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© VIKTOR A. BOYEV, ALISA A. LEZHNINA
vikboev2009@mail.ru

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HEAVY METALS IN THE SNOWPACK OF THE TYUMEN DISTRICT, TYUMEN REGION

SUMMARY. The characteristics of long-term trends in the distribution of heavy metals in the snowpack of the Tyumen district in Tyumen region are described in the article. For the first time for the territory of Tyumen region maps of heavy metals distribution in the snowpack are created.

KEY WORDS. Snow, heavy metals, pollution dynamics.

Currently great value is placed on research of environmental pollution with various pollutants, among which an important place is occupied by heavy metals, which are among the most toxic chemicals. According to N.F. Reimers' classification, heavy metals are those metals which are toxic for living organisms and whose density exceeds 8 g/cm^3. Such metals are Hg, Cd, Co, Zn, Pb, Cu, Ni, Co, Sb, Sn, Bi [1].

Heavy metals are accumulated in depositional environments, which include soil and snow cover, and form extensive technogenic haloes and scattering patterns. Since accumulation of contaminants in the human environment is highly undesirable, studying the dynamics of heavy metals accumulation in depositional environments, including the snow cover, becomes the most important task.

The chemical composition of snow can be used to define the areal distribution and quantity of substances derived from atmospheric fallout in winter. Due to this it is possible to identify sources of pollution and haloes of their influence as well as approximately estimate the number of toxicants, which are carried away with meltwaters from urban and industrial areas into soils and groundwaters.

It is necessary to note the following properties of the snow cover as a depositional environment which is very convenient and informative for studies in the Tyumen district:

1. Simple snow sampling which does not require sophisticated equipment;
2. Stability of the snow cover in the area for a long time;
3. Weak intensification of chemical and biochemical processes in the snowpack produces representative quantitative data on the seasonal atmospheric fallout of polluting elements;

4. High concentration of pollutants in the snow (usually 2-3 times higher than in the air);

5. Snow cover as a natural accumulator provides rather objective data on dry and wet fallouts over the winter (or any other selected period of time while layer-by-layer analysis);

6. Geochemical analysis of the snow cover allows to trace the areal distribution of contaminants in the area in question and obtain a reliable picture of the zones of influence of specific objects on the environment.

The unique ability of the snow cover to attract polluting substances from the air, adsorb dust fallouts on its surface and accumulate them in itself until its own disappearance has been successfully used to assess contamination of both relatively small areas of individual cities and vast territories of regions and republics [2], [3].

In this paper we analyze the content of 7 items in the snowpack, 6 of which are heavy metals according to their chemical properties (Cu, Zn, Pb, Cr, Cd, Hg), and the other (arsenic), although defined as a semimetal, tends to belong to heavy metals judging by its impact on living organisms and human health. Most of the analyzed elements belong to the first three hazard classes, are extremely toxic and characterized by high biochemical activity [4], [5].

The snow cover in the Tyumen district lasts an average of 5.5-6 months. The average date of formation of a stable snow cover is in the first ten days of November, in different years it can shift to the first ten days of October or the second decade of December. The average number of days with snow cover is 161. The average depth of the snow cover in winter is 34cm in the open space and 50 cm in the covered space (in the forest). The maximum depth of the snow cover reaches 65 cm.

In the winter period the area is characterized by the prevalence of south-western wind directions; in the summer period western and north-western wind directions prevail. The average annual wind speed is 5.3 m/s. The average annual precipitation, with instrument correction, is 524 mm, 60% of which is rainfall in the warm season of the year (May to September).

The prevalence of low-land plains in the district and the high degree of wetlands do not contribute to the processes of self-purification of natural landscapes. Correspondingly the potential of the territory resistance to technogenic influence is not high. Pb removal rate, due to natural leaching, erosion and deflation, as well as consumption by plants, is hundreds of times less than the rate of atmospheric and technogenic emissions. The situation is exacerbated by the natural channels of distribution of environmental hazards of natural and anthropogenic origin related to the ecological and geographical location of Tyumen region: due to the westerly flow of pollutants from large industrial enterprises of Sverdlovsk region, which is situated within a close proximity of 250-350 km, and the flow of hydrotechnogenic pollutants in the waters of the Tura river [6].

