HEAVY METALS IN THE ENVIRONMENT OF URBANIZED LANDS

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Abstract
Results of monitoring of environment of the St.-Petersburg region are analyzed: maintenances and spatial distribution in a snow cover of heavy metals which are one of the most dangerous elements for health of the person. Established correlations between the hydrogen index (pH) of snow water index and the total pollution of snow cover; pollution levels of snow cover, surface water and soil. The maps of the spatial distribution of heavy metals and total pollution.

Key words: *urbanized areas, pollution, snow cover, heavy metals, St. Petersburg*

Modern cities are population centers, industry, transport, communications, and the resulting degradation of landscapes and intense pollution. Area anomalies pollutants currently are manmade geochemical province.

The greatest danger to the environment and human health is air pollution. This is due to the fact that many toxic compounds in the atmosphere affect our body throughout life – from the first to the last breath. Found that the total surface of lung alveoli reaches an area of about 100 m^2. Every minute a person breathes in about 20-24 liters of air. In the alveoli inhaled air comes into direct contact with the blood, in which almost all the dissolved compounds in the air from the lungs and the blood flows directly into the systemic circulation, bypassing the main barrier detoxification in the human body – the liver. It was established that poisons ingested by mammals inhalation, affect animals and humans 80-100 times stronger than these poisons entering through the gastrointestinal tract. The difficulty in protection from toxic substances in the atmosphere is that it is possible to abandon the contaminated water or food potentially dirty, but we can not breathe.

Transport of pollutants over long distances is carried out mainly at the expense of the general circulation of the atmosphere. Arriving in her impurity, caught up by air currents may extend to a distance of several hundred to several thousand kilometers.

The presence of a correlation between substances, air pollutants and their content in the snowpack allow the use of this type of storage medium for express geo-ecological assessment of the overall level of pollution in urban areas. Geochemical anomalies in snow cover , essentially reflect the ecological and geochemical state of the atmosphere, summarizing the impact of natural atmogeochemical (degassing of the Earth), natural and man-made atmogeochemical (gas neoplasms buried peat deposits, etc.) and technological factors (emissions enterprises) affecting the dynamics geochemical ecological functions of the lithosphere in time (Trofimov et al, 2006). Snow cover reflects the contours aerogenic pollution for the period of education and gives an indication of the dynamics of the processes taking place. During snowmelt in snow toxicants are migrating to surface water, sediments, soil and their underlying rocks, and their distribution area greatly exceeds the contours of geochemical anomalies in the snowpack.

Most attention when ecogeochemical studies usually given heavy metals (Saet, Revich et al, 1990). This is due to the widespread and indicator value of this type of pollution, as well as the presence of well-established and cheap enough analytical techniques (mainly spectral). In addition, in connection with its high biochemical activity , toxicity, a high cumulative capacity, difficulty excretion of heavy metals are among the most dangerous to human health and other living organisms pollutants. Although the process of urban air pollution are involved not only heavy metals, due to the generality of pollution

sources, the results of this type of pollution exhibit satisfactory agreement with the calculated values of pollution index.

Caught in the environment heavy metal compounds easily penetrate the food chain, accumulating in plants and animals; involved in the metabolic cycles and cause a variety of physiological disorders , including genetic level. To remove heavy metals from the system to a safe level requires a very long period of time, provided the complete cessation of their receipt. The half-life of heavy metals from the human body is usually many months. Physiological effects of heavy metals on humans and animals varies and depends on the nature of the metal compound type, in which it exists in natural environment, and the range of concentrations at which the reaction can be normal metabolic processes.

In this regard, the Department of Geology and Geoecology of Herzen University monitoring of heavy metals in snow and other natural environments of urbanized areas, begun in 2003, are highly relevant (Nesterov et al, 2008, 2009, 2012; Zarina et al, 2009, 2011, 2013).

