

UDC 551.588.467:543.544.5:543.449

DOI: 10.15372/KhUR20160411

Chemical and Granulometric Composition of Particles of Solid Atmospheric Aerosol Including Black Carbon in the Snowpack on the Territory of the Industrial Zone of Novokuznetsk City

N. V. ZHURAVLEVA^{1,2}, E. R. KHABIBULINA^{1,2}, Z. R. ISMAGILOV¹, O. S. EFIMOVA¹, A. A. OSOKINA² and R. R. POTOKINA²¹*Institute of Coal Chemistry and Material Science, Federal Research Center of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia**E-mail: IsmagilovZR@iccms.sbras.ru*²*West-Siberian Testing Centre, Novokuznetsk, Russia**E-mail: zhuravleva_nv@zsic.ru*

Abstract

The qualitative and quantitative composition of 13 polycyclic aromatic hydrocarbons (PAHs) in samples of snow waters on the territory of Novokuznetsk city and the Novokuznetsk district experiencing the maximum load on the environment from the activity of the enterprise of ferrous metallurgy was determined. The distribution of PAHs between the solid and liquid phases of snow water was studied by the method of high performance liquid chromatography (HPLC). It was shown that from 81.2 to 99.5 % of the total content of PAH was present in the solid phase of snow water. The concentration of benzo(a)pyrene amounts the value from 0.092 to 0.748 $\mu\text{g}/\text{dm}^3$. It was established by the laser granulometry method that 90 % of particles of solid atmospheric aerosol in the snowpack were represented by particles, the sizes of which do not exceed 51.0 μm . Samples of snow waters are mainly characterized by the bimodal distribution of nanoparticles by sizes, the bulk of particles (up to 93 %) have the size of 400–600 nm, 7–9 % falls on the proportion of nanoparticles with the sizes of 44–86 nm.

Key words: snowpack, polycyclic aromatic hydrocarbons (PAHs), distribution of particles by sizes, high performance liquid chromatography (HPLC), laser granulometry, method of dynamic light scattering

INTRODUCTION

Novokuznetsk city is one of the biggest industrial centres of Russian Federation. Enterprises of ferrous and non-ferrous metallurgy, coal-mining industry; heat and power generation, located within the city boundaries exert a significant impact on contamination of the environment objects. The major substances contaminating the atmosphere are carbon dioxide, sulphur dioxide, nitrogen oxides, suspended substances, soot and benzo(a)pyrene. Zavodskoy district of the city, on the territory of which 27 enterprises are located, including the biggest enterprise of the ferrous metallurgy Evraz ZSMK JSC, affected by 76.6 % of all emis-

sions of contaminants into the atmosphere of Novokuznetsk, and experiences the maximum load on the environment [1].

According to the observations data of FSBI “Voeikov Main Geophysical Observatory”, the condition of the atmospheric air contamination in Novokuznetsk is assessed as “very high” in 2014 and “high” in 2015, in which, the priority contaminant is benzo(a)pyrene, the average annual concentration of which in 2015 amounted to 4.6 MPC [2].

The major sources of emissions of benzo(a)pyrene in the atmosphere of the city are coke and by-product process at the Evraz ZSMK JSC, aluminium production at the RUSAL Novokuznetsk Aluminium Smelter OJSC, coal

combustion at power stations, local boilers, private house ovens, and auto transport. Benzo(a)pyrene is the most dangerous carcinogenic representative of the class polycyclic aromatic hydrocarbons (PAHs), its maximum permissible concentration (MPC) in atmospheric air in Russia is equal ($0.001 \mu\text{g}/\text{m}^3$) [3], water ($0.00010 \text{ mg}/\text{dm}^3$) [4–6], soil ($0.020 \text{ mg}/\text{kg}$) [7]. The availability of numerous sources of PAHs causes the need of the constant control of compounds of this class in environment objects [8, 9]. The determination of PAH in the snowpack allows obtaining the information about the anthropogenic load degree on the territory and revealing the sources of the environment contamination by compounds of this class [10–13]. The complex assessment of the contamination degree of the snow waters also suggests conducting investigations on the study of the qualitative and quantitative composition of toxic elements [14, 15] and determining the granulometric composition of suspended particles [16].

The control system of the snowpack is a part of the total monitoring system of transboundary and long-range transport of contaminants [17]. Precipitates represent the effective factor of washing out various substances from air, which may lead to the change of the chemical composition of soils, rivers and water bodies [18].

Previously we determined [19] the qualitative and quantitative composition of 13 PAHs in snow waters sampled in the area of meteorological observation stations in Novokuznetsk. It was shown that the concentration of benzo(a)pyrene in snow waters ranged from 0.025 to $0.723 \mu\text{g}/\text{dm}^3$, which exceeded MPC in surface waters ($0.010 \mu\text{g}/\text{dm}^3$) in 2.5–72.3 times. The content of other PAHs (benzo(b)fluoranthene, benzo(g,h,i)perylene) is comparable in order of magnitude with the concentration of benzo(a)pyrene. Suspended substances in the snowpack are represented by particles, the dimensions of which do not exceed $35.5 \mu\text{m}$ (90 %). The fraction of particles with a size of $2.5 \mu\text{m}$ and less amounts to 7.39 %, $10 \mu\text{m}$ and less – 38.46 %.

