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THE INFLUENCE LONG-RANGE AND REGIONAL TRANSFERS OF SUBSTANCES ON THE CHEMICAL COMPOSITION OF THE SNOW COVER BACKGROUND TERRITORIES OF THE EUROPEAN NORTH-EAST OF RUSSIA

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Abstract

The formation of the chemical composition of the snow cover background territories of taiga of the European North-East of Russia (Komi Republic) takes place mainly at the expense of soluble compounds of elements. The coefficients of enrichment (Ke.) elements of the soluble fraction of snow are significantly greater than for the fraction of low-soluble compounds and close to the values of coefficients of accumulation for atmospheric aerosol. Geochemical the ranks of metals for snow cover and soil are differ. These facts shows that the chemical composition of the snow cover background territories of taiga zone is formed mainly through long-distance migrations, the influence of local natural and man-made sources is less important. According to calculations Ke. for items in the snow two groups were allocated to metals terrigenous origin and mixed terrigenous and anthropogenic origin. Rows calculated based on the values Ke. for snow, indicate the specific character of formation of the atmospheric aerosol in the studied area in comparison with the European territory of Russia. There is the influence of anthropogenic emissions and regional geochemical features of the territory. The equity ratio of elements in snow cover on the taiga are estimated. The share of low-soluble forms of metals in the composition of the snow cover decreases with latitude.

Key words: *snow cover, metals, organogenic horizons of soils, aerosol, long-range transport*

INTRODUCTION

Recently interest in theoretical and applied focus of research of snow cover has been growing (Baglaeva, 2012; Bortnikova, 2009; Kalujnyi, 1998; Walker, 2003). Snow cover is effective storage of pollutants that accumulate and persist in it unchanged during the winter. The concentration of pollutants in the snow is usually 2-3 orders of magnitude higher than in the atmosphere. Snow cover, as a natural drive, giving the amount of dry and wet depositions and quantitative parameters of pollution of ecosystems. Analysis of the composition of snow and aerosols, and the ratio of macro - and micro-components provide the necessary information regarding the long-range transport of substances released to the atmosphere. In general, quantitative chemical characteristics of snow cover and aerosols is a reliable marker for evaluation of environmental pollution (Vasilenko, 1985; Vinogradova, 1996).

Research in recent decades show a significant increase in the content of heavy metals in the atmosphere, precipitation, soils and other natural objects, located on a very remote distances from emission sources (Perelman, 1975). The elemental composition of the snow cover background territories is determined coming to the surface aerosol, chemical composition of which is determined by the range of their migration. The formation of the chemical composition of the snow cover background territories caused by pollution in the Russian far and regional transfers of pollutants, and the mass fraction of elements in soils depends not only on the factors of soil formation, but also from the quantitative material composition of snow. Comparing installed geochemical the ranks of accumulation of metals in snow cover and organogenic layer of soil it is possible to identify the role far and regional transfers in the formation of the chemical composition of the snow cover (Walker, 2003).

The enrichment factor (Ke.) often use to determine the sources of metals in aerosols that came to the surface in the composition of the snow cover. It is will have the greatest values for atmospheric aerosol coming background on the territory under significant influence of long-range transport (Baglaeva, 2012). It is known that the ratio of the content of metals in water-soluble compounds and in the composition of suspended particles depends on the degree of environmental pollution. In background areas in the composition of the snow cover is dominated by soluble metal compounds. Near emission sources simultaneously with the increase in the total dust load poorly soluble compounds of most elements is dominated (Beznosikov, 2007; Vinogradova, 1996; Malahov, 1998; Pchelinsev, 1982).

The purpose of this study is to assess the intake of soluble and partially soluble forms of metals and on this basis to define the role of the long-range and regional transfers of substances in the formation of the chemical composition of the snow cover background territory of the taiga of the European North-East of Russia (Komi Republic).

OBJECTS AND METHODS OF RESEARCH

The objects of study were snow cover, atmospheric aerosol and samples organogenic horizons of soils background territories of taiga of the European North-East of Russia (Komi Republic). Sampling conducted by taiga: southern, middle, northern. Scheme of sampling of snow, spray and soil is presented in Figure 1.

