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Trace element composition of snow cover components in the city of Chita and its environs

Evgeniy A. Bondarevich ✉

Chita State Medical Academy, Chita, Russian Federation
✉ bondarevich84@mail.ru

Abstract. The variation in the concentrations of chemical elements of snow cover in melt water and native dust in the urbanized area of Chita and its environs was studied in comparison with the background area and literature data from other regions of Russia and Mongolia. The study of the accumulation of compounds of chemical elements in the components of snow cover makes it possible to assess the degree of pollution of the surface layer of the atmosphere under technogenesis conditions and to identify key sources of pollution. The goal of the work was to compare the amounts of a number of microelements in melted snow water and in native dust residue in areas of different degrees of technogenic load. The materials were dust and snow meltwater, in which the quantitative content of 22 chemical elements was determined using the X-ray fluorescence method of total external reflection on an S2 Picofox spectrometer (Bruker Nano GmbH, Germany). A low content of ionic forms of elements in the aqueous phase of snow was revealed, with an excess of the maximum permissible concentration for Mn by 1.5–2 times under technogenesis conditions. The concentrations of water-soluble forms of trace elements were comparable to data from other regions. The dust fraction of snow, on the contrary, was characterized by significant contamination with sparingly soluble forms of chemical elements, while no excess of the maximum permissible concentration / approximately permissible concentration was noted, and in comparison with the clarke for soils of populated areas, a slight excess of the content of As, Sn and W was noted. The dust fraction of the Chita snow cover, compared to the background, is enriched in Th, Rb, Cr and Ga; in the Chita region, intensive accumulation of Cr, As and Sr in the dust was revealed. Significantly larger amounts of microelements compared to Transbaikal samples were detected for the cities of Ulaanbaatar, Blagoveshchensk, and in somewhat smaller quantities Tyumen and Tobolsk. The mass fraction of water-soluble forms for most microelements was significantly less than 0.1%, while a tendency was revealed to increase the number of ionic forms of elements from the urbanized area to the background areas.

Keywords: snow cover, Eastern Transbaikalia, chemical elements, X-ray fluorescence analysis

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Микроэлементный состав компонентов снежного покрова города Читы и его окрестностей

Е.А. Бондаревич ✉

Читинская государственная медицинская академия, Чита, Российская Федерация»
✉bondarevich84@mail.ru

Аннотация. Исследовано варьирование концентраций химических элементов снежного покрова в талой воде и нативной пыли в условиях урбанизированной территории г. Чита и его окрестностей в сравнении с фоновым участком и данными литературы из других регионов России и Монголии. Изучение накопления соединений химических элементов в компонентах снежного покрова позволяет оценивать степень загрязнения приземного слоя атмосферы в условиях техногенеза и выявлять ключевые источники загрязнения. Цель исследования – сравнение количеств ряда микроэлементов в талой снеговой воде и в нативном пылевом остатке в разных по степени техногенной нагрузке районах. Материалы – пыль и талая вода снега, в которых рентгенофлуоресцентным методом полного внешнего отражения на спектрометре S2 Picofox (Bruker Nano GmbH, Германия) определялось количественное содержание 22 химических элементов. Выявлено низкое содержание ионных форм элементов в водной фазе снега с превышением ПДК по Mn в 1,5–2 раза в условиях техногенеза. Концентрации водорастворимых форм микроэлементов были сопоставимыми с данными из других регионов. Пылевая фракция снега, напротив, характеризовалась существенным загрязнением труднорастворимыми формами химических элементов, при этом превышения ПДК (ОДК) не отмечено, а в сравнении с кларком для почв населенных пунктов наблюдалось незначительное превышение содержания As, Sn и W. Пылевая фракция снежного покрова Читы по сравнению с фоном обогащена Th, Rb, Cr и Ga, в Читинском районе выявлено интенсивное накопление в пыли Cr, As и Sr. Значительно большие количества микроэлементов по сравнению с забайкальскими пробами определялись для городов Улан-Батор, Благовещенск, и в несколько меньших количествах – Тюмени и Тобольск. Массовая доля водорастворимых форм для большинства микроэлементов была существенно меньше 0,1 %, при этом выявлена тенденция увеличения количества ионных форм элементов от урбанизированной территории к фоновым участкам.

