Ecological Geochemical Investigations of the Contents of Heavy Metals in the Snow Cover in the Saint-Petersburg Region with Application of GIS Technologies

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***Abstract*—Results of ecological-cheochemical studies of the snow cover of Saint-Petersburg region of the Russian Federation are studied: evaluation of surface distribution of heavy metals in the snow cover is made; values of regional snow chemical situation for a number of elements and statistical variations of the background are revealed; and snow chemical anomalies of each element under study are shown.**

***Index Terms*—Air pollution, snow cover, heavy metals, ecological-cheochemical studies, ecological monitoring, environment, antropogenic impact.**

I. Introduction

Emissions of harmful substances in the megalopolis atmosphere amount to hundreds of thousands and millions tons. Presense of coorelative dependances between air polluting substanses and their content in snow cover allows using this type of depositing environmet for expressive geoecological evaluation of general pollution of urbanized territories.

Snow chemical anomalies actually reflect ecological-geochemical situation in the atmosphere, summing up the impact of the natural atmogeochemichal atmospheric condition (degassing of the Earth), natural technogenic atmogeochemical (gaseous growths of the peat deposits and others), and technogenic factors (industrial emissions), which influence the dynamics of geochemical ecological functions of the lithosphere during the time [1].

Snow cover reflects the contours of airgenic pollution at the time of its formation and allows judging on dynamics of ongoing processes. Characteristics of technogenic anomalies in such depositing environments as snow cover may serve a relative indicator of the air pool pollution and directly testify the intensity of geochemical transformation of the pre-surface part of the lithosphere. In the period of snow melting toxic materials found in snow move to surface waters, bottom sediments, soils and rocks under them, and the area of their distribution is significantly larger that the outlines of snow chemical anomalies at that.

Relative simplicity of snow chemical land survey allows to carry on large area territorial studies with the aim of evaluation of the spatial distribution of pollutants, definition of the geochemical background and outlining the territories with abnormal values of the parameters under research.

Most attention at ecological-geochemical surveys is usually paid to heavy metals [2]. It is caused by wide distribution and indicational significance of this kind of pollution, as well as presence of well tested and rather cheap analitical methods (mostly spectral). Besides, because of their high biochemical activity, toxicity, high cumulative capacity, difficulty of removing from the organism, heavy metals present one of most hazardous for human health and other living bodies pollutants.

Although not only heavy metals take part in the process of cities atmosphere pollution, due to the commonality of polluting sources, the results of namely this type of pollution show satisfactory likeness to the calculated values of the atmosphere pollution index.

A network of air control stations existing in St. Petersburg and Leningrad oblast (region) does not conduct monitoring of heavy metals variations. Besides, the systems of departmental monitoring are connected mainly with studying of polluting emissions from technogenic sources. At the same time, any ecological-geochemical land survey suggests research of geochemical properties of the environment components at the local (anomalies) and at the regional (provincial) levels.

In this connection the works on the part of the Chair of Geology and Geoecology of The Herzen University of Russia in monitoring of heavy metals content in snow cover and other environs of the St. Petersburg region, that began in 2003, are quite actual.

II. Region and Methods of Research

The region of the research – the St. Petersburg region – Includes the territory of St. Petersburg, a significant part (north-west) of Karelsky isthmus and western part of Leningrad oblast of the Russian Federation. From the west the territory under study is restricted by the coastal line of the Finnish Bay within the town limits of Vyborg – Sosnovy Bor; from the east – by the coast of Ladoga lake from township Kuznechnoye to town Volkhov; the northern boundary is assumed as a conventional direct line from Vyborg to Kuznechnoye, the southern - an arc formed by towns Sosnovy Bor – Luga – Volkhov.

The regional climate is moderately continental with traits of sea influence which is more expressed in the western part of the territory. The winter is rather continuous, moderately cold. In winter the features of sea climate prevail. The coldest month is February. The snow cover holds on 3.5 months on the average (beginning December – mid March). During winter winds of southern, south-western and western directions prevail. The precipitation is mostly of lingering character and falls mainly as snow and sleet, mixed with rain when it thaws.

