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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—**The present paper considers the results of ecological geochemical studies of the snow cover in the region of Saint-Petersburg. The studies have been conducted with application of GIS technologies: spatial distributions of concentrations of heavy metals in snow mantle have been estimated; values of the regional snow-chemical background are presented for a series of metallic elements; for each of the elements examined, the identified territories of snow-chemical anomalies are shown.**

***Keyword:** geoecology, heavy metals, snow-chemical anomalies, GIS Technologies, Saint-Petersburg Region.*

Discharges of poisonous substances to atmosphere in megalopolises amount to hundreds of thousands and millions tons per annum. The presence of correlations between the substances polluting the atmospheric air and their contents in snow cover allow us to use the latter type of depositing medium for fast geochemical estimation of the total level of pollution of urbanized territories [1].

Snow-chemical anomalies, in essence, indicate the ecological and geochemical state of the atmosphere, summing up the effects of natural atmogeochemical (Earth degasification), natural and anthropogenic atmogeochemical (gaseous formations in buried deposits of pit etc.) and purely anthropogenic (industrial emissions), influencing the dynamics of the geochemical ecological function of the lithosphere in time [2]. Snow cover mirrors the contours of the aerogenic pollution within the time-span of its formation, allowing us to make ideas on the dynamics of the processes occurring. The characteristics of anthropogenic anomalies in such depositing mediums as snow cover may be considered as indirect indicators of the pollution of the air basin, directly displaying the intensity of geochemical transformation of the surface section of the lithosphere. During the periods of snow melting, the toxicants present in the snow migrate to the surface waters, bottom deposits, soils and rock substrata, the area of their spread exceeding considerably the contours of the snow-chemical anomalies.

The relative simplicity of snow-chemical surveys enables to conduct large-scale investigations of territories in order to estimate the spacial distribution of polluting substances, determine the geochemical background and to delineate the areas with anomalous values of the parameters under study.

The utmost attention during ecological geochemical surveys is usually paid to heavy metals [3]. This is determined by the wide distribution and indicative significance of this type of pollutiants, as well as the availability of well elaborated and fairly cheap analytical methods (predominantly spectral). In addition, due to their high biochemical activity, toxicity, essential accumulative ability and difficulty of their removal from the organism, heavy metals are among the most noxious pollutants for man and other life forms.

Although not only heavy metals take part in the process of pollution of urban atmosphere, due to the community of the sources of pollution, examination of exactly these pollutants demonstrates satisfactory convergence with the calculated values of the index of atmospheric pollution.

The net of stations for controlling the state of atmospheric air which exist in Saint-Petersburg and Leningrad Oblast do not fulfil observations of distribution of heavy metals. Moreover, the systems of departmental monitoring are occupied mainly with studies of the anthropogenic emission of pollutants. At the same time, any ecological geochemical survey implies investigation of geochemical properties of components of the natural environment both at the local (anomalies) and regional (provinces) levels.

For that reason, the activities of the Chair of Geology and Geoecology of the Russian State A.I. Herzen Pedagogical University (Herzen University), started in 2003 for monitoring of the contents of heavy metals in snow mantle and other natural mediums in the St.-Petersburg region, are of extreme urgency.

The region under studies includes the city of St. Petersburg, a considerable part (north-western) of the Karelian Isthmus and the west of Leningrad Oblast. On the west, the territory in question is bounded by the coastline of the Gulf of Finland within the zone between the cities of Vyborg and Sosnovy Bor, on the east by the banks of Lake Ladoga from the city of Kuznechnoye as far as the city of Volkhov; a conventional straight line from Vyborg to Kuznechnoye was accepted as the northern boundary, and the arc via the cities Sosnovy Bor – Luga –Volkhov accepted as the southern one.

The climate of the region specified above is moderately continental with signs of the maritime influence, the latter being more pronounced in the western part of the territory under consideration. The winters are fairly prolonged. In winter seasons, the features of the maritime climate predominate. The coldest month is February. The snow cover holds on average for 3.5 months (from early December until mid-March). During the winter, the winds of the southern, south-western and western directions are predominant. Precipitations are mostly of steady character, prevailingly in the form of snow or moist snow, with rain when it is thawing.