Ключевые слова: снежный покров, Восточное Забайкалье, химические элементы, рентгенофлуоресцентный анализ

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Introduction

Atmospheric aerosols in the sharply continental climate of Transbaikalia have a significant negative impact on ecosystems and population in the cold period of the year. This is due to the formation of a dense surface layer of smog, which intensifies in frosty windless weather. Sources of atmospheric air pollution in Chita are various types of fuel, solid domestic waste landfills, dust from deforested and disturbed areas of the landscape, transport. Rare snowfalls with little precipitation aggravate the situation, as the removal of suspended particles and pollutant gases occurs for a short time. At the same time there is an accumulation of pollutants in the snow cover of the city and its surroundings, which increases the pollution of soil, surface and groundwater. According to systematic observations, it is known [1] that the average annual amount in the city of Chita is 336 mm, while from November to March inclusive, the amount of solid precipitation is 20 mm, or 6% of the average annual amount. The average thickness of snow cover in the city is 7 cm, snow density is 150 kg/m^3. The combination of these factors leads to significant snow pollution during the snow accumulation period and rapid degradation of the snow cover due to a decrease in albedo in February during thaws. The main insoluble components of snow in the city are soot and other carbon-containing particles, while at a distance from the urbanised area they are inorganic (silicate) dust particles of soil and rocks.

The aim of the study was to compare the amounts of a number of trace elements in melted snow water and in native dust residue in areas with different degrees of anthropogenic load.

Materials and research methods

Snow samples were collected during the period of maximum snow accumulation in the Transbaikalia in the third decade of February to the end of the first decade of March. The snow accumulation time ranged from 95 to 115 days. A total of 63 snow samples were collected in Chita and its environs, of which 3 samples were used as background samples and were collected in the vicinity of the village of Amodovo (Chita region) located 27 km to the west of the city on the windward side. Due to the low snow cover typical for the region, samples were collected with plastic scoops (without removing 1.5 cm of snow from the soil) in polythene bags. The sample was formed by mixing snow cores from several nearby sites, the total sample mass was 4–5 kg.

Determination of chemical elements content was carried out by X-ray fluorescence total external reflection method on S2 Picofox spectrometer (Bruker Nano GmbH (Germany). The melt water was pre-dehydrated and filtered through a blue ribbon paper filter, and after adding the internal standard, 10.0 μl of the sample was applied to a quartz sample holder and dried. The solid precipitate was analysed in the same way. 10.0 mg of dust was placed in a microtube, 100.0 μl of 1.0% Triton X–100 solution and 10.0 μl of standard were added, and then the suspension was applied to a quartz sample holder. The concentration of elements was calculated by the method of internal standard, as which was used a standard sample of germanium salt diluted with deionised water (Ω = 18.2 MOm) with a concentration of 2.50 $мг{\cdot}л^{-1}$.

The analytical data were processed using the programmes 'Microsoft Excel 2019' and 'PAST 3.25'. Data are given in median value with 25 and 75% quartiles. The values of MPC and APC for water and soil are given in accordance with SanPiN 1.2.3685-21 'Hygienic standards and requirements to ensure safety and (or) harmlessness to humans of habitat factors'. Formed samples on the content of chemical elements of different functional zones according to the degree of technogenic load were compared with each other by non-parametric Kraskal – Wallis criterion. Samples with $p \leq 0.05$ were considered significant.

Research results and discussion

Analysis of the data obtained during the study of the chemical composition of melt water did not reveal significant differences in most trace elements between the urbanised area, rural landscape and background (Table). A decrease in the level of soluble forms of trace elements in snow cover from the urban environment to the background areas is observed. The greatest differences are revealed for Mn, Fe, Zn and Sn. Probably, it is caused by geochemical peculiarities of soils of the study area and enrichment of dust particles with the listed trace elements during solid fuel combustion and moving mechanisms of machines. Exceedance of MPC value was revealed only for manganese both for Chita and Chita region in 1.5 and 1.9 times, respectively (Table).