The issues of the interrelationship of distribution of particles by sizes in atmospheric air of the megalopolis and content in them of PAHs were considered in the work [20]. The authors showed that PAHs were adsorbed on

the particles that had the bimodal distribution by sizes with the maxima in the ranges of 0.4–2.1 μm and 3.3–9.0 μm . In the work [21], when studying the atmospheric air contamination near the highway it was shown that the distribution of PAHs on dust particles of a certain size depended on the molecular mass of PAH. The authors explain this dependence by the Kelvin effect that binds the particles diameter and vapour pressure of the substance, at which more volatile PAHs with a smaller molecular mass are bound with particles of a larger size.

Nanoparticles of contaminations, situated in the environment (in atmospheric air, water objects, soil *etc.*) represent risk for health when they enter the human body. Carbon nanomaterials (nanotubes, fullerenes, black carbon), metals particles, oxide nanoparticles, silicates and aluminosilicates nanoparticles, organic polymers nanoparticles *etc.* [22] belong to the priority nanomaterials that are necessary to determine. For some nanomaterials (titanium dioxide, silver, carbon nanotubes nanoparticles), the hygienic standards of their content in the environment objects were established [23]. The technique of identification of nanoparticles in natural, ground water and wastewaters by the transmission electron microscopy (TEM) method is given in the methodological recommendations [24]. This method allows obtaining the information about the shape, structure and size of nanoparticles in the examined water samples, the data on the aggregation degree of the nanoparticles, information about the character of the nanoparticles distribution in the samples, electron microscopic images of particles in water. Another method of determining nanoparticles sizes is the method of dynamic light scattering. In the work [25], a possibilities comparison of the evaluation of the nanoparticles size by dynamic light scattering (DLS) and TEM was conducted. The convergence of results obtained by different methods was shown.

In this work, to study the granulometric composition of atmospheric aerosol particles in samples of snow waters sampled in the Zavodskoy district of Novokuznetsk and the Novokuznetsk district, methods of laser granulometry and DLS were used. The distribution of PAHs in the solid and liquid phases of snow waters was studied by the method of HPLC.

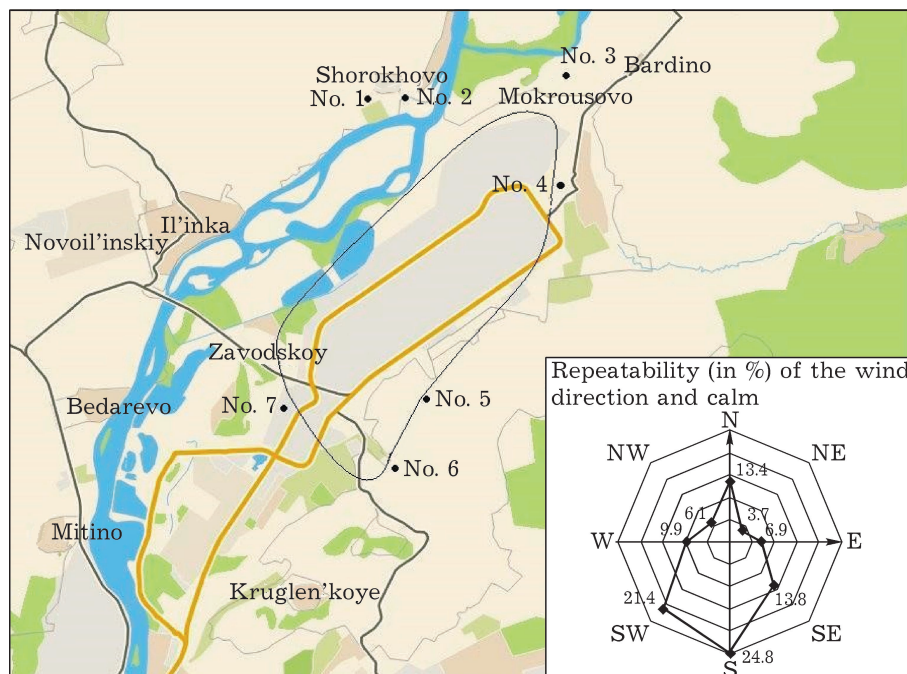


Fig. 1. Map chart of the location of the sampling points of the snowpack in Novokuznetsk and the Novokuznetsk district. The thick line indicates the location district of the industrial area.

EXPERIMENTAL

Snow samples were collected in the Zavodskoy district of Novokuznetsk and Novokuznetsk district, the scheme of the points location is given in Fig. 1. These points are located on the border of the sanitary-protective zone of the north in-

dustrial hub and are experience different degrees of the anthropogenic load on the territory (Table 1). As the reference point, a site located on the south of the Kemerovo Region (Mezhdurechensk district, territory of the State Nature Reserve Kuznetskiy Alatau) was accepted, experiencing the minimum anthropogenic impact.

TABLE 1

Description of sampling points of the snow cores on the territory of Novokuznetsk and the Novokuznetsk district

Sampling Nos.	Location of sampling points of snow samples	Location of the point relatively to the industrial zone*	Additional influence factors
Reference	Mezhdurechensk district, territory of the State Nature Reserve Kuznetskiy Alatau	—	—
1	Novokuznetsk district, Shorokhovo settlement (western outskirts)	Leeward	Emissions from the coal combustion in private house furnaces
2	The same, eastern outskirts	Leeward	The same
3	The same, Mokrousovo village	Leeward	The same
4	The same, Bolshevik village	Leeward	The same
5	Novokuznetsk city, Ul. Goluboy Log	Windward	The same
6	The same, Ul. Chernaya Rechka	Windward	The same
7	The same, Ul. Avtotransportnaya	Windward	Emissions of auto transport

*According to the wind rose in Novokuznetsk.