The study area (St. Petersburg region) includes the territory of St. Petersburg, a significant portion (northwest) west of the Karelian Isthmus and the Leningrad region. In the west, the region is limited coastline within the Gulf of Vyborg – Sosnovy Bor in the east – from the shores of Lake Ladoga for northern border is taken straight from conditional to Vyborg – Kuznechnoe for south – arc Sosnovy Bor – Luga – Volkhov.

The climate – moderate continental with features marine influence, and this influence has a stronger impact in the western part of the territory. Winter is quite long, moderately cold. In winter features marine climate dominated. The coldest month is February. Snow cover on average 3.5 months (from early December to mid-March). During the winter, the winds of the south, southwest and west directions. Precipitation have substantially embedded, widespread in nature and occurs mainly in the form of snow, and sleet, during thaws – rain.

Sampling points were located in areas with minimal impact highways, railways, factories, boilers, etc. (at least 250 m from the edge of the roadway, not less than 1000 m from industrial facilities), in the forest – at large clearings.

Total in 2003-2013 research within the region were taken and analyzed more than 1,000 samples of snow.

With the help of X-ray fluorescence spectrometer method «Spectroscan MAX-GV» in snow samples determined the content of elements: Pb, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Bi. Preference is given to these heavy metals, as they are priority pollutants within the study area and the North-West region as a whole (Lapo AV et al, 1989; Yakhnin EY, 1994; Yanovsky AS, 1995). The majority of the analyzed elements belong to the first three classes is highly active and biochemical toxicity.

The acidity (pH) is an important physico-chemical characteristic of atmospheric water. Along with the measure of the overall mineralization it allows to a certain extent on the local judge of air pollution as the deviation from the index unpolluted precipitation with pH = 5.6 (Israel, 1984).

The main influence on the pH of melt water snow have processes associated with industrial production and combustion of fossil fuels and emission of great quantities of substances, leading to the formation of strong acids such as sulfuric , nitric, hydrochloric and hydrofluoric. Sources of sulfuric and nitric acids – the emissions of oxides of sulfur and nitrogen – inherent in any type of industrial production.

Nevertheless the pH value of melt atmospheric water does not depend on the absolute values of the concentrations of the ions, and the ratio of anions and cations. Therefore, in areas where industrial emissions are dominated compounds having an alkaline reaction (CaO, MgO) and neutralizing the action of acids, we should expect a relatively high pH values of melt water from the snowpack. It can be concluded that the pH of meltwater from snow cover in such areas increases with anthropogenic impact; and in areas where aerosol emissions are small enterprises, due to long-range transport of sulfur and nitrogen occurs acidification of precipitation and snow cover (Glazov et al, 1983).

For eco-toxicological assessment of snow cover was calculated overall pollution index (Zc) which is the sum of the coefficients of concentration (Kc) elements (minus background) included in the geochemical association reflects an excess of the background level of the group of elements and characterizes the level of man-made pollution. When counting Zc uses chemical elements I and class II toxicological hazard (arsenic, cadmium, mercury, lead, zinc, fluorine, boron, cobalt, nickel, molybdenum, copper, antimony, chromium).

As grading scales total pollution of snow and soil covers heavy metals were used developed under the leadership of Yuri Saet indicative scales of the «atmosphere – snow – soil – a man» (Table 1).

Table 1. Pollution levels of snow and soil cover on the total heavy metal contamination (Methodical..., 1990; Saet et al, 1990)

The level of pollution	Total pollution of soils (Zc)	Total pollution snow (Zc)	Drop dust (kg/km^2 day)	Effects on human health
Low	8–16	32–64	100–250	Low morbidity of children, the incidence of functional abnormalities minimal
Average	16–32	64–128	250–450	Increase the overall morbidity
High	32–128	128–256	450–850	High level of overall morbidity, increase in the number of sickly children, children with chronic diseases, disorders of the functional state of the cardiovascular system
Very high	>128	>256	850	High incidence of children, violation of women's reproductive function (increase toxemia of pregnancy, premature birth, stillbirth, neonatal malnutrition)

