

# Snow-cover contamination in urban territories (Lefortovo district, Moscow)

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**ABSTRACT.** The results of snow-cover chemical composition research in Lefortovo District, Moscow, Russia, are considered. The technogenic impact on snow-cover contamination was evaluated using snow sampling, chemical analysis of liquid and solid phases of snow and data processing. Snow meltwaters were slightly acidic, low-mineralized and contaminated with oil products. Contrasting anomalies of chloride, sodium, nitrites, nitrates, oil products and 3,4-benzopyrene are revealed and the main causes of their formation analyzed. The technogenic load on the air and snow cover was mainly due to an extensive road network and the impact of industrial enterprise. Ecogeochemical associations of elements, polluting snow cover by means of the dust component of air, formed the specific types of geochemical zones due to industrial and road-transport emissions. The common type of man-made contamination in snow cover is characterized by the following general association of contaminants: Hg W Mo Cr Ni Co Pb Cu Zn Cd Ag Bi Sn Ba Nb.

## 1. INTRODUCTION

The problem of air contamination in urban territories is becoming increasingly urgent. Difficulties in the air sampling and analysis of a wide range of chemical elements and in the organization of stationary contamination control stations in cities with complex industrial and housing developments prevent reliable information from being obtained about the spatial distribution of pollutants (Ginsburg and others, 1997). This makes it important to study the snow cover depositing the atmospheric precipitations, which allows investigation of the man-made contaminants entering for a short period from the surface boundary layer. Information about snow contamination is also important because the pollutants contained in snow cover can be carried by infiltrating meltwater into the groundwater, with surface runoff into streams and ponds, and also can deposit on the soil cover. The usefulness of snow cover as an indirect indicator of the atmospheric air state in large urban areas with many contamination sources has been proven scientifically by experimental studies (Ginsburg and others, 1997).

This paper presents a study of snow chemistry in the Lefortovo district of Moscow, Russia. The researches were conducted in the framework of the Lefortovo tunnel construction project. Because the tunnel passes under Lefortovo park, a valuable historical site, large-scale reconstruction of the park and restoration of its water system were carried out. The main tasks were: (1) to determine the intensity and composition of air pollution on the basis of snow-cover pollution as a short-term depositing environment, (2) to assess the potential hazard of surface-water, groundwater and soil contamination by snow cover after the snowmelt, and (3) to gain information concerning the reference contaminant concentrations in order to monitor changing environmental conditions after construction of the tunnel and reconstruction of the park.