The snow samples collection was conducted simultaneously during the period of the maximum moisture content (early in March, 2016) immediately before the start of snowmelt. Snow samples were cut in the form of cores on the full depth of the snowpack, placed in plastic bags and brought to the laboratory. Then snow samples were transferred to glass containers, where they melted at room temperature. When determining PAHs snow waters were filtered through a filter "blue ribbon" for the further study of precipitates (solid phase) and filtrates (liquid phase). To determine the granulometric composition of solid particles of aerosol, snow water was subjected to settling, the precipitate was analyzed by the laser granulometry method, and the supernatant liquid – by DLS method.

To extract PAHs from the liquid phase the method of double liquid extraction was applied. The liquid phase (1 dm³) was transferred to a separatory funnel with a volume of 2 dm³, 40 mL of hexane was added, and extraction was carried out using an extractor EL-1 (Labtekh, Russia) with a rate of 1500 rpm/min for 20 min. After the phase separation, the lower layer was transferred to a conical flask, and the upper layer (extract) – in a measuring cup with a volume of 100 mL. The extracts were combined, dried, passing through a layer of anhydrous sodium sulphate. The extract was evaporated under a stream of argon to a solvent volume of 1 mL, then 1 mL of acetonitrile was added and the upper layer of hexane was evaporated.

To extract PAHs from the solid phase filters with precipitates were placed into measuring cups with a volume of 100 and 20 mL of hexane was poured. Samples were placed in an ultrasonic bath for 10 min, after which the solvent was decanted, passed through a filter with a layer of the desiccant. The extracts were combined, evaporated and the solvent was replaced by acetonitrile up to the final volume of 1 mL.

The qualitative and quantitative determination of PAHs in snow water was implemented by HPLC on a device LC-20AD Prominence (Shimadzu, Japan), consisting of the following units: gradient high-pressure pump of the series LC-20AD (mixing system up to four solvents), autosampler SIL-20A (with the possibility of varying the volume of the introduced

sample from 0.4 up to 100 µL), flow-line mobile phase degasser DGU-20A₃, thermostat of columns CTO-10FSvp, fluorescence detector RF-20A, spectrophotometric diode matrix detector SPD-V20A, chromatographic column with the dimensions of 250 × 4.0 mm, filled with the sorbent MZ-PAH C18 5 µm grained (MZ-analytical, Germany).

As the eluents, the first sort acetonitrile (SPC Cryochrom Co. Ltd., St. Petersburg, Russia) and bidistilled water were used. Chromatographing was conducted in the gradient mode: acetonitrile/water from 70 : 30 to 100 : 0 for 12 min, 100 % of acetonitrile with the 12th to 25th min of analysis. The solvent consumption was 0.8 µL/min. The sample injection into the column was carried out automatically; the volume of the injected sample was 20 mL. The thermostating temperature of the column was 40 °C. Detecting was carried out in the following modes: detector on the diode matrix: spectra were removed in the range of 190–400 nm, at quantitative determination the signal was registered at 254 nm; fluorescence detector: programming on the maxima of excitation and emitting for each compound [26].

Identification of PAHs was carried out by the library search with the help of software PostRun. The library contains spectral parameters, the absolute retention times of priority representatives of PAHs. All PAHs have characteristic UV spectra, by which with a big fraction of probability one can identify compounds. The simultaneous use of two detectors in the analysis of samples of the unknown composition eliminates errors of the substance identification and quantitative calculation of their concentration.

The primary and working calibration solutions of analytes in acetonitrile were prepared from standard samples of the enterprise SOP 0101-03-0117-03 (Ekokhim Co. Ltd., St. Petersburg). The determination was carried out using the following standard substances of PAHs: naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene.

The distribution of microparticles by sizes was determined on an ANALYSETTE 22 MicroTec plus analyzer (FRITSCH, Germany),

which allows carrying out measurements in the range of 0.08–2000 μm . Dispergating of the material was carried in a liquid medium (water) with the additive of a surfactant. When dispergating in the liquid medium, the sample material was introduced into a closed liquid circulation contour, after this continuously pumped through a measuring cell. During pumping in the measuring contour, ultrasound was integrated for the destruction of agglomerates and preparation of individual, separated particles. The measurement results were processed in the MaS-control software and presented as differential and integral distribution of particles by sizes.

The size of nanoparticles was determined by an analyzer Zetasizer Nano ZS (Malvern Instruments, England) using technologies of registering backscatter. The operating principle of the analyzer is based on the use of the method of DLS that allows determining the diffusion coefficient of dispersed particles in a liquid by the analysis of the correlation function of intensity fluctuations of scattered light. Further from the diffusion coefficient, the nanoparticles diameter was calculated. The particle size value (average hydrodynamic diameter, D_H) was calculated from the analysis of cumulants in accordance with the International Standard for the method of DLS ISO 13321 [27]. The method allows determining the size of nanoparticles in the range of 0.5 nm to

10 μm . A helium-neon laser with the power of 4 mW operating at a wavelength of 633 nm is used in the analyzer.

Before the nanoparticles measurement, the device was checked according to the latex colloidal system (60 nm). A sample of snow water of a volume of 1.5 μL was selected with a disposable syringe and transferred into a disposable polystyrene cuvette for measurements, hermetically closed and placed into the cuvette compartment of the analyzer. Before measurements, the sample was thermostated at 20 $^{\circ}\text{C}$ for 30 min. To control the results repeatability on each sample, at least, six parallel dimensions were performed, each of which consisted of 20 scans by 10 seconds. The particles distribution by size represents fractions of intensities of the scattered light that belongs to various classes of nanoparticles sizes. The distribution by sizes in the intensity units was obtained from the analysis of correlation functions using the algorithm of the Multi Narrow Modes of the analyzer software.