As a result of pairwise comparison of samples no significant differences were revealed by the Kraskal – Wallis criterion between the pairs 'Chita – Chita region' ($H = 0.60$, $p = 0.44$) and 'Chita – background' ($H = 2.90$, $p = 0.09$), but median content of chemical elements in the pair 'Chita region – background' ($H = 5.03$, $p = 0.03$) were significantly different. These features characterise the greatest differences in concentrations of trace elements in melt water and indicate intensive movement and input of pollutants into the atmospheric air in the Chita region. Such a significant emission of water-soluble forms of trace elements is caused by the wide use of brown coal as fuel in boiler houses in the conditions of low-rise building of suburbs of Chita city and villages of the region.

Median content of chemical elements in melted snow water, in mg·l^{-1}, and dust, mg·kg^{-1}

Chemical element	Melt water. mg·l^{-1} Me / Q_{25}-Q_{75}			MPC[1]	Native dust. mg·kg^{-1} Me / Q_{25}-Q_{75}			Clark urban soils [2]	MPC / APC[2]
	Chita city	Chita district	Background		Chita city	Chita district	Background		
Ti	0.026	0.03	0.01	0.10	730.59	462.61	35.90	4600	—*
	0.02–0.04	0.02–0.03	0.01–0.04		639.37–860.59	369.47–586.43	21.76–50.33		
V	0.02	0.02	0.009	0.10	11.66	7.20	0.65	104.86	150.0
	0.01–0.02	0.02–0.04	0.009–0.02		9.63–16.33	5.37–10.57	0.26–1.03		—
Cr	0.01	0.02	0.007	0.05	8.22	6.46	0.85	80.0	—
	0.01–0.02	0.02–0.04	0.01–0.02		6.52–10.61	4.14–9.36	0.29–0.96		
Mn	**0.15**	**0.19**	0.02	0.10	149.64	147.57	9.54	728.70	1500.0
	0.11–0.21	0.05–0.40	0.02–0.04		125.51–181.52	116.79–242.14	4.79–12.94		—
Fe	0.19	0.25	0.09	0.30	7821.01	5119.13	423.74	$2.2 \cdot 10^4$	—
	0.15–0.25	0.13–0.84	0.08–0.10		$7.2 \cdot 10^3$–$8.6 \cdot 10^3$	$4.0 \cdot 10^3$–$7.0 \cdot 10^3$	243.39–572.55		
Co	0.006	0.008	0.003	0.10	0.62	0.42	0.04	14.09	—
	0.005–0.007	0.006–0.008	0.002–0.004		0.61–0.65	0.39–0.46	0.03–0.05		
Ni	0.005	0.006	0.003	0.02	3.09	3.12	0.26	32.99	—
	0.004–0.005	0.004–0.008	0.002–0.005		1.79–4.31	2.09–5.16	0.16–0.31		20.0–80.0
Cu	0.006	0.007	0.005	1.0	6.73	7.16	0.37	38.97	—
	0.004–0.008	0.005–0.01	0.004–0.009		3.73–12.74	4.36–11.16	0.28–0.49		33.0–132.0
Zn	0.05	0.095	0.03	5.0	47.08	34.49	1.87	158.0	—
	0.03–0.10	0.05–0.34	0.01–0.05		32.12–63.78	21.57–59.36	0.97–2.57		55.0–220.0
Ga	0.003	0.004	0.002	—	4.39	2.52	0.16	16.19	—
	0.003–0.004	0.003–0.004	0.002–0.004		2.98–6.04	2.07–3.14	0.10–0.20		
As	0.003	0.004	0.001	0.01	**5.53**	**5.55**	0.24	15.92	—
	0.002–0.004	0.003–0.007	0.001–0.003		2.94–8.87	3.79–7.51	0.22–0.30		2.0–10.0
Se	0.002	0.003	0.001	0.01	0.14	0.10	0.01	—	—
	0.002–0.003	0.002–0.004	0.001–0.003		0.13–0.15	0.10–0.12	0.008–0.011		
Br	0.005	0.004	0.001	0.20	0.38	0.44	0.04	—	—
	0.004–0.007	0.002–0.005	0.001–0.003		0.23–0.78	0.29–0.69	0.02–0.08		
Rb	0.003	0.004	0.002	0.10	39.91	12.34	0.88	58.0	—
	0.003–0.004	0.002–0.004	0.002–0.003		19.73–61.37	10.21–13.76	0.44–1.21		
Sr	0.19	0.11	0.008	7.0	53.80	81.14	3.45	457.83	—
	0.14–0.24	0.03–0.25	0.003–0.01		26.67–124.18	50.83–136.92	3.08–4.72		
Sn	0.16	0.20	0.08	2.0	**12.34**	**8.25**	0.75	6.77	—
	0.14–0.18	0.17–0.21	0.06–0.15		11.70–13.23	7.79–8.92	0.69–0.89		
Cs	0.05	0.07	0.03	—	4.49	3.02	0.28	—	—
	0.05–0.05	0.06–0.07	0.02–0.07		4.42–4.69	2.88–3.24	0.25–0.33		
Ba	0.09	0.06	0.03	0.70	75.49	112.83	5.40	853.12	—
	0.05–0.14	0.05–0.08	0.02–0.06		33.03–172.16	86.37–159.81	3.78–7.23		
W	0.004	0.006	0.003	0.05	**0.53**	**0.31**	0.02	0.288	—
	0.004–0.005	0.005–0.006	0.002–0.005		0.17–1.31	0.20–0.67	0.01–0.02		
Pb	0.003	0.005	0.002	0.01	8.28	7.55	0.36	54.49	—
	0.003–0.004	0.004–0.013	0.001–0.003		2.38–12.77	5.02–12.46	0.32–0.51		32.0–130.0
Th	0.005	0.006	0.003	—	2.06	0.25	002	—	—
	0.004–0.005	0.005–0.007	0.001–0.004		0.49–4.04	0.22–0.60	0.01–0.03		
U	0.007	0.008	0.004	0.015	0.39	0.28	0.03	—	—
	0.006–0.007	0.007–0.009	0.003–0.006		0.38–0.40	0.27–0.29	0.02–0.004		