At first the investigations were conducted annually on 2 basic plots: the central part of St. Petersburg and Sestroretsk geosystem of Leningrad oblast including lake Sestroretsky Razliv and Sestroretsky marsh [3, 4, 5 and others]. From 2008 the surveyed territory significantly widened. In February 2008 we did a scale selection of the snow cover by means of profile land survey. The samples have been collected from 6 routes radially going out from St. Petersburg in the directions: 1) west – profiles I – St. Petersburg - Kalische, VI – Kronshtadt; 2) north-west – profile II St. Petersburg – Vyborg; 3) north – profile III – St. Petersburg – Kuznechnoye; 4) east - profile V – St. Petersburg – Volkhov; 5) south - profile IV – St. Petersburg – Luga. To get additional information 2 annular routes were organised: 1) VII – Southern semiring; 2) VIII – Northern semiring.

Selection and preparation of samples were carried out according to the officially approved methods developed by us in full correspondence with the world standards [6, 7, 8, 9], accompanied with detailed documentation to the selected material. GPS-navigator eTreex Venture HC was used to tie up the coordinates.

The points for taking samples were placed on plots with minimum influence of motorways, railroads, industries, boilers etc. (at a distance not less than 250 m from the edge of motorways, not less than 1000 m from industrial objects), in forests - on large glades.

In total, on the basic points, radial and annular routes more than 350 snow cover samples were taken, and about 4000 element definitions were made.

Laboratory-analytical works were performed on the basis of the laboratory of Environmental Geochemisty A.N.Fersman of the Chair of Geology and Geoecology of the Faculty of Geography of the Hezen State Pedagogical University of Russia.

Preparation of samples was performed in the following sequence: defining pH of thawed water for definition of the snow cover acidification degree; filtering through «red ribbon» filter with large size of pores to remove rubbish; filtering through preliminary weighed membrane filter «blue ribbon» (pore diameter 1 mkm), that holds only badly soluble fraction of polluting materials, for further definition of the dust fraction mass; measuring the volume; mixing the sample; heating 300 cm^3 of thawed water to temperature 60^0C; distillation of the sample on liquid sample concentrator D-01, that results in forming thin layer concentrates of heavy metals water soluble phase on sorption cellulose DETATA-filters.

Heavy metals in thawed water are present in two phases: in composition of insoluble suspension and in water soluble form. Time-space specifics of chemicals in these 2 phases depend on different causes. Soluble compounds of heavy metals are most biologically active. Being easily assimilated by organisms they are stored in all links of the trophic chains and are most hazardous for living organisms including human ones. Besides, solubility of toxic elements makes polluted areas of other environments larger in the period of snow melting. So in the course of our work we were paying most attention to heavy metals water soluble phase.

Prepared samples were analyzed with X-ray fluorescent method on spectrometer «Spectroscan MAKS» using methods which allow to define mass concentrations of heavy metals. The following elements content was analyzed: V, Cr, Fe, Ni, Cu, Zn, Pb, Bi. Preference was given to these heavy metals on the ground that they present top pollutants within the territory under study and the whole North-Western region. Apart from that, majority of them belong to the first three classes of toxicological danger.

III. Results and Discussion

First results of the received data processing let us make a conclusion of a relatively low general level of the St. Petersburg snow cover pollution with heavy metals. Thus, comparison of heavy metals contents with maximum permissible concentrations (MPC) for water of drinking, household, cultural and industrial water resources showed that thawed water metal content is 1-2 times lower than MPC values (Table I) [10].

TABLE I. Heavy Metals Average Content in the St. Petersburg Region Snow Cover mg/l

Zone	Bi	Pb	Zn	Cu	Ni	Fe	Cr	V
St.Petersburg	0.012	0.011	0.028	0.019	0.003	0.025	0.007	0.006
30 km	0.012	0.010	0.020	0.016	0.003	0.014	0.006	0.005
60 km	0.012	0.010	0.012	0.014	0.002	0.014	0.006	0.004
90 km	0.013	0.010	0.010	0.017	0.003	0.010	0.006	0.005
>90 km	0.011	0.009	0.020	0.019	0.003	0.013	0.006	0.004
MPC [11]	**0.5**	**0.1**	**1.0**	**1.0**	**0.1**	**0.5**	**0.5**	**0.1**

The trends of the heavy metal snow cover total pollution of the central part of St. Petersburg received by the authors were compared with the data of the Automatic system atmospheric air monitoring (ASAAM). ASAAM N10 is situated in the center of St. Petersburg. Its data characterizing atmospheric air pollution was taken for comparison. Althouth ASAAM does not define heavy metal content, but only registeres the levels of carbon oxide, nitrogen oxide, sulpher dioxide and suspended substances total, a high correlativity of our and ASAAM data excluding the year 2007 was established (Fig.1) [12].