RESULTS AND DISCUSSION

The determination results of PAHs in the solid and liquid phases of snow waters are given in Tables 2–4. At the reference point (Mezhdurechensk district, the territory of the State Nature Reserve Kuznetskiy Alatau) PAHs were not detected.

TABLE 2
Concentrations of PAHs in the solid phase of snow waters

PAHs	Test results of the solid phase, $\mu\text{g}/\text{dm}^3$							
	Background	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Naphthalene	<0.020	0.550	1.469	3.901	2.53	6.495	1.810	1.385
Fluorene	<0.006	0.150	0.338	0.638	0.330	1.497	0.113	0.550
Phenanthrene	<0.006	1.585	1.518	4.534	2.848	9.659	2.127	4.378
Anthracene	<0.001	0.103	0.098	0.425	0.271	0.839	0.158	0.224
Fluoranthene	<0.006	0.687	0.557	3.545	2.510	6.364	2.768	2.271
Pyrene	<0.020	0.595	0.522	2.202	1.599	4.120	1.757	1.505
Benzo(a)anthracene	<0.006	0.073	0.052	0.220	0.191	0.442	0.516	0.274
Chrysene	<0.003	0.254	0.256	0.949	0.769	1.828	1.877	1.174
Benzo(b)fluoranthene	<0.006	0.161	0.162	0.488	0.440	1.062	1.416	0.756
Benzo(k)fluoranthene	<0.001	0.031	0.027	0.010	0.010	0.235	0.030	0.183
Benzo(a)pyrene	<0.001	0.092	0.089	0.269	0.294	0.579	0.745	0.403
Dibenzo(a,h)anthracene	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Benzo(g,h,i)perylene	<0.006	0.095	0.114	0.246	0.256	0.549	0.932	0.451

TABLE 3
Concentrations of PAHs in the liquid phase of snow waters

PAHs	Test results of the liquid phase, $\mu\text{g}/\text{dm}^3$							
	Background	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Naphthalene	<0.020	0.512	0.371	0.399	0.562	1.337	0.473	0.449
Fluorene	<0.006	0.416	0.240	0.422	<0.006	0.273	0.222	0.158
Phenanthrene	<0.006	0.007	0.045	0.112	0.076	0.084	0.083	0.106
Anthracene	<0.001	0.014	0.009	0.018	0.020	0.024	0.021	0.022
Fluoranthene	<0.006	0.008	<0.006	0.009	0.009	0.018	0.055	0.009
Pyrene	<0.020	<0.020	<0.020	<0.020	0.040	0.047	0.065	0.044
Benzo(a)anthracene	<0.006	0.011	<0.006	0.049	0.007	<0.006	0.014	0.010
Chrysene	<0.003	<0.003	<0.003	<0.003	0.007	0.011	0.011	0.007
Benzo(b)fluoranthene	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Benzo(k)fluoranthene	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Benzo(a)pyrene	<0.001	0.003	0.003	0.004	0.003	0.003	0.003	0.003
Dibenzo(a,h)anthracene	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Benzo(g,h,i)perylene	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006

The maximum content of cancerogenic and toxic PAHs was found in the sample selected in point No. 5 (Novokuznetsk, Ul. Goluboy Log), despite the fact that this point is located from the windward side from the industrial zone. Peculiarities of the terrain relief at the given point contribute to weak scattering of emissions of private house furnaces. This fact reflects the entire complexity of the influence assessment

of PAHs emissions from the industrial zone of the metallurgical enterprise taking into account additional emission sources. The largest content of pollutants in this point is noted for the both analyzed phases: in what connection, concentrations in the solid phase are in 35–350 times higher than in the liquid phase for anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)pyrene. Benzo(b)fluoranthene,

TABLE 4
Total content of PAHs in snow waters

PAHs	Test results, $\mu\text{g}/\text{dm}^3$							
	Background	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Naphthalene	<0.020	1.062	1.840	4.300	3.092	7.832	2.283	1.834
Fluorene	<0.006	0.566	0.578	1.060	0.330	1.770	0.335	0.708
Phenanthrene	<0.006	1.592	1.563	4.646	2.924	9.743	2.293	4.484
Anthracene	<0.001	0.117	0.107	0.443	0.291	0.887	0.179	0.246
Fluoranthene	<0.006	0.695	0.557	3.554	2.519	6.382	2.823	2.280
Pyrene	<0.020	0.604	0.537	2.202	1.639	4.167	1.822	1.549
Benzo(a)anthracene	<0.006	0.084	0.052	0.269	0.198	0.442	0.530	0.284
Chrysene	<0.003	0.284	0.256	0.949	0.776	1.839	1.888	1.181
Benzo(b)fluoranthene	<0.006	0.161	0.162	0.488	0.440	1.062	1.416	0.756
Benzo(k)fluoranthene	<0.001	0.031	0.027	0.010	0.010	0.235	0.030	0.183
Benzo(a)pyrene	<0.001	0.095	0.092	0.273	0.297	0.582	0.748	0.406
Dibenzo(a,h)anthracene	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Benzo(g,h,i)perylene	<0.006	0.095	0.114	0.246	0.256	0.549	0.932	0.451
Total content of PAHs	–	5.386	5.885	18.440	12.772	35.494	15.284	14.364

benzo(k)fluoranthene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene in the liquid phase are contained in concentrations below the detection limit on the method.