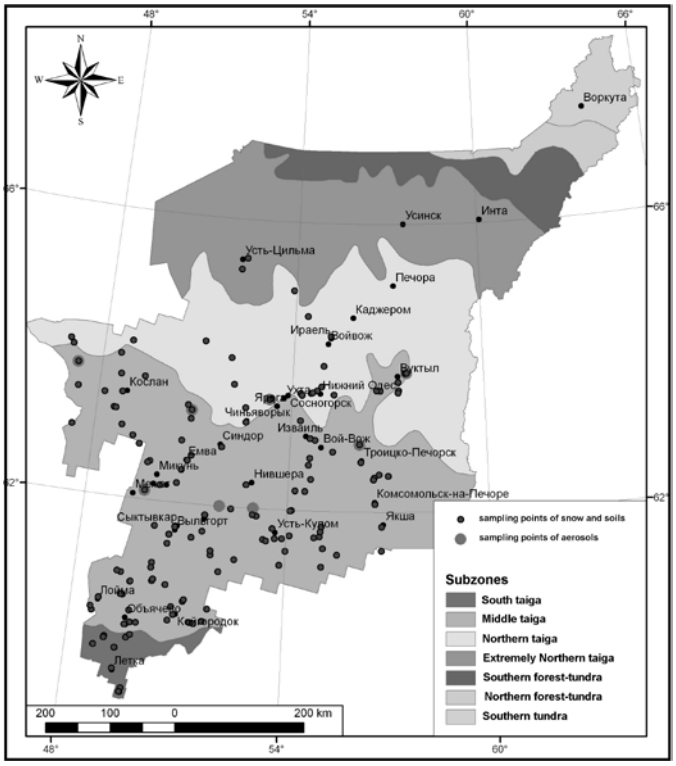


Figure 1. Scheme of the sampling points locations of the snow cover,

atmospheric aerosol and soils

Sampling, sample storage of snow cover, chemical analysis of melt water and aerosols were performed in accordance with the guidelines for the control of atmospheric pollution. Samples of atmospheric aerosol were collected in few paragraphs dedicated to the sampling of snow cover. Selection of aerosols carried out by filtering a fixed amount of air through the cellulose acetate filters with the three-way aspirator. The air intake is carried out at a height of 1.5-2 m above the ground in the direction of the wind. The duration of the selection of one of the sample ranged from 1.5 to 2 hours, and the volume of pumped through the air filter for a test – not less than 20 m^3. The mixed samples consisting of 15 individual samples were selected to assess the variability of metals organogenic horizons of the soils.

Quantitative chemical analysis of metals is carried out by the method of atomic emission spectrometry with inductively coupled plasma. Following elements in the snow and aerosols were determined: Na, K, Ca, Mg, Mn, Zn, Cd, Cu, Ni, Pb, Fe, Al, Cr; in soil samples − Mn, Zn, Cd, Cu, Ni, Pb. The contents of the examined components in snow water was estimated in units of mass concentrations in mg/dm^3. Obtained results were calculated at the appropriate values exposure levels substances mg/m^2 (g/m^2) for more correct interpretation.

Chemical-analytical researches were carried out on the basis of instrument-methodical base of eco-analytical laboratory of the Institute of biology, Komi scientific center, accredited in relation to objects of quantitative

chemical analysis for the purposes of the industrial ecological control, monitoring of environmental pollution and scientific research.

DISCUSSION OF RESULTS

The obtained results showed that in snow cover background landscapes taiga zone dominated by water-soluble compounds as macro (Na, K, Ca, Mg)and micro-components (Ni, Cd, Zn, Mn, Cu, Pb) (Table 1).

