Analysis of Aerosol Pollution Near the Novosibirsk Tin Plant

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Abstract

The major results of investigation of the arsenic pollution of snow cover near the Novosibirsk Tin Plant at the end of winter seasons of the years 1994–1995 and 2000–2001 are presented. The data of natural observations are interpreted on the basis of the formulation of inverse problems of the transport of aerosol admixtures. Quantitative regularities of the pollution of territory are revealed. The structure of aerosol precipitation is analyzed and the levels of arsenic concentration in the snow in winter seasons under consideration are compared.

INTRODUCTION

The Novosibirsk Tin Plant (NTP) is situated at the left bank of the river Ob' in the industrial region of the Kirovsky District of Novosibirsk. The major activities of the plant are aimed at the manufacture of commercial tin, as well as tin-based alloys, solders and babbits. Tin concentrates, lead- and tin-containing minerals with tin content from 10 to 60 % are used as the initial raw material. In addition to tin, the initial raw material contains lead, arsenic, sulphur, zinc, indium, iron, *etc.*

The raw material is processed at the plant according to the following scheme: pretreatment of concentrates – roasting – reductive fusion – refinement. Lean raw material, middling and slag are processed by fuming, while the removals of refinement are processed by electric fusion. The major toxicants emitted into the environment during tin manufacture are arsenic, lead, zinc, sulphur oxides. Suspended matter is emitted from riddles, crushers, bunkers, conveyers, grainers, as well as drying, roasting, electrofusion and fuming ovens, middling tailings.

Dust is partially removed from the air of exhaust ventilation systems. No purification from sulphur oxides is performed. To remove dust and to purify gases, electric filters are used along with bag filters, Ventury scrubbers, cyclones, full scrubbers. Multistep dust capturing systems are used to purify the most heavily polluted gases. The efficiency of the basic dust removing installations is rather high. For example, for dust removal from fuming gases, it reaches 99.6 %; for electric oven gases, 99.9 %; for refinement gases, 99.8 %.

The major amount of hazardous substances is emitted into the atmosphere through a chimney which is 100 m high. On the one hand, its substantial height allows efficient scattering of the hazardous admixtures; on the other hand,

this may lead to substantial gas and aerosol pollution of the city territory.

MODEL TO ESTIMATE AEROSOL POLLUTION OF A TERRITORY

In order to estimate long-term (month, season, year) pollution of the territory by a point source, the following regression equations were proposed and tested:

$$p(r, \varphi, \bar{\Theta}) = g(\varphi + 180^\circ) \cdot f(r, \Theta_1, \Theta_2) \quad (1)$$

$$f(r, \Theta_1, \Theta_2) = \Theta_1 r^{\Theta_2} \exp(-c/r) \quad (2)$$

Here p is specific content of an admixture in snow (soil, air); r, φ are polar coordinates of the calculated point, with the point of origin at the source location; $g(\varphi)$ is climatic recurrence of wind directions for the time interval under consideration; c is a parameter depending on the height of the source, temperature and volume of the emitted air gas admixture and wind velocity; $\bar{\Theta} = (\Theta_1, \Theta_2)$ is a vector of unknown parameters.

The Θ_1 component is proportional to the emission productivity; it exhibits rather complicated dependence on climatic characteristics, wind velocity, turbulent exchange coefficients, source height, and sedimentation rate of the aerosol admixtuire;

$$\Theta_2 = -2 - w/[k_1(n + 1)] \quad (3)$$

where w is the rate of sedimentation of aerosol particles; k_1 is vertical turbulent diffusion coefficient at the height of 1 m; n is power in the approximation of the horizontal component of wind velocity by the power series profile.

For $\Theta_2 \to -2$ $w \to 0$, which corresponds to the case of weakly settling admixture. If the climatic information on wind velocity and the data on geometric and thermodynamic characteristics of the source are available, the c value can be calculated preliminarily using the eq. (3) as $c = 2r_{\max}$ or determined using the results of observations of the surface concentration field for weakly settling admixture, where $r_{\max}$ is the point of maximal surface concentration for a weightless admixture. In the opposite case, c should be related to the number of the estimated parameters of the model (1).