The minor content of the analytes in the liquid phase is explained by their low solubility in water that decreases with increasing the number of condensed rings of the PAHs molecule. In this regard, the highest values were recorded for binuclear naphthalene and trinuclear fluorene (their content is in the range of 39.4–77.6 % and 15.2–42.4 % from the sum of all PAHs in the liquid phase, respectively). At the analysis of the ratio of individual PAHs in the solid and liquid phases of snow waters the following regularities were revealed: 5,6-nuclear compounds to a greater extent become apparent in the solid phase (about 60–80 % of the total concentration), which is due to their low solubility in water.

An analogous distribution of PAHs in the snowpack was obtained also for the samples selected in other points. According to the investigation results, it was established that the majority of the examined PAHs had a high concentration in samples of the solid phase, except for naphthalene and fluorene, which is due to the different solubility of these compounds in water.

The distribution of the total content of polycyclic aromatic hydrocarbons between the solid and liquid phases of snow waters is represented in Fig. 2. The prevailing values of analytes were found for the solid phase (81.2–99.5 % from the total concentration), the largest contribution to which is made by naphthalene (0.550–6.495 $\mu\text{g}/\text{dm}^3$), phenanthrene (1.518–9.659 $\mu\text{g}/\text{dm}^3$), fluoranthene (0.557–6.364 $\mu\text{g}/\text{dm}^3$), pyrene (0.522–4.120 $\mu\text{g}/\text{dm}^3$), chrysene (0.161–1.877 $\mu\text{g}/\text{dm}^3$).

The largest concentrations of PAHs in snow water (see Table 4) were obtained for naphthalene (1.062–7.832 $\mu\text{g}/\text{dm}^3$), phenanthrene (1.563–9.743 $\mu\text{g}/\text{dm}^3$), fluoranthene (0.557–6.382 $\mu\text{g}/\text{dm}^3$), pyrene (0.537–4.167 $\mu\text{g}/\text{dm}^3$), and chrysene (0.256–1.688 $\mu\text{g}/\text{dm}^3$). These hydrocarbons are prevailing components of systems emissions associated with pyrolysis of organic substances. The concentration of benzo(a)pyrene amounts the value from 0.092 to 0.748 $\mu\text{g}/\text{dm}^3$.

In Russia, out of all the analyzed substances, MPCs in surface waters were established for benzo(a)pyrene (0.010 $\mu\text{g}/\text{dm}^3$) and naph-

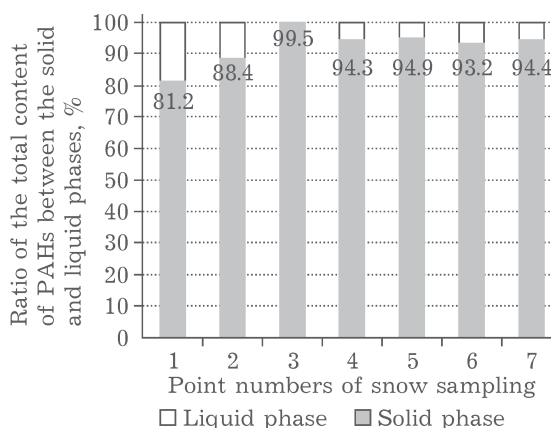


Fig. 2. Distribution of the total content of PAHs between the solid and liquid phases of snow waters.

thalene (4 $\mu\text{g}/\text{dm}^3$). The concentration of benzo(a)pyrene in snow waters ranges from 0.092 to 0.748 $\mu\text{g}/\text{dm}^3$, which exceeds the MPCs in surface waters in 9.2–74.8 times (Table 5). The content of other PAHs (benzo[b]fluoranthene, benzo(g,h,i)perylene) is comparable in order of magnitude with the concentration of benzo(a)pyrene. It is obvious, that normalizing the content of only benzo(a)pyrene does not reflect the real cancerogenicity of samples. The total content of naphthalene exceeds the MPC in points No. 3 (1.08 times) and 5 (1.96 times).

It should be noted that in the flood period a substantial amount of PAHs with melt waters enters into the sources of drinking water supply and deep soil layers, while solid particles adsorbed in themselves a part of PAH remain on the surface (upper soil layers). Thus, knowing in what proportion concentrations of pol-

TABLE 5

Total content of benzo(a)pyrene in the solid and liquid phases of snow waters

Sampling points numbers	Content of benzo(a)pyrene, $\mu\text{g}/\text{dm}^3$	Repetition factor of exceeding the MPC, times
Background	<0.001	Does not exceed
1	0.095	9.5
2	0.092	9.2
3	0.273	27.3
4	0.297	29.7
5	0.582	58.2
6	0.748	74.8
7	0.406	40.6

lutants are distributed between the solid and liquid phases, one can prognosticate and assess the pollution possibility of environmental objects.

The results obtained by us about the PAHs distribution, preferentially on solid particles of snow aerosol condition the necessity of carrying out investigations of the granulometric composition of micro- and nanoparticles. These data are important for both optimizing analytical procedures of the sample preparation (selection of filtering systems *etc.*), and for sanitary and hygienic assessments.

The distribution of microparticles by sizes in samples of snow waters for all the studied points is characterized by close values. A typical particles distribution by sizes is shown in Fig. 3. The size of suspended particles in snow waters samples ranges from 0.08 μm to 100 μm . The bulk of the solid phase of snow water is formed by the particles with the sizes up to 18.70 μm (50 %) and to 51.0 μm (90 %) (Table 6). The particles up to 2.5 μm amount to the maximum of 4.75 %, up to 10.0 μm – 33.56 % (Table 7).