In the Tyumen district there are over 1,500 industrial enterprises and organizations, but the greatest contribution to the pollution of the environment of the studied area is made by its administrative center — the city of Tyumen.

A special place in the complex of geo-environmental problems of Tyumen region is occupied by heavy metal pollution of the snow cover and soil and the increasing acidity of soils, which is facilitated by:

- cross-border transportation of acidic pollutants;
- emissions of urban heating plants operating on gas;
- high rates of automobile fleet growth.

Cross-border regional transportation of acidic pollutants is associated with the position of Tyumen region near relatively large industrial centers of Sverdlovsk region (the cities of Yekaterinburg, Nizhniy Tagil, Kamensk-Uralskiy, etc.). Stationary industrial sources of the region annually emit about 1,500 tons of pollutants into the air, which is over 7% (second place) in the Russian Federation.

Heavy metals are priority pollutants of soils; among them lead holds a special position. A sharp increase in the content of lead in the technogenic emissions on the territory of the Tyumen district has been registered since 1950s. The intensity of lead pollution of soils in Tyumen is 4-800 times more than worldwide. It considerably surpasses the number of lead fallout characteristic for industrially developed regions, outside the direct influence of technogenic sources, of Poland, Germany, and many US states.

Until the early 1990s industrial contribution to lead pollution of the environment was predominant. In fact, the real problem of lead contamination of soils in Tyumen district was created in the previous few decades due to joint «efforts» of more than 180 industrial enterprises — sources of lead.

Due to sharp reduction of industrial production, harmful emissions decreased by one third in 2010. However, because of deterioration in the operation of waste treatment facilities of companies and a significant increase in the air pollution caused by automobile vehicles, human pressure on the environment is not reduced. The total discharge of harmful substances into the atmosphere of Tyumen region is maintained within 280-290 million tons per year. Studies show that air pollution causes up to 44.6% of total morbidity. Respiratory diseases, diseases of the endocrine system, diseases of the blood and blood-forming organs, diseases of the nervous system and sense organs, congenital anomalies dominate in Tyumen region, i.e. human pathology is dependent on ecological processes. The report data of the Tyumen Center of the State Sanitary and Epidemiological Supervision also suggest that the most dangerous for the environment is lead, which affects the nervous system, lowers intelligence, causes negative changes in human physical activity, coordination, hearing ability, and affects the cardiovascular system and blood-forming organs.

Snow cover sampling and preparation

These studies were carried out on the territory of Tyumen region in 2001-2010. The survey was conducted once a year in late winter, before the spring thaw, when the snow moisture content is close to maximum. Sampling was carried out at the reference sites of the Federal State Institution "The State Station of Agrochemical Service "Tyumenskaya".

Snow samples were collected at the reference sites in places of boreholes laying. Snow sampling and snow water analysis were conducted on the basis of the regulatory document RD 52.04.186-89 (Guidelines for air pollution control, part 2, p. 5.1.2.).

The samples were analyzed on spectrophotometer «Saturn» by the method of atomic absorption spectrophotometry (acc. to RD 52.04.186-89, part 2, p. 4.5.12.).

In samples of snow water we measured pH, solids, conductivity, heavy metal content (Zn, Cr, Cd, As, Cu, Pb, Hg) by atomic absorption spectrophotometry.

Analysis of the distribution of heavy metals and assessment of the environmental and geochemical condition of the snow cover of the Tyumen district

After several years of study (2001-2010) we received information on the distribution of heavy metals in the snowpack of the Tyumen district.

Comparing the annual results of the analysis of melt water samples for heavy metal content, it can be seen that over the study period as a whole there are constant values of the elements under study, except in 2002 (Fig. 1).