For a comparative analysis of the distribution of heavy metals in the snow cover, as well as for the correlation analysis between the pH value (pH) and the overall pollution index (Zc) study area was divided into five zones, the distance from St. Petersburg:

1) St. Petersburg in its administrative boundaries, Kurortnii, Petrodvorets, Pushkin, Kolpinskiy areas (52 sampling points);

2) the 30-kilometer zone, which includes the territory to Oselki sampling stations in the north-east, east and Peri, Verevo in the south (17 sampling points);

3) 60-kilometer zone, which includes the territory to Ushkovo sampling stations in the north-west, Lembolovo in the northeast, east and Zhikharevo, Siverskaya in the south (53 sampling points);

4) 90-kilometer zone, which includes the territory to Zahodskoe sampling stations in the north-west, Petyayarvi in the northeast , east and Pupyshevo, Rosinka in the south (34 sampling points);

5) area, over 90 km from St. Petersburg , including Kalishche territory to the west of Vyborg in the north-west, 152 km north-east, east and Volkhov, Luga in the south (56 sampling points) .

The results of analyzes are shown in Table 2 and Fig. 1-3.

Table 2. The results of geochemical studies of snow cover of the St. Petersburg region

Zone	Bi, mg/l	Pb, mg/l	Zn, mg/l	Cu, mg/l	Ni, mg/l	Fe, mg/l	Cr, mg/l	V, mg/l	Dust, mg/m^2	pH	Zc
St. Petersburg	0.0121	0.0107	0.0278	0.0191	0.0031	0.0252	0.0065	0.0057	0.37	6.69	12.0
30 km	0.0120	0.0101	0.0203	0.0159	0.0025	0.0136	0.0061	0.0045	0.62	6.13	8.0
60 km	0.0117	0.0097	0.0123	0.0141	0.0018	0.0136	0.0058	0.0042	0.28	6.32	7.9
90 km	0.0128	0.0102	0.0104	0.0166	0.0032	0.0099	0.0061	0.0045	1.62	6.39	7.7
>90 km	0.0105	0.0094	0.0202	0.0185	0.0027	0.0125	0.0056	0.0042	0.35	6.57	11.0
MAC*	**0.5**	**0.1**	**1.0**	**1.0**	**0.1**	**0.5**	**0.5**	**0.1**	-	-	-
Yakutia **	-	0.0020	-	0.0020	0.0020	-	0.0050	0.0020	-	-	-

* Hygienic ..., 2003; ** Makarov et al, 1990.

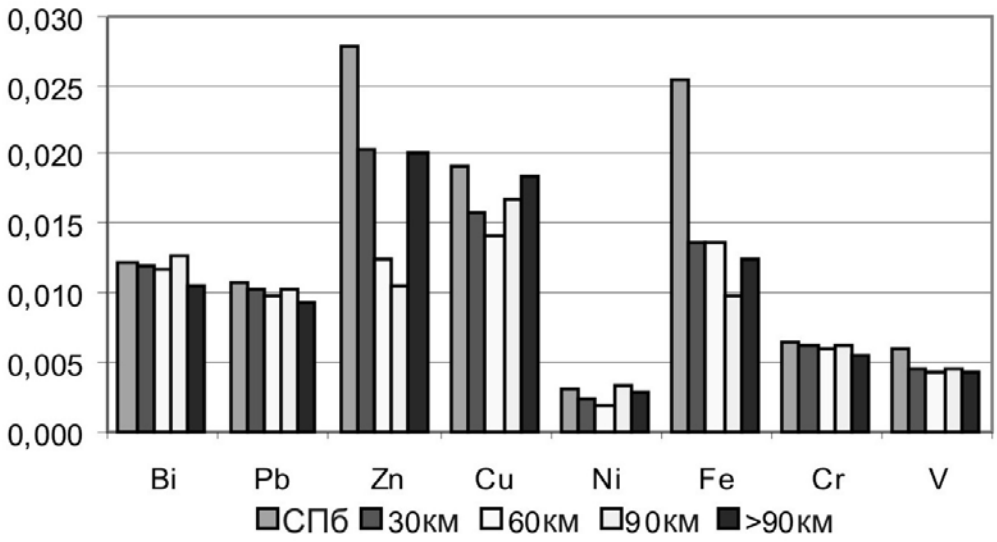

Fig. 1. Average content of heavy metals snow cover St. Petersburg region, mg/l

For sanitary assessment of snowpack in Table 2 shows the maximum allowable concentration (MAC) of a number of elements.