Table 1. The ratio of the elements in the fractions of melt snow water

Element	Soluble fraction			Poorly soluble fraction		
	1	2	3	1	2	3
Na	0.0219 ±0.0002*	0.0171 ±0.001	0.0245 ±0.002	0	0	0
	100**	**100**	**100**	0	0	0
K	0.0064 ±0.0008	0.0097 ±0.0003	0.0171 ±0.0016	0.0009 ±0.0001	0.00120 ±0.00004	0.0005 ±0.0001
	87.7	**89.0**	**97.2**	**12.3**	**11.0**	**2.8**
Ca	0.0161 ±0.0014	0.021 ±0.001	0.0388 ±0.003	0.0017 ±0.0002	0.00160 ±0.00004	0.0008 ±0.0001
	90.4	**92.9**	**98.0**	**9.6**	**7.1**	**2.0**
Mg	0.0027 ±0.0002	0.0026 ±0.0001	0.0045 ±0.0003	0.00030 ±0.00003	0.00090 ±0.00002	0.00030 ±0.00002
	90.0	**74.3**	**93.8**	**10.0**	**25.7**	**6.3**
Ni	0.076 ±0.008	0.068 ±0.002	0.056 ±0.004	0.046 ±0.005	0.025 ±0.001	0.0179 ±0.0014
	62.3	**73.1**	**75.8**	**37.7**	**26.9**	**24.2**
Cd	0.020 ±0.002	0.026 ±0.001	0.011 ±0.001	0.035 ±0.004	0.0130 ±0.0004	0.0033 ±0.0003
	36.4	**66.7**	**76.9**	**63.6**	**33.3**	**23.1**
Zn	0.79±0.07	0.85±0.02	0.88±0.06	0.37±0.03	0.500±0.012	0.29±0.02
	68.1	**63.0**	**75.2**	**31.9**	**37.0**	**24.8**
Mn	0.19±0.02	0.44±0.01	0.52±0.03	0.036±0.003	0.059±0.001	0.040±0.003
	84.1	**88.2**	**92.9**	**15.9**	**11.8**	**7.1**
Cu	0.091 ±0.010	0.138 ±0.004	0.169 ±0.013	0.0080 ±0.0009	0.0051 ±0.0001	0.0031 ±0.0002
	91.9	**96.4**	**98.2**	**8.1**	**3.6**	**1.8**
Pb	0	0.023 ±0.001	0.032 ±0.002	0.033 ±0.004	0.024 ±0.001	0.0159 ±0.0012
	0.0	**48.9**	**66.8**	**100.0**	**51.1**	**33.2**
Al	0.71±0.07	0.78±0.02	0.21±0.02	1.29±0.14	1.23±0.04	1.20±0.09

	35.5	**38.8**	**14.9**	**64.5**	**61.2**	**85.1**
Fe	0.84±0.01	0.74±0.02	0.58±0.04	0.60±0.07	0.88±0.03	1.07±0.08
	58.3	**45.7**	**35.2**	**41.7**	**54.3**	**64.8**
Cr	0.060 ±0.006	0.0212 ±0.0006	0.0311 ±0.0023	0.070 ±0.008	0.0334 ±0.0010	0.0349 ±0.003
	46.2	**38.8**	**47.1**	**53.8**	**61.2**	**52.9**

1, 2, 3 – the southern, middle and northern taiga;

* − module of receipt of the item (Na^+, K^+, Ca^{2+}, Mg^{2+} – g/m^2, other – mkg/m^2);

** − mass share, %.

The exception are terrigenous elements Al, Cr and Fe. In addition, the mass fraction of soluble elements with the latitude increases. The most significant changes in the ratio of the share of soluble and insoluble compounds mentioned in the snow for cadmium. It is established that Ni, Cd, Cu, Zn are mainly in the composition of the soluble compounds, and for Al and Fe is dominated their hard-soluble forms. This is consistent with data obtained by other authors (Vinogradova, 1996).

The contribution of aerosols of different origin in the formation of the chemical composition of precipitation (snow) were estimated by calculating the values of the coefficients of aerosol enrichment of snow elements regarding the content in the earth crust. For each element enrichment factor was calculated by the formula:

$$K_{e.} = \frac{[\omega(E)_i/\omega(Al)]_{sample}}{[\omega(E)_i/\omega(Al)]_{earth\ crust}},$$

$\omega(E)_i$ – mass concentration of element in the atmospheric aerosol and the earth's crust;

$\omega(Al)$ – mass fraction of aluminum in the atmospheric aerosol and the earth's crust (Poslovin, 1984).

The values of element content, in the form of dissolved compounds, and in structure of poorly soluble in melt water of suspended particles were used to calculate the coefficients of enrichment. The values Ke. considered elements can be divided in terrigenous (Ke. < 10) and anthropogenic (Ke. > 10) (Mason, 1952). The mean values of the coefficients of enrichment presented in table 2.