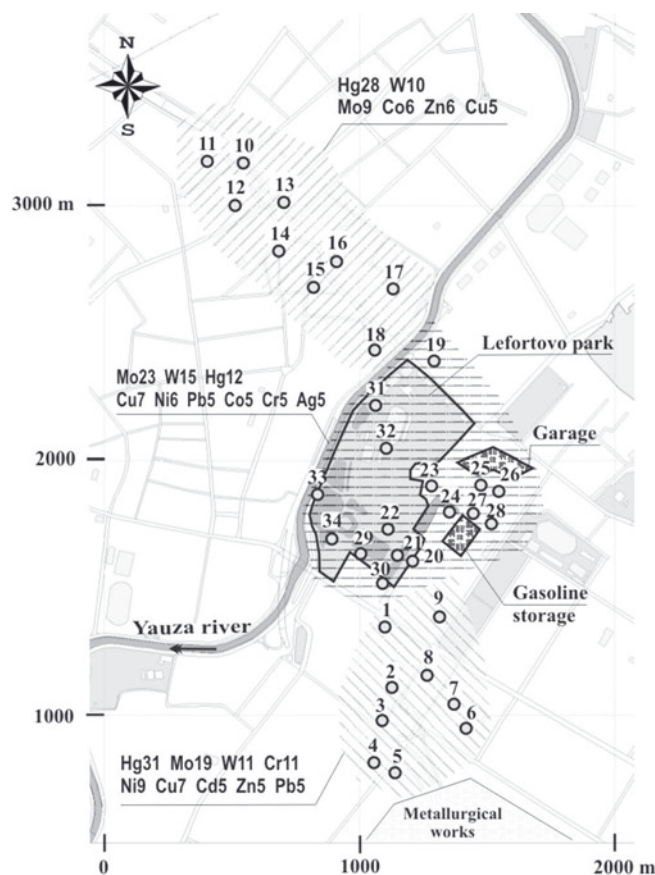
## 2. MATERIALS AND TECHNIQUE

Snow samples were collected in Lefortovo park and surrounding areas along the route of the projected tunnel

(Fig. 1). The location of 34 sampling points in the park was chosen taking into account the direction of surface runoff to the ponds and river and the location of pollution sources (garages, car washes, etc.). The distance between sampling points along the roads under the projected tunnel was generally ~100 m. Snow samples were collected before the period of heavy snowmelt from the pit, revealing the entire thickness of snow cover. Samples were defrosted in the laboratory at room temperature. The meltwater was filtered through the pre-weighted filter. The filter with the sediment was dried and weighed, and the volume of filtered water measured.

pH,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{PO}_4^{3-}$ , Fe, Mn, Zn, Sr, Cu, Ba, Pb, Cd, Ni, Cr, Mo, Co, As, Ag, Be and V were analyzed in filtered meltwater. Oil products, phenols and polycyclic aromatic hydrocarbons (PAHs; 3,4-benzopyrene, 1,12-benzoperylene, 11,12-benzofluoranthene, perylene, chrysene, phenanthrene, pyrene, anthracene) were analyzed in unfiltered snow samples. In the solid phase of snow, 71 chemical elements were determined using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

When assessing the degree of snow meltwater contamination, i.e. the excess of the actual concentration compared with standards, it was taken into account that the meltwater is a source of potential groundwater, river-water and pond contamination. We therefore compared chemical concentrations with hygiene standards and the thresholds for fishery water reservoirs. Snow contamination by solid-phase depositions was assessed using coefficients of dust load, concentrations and masses of the chemical elements in the dust. Levels of abnormality for individual contaminants were determined using the concentration coefficient  $K_c$ , calculated as the ratio of element concentration in the snow sample to its background value. To assess the multi-element contamination, the total contamination index,  $Z_c$ , was calculated for metals in hazard classes I–III as  $Z_c = \sum K_c - (n - 1)$ , where  $n$  is the number of elements.



**Fig. 1.** Scheme of snow-cover sampling points, main sources of contamination, and geochemical associations of elements in solid phase of snow.

The soil contamination hazard was determined by comparing the chemical-element concentration in solid-phase snow with the background concentration and hygiene standards for soils. The background values of solid precipitation, dust load, chemical elements in meltwater and soil were obtained on the basic principle using the ECOSCAN program (Burenkov and others, 1997).

### 3. RESULTS AND DISCUSSION

#### 3.1. Snow meltwater contamination

Snow meltwater was slightly acidic (pH in 74% of the samples of snow water did not exceed 6.0) and low-mineralized. The anomalies of chloride, sodium, nitrites, nitrates, oil products and 3,4-benzopyrene were revealed and the causes of their formation analyzed.

The salinity of snow meltwater ranged from 4.19 to 116 mgL<sup>-1</sup> (up to 12 times higher than the background value), but the range of variation in 73% of samples was 20.5–47.5 mgL<sup>-1</sup>. Increased salinity values were caused by the higher concentrations of Cl<sup>-</sup> and Na<sup>+</sup>, which were associated with the use of deicing salt. Analysis of the distribution of metals showed that only zinc, copper and cobalt were above the sensitivity of analysis in meltwater. However, even negligible quantities of heavy metals exceeded the fishery water reservoir standards: for zinc by up to 26 times, for copper by up to 40 times and for cobalt by up to 4 times. The assessment of zinc distribution between the liquid and solid phases of snow showed that

>50% of the samples contained zinc chiefly in the liquid phase. Zinc migration in the atmosphere occurs mainly in the solid phase in aerosols (97–99%; Tutunova, 1987), so in our case, zinc in the liquid phase seems to be available because a portion of solid particles of zinc are contained in easily soluble forms: chlorides, bromides and sulfates, arriving with vehicle emissions. Copper, unlike zinc, was predominantly found in the solid phase and can be represented by copper-bearing minerals and sorbed forms. The transition of metals to the liquid phase was carried out by oxidation and leaching from solid particles, and desorption of formerly adsorbed ions.