Maximum permissible concentrations (MPC) of chemical substances in drinking water from centralized, including hot, and non-centralized water supply systems, water from underground and surface water bodies for domestic, drinking and cultural water use, water from swimming pools and water parks.
The value of the MPC/APC (mg·kg^{-1}) taking into account the background (clarke).
*— there is no standard indicator.
Source: compiled by E.A. Bondarevich.

The detected median concentrations for a number of trace elements are comparable to those of other settlements and regions of Russia. For copper, bromine, lead arsenic and selenium, similar data are given for melt water in Altai Krai [3], as well as for nickel, cobalt, manganese and iron in Blagoveshchensk [4; 5]. For cobalt, copper, manganese, iron, lead and nickel in Arkhangelsk [6], for arsenic, copper, strontium and zinc in Ulaanbaatar [7], for zinc, copper and iron in Kyzyl [8] and for lead, nickel, copper and cobalt for Lake Baikal [9]. For a number of trace elements in the conditions of the urbanised territory of Chita, significant exceedances of the content were revealed, which can reach 1–3 orders of magnitude. For instance, the content of manganese, barium, vanadium, chromium, iron, zinc, and titanium is significantly higher in snow melt water in Chita compared to the snow water of Lake Baikal water area [9]. The concentrations of cobalt, chromium, nickel, lead and vanadium are one order of magnitude higher compared to Ulaanbaatar [7]. The amount of thorium is three orders of magnitude and uranium one order of magnitude higher than in the snow cover of Blagoveshchensk [4]. The soluble forms of titanium, manganese, iron, and zinc in the melt water of Chita exceeded the values for the Altai Krai by 1–2 orders of magnitude [3]. The greatest differences in the concentrations of water-soluble forms of chemical elements in melt water of Chita were with the data of background concentrations of the central sector of Western Siberia and exceeded by 1 order of magnitude the values for titanium, cobalt, selenium, strontium, and by 2–3 orders of magnitude for vanadium, chromium, and tin [10].