Initially the studies were conducted annually at two reference areas: the Central districts of Saint-Petersburg and the Sestroretsk geosystem including Lake Sestroretsk Razliv and the Sestroretsk Marsh [4, 5, 6].

Since 2008, the territory of observations has been considerably expanded. In February 2008, we carried out large-scale sampling of snow cover by means of profile surveys. The samples were taken along 6 routes radially divergent from St.-Petersburg: 1) western – profiles I – St.-Petersburg – Kalishche, VI – Kronstadt; 2) north-western – profile II St.-Petersburg– Vyborg; 3) northern – profile III – St.-Petersburg – Kuznechnoye; 4) eastern – profile V – St.-Petersburg – Volkhov; 5) southern – profile IV – St.-Petersburg – Luga. In order to obtain additional information, two circular routes were chosen: 1) VII – Southern Semiring; 2) VIII – Nothern Semiring.

Sampling was conducted according to procedures worked out by us and officially approved [7, 8, 9], all the samples being carefully documented. For coordinate tying of the sampling points, a GPS navigator eTrex Venture HC was used.

The points of sampling were arranged in areas with the minimum effects of highways, railways, industrial plants, boilers, etc. (at a distance of at least 250 m from the edge of a roadway, over 1000 m from industrial units), on large clearings if in forest.

In the reference areas throughout radial and circular routes, a total of 350 samples of snow cover have been collected and about 4,000 identifications of chemical elements carried out.

The analytical studies were conducted in the A.E. Fersman Laboratory of Geochemistry of the Environment at the Chair of Geology and Geoecology of Herzen University.

Preparation of samples was conducted according to a certified "Procedure of measuring mass concentrations of V, Bi, Fe, Co, Mn, Cu, Ni, Pb, Cr, Zn in drinking, natural and waste waters by means of the X-ray fluorescence method after concentrating the solutions on cellulose DETATA filters M049-B/03" ("NPO "Spectron"" Limited, St.-Petersburg) and using the corresponding procedures of RSPU in the following sequence: measuring of pH of thaw water for determination of the extent of acidulation of snow cover; filtration through filters "Red Tape" with pores of large size in order to remove solid particles, filtration through pre-weighed membrane filters "Blue Tape" (pore diameter 1 μm) which retain only poorly soluble fractions of pollutants in order to subsequent defining of the mass of the dust fraction; measuring the volume; stirring of the sample; heating of 300 cm^3 of thaw water to the temperature of 60 °C; distillation of the sample in concentrator of liquid samples D-01 with formation of thin-film concentrates of heavy metals on sorption cellulose filters DETATA.

The prepared samples were analyzed by X-ray fluorescence method in spectrometer "Spectroscan MAX", "Spectron" Company, according to a procedure enabling to determine mass concentrations of heavy metals. Water-soluble phases of the following elements were determined: V, Cr, Fe, Ni, Cu, Zn, Pb, and Bi. Preference was given exactly to these heavy metals since they are the predominant pollutants within the territory under study and the entire North-Western region. Moreover, most of them belong to the first three classes of toxicological hazard.

The first results of processing the data of sampling suggest a relatively low general level of pollution of snow cover with heavy metals in St.-Petersburg region. For instance, comparison of the contents of heavy metals with their maximum permissible concentrations in water bodies of economic/drinking, cultural and community services has demonstrated that in thaw water the contents of metals are by one to two factors of ten below the values of MPC [10].

The further investigations were aimed at estimation of regional background values for heavy metals and detection of snow-chemical anomalies [11, 12]. This problem is of high scientific and practical significance and can be solved only with the use of modern GIS technologies [13].

In order to investigate the territorial distribution of heavy metals in snow mantle, GIS ArcGIS was applied. Geographic Information Systems (GIS) are computer systems for gathering, storing, administration, analysis and representation of spatially determined information. GIS are applied in a wide spectre of tasks concerned with analysis and forecast of phenomena and events of the surrounding world, e.g. in planning environment protection activities.

For storage of the complete initial information on the contents of heavy metals in the nival mantle of St.-Petersburg region, a geographical database in a new data format was used. This format received its name after the base of geographic data and is employed in modern versions of software ArcGIS 9.x. A geodata base is a spatial database comprising sets of data which bear geographic information pertaining to the general GIS model (vector objects, dot matrices, topology, grids etc.).