Thus, it was shown by us that the solid part of the atmospheric aerosol of snow waters was represented on one-third by particles with the size of less than 10 μm that contain on their surface adsorbed carcinogenic PAHs. For suspended particles in atmospheric air with the sizes of 2.5 and 10 μm , maximally one-time, mean daily, and annual average MPCs were established [3]. In Novokuznetsk, monitoring aerosol particles of this size in atmospheric air is not conducted, whereas the data obtained point out to their significant content in the total amount of suspended particles. This should serve as the basis for the inclusion of granulometric analysis of suspended impurities in the list of mandatory indexes for monitoring pollution of objects of the environment of Novokuznetsk.

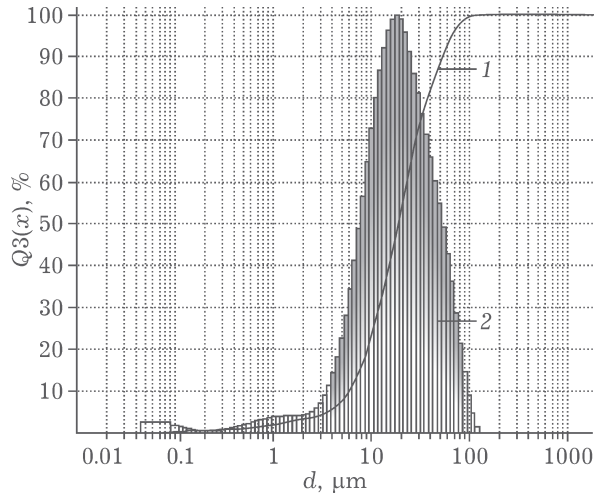


Fig. 3. Integral (1) and differential (2) particles distribution curves by sizes in the sample of snow waters (point No. 4).

The distribution of nanoparticles by sizes (in intensity units) in solid aerosol of snow waters is represented in Table 8. A typical distribution curve is given in Fig. 4. Samples Nos. 1–4, 6 are characterized by the bimodal distribution of particles by sizes, the major fraction of nanoparticles (up to 93 %) has the size of 400–600 nm, 7–9 % falls on the fraction of particles with the sizes of 44–86 nm. When studying the granulometric composition of nanoparticles in the snowpack in the influence zone of metallurgical enterprises close values were received by the authors [28] and it was shown that the particles had the polydisperse composition with the average values in the range from 290.5 to 620.5 nm.

Sample No. 5 has the monomodal distribution with a peak of the basic mode at 491 nm. Sample No. 7 contains larger particles with a peak of the basic mode at 842 nm and peak of the second mode at 249 nm (Fig. 5). This sam-

TABLE 6

Distribution of particles by sizes in the solid phase of snow samples

Q3(x), %	Particles sizes in the respective sampling points of the snow samples, μm						
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
10.00	5.10	5.30	6.00	4.60	5.10	5.30	5.80
50.00	15.10	15.40	18.40	14.19	17.50	16.30	18.70
90.00	33.00	35.30	51.00	36.00	46.00	36.30	46.90

TABLE 7

Distribution of particles with sizes less than 2.5 and 10.0 μm in solid phase of snow samples

Particles size, μm	Content of particles in sampling points of snow samples, %						
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
< 2.5	4.03	4.50	3.77	4.75	3.16	3.52	3.81
< 10.0	25.94	29.59	24.91	33.56	28.55	24.88	26.52

TABLE 8

Distribution of nanoparticle by sizes as fractions from the total intensity of the scattered light that belong to appropriate sizes of particles in samples of snow waters

Samples No.	Peak position of distribution mode, nm	Proportion of intensity characterizing mode peak
1	452	0.92
	62	0.08
2	401	0.91
	60	0.09
3	501	0.93
	44	0.07
4	596	0.92
	86	0.08
5	491	1
6	424	0.92
	61	0.08
7	842	0.61
	249	0.39

pling point is characterized by the proximity of the motorway with a heavy traffic.

The results obtained when studying the distribution of nanoparticles in snow aerosol allow suggesting that the PAH content in the liquid phase of snow water is conditioned by their partial sorption on the surface of nanoparticles.

CONCLUSION

The qualitative and quantitative composition of 13 PAHs in snow waters sampled in Novokuznetsk and Novokuznetsk district experiencing the largest load on the environment from ferrous metallurgy enterprises was determined. In the composition of PAHs in the snowpack 3,4-nuclear compounds – pyrene, chrysene, phenanthrene, fluoranthene – prevail. The concentration of benzo(a)pyrene in snow waters ranges from 0.092 to 0.748 $\mu\text{g}/\text{dm}^3$, which exceeds the MPC in surface waters (0.010 $\mu\text{g}/\text{dm}^3$) in 9.2–74.8 times.

The maximum total concentration of 13 PAHs (35.494 $\mu\text{g}/\text{dm}^3$) was determined in the point located from the windward side relatively to the industrial zone, however, experiencing an additional load on the environment in the form of emissions of private house furnaces.

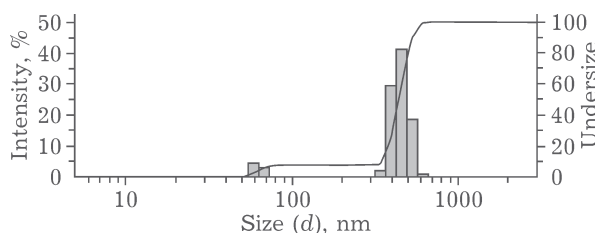


Fig. 4. Bimodal particle distribution with peaks of mode at 62 and 452 nm in intensity units (sample No. 2).