EXPERIMENTAL

Sampling procedure

The major source of pollutants at the NTP territory is a chimney of 100 m high with the mouth 3.7 m in diameter. The rate of gas-dust mixture coming out of the chimney can reach 5–6 m/s; its temperature is 80–90 °C. The present characteristics of the chimney allow us to estimate the r_{max} value. In this case, it is about 1.5 km [3].

The snow cover was sampled over its whole depth by a standard procedure using a snow sampler. In March 1995, sampling was performed along several radial routes (Fig. 1). The data of these studies are presented in [4]. Taking into account the highest recurrence of the southern wind in winter, the major number of sampling points was located to the north of the plant territory. The distance from the chimney to sampling sites was 0.4–2.5 km. This allowed us to reveal the nearby and remote regions of aerosol precipitation of arsenic at the substantial differentiation of particle size. This procedure helps obtaining a more efficient estimation of the parameters of regression function (1) depending on the distance scales under consideration. It should be noted that at the known particle size distribution or gravitational sedimentation rates, it is unnecessary to distinguish precipitation regions specially. In this case, it is reasonable to carry out an optimal positioning of sampling sites using mathematical planning of experiment [5, 6].

On the beginning of March 2001, snow was sampled along three radial routes of the northern direction. At these routes, snow was sampled in the same sites as in 1995 (see Fig. 1). The major results of experimental investigations of the years 1995 and 2001 are shown in Table 1.

Chemical analysis

The primary sample preparation for analysis involved melting with a water bath at a