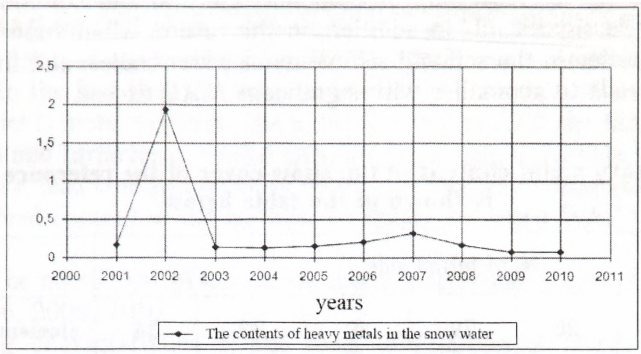

Fig. 1. The contents of heavy metals in the snow water of the Tyumen district over the decade of the research (2001-2010) (mg/l)

The figure shows a sharp rise of the heavy metals in the snow water in 2002. 2002 is characterized by the excess of maximum allowable concentration (MAC) for Pb for all reference sites and Cd for 2 reference sites near Roshchino and Uspenka.

In general, we observed positive dynamics of reduction in the content of heavy metals in the snow in the Tyumen district from 2002 on. It should be noted that their minimum content for the ten-year study period was recorded in 2009 and 2010.

The range of heavy metals according to their increasing MAC (Maximum concentration limit) average values over the study period from 2001 to 2010 is as follows: Zn <Cu <Pb <Cr <As <Cd <Hg.

The average content of heavy metals in the snowpack of the Tyumen district is shown in Fig. 2.

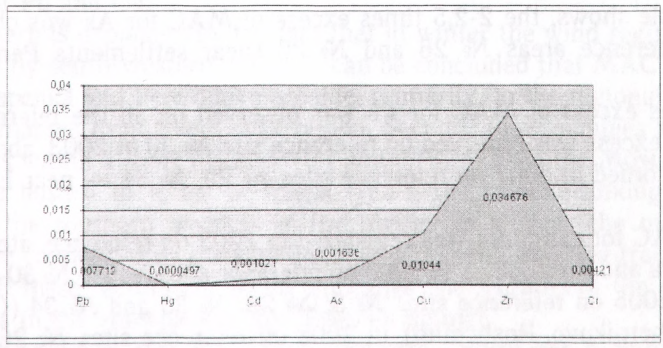

Fig. 2. The average concentrations of heavy metals in the snowpack of the Tyumen district (2001-2010)

As it follows from Fig. 2, long-term average concentrations of heavy metals in the reference sites of the Tyumen district are within 0.0058-0.0118 mg/l.

Comparison of the content of heavy metals in the snowpack of the Tyumen district and the MAC for water bodies of drinking and social amenities suggests relatively low snow cover pollution with heavy metals. The ten-year study observed excess of MAC for the elements such as As — 2001, Pb — 2002, 2003, 2007, Cd — 2002, 2003, 2005 and 2008.

Although the obtained data show that the content of heavy metals insignificantly exceeded MAC set for reservoirs of economic, cultural and communal purposes, pollution of air is significant. In addition, in the future, when snow melts, heavy metals are deposited in the soil and sediments of water bodies, and their long-term accumulation leads to anomalies with significant MAC excess.

Table

The heavy metal content in the snow cover of the reference sites is shown in the table below

№ of tetrad side								
year	3	26	29	30	**33**	**34**	**element**	**MAC**
2001	0,003	**0,022**	0,005	**0,026**	0,003	0,0026	arsenic	MAC=0,01
2002	**0,025**	**0,021**	**0,027**	**0,028**	**0,024**	**0,026**	lead	MAC=0,01
2002	0,001	0,001	0,001	**0,002**	0,001	**0,002**	cadmium	MAC=0,001
2003	0,00007	**0,0175**	0	**0,0015**	0,00004	0,0002	cadmium	MAC=0,001
2003	0,0043	0,011	0,0023	**0,056**	0,0003	0,0057	lead	MAC=0,01
2004								
2005	**0,0017**	0,0004	**0,0025**	0,0005	**0,0037**	**0,003**	cadmium	MAC=0,001
2006								
2007	0,0027	0,002	**0,0163**	0,0023	0,0042	**0,0143**	lead	MAC=0,01
2008	0,00059	**0,002**	**0,0012**	**0,0016**	0,001	0,0005	cadmium	MAC=0,001
2009								
2010								
the bold print indicates MAC excess (acc. to doc. GN 2.1.5.1315-03)								

As the table shows, the 2-2.5 times excess of MAC for As was observed only in 2001 in reference areas № 26 and № 30 (near settlements Perevalovo and Uspenka).

