 μg/L. The snow dust enrichment in lead reported from SPs 20 and 22 showed Pb concentrations to be significantly higher than the background value. Although SPs 5 and 22 are located at different parts of the study area, but in proximity to highways with heavy traffic flow, they show explicable high lead levels. Sampling points 20, 21 are 1.5–3.0 km away from the highways, which makes dry washout of lead from snowpack of these points unlikely. Results of the field studies conducted around the Norilsk Mining and

Metallurgy Combine have shown a mosaic pattern of Pb deposition into snowpack [*Onuchin et al., 2014*]. Analyses of lead input in the snowpack of Tyumen showed its concentration in the solid phase, with the levels varying within a wide range, from 0 to 214 μg/L [*Krest'yannikova et al., 2015*]; its abnormal concentrations are localized.

At the studied sampling points (5, 6, 9, 10, 13–16), copper pollution encompasses the background sites located around the SCC, Tomsk Petrochemical Plant (Tomskneftekhim), where Kc > 1. Copper concentrations average (7.3 ± 0.8) μg/L. The value of Kc is reported to be high for SP 20 (Batkat village). In coals utilized as fuel, one can hardly expect high levels of copper. Enrichment of Siberian coals in lithophile and siderophile chemical elements (Cr, Ni, Co) and their depletion in chalcophile elements (Cu, Pb, Zn, Cd, etc.) is noted [*Arbuzov, 2007*]. Consequently, Cu enters the Batkat snowpack from other sources. Given that manganese is commonly used in the chemical industry, its anomalous abundancy relative to the background value should be expectable in the vicinities of SCC and Tomskneftekhim. The mean value is (34.2 ± 7.3) μg/L, the background value is 18.4 μg/L. At the sampling points (4, 5, 9, 10, 13–16) around chemical plants, Mn concentrations are 2–3 times higher than background values. At points 20, 21, the Kc values are shown to be high (3.6 and 1.8), which

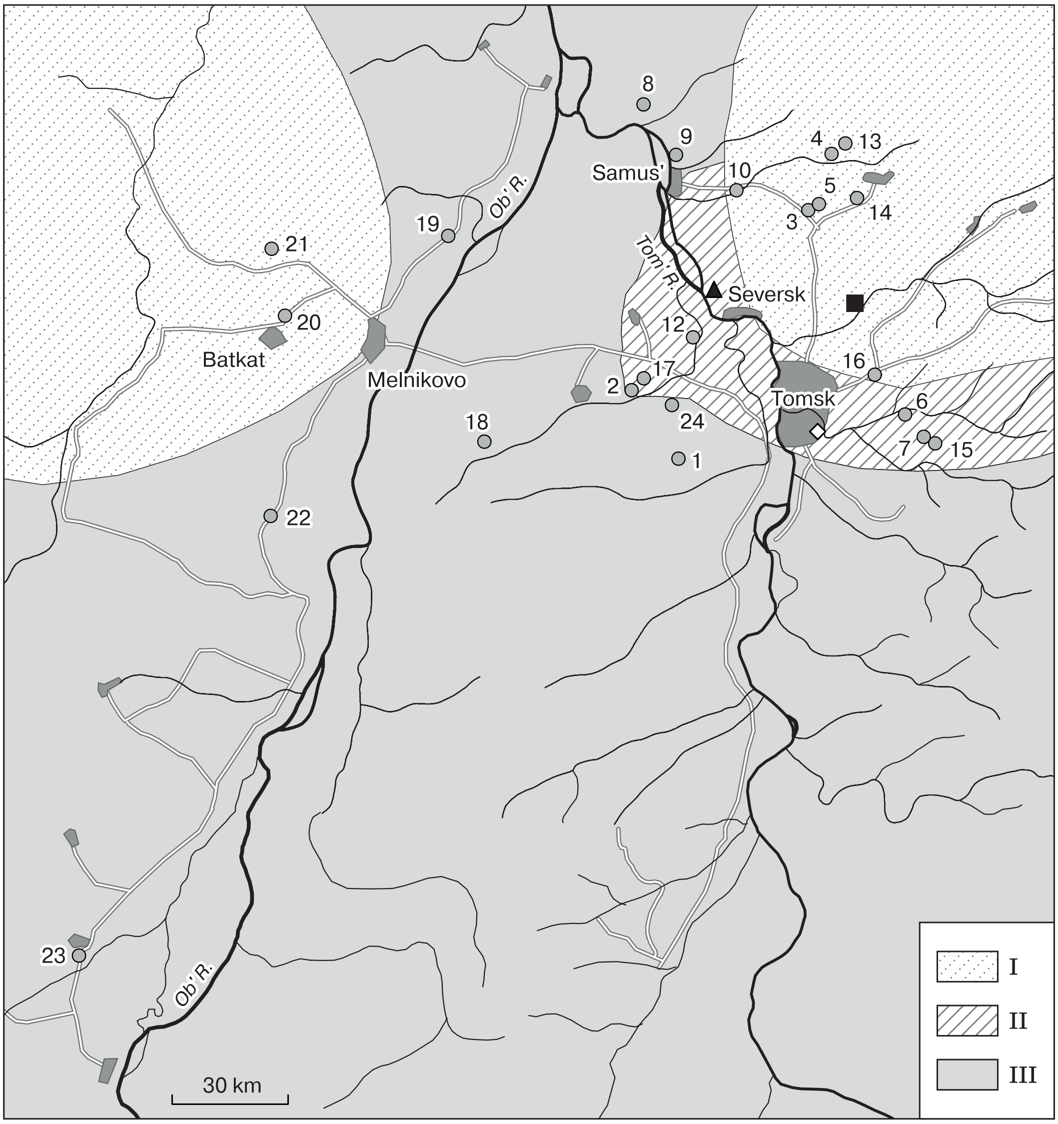

Fig. 3. Distribution of mean annual values of multivariate cluster analysis of trace element inventory (Ni, Co, Cu, Mn, Zn, Pb, Cr, Cd) in the territory of the Tomsk Oblast.