Table 2. The mean values of the coefficients of enrichment of aerosols snow macro - and microelements relatively clark in the earth's crust (*n=227, 2005-2007 гг.*)

Элемент	Total content of elements	Soluble fraction 2	Poorly soluble fraction
Na	33±9	29±8	-
Mg	7±2	6±2	1±0.4
K	19±5	17±5	2±0.5
Ca	26±7	26±7	2±0.5
Ni	73±19	45±12	29±8
Cu	94±25	83±22	16±4
Cd	8000±2100	4400±1200	2510±660
Zn	430±110	284±75	182±48
Mn	24±6	20±5	3±0.7
Fe	1±0.4	1±0.1	1±0.2
Pb	88±23	88±23	62±16
Cr	10±3	5±1	8±2

There is an increase of coefficient values due to the contribution of low-soluble fractions, which is determined by the local pollution of snow cover for the total metal content in the snow. However the values Ke. for elements in the composition of suspended particles are much smaller than for the soluble forms.

For the total metal content in the snow lowest values of the coefficients of enrichment obtained for magnesium (Ke. = 7) and chromium (Ke. = 10). Although sodium, potassium and calcium are macronutrients and found in large quantities in the earth's crust, their coefficients enrichment exceeded the limit value (10) for terrigenous items and amounted to 34, 19 and 26, respectively. The maximum values of the coefficients of enrichment obtained for the cadmium content in the snow background areas is minimal.

The second largest is the Ke. belongs to zinc - element, dominant in winter precipitation in the study area.

The increase in the values of coefficients of enrichment for total content of elements is observed at the expense of the contribution of low-soluble fractions, which is determined by the local pollution of snow cover.

To visualize the values of the coefficients of enrichment snow elements was built geochemical a number of metals (1) and compared with that obtained in the work S. Malakhov and S. Makhanko (1997) for background territories of the European zone of Russia (2). A comparison of the two series has shown, that the investigated territory is characterized by the rejection of the values of the coefficient of enrichment for such elements as manganese, calcium and nickel upwards:

$$Fe < Mg < Cr < K < Mn < Ca < Na < Ni < Pb < Cu < Zn < Cd \quad (1)$$

$$Fe < Mn < Ca < K < Mg < Ni < Cr < Na < Cu < Zn < Pb < Cd \quad (2)$$

High manganese content in snow cover due to the possible penetration of dissolved forms of organogenic horizons of soils, in which the content of compounds of manganese much (Mason, 1952). The distribution of this element in snow cover of taiga looks fairly homogeneous fields with several local maxima. The content of calcium, according to the average value of factor of enrichment, the area is also higher due to the influence of local background (Bortnikova, 2009). High nickel content, probably due to specific technogenic impacts on the area and a long lifetime in the atmosphere. Maximum modules receipt of nickel marked around large settlements and industrial centers that possibly caused by emissions of heat power engineering and transport.

Calculations Ke. allowed to separate chemical elements into two groups: 1 – typical of the earth's crust (Fe, Mg, Cr, K, Mn, Ca, Na); 2 – mixed terrigenous and anthropogenic origin (Ni, Pb, Cu, Zn, Cd). There is consistency in the distribution of dissolved forms of metals in snow cover in the taiga subzone. Geochemical a number of elements according to the values of their content (mol/m^2) as follows: Zn > Mn > Cu > Ni > Cd > Pb.

Dissolved form elements characterize the contribution of long-range transport, so there are minor variations in the ratio relative to the component with minimal content in different subzones. The greatest variability are characterized by a series of distribution of poorly soluble metal compounds. In the southern taiga subzone high content of nickel in suspended particles is characterized.

In the northern taiga subzone of the observed increase in the concentration of lead in the composition of suspended particles. Received geochemical series for soluble compounds and total concentrations are similar, because in the samples of snow cover mainly dominated by dissolved form elements. This represents a slight impact of local pollution sources on the accumulation of heavy metals in snow cover background territories of taiga zone of the region.

The accumulation of heavy metals in the litter (A0), organogenic (O) and sod (A1) horizons of the soilsis investigated to evaluate the role of long-range transport, since the results of studies of higher levels of background soils, slightly exposed to anthropogenic impact reflect the level items arrive from the atmosphere for a long time. Geochemical series of heavy metals for snow cover and soil subzone were built (table 3). The umbric albeluvisols, stagnic histic albeluvisols and albic podzols in the southern taiga were analyzed; stagnic histic albeluvisols, haplic albeluvisols and albic podzols – in the medium taiga haplic albeluvisols, stagnic albeluvisols (siltic) and albic podzols – in the north taiga.