2-2.5 times excess of MAC for Pb was observed on all the reference sites in 2002, 5 times excess was observed on reference site № 30 in 2003, about 1.5 times excess was recorded in 2007 on reference sites № 29, № 34 — near Embaevo and Roshchino.

Excess MAC for cadmium was registered in 2002 on reference sites № 30 and № 34 (Uspenka and Roshchino), in 2003 on reference sites № 26, № 30 (Perevalovo, Uspenka), in 2005 on reference sites № 3, № 29, № 33 and № 34 (Chervishevo, Embaevo, Reshetnikovo, Roshchino), in 2008 on reference sites № 26, № 29 and № 30 (Perevalovo, Embaevo, Uspenka).

Excess MAC for cadmium on the reference sites ranged from 1.2 to 17.5 times. Such patterns of cadmium behavior may be due to various causes: including the transfer of regional enterprises of Sverdlovsk region or sampling during periods of thaw, etc.

An anomalous concentration of cadmium in 2003 (17.5 times excess MAC) was reported on reference site № 26, near village Perevalovo. Given that the average long-term dynamics of the content of cadmium gives an indication of a very low contamination of the snow cover and insignificant MAC excess (about 1-3 times) in certain areas of reference, the excess can be attributed to a measurement error.

Excess MAC for lead on all reference sites in 2002 (about 2-2.5 times), 5 times excess MAC for lead (near reference site № 30) in 2003, and a slight excess in 2007 is due to the fact that the main source of lead contamination of snow in the Tyumen district is motor vehicles. Due to the fact that in 2003 the Act on "Prohibition of production and turnover of leaded gasoline (including tetraethyl lead) in Russia" came into force, lead concentrations in the snow cover have decreased significantly. Since 2003, lead content in the snowpack slightly exceeded MAC (1.5 times) only in 2008.

It should be noted that MAC excess was not recorded in any of reference sites in 2004, 2006, 2009, 2010.

Analyzing characteristics of the areal distribution of heavy metals in the snowpack of the Tyumen district, one can make the following conclusions: the absolute quantitative content in the snow cover out of all studied heavy metals belongs to Zn (content in the snow cover over the period of a decade of observations is 2.0737 mg/l). The least represented is Hg (the content in the snow of the Tyumen district for ten years).

It was revealed that the highest levels of heavy metal concentration were recorded to the south-west of Tyumen in the immediate vicinity of village Uspenka. The elemental composition is dominated by As, Cd, Pb.

The second distinct maximum of the concentrations of the majority of the investigated heavy metals was registered to the north-west of Tyumen in the immediate vicinity of Roshchino. Excess MAC for Pb and Cd on reference site № 34 near Roshchino is due to the proximity of the aerodrome (7 km).

The third area include reference sites № 26 and № 29 which are near Perevalovo and Embaevo. The elemental composition of this zone is characterized by the prevalence of Pb and Cd.

This pattern is explained by the fact that in winter the wind regime in the area is dominated by south-western winds. It can be concluded that MAC excess on the sites near Uspenka and Perevalovo are due, primarily, to the regional movement of polluted air masses from Sverdlovsk region. Second, snow samples were collected on these sites within a short distance (0.1 and 0.16 m) from the Moscow tract road, which is the busiest in terms of traffic. Third, the railway linking the Tyumen district and the southern districts of the region, as well as the most important centers of the country, runs through Tyumen along the Moscow tract road around Embaevo. All these factors combined determine the features of the distribution of heavy metals in the snowpack of the Tyumen district.

It should be noted that the city of Tyumen, clearly has a significant impact on the pollution of the snow cover of the district. Studies show a clear tendency

of reduction of the absolute and maximum permissible concentrations of heavy metals in the snowpack with respect to the distance from the city. The purest of the reference sites, as the research shows, is site № 3 (north of Tyumen, near village Chervishevo).

Thus, the analysis of the areal distribution of heavy metals in the snowpack of the Tyumen district reveals a general pattern: the tendency to accumulate in the areas of maximum traffic load against the background of the overall pollution of the study area with the air masses coming from Sverdlovsk region.

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