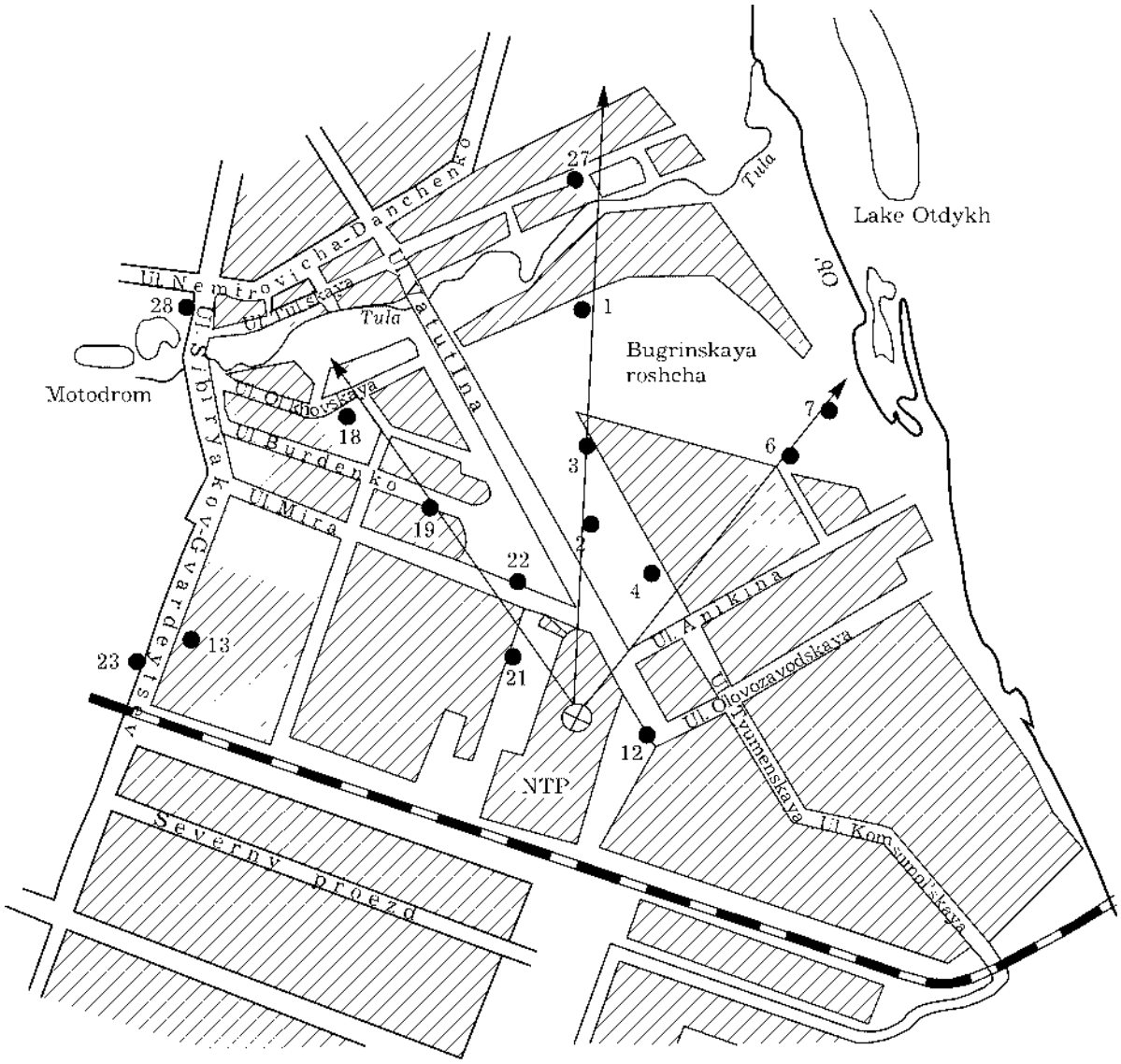

Fig. 1. Scheme of snow sampling sites in the vicinity of the Novosibirsk Tin Plant: ⊗ is the plant chimney; arrows indicate the major sampling routes.

temperature of 50–60 °C followed by filtering the melted water. To isolate coarse and fine solid fractions from the water-soluble part of samples, the samples were filtered sequentially through the paper filters (blue ribbon, pore diameter 1–3 μm), and membrane filters (pore diameter 0.45 μm).

To determine arsenic content of the separated fractions, atomic emission analysis was applied. The filters with precipitates were subjected to the acidic leaching at elevated pressure. The solutions obtained after leaching, and the water-soluble fraction were evaporated with a graphite collector with sodium chloride added. For quantitative calculations, calibration samples based on graphite powder with the addition of microelements were used. The correctness was checked by varying the weighed portion. The analysis was performed with the PGS-2 spectrograph (Karl Zeiss, Yena) with the arc excitation source; emission spectra were recorded with the multi-channel analyzer of emission spectra. The error of determining arsenic within the concentration range 6–1250 mg/l is 35 to 15 %, respectively.

TABLE 1
Characteristics and results of the analysis of snow sampled near the Novosibirsk Tin Plant

Index	Reference point No.								
1	2	3	4	6	7	18	19	22	
Distance from the chimney, km	1.9	1.05	1.4	0,45	1.3	1.6	1.76	1.28	0.4
Snow mass, kg	2.6/0.65	1.9/0.71	2.5/0.68	2.2/0.72	2.25/0.64	2.8/0.72	3.05/0.64	2.05/0.67	1.9/0.74
Sampling area, dm^2	4.8/0.39	3.2/0.39	4.0/0.39	4.0/0.39	2.4/0.39	2.4/0.39	3.2/0.39	4.8/0.39	4.0/0.39
Arsenic concentration, μg/l	17.3/223	63.2/402	44/248	63.6/1360	62.2/357	57.1/247	13.8/70.5	26.8/38	6.3/229

Note. The numerator shows experimental data for 1995, denominator shows the data for 2001.