Data Table 2 and Fig. 1 show that the content of heavy metals is the most polluted snow within St. Petersburg, as the distance from the city pollution level is reduced , although in the area for more than 90 kilometers, the values Zn, Cu, Fe grow again. Increasing the zinc content in this area due to the fact that there are regional centers of the region – Vyborg, Volkhov, Luga and Kalishche who are making their "contribution" to the state of the snow cover.

Comparing the results of the analyzes with the official regulations (MAC), we can come to a definite and quite unexpected conclusion about the relatively low level of pollution of snow cover the central part of St. Petersburg with heavy metals. In the melt water content of metals by 1-2 orders of magnitude lower than the level of maximum allowable concentration for water bodies of drinking and cultural purpose. It should be noted, however, that the content of heavy metals, however, one or two orders of magnitude higher than that observed for the background for the Russian regions of Yakutia (Table 2).

Average pH snow samples designated zones of the St. Petersburg region vary in a relatively narrow range of 6.13 to 6.69, which characterizes the melt water as slightly alkaline compared with non-contaminated sediments.

Fig. 2 shows the distribution of samples for pH range in the snow water of the St. Petersburg region. As can be seen from the figure, the maximum number of samples with a pH above 5.5 is necessary for a range of values of 6.5-7.0 (35%), which is typical for industrial development areas (Yakhnin 2003, Abdullaev et al, 2010). Occurrence of samples with pH> 7.0 is 24%, and it should be noted that the samples with the highest values of pH (7,85-9,78) were selected near Volkhov aluminum factory – the only major steel plant in the study area.

Minimum pH values typical for samples taken in areas with low anthropogenic load.

The obtained data are fully consistent with the results of the Research Center for Ecological Safety, obtained in the study of snow cover the Leningrad region and South-East Finland, 1992-2001 (Yakhnin, 2003). The authors of these studies note that all areas of technogenic pollution compared to the background areas are characterized by higher pH values snow water, the maximum value of the pH value, as in our study, it was found in the zone of influence of the Volkhov aluminum smelter, where individual samples had snow water alkaline reaction 8.0-9.0 (Yakhnin 2003, Zarina et al, 2012).

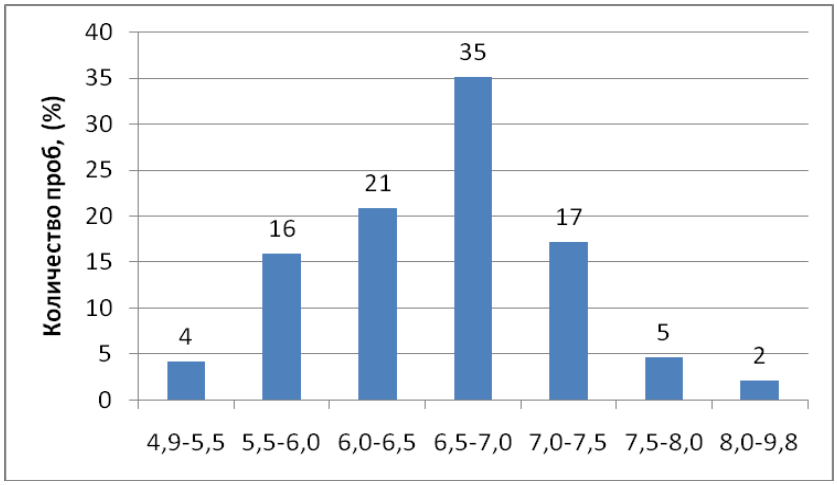

Fig. 2. Interval Distribution of pH values in the snow samples of the St. Petersburg region