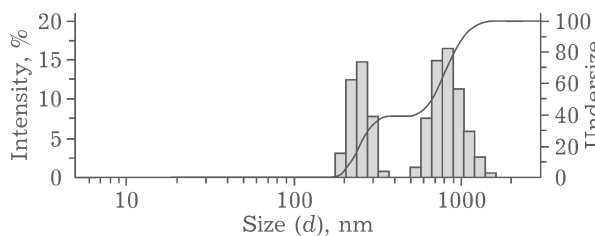


Fig. 5. Bimodal particle distribution with peaks of mode at 249 and 842 nm (sample No. 7).

The solid phase of the snowpack is represented by microparticles, sizes of which do not exceed 51.0 μm (90 %). The fraction of particles with the size of 2.5 μm and less amounts to 4.75 %, 10 μm and less – 33.56 %.

The nanoparticles distribution by sizes in snow waters is mainly bimodal, the major fraction of nanoparticles (up to 93 %) has the size of 400–600 nm, 7–9 % falls on the fraction of particles with the sizes of 44–86 nm.

REFERENCES

- 1 Doklad o Sostoyanii Okruzhayushchey Sredy g. Novokuznetska za 2014 god, Komitet Okhrany Okruzhayushchey Sredy i Prirodnikh Resursov Administratsii Goroda Novokuznetska. Novokuznetsk, 2015. URL: http://eko-nk.ru/user_images/File/doklad/DOKLAD-2014.pdf (Accessed 2016-06-14).
- 2 Spisok Gorodov Rossii s Naibol'shim Urovnem Zagryazneniya Atmosfernogo Vozdukha. URL: <http://voeikovmgo.ru/ru/izmenenie-klimata-v-rossii-v-xxi-veke.html?id=681> (Accessed 2016-06-15).
- 3 Gigiyenicheskiye Normativy GN 2.1.6.2604–10. Predel'no Dopustimye Kontsentratsii (PDK) Zagryaznyayushchikh Veshchestv v Atmosfernom Vozdukh Naselennykh Mest. Utv. Postanovleniyem Glavnogo Gosudarstvennogo Sanitarnogo Vrach Rossiyskoy Federatsii ot 19 Aprelya 2010 g., No. 26.
- 4 GN 2.1.5.2280–07, Predel'no Dopustimye Kontsentratsii (PDK) Khimicheskikh Veshchestv v Vode Vodnykh Ob'yektov Khozyaystvenno-Pit'yevogo i Kul'turno-