NUMERICAL MODELING

Preliminary analysis of the data shown in Table 1 and the geometric characteristics of the chimney indicate that the concentration of arsenic in the nearby region of the action of source (points No. 2, 4, 22) is rather high, compared to remote observation points. We can assume that this is a result of sedimentation of coarse particles containing arsenic. On the other hand, rather high concentrations of arsenic in the remote region are the evidence of the fact that the disperse composition of the emitted mixture is variable. So, it is reasonable to estimate the parameters Θ_1 and Θ_2 of the regression dependence (1) separately for the nearby and remote regions, which allows us to provide a more precise description of the spatial distribution of aerosol precipitation of arsenic.

The results of estimation of the unknown parameters of model (1) according to the observation data of the years 1995 and 2001 are listed in Table 2. To increase the accuracy of estimation, two approaches were used. In the first one, the reference observation points were chosen both in the nearby and in the remote regions; in the second one, in the case of the availability of additional information on arsenic content of fractions, the parameters were estimated in more detail, *i. e.* separately for each fraction.

The arsenic concentrations calculated according to eq. (2) using the determined parameters are shown in Figs. 2 and 3. The observation data are normalized by the corresponding winter mean recurrence of wind directions with respect to the source [7]. It should be noted that in order to estimate parameters according to [5, 6], it is sufficient to use a limited set of the reference observation sites. This circumstance provides an additional possibility to test the adequacy of the model over the rest sampling sites which serve as the reference ones. In general, judging from Figs. 2 and 3, calculations and observations are consistent wich each other quite satisfactorily. Deviations in some reference points can be linked with different reasons, in particular with the possible capture of soil particles during sampling, errors of sample preparation and chemical analysis, de-

TABLE 2

Estimation of the parameters Θ_1 and Θ_2 of the regression (1) according tj the observation data of the years 1195 and 2001.

Year	Reference point No.	Fractional composition*	$\Theta_1 \cdot 10^{-3}$	Θ_2
1995	4, 6	Sediment + filtrate	5.8	−4.15
1995	6, 27	The same	3.5	−2.05
2001	4, 6	Coarge fraction	38.7	−5.54
2001	2, 7	The same	27.1	−3.93
2001	2, 7	Fine fraction + filtrate	6.9	−4.31

*The data on arsenic content of the mentioned fraction were used.

viations between the mean climatic and the current winter wind recurrence, *etc*.

The analysis of the data presented in Table 2 shows that the Θ_2 values change substantially with increasing distance from the source to the reference points. This confirms the assumption concerning substantial variation of the disperse composition of aerosol emission. Taking into account eq. (3) and comparing esti-

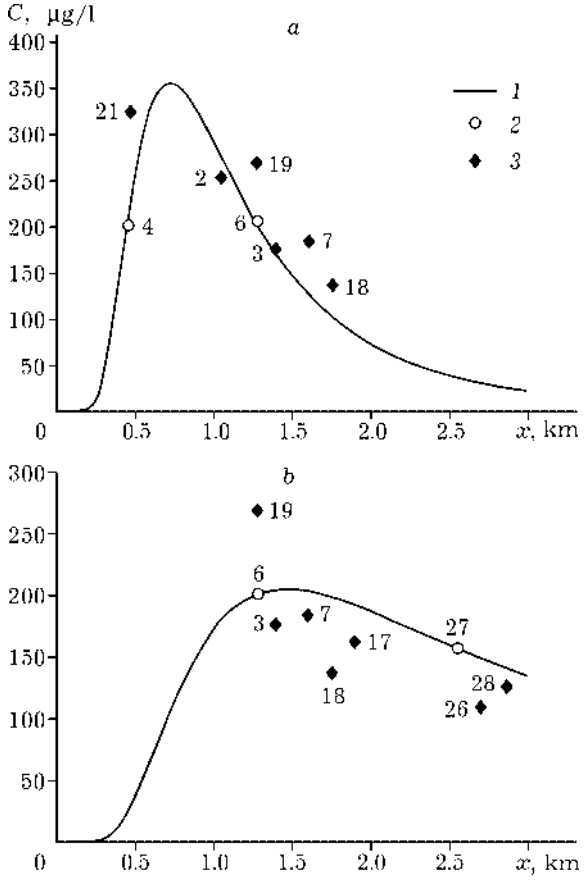

Fig. 2. Arsenic distribution in the nearby (*a*) and remote (*b*) regions of the action of the source recovered according to the observation data of 1995: *1* − numerical modeling; *2, 3* − supporting and reference observation sites.