Main sources sending to atmosphere toxic materials from human economic activity in St. Petersburg are autotransport, thermal power stations, metallurgical shops at machine building industrial enterprises. As you can see in Fig.1, the levels of atmospheric air and snow cover pollution in St. Petersburg in latest years distinctly tend to get lower. It is connected with federal measures aimed at toughening of ecological politics within the frames of international agreements, Kioto protocols including. These measures are targeted at lowering of polluting emissions from industry and autotransport to the environment, and include setting up dust and gas cleaning equipment and filters at the sources of emissions, modernization of the equipment, perfecting technologies of production, renewing machine stock, etc.

Further research was aimed at defining regional background values for heavy metals and exposing snow chemical anomalies [12, 13]. This task has an important scientific and practical meaning and can be effectively solved only with the help of modern geoinformational systems (GIS) of mapping geoecological situation [14].

For studying of territorial heavy metal distribution in snow cover we used GIS ArcGIS. Geographical Informational

Systems (GIS) are computer systems for collecting, storing, monitoring, analysis and presentation spatially definite information. GIS are used in a wide range of tasks connected with analysis and forecasting of phenomena and events of the world around, for instance, with planning of nature protective actions.

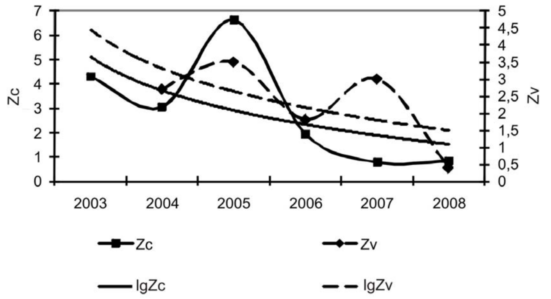


Fig. 1. Correlativity of total snow cover (*Zc*) and level of atmospheric air (*Zv*) pollution trends in the center of St. Petersburg. 2003-2008 (data of February 15 of each year)

For storing all incoming data on heavy metal content in the St. Petersburg region snow cover the geodata database was used - a new data format named after the base of geographical data which is used in modern versions of program products ArcGIS 9.x. Geodata database is a spatial database containing sets of data which present geographical information in the context of the general model of GIS (vector objects, rasters, topology, networks etc.)

At the first stage of work with the program we tied up the raster of a typical (paper) map of the area of the research. Tying up the raster is essential to establish the correspondence between the dots of the image and the locality in the set system of coordinates. Gauss-Krjuger projection *Pulkovo 1942 3 Degree GK M 30E* was chosen for territory mapping.

A raster image in BMP format was used as initial. The image was created by way of scanning a tourist map of Leningrad oblast (scale 1:800000). Tying up was made to 4 basic points. The first one (TP-1) is situated near railroad station Ljaypsuo (Vyborg direction), the second one (TP-2) is also on Karelsky isthmus near railroad station Sosnovo (Priozersk direction), the third (TP-3) is in town Pikalevo (west of town Volkhovstroy), the fourth (TP-4) - on railroad station Mshinskaya (Luga direction).

At the next stage of designing the database in the format of a geodata database we were creating a dBASE table for every test profile with the following fields: latitude and longitude coordinates for test points in the tenth degrees for Krasovsky ellipsoid; a text field with the name of the test point (station, number of point); a data field for defined concentration of Bi, Pb, Zn, Cu, Ni, Fe, Cr, V; an integer field with the number of the profile (1-8). Then the tables were combined into a single table.

The initial document of the map is represented by a raster base sheet of the map of Leningrad oblast in Gauss-Krjuger projection with marked vector test points showing some chosen names of stations. The map also shows a kilometer step net of the area 30x30 km.