Zones showing similarity in the chemical composition: I – industrial zone, II – industrial-residential zone, III – relatively pure areas. See Fig. 1 for notations.

does not permit us to relate this phenomenon with the chemical composition of solid fuel utilized by the boiler house. Territorially, the pollution points gravitate to Tomskneftekhim and Tomsk city. Anomalies in chromium contents in the snowpack are primarily associated with the foundry production facilities [*Sergeeva, Kuimova, 2011*]. The authors attribute the chromium contamination of snowpack in Blagoveshchensk city to transboundary transmission from China, where thermal power plants are coal-fired. Although the foundry facilities remained within the Tomsky Instrument factory, the contamination did not spread beyond the city limits. However, HPP-2, which in the 1990s was partially coal-fired may continue to be the source of chromium pollution. The average cadmium content is (1.0 ± 0.2) μg/L within the snowpack. Abnormally high cadmium concentrations within snowpack are associated with the industrial and residential-transport zones [*Sergeeva, Kuimova, 2011*]. The Kc value reached maximum (1.3–2.0) at SPs 16, 2, and 9, and minimum (1.1–1.3) at SPs 15, 12, 19, and 23. All these points are located in proximity to highways, and the sampling points in proximity to the industrial zone report the highest values.

The mean value of total Zc pollution index is 8.5 ± 1.3, which varies widely (the variation coefficient is 73 %). The level of pollution is regarded as low and non-hazardous at Zc < 32 [*Kasimov et al., 2012*].

The K-means cluster analysis was used for classification of the sampling points. For simplicity, they were split into three clusters to provide a fit to the existing at the time trace elements distribution patterns in the territory of Tomsk Oblast. The averaged over the years Euclidean distances between the multivariable centers of clusters were mapped in using the QGIS (Fig. 3). For convenience, results of the classification are shown in black and white shading (notations I–III in Fig. 3). The points grouped in northeast and southeast of SCC and near Tomskneftekhim (points 10, 3, 5, 14, 4, 16) correspond to Zone I. The points 20 and 21 located at a considerable distance (70 km) from SCC are characterized by a close chemical composition. A similar situation is observed in Bratsk, where the aluminium smelter (BrAZ) is known to be a heavy metal pollution source [*Yanchenko et al., 2013*]. The sampling point located 29 km from the source shows a high concentration of contaminants, even higher than at a distance of 3 km from the production facilities. Assumingly, the pollution is caused by the boiler house, rather than the BrAZ facilities. We think, heavy metals uptake and translocation from the facilities over such distance is possible, in view of the revealed similarity in the chemical composition and elements concentrations (spectrum) at a distance of 29 km and near BrAZ.

Zone II encompasses the transitional group (points 2, 3, 6, 7, 12, 15) biased toward HPP-2 and the city-specific trace element contamination. The sampling points which are highlighted within Zone III are relatively pure in terms of elemental composition (points 1, 8, 9, 13, 18, 22–24), which largely overlaps the points within the interval below the mean Zc content.

CONCLUSIONS

1. Although the average snow depth is evenly distributed within the studied area, its variability over the years of observation is remarkable. The average snow-captured dust content is (6.8 ± 1.2) mg/L, dust load is (8.5 ± 3.6) mg/(m^2·day).

2. The variability may be regarded as moderate with respect to some parameters (snow depth, pH), or high (>100, e.g., contents of dust particles, P_2O_5, Mg, NO_3^-).

3. Comparison of snowpack in the forest and in land-use area revealed a significant difference between snow depth, contents of dust, NH_4^+, P_2O_5, Mg (towards their enhancement for the forest area).

4. Trace element levels tend to increase near the industrial zone of the Tomsk city agglomeration. Lead has a mosaic distribution pattern throughout the territory and its concentrations are confined to observation points located near highways, while cadmium concentration coefficient is reported to be high in snow samples both from the background sites and from within the industrial zone.

5. The multivariate cluster analysis allowed us to establish three groups of the observation points, namely: industrial and industrial-residential areas, and relatively pure areas.

6. Snowpack of some observation points (Batkat settlement and Komarovo swamps) which are more than 70 km away from the SCC and Tomskneftekhim facilities is shown to have anomalous contents of dust and heavy metals (1.5–2 times higher relative to the background values), whose composition is similar to those observed in the northeast of the Tomsk-Seversk agglomeration.

7. The total pollution index value indicates that all the background sites have an average value of Zc < 32, suggesting a low level of snowpack contamination with heavy metals. Thus, pollutants deposition in the studied snowpack has a focal pattern both within a 30-kilometer impact zone of the industrial facilities and at a considerable distance from them (more than 70 km).

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