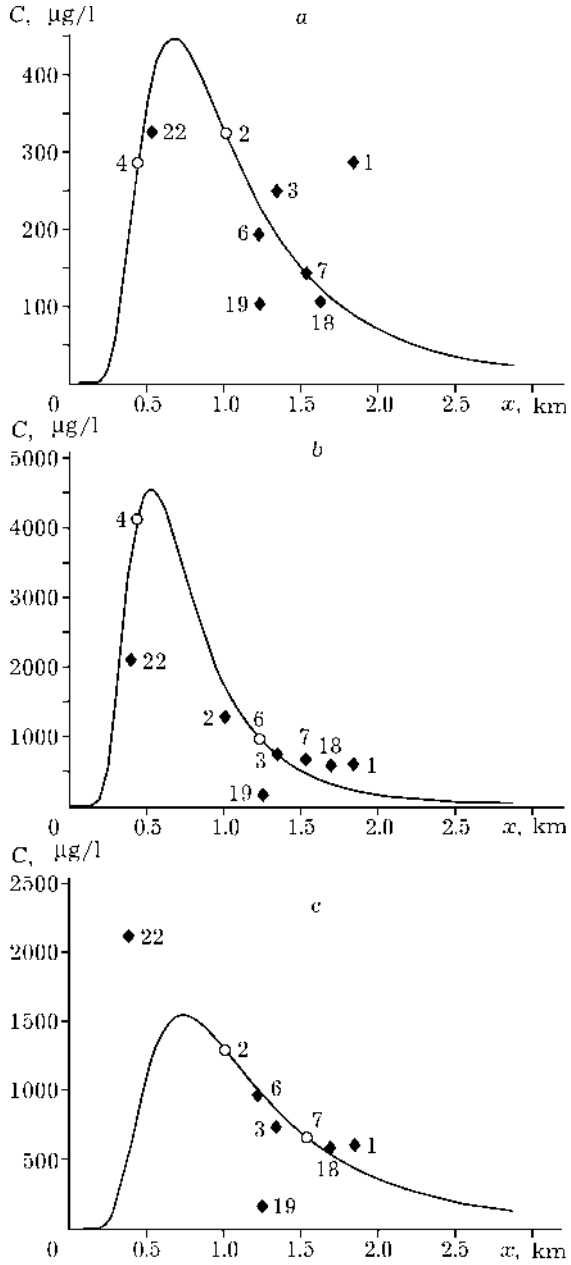

Fig. 3. Level of arsenic precipitation in winter 2000−2001 in the fractions: *a* − total in fine and water-soluble; *b, c* − in coarse (*b* − nearby region, *c* − remote region).

mations of Θ_2, mean rate of sedimentation of the dust particles containing arsenic was much higher in winter 2000–2001 than in winter 1994–1995. As a result, the maximum of sedimentation shifted noticeably towards the chimney and occurred at a distance of about 0.5 km. In winter 1994–1995, the maximum of sedimentation occurred at a distance of 0.8–0.85 km to north-east. It should also be noted that in winter 1994–1995, the rate of particle sedimentation in the remote region was low. According to the data shown in Fig. 2, *b*, this means that a substantial part of the territory of Novosibirsk was under the influence of the NTP.