The module Spatial Analyst was used for mapping heavy metal distribution within the research territories. The technology of mapping the distribution parameter includes the following main steps: an interpolation of the raster using a definite method and a choice of the classification interval boundaries.

Making distribution maps of any area parameter in module Spatial Analyst ArcGIS is based on raster interpolation. The essence of interpolation is to calculate parameter values between measure points in a denser network defined by a required accuracy of the studied object (phenomenon) interpretation while using as initial data measurement points of the research parameters distributed in a certain scheme (in our case – heavy metal content in the snow cover at places of sampling). The starting points, containing the values of the parameter (characteristic) under study, may be distributed either evenly or at random. As a result of interpolation all research area is split up by a regular net of cells of relatively small size. Each cell has its world coordinates.

For interpretation of the data of observation for heavy metal content in snow cover, taking into account density of points of monitoring network and its total number, we chose the method of back weight distances (BWD), where the value of each cell is calculated on the average from the total value of measurement points which are found near each cell. The closer the point to the center of an evaluating cell is, the more weight or influence it has in the process of calculating the average. This method suggests that the influence of the value of the measured variable lessens while the distance from the measurement point grows.

As the main interpolation options were chosen: the fixed radius of the search of 17000 m, the size of the cell of the outgoing raster – 500 m.

Figure 2 shows the map of Pb distribution within the limits of the surveyed territory.

Substantiation and choice of classification intervals of the research parameter have significant meaning at interpretation of statistically processed data. Fig. 3 shows frequency characteristics of Pb content distribution in the cells of the interpolated raster. Four classification intervals were set. The interval boundaries were defined by Jenks natural breaks method.

The first two classes of Pb content (in this case up to 0.008 and from 0.008 to 0.011 mg/kg) correspond to background values of the pollutant. The other two classes – to snow chemical anomalies.

As one can see in figure 2, on the most part of the research territory Pb content corresponds to the background values. At the same time snow chemical anomalies were marked on the territories of the suburbs of St. Petersburg and Volkhov as well as in the whereabouts of stations Mullyupelto, Lebedevka, Ushkovo.

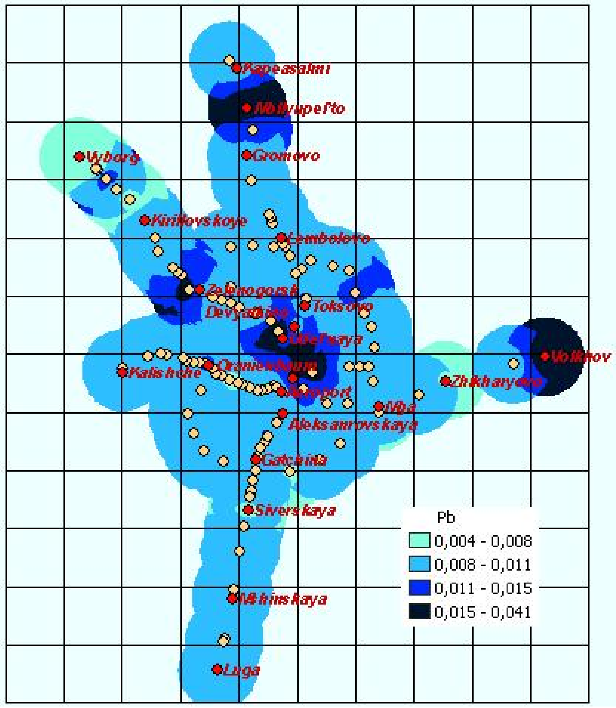


Fig. 2. Map of Pb content distribution (mg/kg) in snow cover of St. Petersburg region

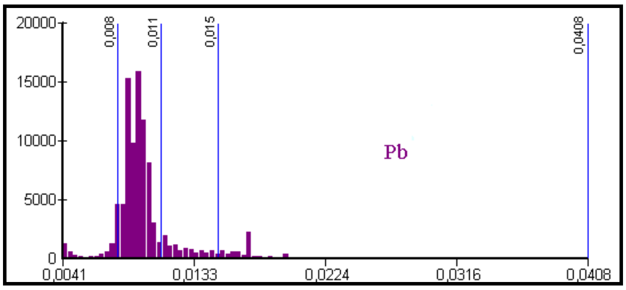


Fig. 3. Frequency characteristics of Pb content distribution and boundaries of classification intervals

The results of the analysis of other metals distribution on the research territory show the following. Like lead, iron forms snow chemical anomalies in St. Petersburg suburbs, especially pronounced in the neighbourhood of stations Udelnaya, Airport. In the north of the territory, increased iron content was noticed near station Lyaipyasuo, in the south - at the station Suyda and in town Luga (fig. 4).