In comparison with cities and regions with similar natural-climatic and anthropogenic factors, no significant differences in the content of water-soluble forms of trace elements were revealed. Comparison of data sets by the Kraskal – Wallis criterion no significant results were recorded in pairs Chita – Kyzyl ($H = 2.82$, $p = 0.09$), Chita region – Kyzyl ($H = 1.46$, $p = 0.23$), significant differences were observed in Kyzyl background (Amodovo village) ($H = 7.17$, $p = 0.007$) (elements Mn, Fe, Co, Ni, Cu, Zn, As and Pb). The Chita – Ulaanbaatar' and background – Ulaanbaatar pairs also showed no significant differences ($H = 3.60$, $p = 0.06$ and $H = 1.22$, p = 0.27, respectively), while in the Chita region – Ulaanbaatar pair the criterion revealed significant differences ($H = 4.68$, $p = 0.03$) (elements V, Cr, Co, Ni, Cu, Zn, As, Sr and Pb). In all pairs of comparisons between Transbaikal samples and samples from Blagoveshchensk, no significant differences were found for a set of concentrations of Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb ($H = 0.01–2.48$, $p = 0.11–0.91$). Significant differences in concentrations of water-soluble forms of elements in all compared pairs were found with data from Lake Baikal: Chita – Baikal $H = 8.93$, $p = 0.003$, Chita region – Baikal $H = 9.73$, $p = 0.002$ and background – Baikal $H = 5.13$, $p = 0.02$ (elements Ti, V, Cr, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr and Pb). Also, there was noted a decrease in the concentration of ions of the studied elements for iron, strontium, and bromine in the conditions of Chita compared to the winter period of 2020–2021 [11].

Analysis of data on the content of trace elements in the dust fraction of snow cover revealed significant differences between the samples of Chita city and Chita region relative to the background area. The highest content of thorium (103 times) and rubidium (45 times) in the native dust of Chita relative to the background was observed, other trace elements were exceeded from 9.67 times (Cr) to 27.4 times (Ga). In samples of Chita region, the multiplicity of exceedance of background concentrations was somewhat lower and varied from 7.6 times (Cr) to 23.1 times (As) and 23.5 times (Sr) (Table). There is no standardisation of the content of chemical elements and their compounds in snow dust and solid residue, for this reason one can be guided by the corresponding clarke values, MPC/APC for urban soils [2]. The study revealed an insignificant excess of the norming indicator (soil clarke) for arsenic, tin and tungsten, while for other trace elements, even in the conditions of urbanised territory, the amount was 1–2 orders of magnitude lower than the clarke content and MPC(APC) (Table).

Pairwise comparison of data sets by the Kraskal – Wallis test showed no significant differences in median trace element content in the Chita – Chita region groups ($H = 0.25$, $p = 0.61$), but the Chita – background ($H = 11.91$, $p = 0.0006$) and Chita region – background ($H = 8.96$, $p = 0.003$) pairs were significantly different.