Fig. 3 shows the dynamics of pH and Zc with distance from St. Petersburg. The highest values of total index (Zc) are characteristic of snow cover in the vicinity of St. Petersburg. As the distance from the city pollution level decreases and increases again at a distance of over 90 kilometers, where the regional centers of the Leningrad region – Vyborg, Volkhov, Luga and Kalishche, contributing their "contribution" to the pollution of the snowpack. Similarly behaves the pH. The correlation coefficient between pH value and total pollution index is 0.89, which indicates a high degree of direct correlation between them.

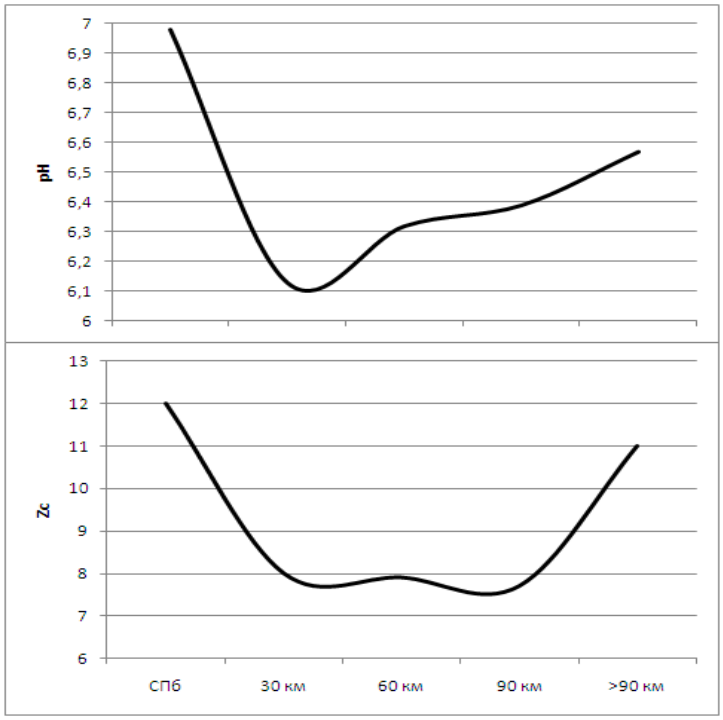

Fig. 3. Changing the pH value (pH) and the overall pollution index (Zc) as the distance from Saint Petersburg

To identify patterns of spatial distribution of heavy metals in the snow cover of the St. Petersburg region, we have constructed maps for each of the chemical elements. Due to the fact that in the outlying parts of the region studied the density of sampling points is not sufficient to create high reliability mapped schemes , the area has been limited in the west – the sampling stations and Bronk Ushkovo the north – Georgian , in the east – and Pupyshevo Kirovsk , in the south – Gatchina .

Analyzing the characteristics of the spatial distribution of heavy metals in the snowpack in the region, we can draw the following conclusions:

The maximum values of lead and zinc in the snowpack are characteristic in St. Petersburg, Leningrad region surrounding areas have a significantly less pollution. Moreover, for the territory of St. Petersburg characteristic patchiness in the spatial distribution of these elements. Maximum values of the zinc content in the snow cover (above 0.1 mg/l) were in the northeastern part of St. Petersburg and the adjacent territory of the Leningrad region. For the center, south and south- west of the city is characterized by the concentration of zinc in the melt water of the order of 0.04 mg/l. For the rest of the Greater St. Petersburg marked zinc content 0.001-0.002 mg/l. Isoline 0.01 mg/l in general outlines the boundaries of the city, except the north-eastern part. For the territory lying outside of St. Petersburg characteristic values of zinc content of less than 0.01 mg/l.

With a view to ecological and geochemical assessment of the territory we have constructed maps of their total pollution (Zc) snowpack St. Petersburg region in their content of heavy metals I and II hazard classes (Fig. 4).