Estimations of the parameters of regression (2) shown in Table 2 allow us to obtain the spatial image of arsenic aerosol precipitation. It is sufficient to use eq. (1) uniting sequentially the concentration fields of the nearby (up to 1 km) and remote regions. A similar procedure can be made with the coarse fraction in the case of the winter 2000–2001. Then, the obtained field must be summed with the concentration field formed by small and water-soluble fractions.

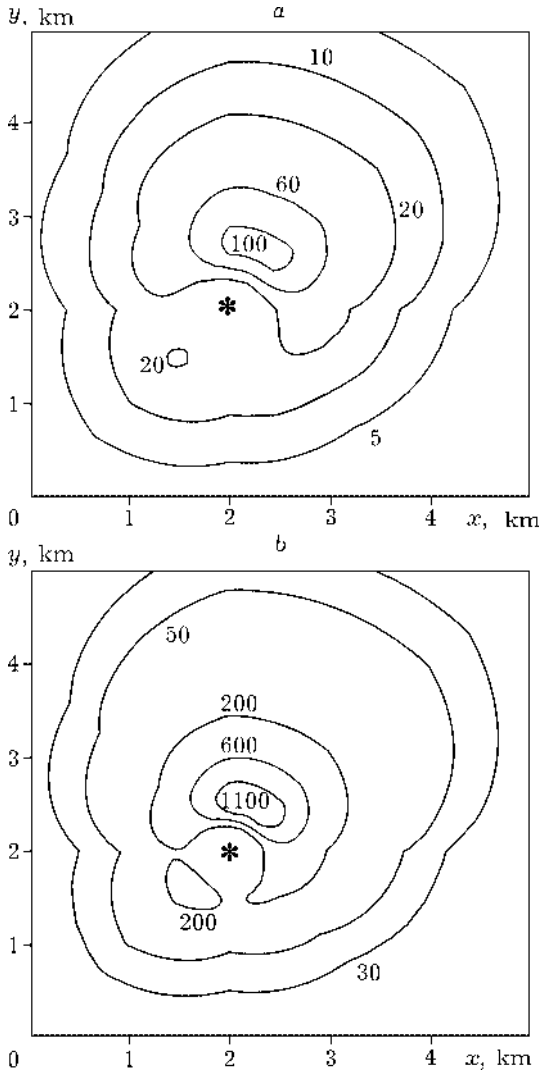

Fig. 4. Arsenic concentration (μg/l) in winter at the end of winter 1995 (*a*) and 2001 (*b*).

The fields of aerosol precipitation of arsenic during winter seasons under consideration are shown in Fig. 4. One can see that rather large region of increased concentration is formed to the north of the source. The intensity of precipitation in this region was much higher in 2001 than in 1995.

The obtained precipitation fields can be used to estimate total emission of arsenic during the winter seasons under consideration. In order to do this, it is necessary to perform additional investigations to determine moisture capacity of snow, time of the stable snow cover bedding, wind rose for a specific winter season, disperse composition, *etc*.

CONCLUSIONS

The experimental investigation and numerical modeling allow us to make the following conclusions.

1. Recovery models provide quite adequate description of the aerosol pollution of snow cover in the vicinity of the NTP by arsenic.

2. Particle size distribution for the arsenic-containing dust is rather broad, which causes relatively high pollution of the territories both near the NTP and remote ones. This circumstance brings about the necessity to place sampling sites more densely in the vicinity of the source. If the data on the particle size distribution is available, the recovery model should be additionally corrected and the position of sampling sites should be optimized on the basis of numerical methods of planning experiments.

3. The numerical analysis of the data of snow monitoring of the pollution in 1995 and 2001 allows us to perform a comparison. In winter 2000–2001, the emission of arsenic into the atmosphere from the NTP territory occurred in much larger aerosol fractions than during

the season 1994–1995. Total precipitation of this element in winter 2000–2001 exceeds that of 1994–1995 substantially, especially in the nearby region.

The obtained regularities of arsenic distribution in snow cover in the vicinity of the NTP can be used to analyze the data on aerosol pollution of the atmospheric air and soil.

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