The content of trace elements in the dust fraction of the snow cover in Chita significantly exceeded the values for other regions and settlements by most indicators. Thus, for the background territories of Western Siberia [10; 12], the content of Co in Transbaikal samples was 3 orders of magnitude higher, Ni, Zn, Cu, and Pb – 4 orders of magnitude higher, V, Cr, Mn, Fe, As, Sr, Ba, and U – 5 orders of magnitude higher, and Rb, Cs, and Th – 6 orders of magnitude higher. Also, low values of trace elements accumulation in dust were recorded in Kyzyl [8], Blagoveshchensk [4] and Altai Krai [3], and the differences were 1–3 orders of magnitude compared to Chita, but iron in the dust fraction of Tuva samples was 5 orders of magnitude, and in Altai samples 4 orders of magnitude less. The values of trace elements in the dust of Ulaanbaatar [7] and Blagoveshchensk [5] were significantly higher. Thus, the content of As in the conditions of Ulaanbaatar city was 4.4 times higher, and V, Cr, Zn, Sr and Pb differed by 1 order of magnitude, while Co, Ni and Cu were higher by 3 orders of magnitude [7]. For Blagoveshchensk, higher amounts of Ni, Cu and Pb (by 1 order of magnitude) and a 6–8-fold excess of Cr and Zn were recorded [5]. The results from the cities of Tyumen and Tobolsk were the closest in terms of the median content of trace elements in the dust fraction of the snow cover [13]. The amounts of V, Zn, As, Sr, Sn, Ba, W were comparable, but the amounts of Cr, Ni, and Cu in these settlements exceeded the Transbaikal indicators by 1 order of magnitude.

Thus, the content of trace elements in the dust fraction in different regions of the country has a huge range of indicators, but for ecologically clean areas the values had minimal indicators, while technogenically disturbed landscapes were characterised by strong pollution. In the conditions of Chita city, significant dust pollution was revealed, which differed significantly by the Kraskal – Wallis criterion in comparison with the samples of Kyzyl, Blagoveshchensk, and Ulaanbaatar cities. According to this criterion, there are no significant differences in pairs Chita – Tyumen ($H = 1.6$, $p = 0.21$ for V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Sn, Cs, Ba, W and Pb), Chita region – Tyumen, Chita – Tobolsk ($H = 2.05$, $p = 0.15$), Chita region – Tobolsk ($H = 2.9$, $p = 0.09$), whereas in pairs Tyumen –

Amodovo (background) and Tobolsk – Amodovo (background) this criterion revealed significant differences (H = 16.35 and H = 17.36 at p < 0.001, respectively).

The ratio of water-soluble forms of trace elements to their content in the Chita snow dust had values less than 0.1 %, except for Co, Se, Br, Sn, Cs and U, with a significant increase in trace element ions detected in the conditions of the background area. This is due to the low values of accumulation of element compounds in dust and the absence of their thermochemical conversion in fuel combustion systems with the formation of insoluble substances (oxides, sulfides, silicates, etc.).

Conclusions

1. The microelement composition of melt water and dust fraction of snow cover of Chita and its surroundings was studied by the method of non-destructive X-ray fluorescence analysis. No significant differences in the concentration of water-soluble forms of elements between the city and rural settlements of Transbaikalia were revealed. The amount of trace elements in the background conditions was minimal, however, even in the conditions of the urbanised area no exceedance of MPC was observed, except for Mn.

2. Compared to cities and regions with similar natural-climatic and anthropogenic factors, no significant differences in the content of water-soluble forms of trace elements were observed.

3. A comparison of data between the 2021 and 2024 winter seasons found decreased concentrations of iron, strontium, and bromine compounds in snowmelt water.

4. The dust fraction of Chita snow cover is enriched with thorium, rubidium, chromium and gallium compared to the background, in Chita region intensive accumulation of chromium, arsenic and strontium in dust was detected. No exceedances of MPC (APC) and clarke indicators for soils in the dust fraction were noted.

5. Dust from the snow cover of Chita contained significantly higher amounts of trace elements than dust in most other cities and regions for which data are available in the literature. Close quantitative indicators were recorded for the cities of Tyumen and Tobolsk, and the greatest differences were noted in comparison with the Katunsky Reserve (Altai Republic) and the central sector of Western Siberia.

6. The mass fraction of water-soluble forms for the majority of trace elements was significantly less than 0.1%, at the same time the tendency of increasing the number of ionic forms of elements from the urbanised area to background sites was revealed.

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Bio note:

Evgeniy A. Bondarevich, Candidate of Biological Sciences, Associate Professor, Associate Professor of the Department of Chemistry and Biochemistry, Chita State Medical Academy, 39a St. Gorky, Chita, 672000, Russian Federation. ORCID: 0000-0002-0032-3155. E-mail: bondarevich84@mail.ru