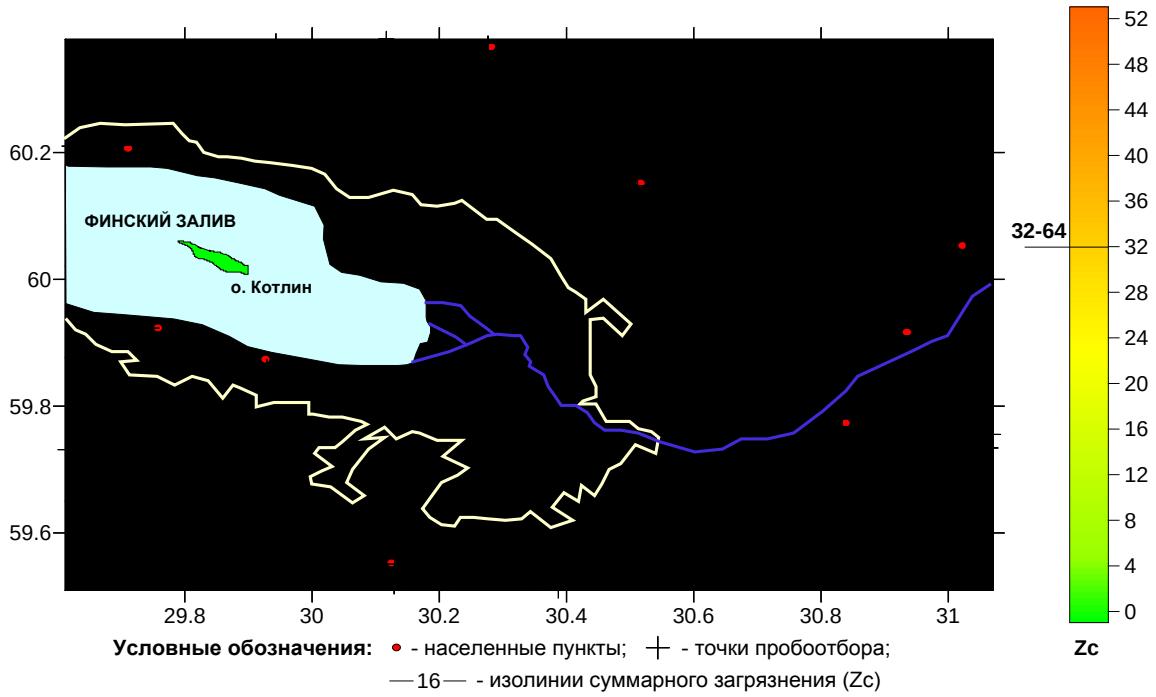

Fig. 4. Schematic map of the level of overall pollution (Zc) of the snow cover of the St. Petersburg region

Overall, the analysis maps of their total pollution of snow cover in the region reveals a number of patterns:

For the territory of St. Petersburg typical mosaic distribution zones of high and low concentrations of pollutants. Pollution indices in this part of the region vary from 8 to 56 (sampling station Kondakopshino), while the rest of the study area is a kind of relatively uniform distribution of background contamination with the lowest index Zc within 0,01-4. Marked maxima values Zc sampling stations: Dachnoe (Zc = 40), Volodarskaya (Zc = 33), Verevo (Zc = 30) , Ulyanka (Zc = 28), Specific (Zc = 20), Predportovaya (Zc = 20). Patchiness and high anomalous values Zc within St. Petersburg themselves testify to the main contribution to the pollution impact of the urbanized environment.

Outside of St. Petersburg have low levels of contamination. Exceptions are areas Toksovo sampling station and the Georgian, where the index value exceeds Zc 9. Along the northern coast of the Neva River outside of St. Petersburg is scheduled band with minimum values of Zc, which may be due to the impact of the flow of air currents that contribute to removal of contaminants in the neighborhood.