A major problem in the study area is environmental contamination by oil products and PAHs caused by the impact of heavy traffic, garages, car washes, car parks, etc. The concentration of oil products ranged from 0.04 to 1.36 mgL<sup>-1</sup>, thus exceeding the maximum permissible concentration (0.3 mgL<sup>-1</sup>) at several sites. The highest concentrations were observed in the south and north of the study area, and in Lefortovo park.

Atmospheric precipitation, especially snow, intensively absorbs PAHs. According to Gregor (1991), PAH concentration is five times higher in snow than in rain. The total amount of PAHs in the meltwater was varied in a large range, (7.2–1209) × 10<sup>-6</sup> mgL<sup>-1</sup>. The maximum value was recorded at Lefortovo park and was associated with emissions by construction machines, as well as fuel spillages during reconstruction of Lefortovo ponds.

The typical association of individual PAH represented by anthracene, 3,4-benzopyrene, 1,12-benzoperylene, 11,12-benzofluoranthene, perylene, chrysene, phenanthrene and pyrene was ascertained. The only normalized component of PAHs is 3,4-benzopyrene. As noted above, the extraction and analysis of PAHs was carried out from unfiltered snow samples, so it is necessary to know the ratio of the component contained in the liquid and solid phases. According to Vasilenko and others (1988), PAHs with a molecular weight of <228 – phenanthrene, anthracene, fluoranthene, pyrene, chrysene – are in a dissolved state in snow cover, while PAHs with a molecular weight of >228 – 11,12-benzofluoranthene, 3,4-benzopyrene and 11,12-benzofluoranthene – are ~90% in solid phase. Because 3,4-benzopyrene is mainly contained in solid-phase precipitation, the most significant risk comes from increased soil contamination after the snowmelt period. However, as shown below, the 3,4-benzopyrene hygiene threshold in soil was not exceeded.

In water systems in Lefortovo park, hygiene thresholds were exceeded for oil products to 3.2 MPC (maximum permissible concentration). Water-use fishery thresholds were exceeded for oil (up to 19.4 MPC), copper (up to 30 MPC), zinc (up to 3 MPC), nitrite (up to 4.3 MPC) and 3,4-benzopyrene. In the adjacent areas along the roads, hygiene thresholds are exceeded not only for oil products (up to 4.5 MPC), but also for 3,4-benzopyrene (up to 3.5 MPC). Upper limits for fishery water reservoirs were exceeded for oil products (up to 27 MPC), nitrite (up to 5 MPC), copper (up to 40 MPC), zinc (up to 26 MPC) and cobalt (up to 4 MPC). It should be emphasized that we only define the components, dangerous for surface water and groundwater. However, if we want to quantify the concentration of pollutants in the ponds, river and groundwater after snowmelt, it is necessary to simulate these processes.

### 3.2. Assessment of dust load and load of trace elements on the study area

The dust load in the study area mainly ranged from 21.0 to 203 kg km<sup>-2</sup> d<sup>-1</sup>. Background sites were located in the south of the area (sampling points 1 and 2), in Lefortovo park near the upper lakes, and to the north from point 31 to point 17. The sites with high levels of abnormality (>3) were located in the north of the study area at sampling points 12 and 13, and in the central part at sampling point 19 (where the highest level of dust-load abnormality was observed).