Table 3. Geochemical a number of metals accumulation in snow cover and organogenic horizons of soils and aerosol

Taiga subzone	Geochemical a number of metals	Object
South taiga	Zn > Mn > Ni > Cu > Pb > Cd 193 > 44 > 23 > 21 > 2 > 1	snow, n = 14
	Mn > Zn > Cu, Ni, Pb, Cd 65 > 7 > 1	albic podzols, n = 24
	Mn > Zn > Ni > Cu > Pb, Cd 311 > 10 > 3 > 2 > 1	umbric albeluvisols, n = 19
	Mn > Zn > Ni > Cu, Pb, Cd 66 > 5 > 2 > 1	stagnic histic albeluvisols, n = 30
	Mn > Zn > Ni > Cu, Pb >> Cd 95 > 5 > 2 > 1 >> 0.05	average for soil
Average taiga	Zn > Mn > Cu > Ni > Cd, Pb 92 > 40 > 10 > 7 > 1	snow, n = 186
	Mn > Zn > Cu > Ni, Pb >> Cd 32 > 7 > 2 > 1 >> 0.02	albic podzol, n = 37
	Mn > Zn > Ni, Cu, Cd, Pb 105 > 2 > 1	haplic albeluvisols, n = 25
	Mn > Zn > Ni, Cu > Pb, Cd 117 > 7 > 2 > 1	stagnic histic albeluvisols, n = 64
	Mn > Zn > Ni, Cu, Pb >> Cd 100 > 7 > 1 >> 0.1	average for soil
North	Zn > Mn > Cu > Ni > Pb > Cd	snow, n = 27

taiga	147 > 83 > 22 > 10 > 2 > 1	
	Mn > Zn > Ni, Cu, Pb >> Cd 103 > 9 > 1 >> 0.05	albic podzol, n = 23
	Mn > Zn > Ni > Cu > Pb >> Cd 92 > 15 > 5 > 2 > 1 >> 0.04	stagnic albeluvisols (siltic), n = 30
	Mn > Zn > Ni > Cu, Pb >> Cd 21 > 5 > 2 > 1 >> 0.02	stagnic histic albeluvisols, n = 38
	Mn > Zn > Ni > Cu, Pb > Cd 59 > 9 > 3 > 1 >> 0.03	average for soil
The average for taiga zone	Cu > Ni > Zn > Mn > Pb > Cd 251 > 148 > 59 > 29 > 17 > 1	aerosol, n = 8

In general, it can be noted that the sequence of elements in geochemical series for soil and snow cover basically does not change while advancing from the south to the north. For organogenic horizons soil has a high content of manganese (Shevchenko, 2000), zinc dominates in the snow. The share of copper and cadmium in the common module of heavy metals on the snow cover more than in soil. The prevalence of zinc composition of the snow cover indicates the priority role of long-range transport, the supply of manganese mainly due to natural processes in the taiga. The high content in melt water manganese may be a consequence of its receipt of dissolved forms of litter and organogenic horizons in the beginning of snow cover. The prevalence in the snow zinc over manganese may be due to the fact that the great migration of this element from lower latitudes in the process of wind erosion, where his lot is contained in the soil and rocks (Malahov, 1990).

Another theory explaining the difference in the distribution of elements in geochemical the ranks of the investigated objects, based on different behavior of metals in the process of acid leaching from soils. Nickel and manganese are at a lower level than copper and zinc in a series of leaching of various components: Cu > Zn > Ni > Mn (Beznosikov, 2007). However, zinc precipitation contains more than copper, and geochemical range of this element dominates. Based on differences in the accumulation of metals in the snow and organogenic horizons of the soils can be argued about the preferential formation of the chemical composition of the snow cover background territories at the expense of aerosols involved in the long-range transport.

The formation of the chemical composition of atmospheric aerosol happens regardless of soil erosion factor (sampling carried out in March), and therefore it has a completely different geochemical a number of elements.The results of correlation analysis showed that similar mechanisms of metals distribution of in the aerosol and snow are characteristic only for sodium and copper. High significant correlation coefficients for copper ($r = 0.49$, $r_{5\%} = 0.40$, $P = 0.95$) and sodium ($r = 0.68$, $r_{5\%} = 0.40$, $P = 0.95$) indicate that the accumulation of these elements in the snow probably due to local environmental factors, rather than as a result of long-range transport. The other elements are not reliable affinity. These discrepancies may be due to the fact that the results of the chemical composition of aerosol and snow reflect the state of the atmosphere for different time periods.