At the initial stage of employing the software, tying of the dot matrix of ordinary (paper) map of region under study was carried out. The procedure of tying the raster dataset is necessary for establishing correspondence between the dots of a representation and locality in a given coordinate system. For mapping the territory in question, the Gauss-Krüger projection Pulkovo 1942 3 Degree GK M 30E was chosen.

As the initial, the pixel representation in the BMP format was used which has been obtained by scanning a tourist map of Leningrad Oblast (scale 1:800,000). The ties were obtained in four reference points. The first (TP-1) is located near the railway station of Lyaypyasuo (railroad branch to Vyborg), the second (TP-2) is also on the Karelian Isthmus near the railroad station of Sosnovo (Priozersk railroad branch), the third (TP-3) is the city of Pikalevo (to the west of the city of Volkhovstroy), the fourth (TP-4) – at the railroad station “Mshinskaya” (Luga branch).

At the next stage of designing the database, for each profile of sampling a dBASE spreadsheet was filled in the geodata format. The spreadsheet included the following fields: latitude and longitude values of the sampling points in decimal degrees for Krasovsky ellipsoid of 1940; a text field with the name of the sampling point (station, the number of the point); data fields with determined concentrations of Bi, Pb, Zn, Cu, Ni, Fe, Cr, V; an integer-valued field with the number of the profile (1 to 8). Further on, the spreadsheets for separate profiles were integrated into a single composite datasheet.

The initial document of the map is represented by a raster background map of Leningrad Oblast in the Gauss-Krüger projection and vector representations of sampling points with selectively shown names of stations. In the map, also a kilometre grid measuring 30 x 30 km is shown.

For building maps of distribution of the contents of particular metals within the territory studied, the Spatial Analyst toolbar of the software was used. The technology of building the map of distribution of a parameter includes the following stages: interpolation of the raster representation according to a given procedure and selection of the limits of the classification ranges.

Creation of maps of distribution of a certain parameter over an area using the Spatial Analyst toolbar of ArcGIS is based on interpolation of raster datasets. The essence of the interpolation is in calculation of the values of the parameters (in our case, the contents of heavy metals in sampling points of the snow mantle) between the measurement points with a denser grid determined by the necessary precision of interpretation of the object (phenomenon) under consideration. As the source data for the interpolation, the sampling points for the parameters under study distributed according to a certain scheme are used. The original points containing the values of the parameter (property) under study may be distributed uniformly or in a random way. As the result of the interpolation, the surveyed area is divided into a regular grid of cells of relatively small dimensions. Each cell possesses its own world coordinates.

For interpretation of the observed data on the contents of heavy metals in snow cover with account of the density of the grid of monitoring points, we chose the Inverse Distance Weighted (IDW) interpolation. IDW estimates cell values by averaging the values of sample data points in the neighbourhood of each processing cell. The closer a point is to the centre of the cell being estimated, the more influence, or weight, it has in the averaging process. The method thus implies that the influence of the measured variable decreases with the distance from the sampling point.

As the main options of the interpolation, the function with a fixed search radius of 17,000 m was chosen with the cells of the produced point dataset measuring 500 m.

Figure 1 shows a map of distribution of lead contents within the territory under study.

Of no small significance in interpretation of the results of statistic processing is the choice and grounding of the classification intervals for the parameter under study. Figure 2 presents the frequency characteristic of distribution of lead contents throughout the cells of the interpolated raster dataset. Four intervals of classification were set. The boundaries of the intervals were determined by the Jenks Optimization method (Jenks Natural Breaks Classification).

The first two classes of the contents of lead (in our case, up to 0.008 and from 0.008 to 0.011 mg/kg) correspond to the background values of the pollutant contents. The other two classes are snow-chemical anomalies.

As shown in fig. 1, over the most of the territory studied, the contents of lead are at background values. At the same time, there are snow-chemical anomalies recorded in the territories of suburbs of St.-Petersburg and the city of Volkhov, as well as around the railway stations of Myullyupelto, Lebedevka and Ushkovo.