The total load of trace elements varied from 97.1 to 812.5 g km<sup>-2</sup> d<sup>-1</sup>. Maximum values of trace element load were found in the south of the area. The prevalent trace elements were zinc (in 58.8% of samples), barium (14.7%), nickel (14.7%), chromium (8.8%) and lead (2.9%). The following trends can be identified from the ratio between the main trace elements. Zinc, barium and manganese were prevalent in the northern part (sampling points 10–17). Further south (18 and 19), barium became most prevalent (Ba Zn Mn), in the central part (sampling points 23–27, 30–34), the role of nickel and chromium significantly increased (Zn Ni Ba, Zn Ba Ni, Ni Zn Cr) and in the southern part (sampling points 3–8) chromium and nickel took the leading positions (Cr Zn Ni, Ni Cr Zn, Zn Cr Ba, Zn Cr Mn). Spatial variation of metal concentrations was well correlated with the composition of emissions from industrial enterprises located in the south of the study area, in the first place from the 'Sickle and Hammer' metallurgical works. 'Wind Rose' in Moscow is located so that the winds blow mostly from the southwest and south, and accordingly from the metallurgical works to the study area.

However, the absolute contents of elements do not reflect the levels of element accumulation and do not allow us to estimate the degree of snow-cover contamination caused by man-made factors. Therefore the determination of actual concentration excess compared to the background is of particular importance.

### 3.3. Assessment of snow solid-phase contamination

Solid-phase contamination was studied using the concentration coefficient  $K_c$  and the total contamination index  $Z_c$ . The results of calculating trace element concentration in the dust captured by snow cover compared to appropriate background values allowed us to characterize the levels of abnormality of chemical elements. The highest-contrast contamination zones ( $K_c > 10$ ) in the study area were created by mercury, tungsten, molybdenum, chromium, nickel, cobalt, lead and copper. Middle-contrast contamination zones ( $10 < K_c < 3$ ) were created by accumulation of zinc, cadmium, silver, bismuth and tin, and low-contrast contamination zones by accumulation of barium, niobium and lithium. Manganese, gallium, ytterbium, beryllium, scandium, vanadium, yttrium and zirconium did not create anomalous zones in the study area.

Very high concentrations of mercury, molybdenum and tungsten were the main features of snow-cover contamination. The element most associated with pollutants was mercury, at 50% of the sampling points. Anomalous concentrations of mercury may be due to dust and gas emissions by heat-and-power engineering enterprises. In addition, many highly toxic mercury anomalies in the soil cover were revealed, so mercury can accumulate in snow cover because of mercury vapor. Anomalous contamination by molybdenum and tungsten is related to industrial emissions.

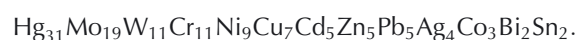
Due to disagreement about mercury accounting,  $Z_c$  was calculated in two ways: (1) for metals in hazard classes I–III excluding mercury, and (2) for metals in hazard classes I–III including mercury. In the first variant,  $Z_c$  varied from 10.6 to 123.6 and the area was characterized by low and medium levels of contamination. In most cases, tungsten was the only element in hazard class III, which in the study area belongs to a group of elements with the highest levels of abnormality. In the second variant,  $Z_c$  increased from 14 to 192. This increased the number of sites with high and average contamination levels, so the areas with low contamination level reduced.

As a result of snow melting, the solid-phase particles remain in the soil, so it is advisable to assess the potential risk of soil contamination. With respect to the background value of solid phase, ~5% of the area was characterized by a low pollution level, and 88% by a high pollution level (at sampling points 20 and 26). However, the hygiene threshold was observed to be exceeded only for cadmium (up to 3.6 MPC) and chromium (up to 4.3 MPC).

### 3.4. Geochemical associations of elements in solid-phase deposition of snow cover

The technogenic associations of elements, polluting snow cover by means of the dust component of air, formed the specific types of geochemical halos in snow. Based on study of the spatial distribution of the chemical elements and the structure of snow contamination, the territory was divided into three regions (south, north and central).