Estimating snow cover in the region in terms of toxicological hazard to living organisms overall pollution index (Zc) heavy metals 1-2 hazard class, it can be concluded that the snow cover throughout the contamination is low, even with a maximum in the southern part of St. Petersburg on the value 2 times less than the lower bound moderately dangerous levels of pollution (pollution levels from Table. 1).

For the purpose of comparative analysis, we studied snow samples selected on the east of the Leningrad region (Oleshi village neighborhood, south-eastern slope of the hill Vepsskaya) Solovki Archipelago (Big Solovetsky Island), Antarctica (Station Progress in the Alps (Zugspitze, Bavaria). Averaged data X-ray analysis of samples to determine the concentration of heavy metals and the index of overall pollution of snow cover areas of research are given in Table. 3.

From the analysis of the data obtained (Table 3), it can be argued that the most contaminated regions is characterized of snow cover, which means that the airspace and the St. Petersburg region, with the largest concentration of Pb, Zn, Cu characteristic of the central part of the support portion St.

Petersburg, and the largest concentration of Bi, Ni, Cr – for the St. Petersburg region. For the region as a whole is marked and tested to the maximum level of total areas of snow cover pollution (Zc = 7.2). The least contaminated snow and air environment of the southeast hill Vepsskaya (Zc = 0.1). Comparing areas with minimal (east of the Leningrad region, the highlands of the Bavarian Alps, Solovetsky Islands, Antarctica) and maximum (St. Petersburg region) anthropogenic impacts, it should be noted that the analysis of samples taken shows comparable results for most elements.

Table 3. Mean values of heavy metals class I and II hazards and overall pollution index (Zc) of snow cover parts of the world

Region	Heavy metals, mg/l						Z_c
	Bi	Pb	Zn	Cu	Ni	Cr	
St. Petersburg (center)	0.0102	0.0110	0.0496	0.0338	0.0024	0.0050	3.8
St. Petersburg Region	0.0118	0.0098	0.0117	0.0145	0.0031	0.0065	7.2
Oleshi (east Leningrad region)	0.0107	0.0089	-	0.0124	0.0012	0.0055	0.1
Solovetsky Islands	0.0113	0.0090	0.0228	0.0187	0.0023	0.0055	3.6
Progress (Antarctica)	0.0105	0.0097	0.0212	0.0148	0.0023	0.0052	3.0
Zugspitze (Bavarian Alps)	0.0113	0.0083	0.0047	0.0137	0.0019	0.0057	0.6

The results obtained by the authors in the study of the "atmosphere – snow – surface water" indicate that the difference in the density of the heavy metal concentrations in snow and surface waters between the relatively "clean" and lakes Gorovaldayskoe Sestroretsky spill (suburbs of St. Petersburg) and "dirty" Ohtinskii spill (St. Petersburg) can reach 5 or even 10 multiple values for snow and surface water , respectively. Thus, significant concentrations of heavy metals in the snowpack and surface waters Okhtinsky spill indicates strong anthropogenic pressure, produced by the combined influence of man-made, including by the aerosol deposition.

When analyzing the total soil pollution in the region identified patterns generally reflect the patterns of spatial distribution of contaminants in the snow cover area is St. Petersburg sharply mosaic and beyond appear background values with index 5. For western, north-eastern and eastern suburbs of St. Petersburg, as well as for most of the city is marked by low (Zc < 16) level of soil contamination. For a large part of St. Petersburg, Gatchina and Georgian areas characterized by average (Zc = 16-32) and high (Zc = 32-128) levels of soil contamination, which is consistent with elevated concentrations of toxicants in the snowpack.

Thus, although the findings suggest that the content of heavy metals in snow samples rarely exceed maximum allowable concentrations established for the water reservoirs of the economic and cultural purpose , but in the future, when snow melts, heavy metals deposited in the soil cover surface water and sediments. Perennial their accumulation leads to anomalies with significant exceedance, evidenced by the study authors for the transit of heavy metals in natural environments (Nesterow et al., 2009, 2012; Zarina et al., 2013, etc.)

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