The results of analysis of distribution of other metals in the territory under consideration are as follows. Similarly to lead, iron constitutes snow-chemical anomalies in suburbs of St.-Petersburg, especially remarkable in the vicinity of stations Udelnaya and Airport. In the north, increased contents of iron are recorded around the Lyaypyasuo station; in the south – at the station of Suyda and in the town of Luga.

Of a similar character, within the territory studied, are the distributions of Cr, Ni, Cu and Zn: the snow-chemical anomalies of these elements are recorded mainly in the northern part of the region (Cr – town of Vyborg; Ni – Lebedevka and Pettyayarvi; Cu – Kapeasalmi and Lebedevka; Zn – Lebedevka and Otradnoye). Anomalous contents of nickel and copper are observed also at outskirts of St.-Petersburg – the districts of Dachnoye and Ozerki respectively.

In the southern area of the region, a considerable bismuth anomaly has been recorded in the vicinity of stations Divenskaya (Luga railway branch). Vanadium constitutes small-area anomalies near the station of Solnechnoye (Vyborg railway).

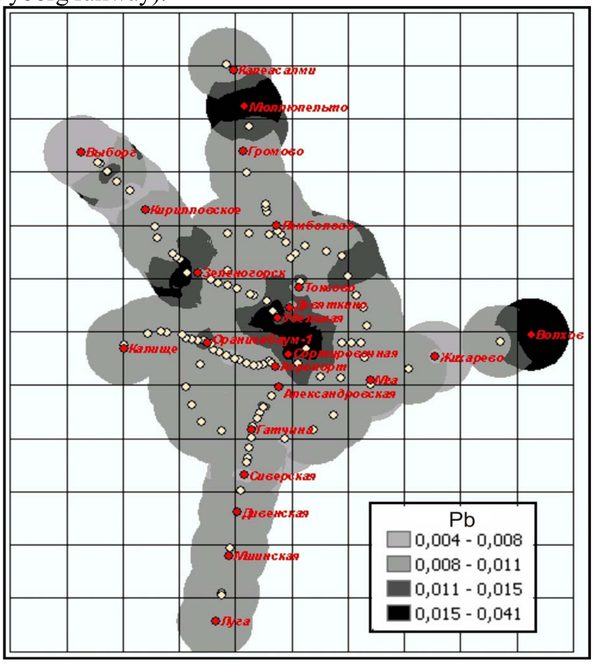

Figure 1. Map of distribution of Pb contents (mg/kg) throughout snow cover in Saint-Petersburg region.

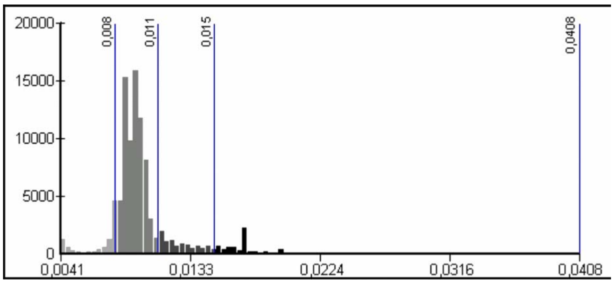

Figure 2. Frequency characteristic of the distribution of Pb contents and the boundaries of the classification intervals.

A statistical treatment of the results has enabled to define, on the basis of the character of the spatial distribution of heavy metals throughout the region, the background contents of the elements (mg/kg) and the absolute mean-square error of the background definitions (σ). The results of the statistical treatment are presented in the table 1.

Thus, on the basis of employment of GIS technologies, the spatial distribution of concentrations of heavy metals in snow mantle of the Saint-Petersburg region has been first estimated. For the elements V, Cr, Fe, Ni, Cu, Zn, Pb, and Bi, the values of the regional snow-chemical background have been obtained and their statistically significant variations determined. For each of the elements examined, the areas of snow-chemical anomalies have been identified.

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TABLE I. BACKGROUND CONCENTRATIONS OF METALLIC ELEMENTS AND THE MEAN-SQUARE DEVIATIONS FROM THE 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
Mean square error (σ)	0.001	0.001	0.004	0.001	0.005	0.010	0.001	0.003