As it has been already noticed, important meaning in interpretation of the data of statistical processing has substantiation and choice of the classification intervals of the research parameters. Figure 5 shows frequency characteristics of Fe content distribution in the cells of the interpolated raster.

As it is seen in fig. 5, frequency characteristics of Fe content distribution differs from that of Pb. Nevertheless, this fact should not tell on the substantiation of the method of calculation of background values of the analyzed elements. As it is known, the background is defined by the actions of many factors. So, according to the central limit theorem by Lyapunov[1], it may be assumed that the background metal content can be calculated from the assumption of the normal distribution of the research parameter.

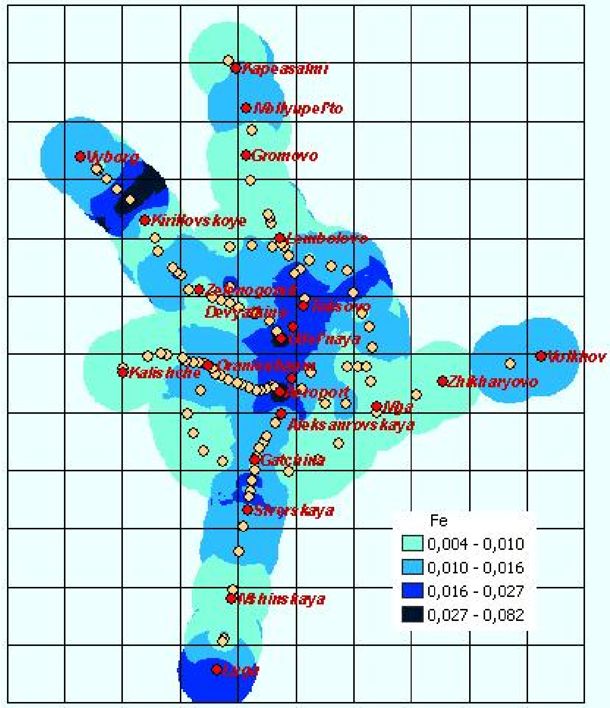


Fig. 4. Map of Fe content distribution (mg/kg) in snow cover of St. Petersburg region

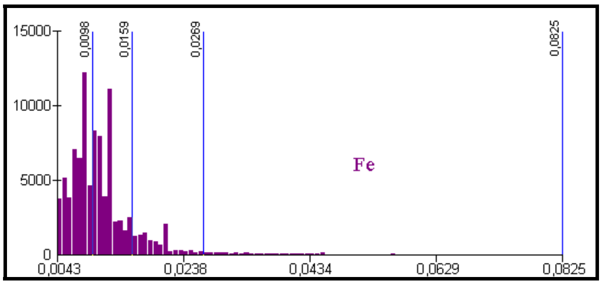


Fig. 5. Frequency characteristics of Fe content distribution and boundaries of classification intervals

Distributions of Cr, Ni, Cu, Zn on the examined territory have similar character: snow chemical anomalies of these elements are observed mainly in the northern part of the region (Cr – Vyborg, Ni – Lebedevka, Pettyayarvi, Cu – Kapeasalmi, Lebedevka; Zn – Lebedevka, Otradnoye). Anomalous values of Ni and Cu are noticed also in the neighbourhood of St. Petersburg suburbs - Dachnoye and Ozerki correspondingly.

In the southern part of the region a significant bismuth anomaly is observed near station Divenskaya (Luga direction). Vanadium forms insignificant areas of anomalies in the neighbourhood of station Solnechnoye (Vyborg direction).