At the southern site (sampling points 1–9), snow-cover contamination was characterized by an association that included the highest levels of abnormality for Mo, Ni, Cr, W, Hg. Association of elements by the average values of  $K_c$  can be represented as



This association was due mainly to the influence of anthropogenic aerosol emissions from the metallurgical works (Ginsburg and others, 1997), as evidenced by the maximum concentrations of metals in aerosol dusts, reaching the following values: Ni 4000 mg kg<sup>-1</sup> ( $K_c = 40$ ); Cr 2000 mg kg<sup>-1</sup> ( $K_c = 20$ ); Mo 40 mg kg<sup>-1</sup> ( $K_c = 13.3$ ); W 60 mg kg<sup>-1</sup> ( $K_c = 10$ ); Pb 500 mg kg<sup>-1</sup> ( $K_c = 8.3$ ); Cu 300 mg kg<sup>-1</sup> ( $K_c = 5$ ); V 1000 mg kg<sup>-1</sup> ( $K_c = 4$ ); Co 40 mg kg<sup>-1</sup> ( $K_c = 4$ ).

At the northern site (sampling points 10–19) the technogenic anomaly in snow cover was characterized by an association (average value of  $K_c$ ) that can be represented as



The increased level of cobalt abnormality was the main feature of the association. At the northernmost point, cobalt was the element most associated with contaminants. Emissions by industrial enterprises located to the north or northwest of the study territory affected the formation of this anomaly. Compared with the southern site, the average level of mercury anomaly was virtually unchanged, but the molybdenum, tungsten, chromium and copper markedly reduced, indicating a weakening of the impact of metallurgical works.

At the central site (sampling points 20–34) the technogenic anomalies in snow cover were characterized by an association (average value of  $K$



A specific feature of contamination at the central site was



relatively low mercury concentrations: in most cases mercury did not have the leading position in the association. Compared with the southern site, levels of abnormality of chromium and nickel were markedly reduced, while the level of cobalt abnormality increased. In the east of the central site a small anomalous area with heightened concentration of lead ( $K_c$  increases up to 14) was found, which was due to the influence of road transport emissions at the garages located here.

The contents of pollutants in the atmospheric air were calculated using regression equations (Valetdinov and others, 2009). The lead excess in air was up to 2.2 MPC at sampling points 19, 25 and 28, and nickel excess was up to 2.1 MPC at sampling points 5 and 6. The contents of the other elements comply with the standards. It should be noted that so-called 'alerted' concentration ( $>0.5$  MPC) was found for zinc (0.97 MPC) at sampling point 13 and chromium (0.6 MPC) at sampling points 5 and 6.

#### 4. CONCLUSION

The results of research in Lefortovo district allowed us to determine the chemistry of the liquid and solid phases of snow, establish the type of man-made contamination of snow cover, evaluate the main characteristics of snow contamination and their spatial variations, and assess the hazard of snow contamination to other natural environments.

Snow cover in the study area was mainly characterized by an average level of contamination consistent with the total contamination index. Ecogeochemical associations of elements, contaminating the snow cover over the dust component of air, formed the specific geochemical halos. A similar structure of the ecogeochemical field arose as a result of mixing of industrial and highways emissions. The common type of man-made contamination in snow cover is characterized by the following general association of contaminants:

Hg W MoCr Ni Co Pb Cu Zn Cd Ag Bi Sn Ba Nb.

Non-compliance with standards in atmospheric air, calculated using regression equations, was determined only for nickel and lead. Assessing the snow-contamination hazard to surface and groundwater, hygiene thresholds were exceeded for oil products and 3,4-benzopyrene, and water-use fishery thresholds for copper, zinc and nitrite. Soil hygiene thresholds were exceeded only for cadmium

and chromium. In this paper, we only define the components that are dangerous for other natural environments. To quantify the concentration of pollutants in ponds, river, groundwater and soils after snowmelt, it is necessary to simulate these processes, and we propose to consider these results in a subsequent paper.

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