Ke. relative clark in the earth's crust by B. Mason (1952) for the evaluation of the mechanisms of formation of the chemical composition of atmospheric aerosol were calculated. The obtained values of the coefficients of

enrichment is much lower than for snow cover. The highest value Ke. marked for cadmium. Diagrams reflecting the average values Ke. for atmospheric aerosol and total content of elements in the snow have considerable similarity, which is confirmed by the correlation coefficient r = 0.85 (n = 12, $r_{5\%}$ = 0.58, P = 0.95) (Fig. 2).

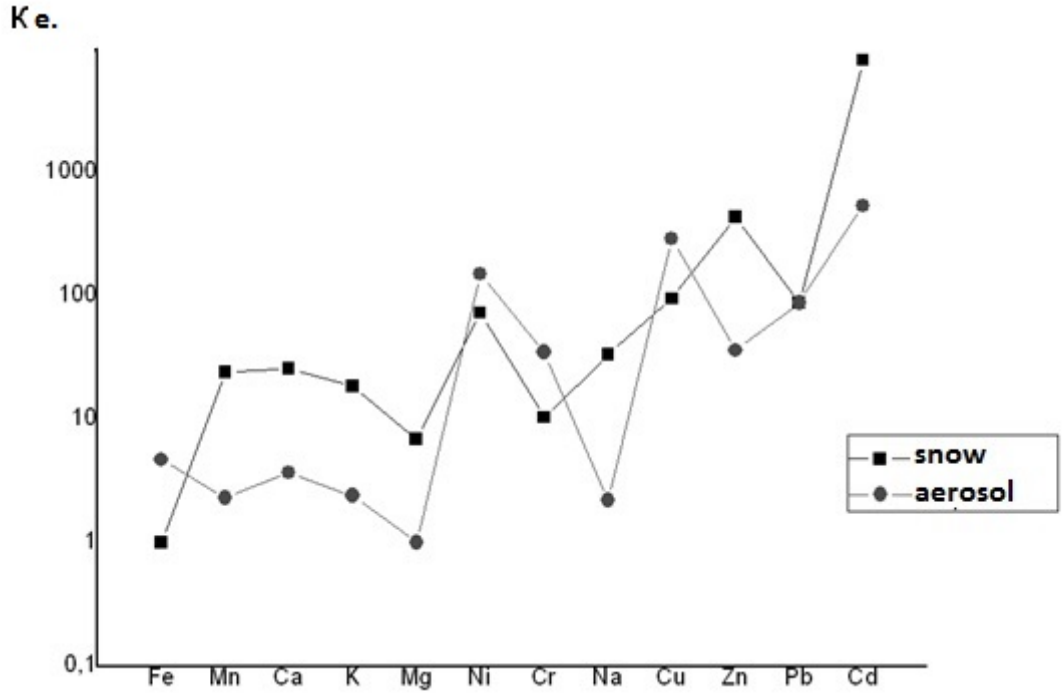


Figure 2. The values of the coefficients of enrichment of elements for atmospheric aerosol and total content in snow cover

CONCLUSION

The formation of the chemical composition of the snow cover of the taiga zone background territories of the Komi Republic is mainly due to soluble compounds of elements. Factors enrichment elements soluble fraction much more than for a fraction of low-soluble compounds and close to the values of coefficients of accumulation for atmospheric aerosol. Geochemical the ranks of metals for snow cover and soil differ. These facts shows that the chemical composition of the snow cover background territories of taiga zone is formed mainly through long-distance migrations, the influence of local natural and man-made sources is less important. The geochemical series of items, calculated based on the values cob for snow, indicate the specific character of formation of the atmospheric aerosol in the studied area in comparison with the European territory of Russia. There are the influence of anthropogenic sources and regional geochemical features. According to calculations cob for items in the snow were allocated to two groups – metals terrigenous origin (Fe, Mg, Cr, K, Mn, Ca, Na) and mixed terrigenous and anthropogenic origin (Ni, Pb, Cu, Zn, Cd). Equity ratio of elements in snow cover in the taiga were evaluated. The share of low-soluble forms of metals in the composition of the snow cover decreases with latitude

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