Statistical processing of the research materials allowed to define background values of the elements (mg/kg) and the average square absolute error of definition of the background (σ), proceeding from the character of spatial heavy metal distribution within the region limits. The results of statistical processing are shown in Table 2.

For detailed analysis of spatial distribution of toxic elements content in snow cover of St. Petersburg region we calculated the concentration coefficients (K_c) of the elements under study in relation to the received background values (tab. 3, fig. 6).

[1] Lyapunov central limits theorem: If a random value X presents a sum of a very big figure of mutually independent random values, influence of each of which is infinitesmally small, then X has a distribution close to normal.

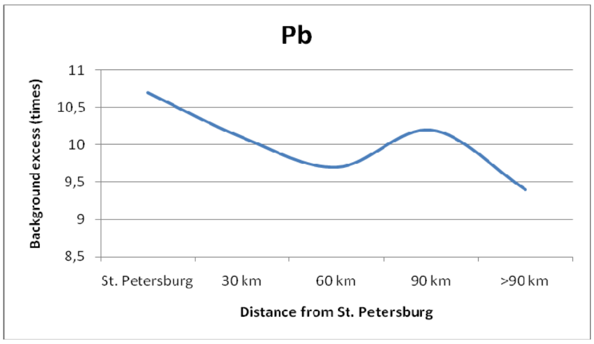
TABLEII:. BACKGROUND VALUES OF THE ELEMENTS AND AVERAGE SQUARE DEVIATION FROM BACKGROUND MG/KG

	V	Cr	Fe	Ni	Cu	Zn	Pb	Bi
Background	0.004	0.006	0.011	0.002	0.015	0.013	0.009	0.012
Average square error (σ)	0.001	0.001	0.004	0.001	0.005	0.010	0.001	0.003

TABLE III. CONCENTRATION COEFFICIENTS (K_c) OF THE ELEMENTS IN SNOW COVER OF ST. PETERBURG REGION (IN BACKGROUND UNITS)

Zone	Bi	Pb	Zn	Cu	Ni	Fe	Cr	V
St. Petersburg	4.0	10.7	2.8	3.8	1.6	2.3	1.1	1.4
30 km	4.0	10.1	2.0	3.2	1.3	1.2	1.0	1.1
60 km	3.9	9.7	1.2	2.8	0.9	1.2	1.0	1.1
90 km	4.3	10.2	1.0	3.,3	1.6	0.9	1.0	1.1
>90 km	3.5	9.4	2.0	3.7	1.4	1.1	0.9	1.1

As one can see from Table 3, the highest values of the concentration coefficients are characteristic for Pb, and insignificant decrease is noticed at a distance of 60 km from St. Petersburg. A little lower values K_c have Bi, Cu and Zn – up to 4, concentration coefficients (K_c) Cr and V are marked within limits 1 (i.e. correspond to background values).



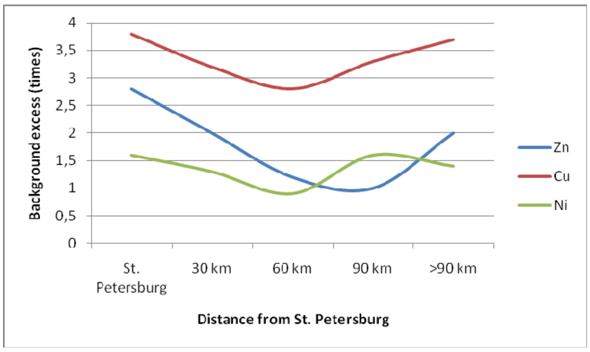


Fig. 6. Variations of concentration coefficients (K_c) in relation to the local background while increasing distance from St. Petersburg

As figure 6 shows, in St. Petersburg neighborhoods snow cover is the dirtiest in heavy metal content in the water soluble phase. While increasing distance from St. Petersburg the level of pollution lowers and grows again in the zone of over 90 km, where regional centers of Leningrad oblast are situated – Vyborg, Volkhov, Luga and Kalische, which make their «contribution» to the state of the snow cover. This pattern especially distinctly reveals in relation to Pb, Zn, Cu and Ni. Significant excess of the background values of Pb concentration practically all over the research territory attracts attention.

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