- Bytovogo Vodopol'zovaniya. Dopolneniya i Izmeneniya No. 1 k GN 2.1.5.1315-03. Utv. Postanovleniyem Glavnogo Gosudarstvennogo Sanitarnogo Vrachha Rossiyskoy Federatsii ot 28 Sentyabrya 2007 g., No. 75.
- 5 GN 2.1.5.1315-03. Predel'no Dopustimye Kotsentratsii (PDK) Khimicheskikh Veshchestv v Vode Vodnykh Ob'yektov Khozyaystvenno-Pit'yevogo i Kul'turno-Bytovogo Vodopol'zovaniya. Utv. Postanovleniyem Glavnogo Gosudarstvennogo Sanitarnogo Vrachha Rossiyskoy Federatsii ot 27 Aprelya 2003 g.
- 6 Normativy Kachestva Vody Vodnykh Ob'yektov Rybokhozyaystvennogo Znacheniya, v tom Chisle Normativy Predel'no Dopustimykh Kotsentratsiy Vrednykh Veshchestv v Vodakh Vodnykh Ob'yektov Rybokhozyaystvennogo Znacheniya. Utv. Prikazom Federal'nogo Agentstvapo Rybolovstvu No. 20 ot 18.01.2010.
- 7 GN 2.1.7.2041-06. Predel'no Dopustimye Kotsentratsii (PDK) Khimicheskikh Veshchestv v Pochve. Gigiyenicheskiye Normativy, Federal'ny Tsentr Gigiyeny i Epidemiologii Rospotrebnadzora, Moscow, 2009.
- 8 Rovinskiy F. Ya., Teplitskaya T. A., Alekseeva T. A., Fonovy Monitoring Politsiklicheskikh Aromaticeskikh Uglevodorodov, Gidrometeoizdat, Leningrad, 1988.
- 9 Rubailo A. I., Oberenko A. V., *J. Sib. Fed. Univ. Chem.*, 4 (2008) 344.
- 10 Raputa V. F., Sadovskiy A. P., Ol'kin S. E., Reznikova I. K., *Opt. Atmos. Okeana*, 13, 9 (2000) 886.
- 11 Kokovkin V. V., Raputa V. F., Shuvueva O. V., Morozov S. V., *Opt. Atmos. Okeana*, 13, 8 (2000) 788.
- 12 Raputa V. F., Kokovkin V. V., Sadovskiy A. P., Ol'kin S. E., Reznikova I. K., Morozov S. V., Kuznetsova I. I., Chirkov V. A., *Opt. Atmos. Okeana*, 16, 5-6 (2003) 546.
- 13 Raputa V. F., Khodzher T. V., Gorshkov A. G., Koutsenogii K. P., *Opt. Atmos. Okeana*, 11, 6 (1998) 650.
- 14 Pavlov V. E., Sutorikhin I. A., Khvostov I. V., Zinchenko G. S., *Opt. Atmos. Okeana*, 22, 1 (2009) 96.
- 15 Raputa V. F., Kokovkin V. V., Morozov S. V., *Chem. Sustain. Dev.*, 18, 1 (2010) 63.
URL: <http://www.sibran.ru/en/journal/KhUR>
- 16 Artamonova S. Yu., Lapukhov A. S., Miroshnichenko L. V., Razvorotneva L. I., *Chem. Sustain. Dev.*, 15, 6 (2007) 643. URL: <http://www.sibran.ru/en/journal/KhUR>
- 17 RD 52.04.186-89. Rukovodstvo po Kontrolyu Zagryazneniya Atmosfery, Goskomgidromet SSSR, Moscow, 1991.
- 18 Adamies E., Wieszala R., Strzebońska M., Jarosz-Krzemińska E., *Geol., Geophys. Environ.*, 22, 1 (2009) 96.
- 19 Zhuravleva N. V., Potokina R. R., Ismagilov Z. R., Khabibulina E. R., *Khim Ust Razv.*, 22, 5 (2014) 445.
- 20 Lu Y., Li X., Xu T. T., Cheng T. T., Yang X., Chen J. M., Iinuma Y., Herrmann H. *Atmos. Chem. Phys.*, 16 (2016) 2971.
- 21 Hoshiko T., Yamamoto K., Nakajima F., Prueksasit T., Temporal Variation of Particle Size Distribution of Polycyclic Aromatic Hydrocarbons at Different Roadside Air Environments in Bangkok, Thailand.
URL: <http://dx.doi.org/10.5772/48432>.
- 22 MR 1.2.0043-11. Kontrol Nanomaterialov v Ob'yektakh Okruzhayushchey Sredy: 1.2. Gigiyena, Toksikologiya, Sanitariya: Metodicheskiye Rekomendatsii, Rospotrebnadzor, Moscow, 2012.
- 23 GN 1.2.2633-10. Gigiyenicheskiye Normativy Soderzhaniya Prioritetnykh Nanomaterialov v Ob'yektakh Okruzhayushchey Sredy. Utv. Postanovleniyem Glavnogo Gosudarstvennogo Sanitarnogo Vrachha Rossiyskoy Federatsii ot 25 Maya 2010 g., No. 60.
- 24 Ispolzovaniye Metodov Kolichestvennogo Opreddeniya Nanomaterialov na Predpriyatnykh Nanoindustrii: Metodicheskiye Rekomendatsii, Federal'ny Tsentr Gigiyeny i Epidemiologii Rospotrebnadzora, 2010.
- 25 Anderson W., Kozak D., Coleman V. A., Jamting E. K., Trau M., *J. Colloid Interface Sci.*, 405 (2013) 322.
- 26 PND F 14.1:2:4.70-96. Kolichestvenny Khimicheskiy Analiz Vod. Metodika Izmereniy Massovykh Kotsentratsie Politsiklicheskikh Aromaticeskikh Uglevodorodov v Pit'yevykh, Prirodnykh i Stochnykh Vodakh Metodom Vysokoeffektivnoy Zhidkostnoy Khromatografii, Federal'naya Sluzhba po Nadzoru v Sfere Prirodopol'zovaniya, Moscow, 2012.
- 27 ISO 13321:1996. Particle size analysis. Photon correlation spectroscopy.
- 28 Marsalek R., *Int. J. Chem., Molec., Nucl., Mat. Metal. Eng.*, 8, 12 (2014) 1291.

УДК 551.588.467:543.544.5:543.449

DOI: 10.15372/KhUR20160411

Химический и гранулометрический состав частиц твердого атмосферного аэрозоля, включающего черный углерод, в снеговом покрове на территории промышленной зоны Новокузнецка

Н. В. ЖУРАВЛЕВА^{1,2}, Е. Р. ХАБИБУЛИНА^{1,2}, З. Р. ИСМАГИЛОВ¹, О. С. ЕФИМОВА¹, А. А. ОСОКИНА², Р. Р. ПОТОКИНА²

¹Институт углехимии и химического материаловедения
Федерального исследовательского центра угля и углехимии Сибирского отделения РАН,
Кемерово, Россия

E-mail: IsmagilovZR@iccms.sbras.ru

²ОАО “Западно-Сибирский испытательный центр”,
Новокузнецк, Россия

E-mail: zhuravleva_nv@zsic.ru

Аннотация

Определен качественный и количественный состав 13 полициклических ароматических углеводородов (ПАУ) в пробах снеговых вод на территории Новокузнецка и Новокузнецкого района, испытывающего максимальную нагрузку на окружающую среду от деятельности предприятия черной металлургии. Изучено распределение ПАУ между твердой и жидкой фазами снеговой воды методом высокоэффективной жидкостной хроматографии. Показано, что 81.2–99.5 % суммарного содержания ПАУ находятся в твердой фазе снеговой воды. Концентрация бенз(а)пирена варьирует от 0.092 до 0.748 мкг/дм³. Методом лазерной гранулометрии установлено, что 90 % частиц твердого атмосферного аэрозоля в снеговом покрове представлены частицами, размеры которых не превышают 51.0 мкм. Пробы снеговых вод характеризуются преимущественно бимодальным распределением наночастиц по размерам, основная доля частиц (до 93 %) имеет размер 400–600 нм, на долю наночастиц с размерами 44–86 нм приходится 7–9 %.

Ключевые слова: снеговой покров, полициклические ароматические углеводороды, распределение частиц по размерам, высокоэффективная жидкостная хроматография, лазерная гранулометрия, метод динамического рассеяния света

