Organic Carbon in the City Territories of the South of West Siberia

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Abstract

The results of conjugated studies of contaminations of snowpack and atmosphere air by polyaromatic hydrocarbons (PAH) and soot in a number of major cities of the south of West Siberia are presented. Snow samples selected at the stationary observation stations were analyzed by the method of gas chromatography mass spectrometry (GC-MS) on the content of PAH. The results obtained were compared with the data of the Federal Service for Hydrometeorology and Environmental Monitoring of Russia (Roshydromet) on soot and benzo(a)pyrene in air. Linear correlations between concentrations of considered impurities in conjugated environments were established. The data of ground monitoring snowpack contamination by PAH were compared with the results of winter space image processing by tones of the grey colour.

Key words: atmosphere, snowpack, polyaromatic hydrocarbons, soot, observational data, correlation analysis

INTRODUCTION

The organization of systematic instrumental observations of atmospheric air long-term contamination at urban territories present certain difficulties [1–4]. In this regard, natural plane-tables that are accumulators of aerosols are widely used in monitoring urban environment. One of the effective ways of experimental studies of atmospheric transfer processes of organic compounds (OC) is the study of snowpack as a natural tablet-accumulator [5–8]. Black carbon is highly dispersed co-faction in fossil fuel combustion processes. Its presence is traced in the composition of the deposited aerosols at different types of anthropogenic sources as coal boiler-houses and CHP plants, industrial plants, highways. In the composition of fallouts of OC, polyaromatic hydrocarbons (PAHs) are also present [9–13]. An especially large amount of PAH emissions is observed in the winter season after burning coal and mazut at thermal power plants and in private sector housing. Auto transport also makes a significant contribution into the urban atmosphere contamination.

The structure of the space-time distribution of sources of PAH emissions into the city atmosphere is a quite heterogeneous. The pres-

ence of PAHs in air can be judged by benzo(a)pyrene and soot. Levels of atmospheric contamination by these impurities are determined at stationary posts of Roshydromet [1, 3, 14−16]. It should be noted, that the effectiveness of the used stationary posts systems is very limited: new sources appear at the city territory, autopark expands in rapid temps, road network and building construction areas change. As a consequence, there is a need for a significant extension and optimization of the system of the observation stations.

The numerical analysis of monitoring data of prolonged contamination of snowpack on the basis of space dynamics of processes of the atmospheric transport from OC emission sources

allows reconstructing precipitation fields, assessing the total emissions and characteristics of the disperse composition [5, 6, 17]. This approach allows significantly complementing the system of the air contamination control.

Alongside with ground monitoring, methods of remote sounding snowpack contamination are intensively developed over several decades [18−20]. They allow operatively identifying the detailed contamination space structure from various sources at wide territories. In this regard, it is important to establish functional relations between these two monitoring kinds.

The aim of this work is to conduct paired studies on the establishment of quantitative regularities in the distribution of OC in the
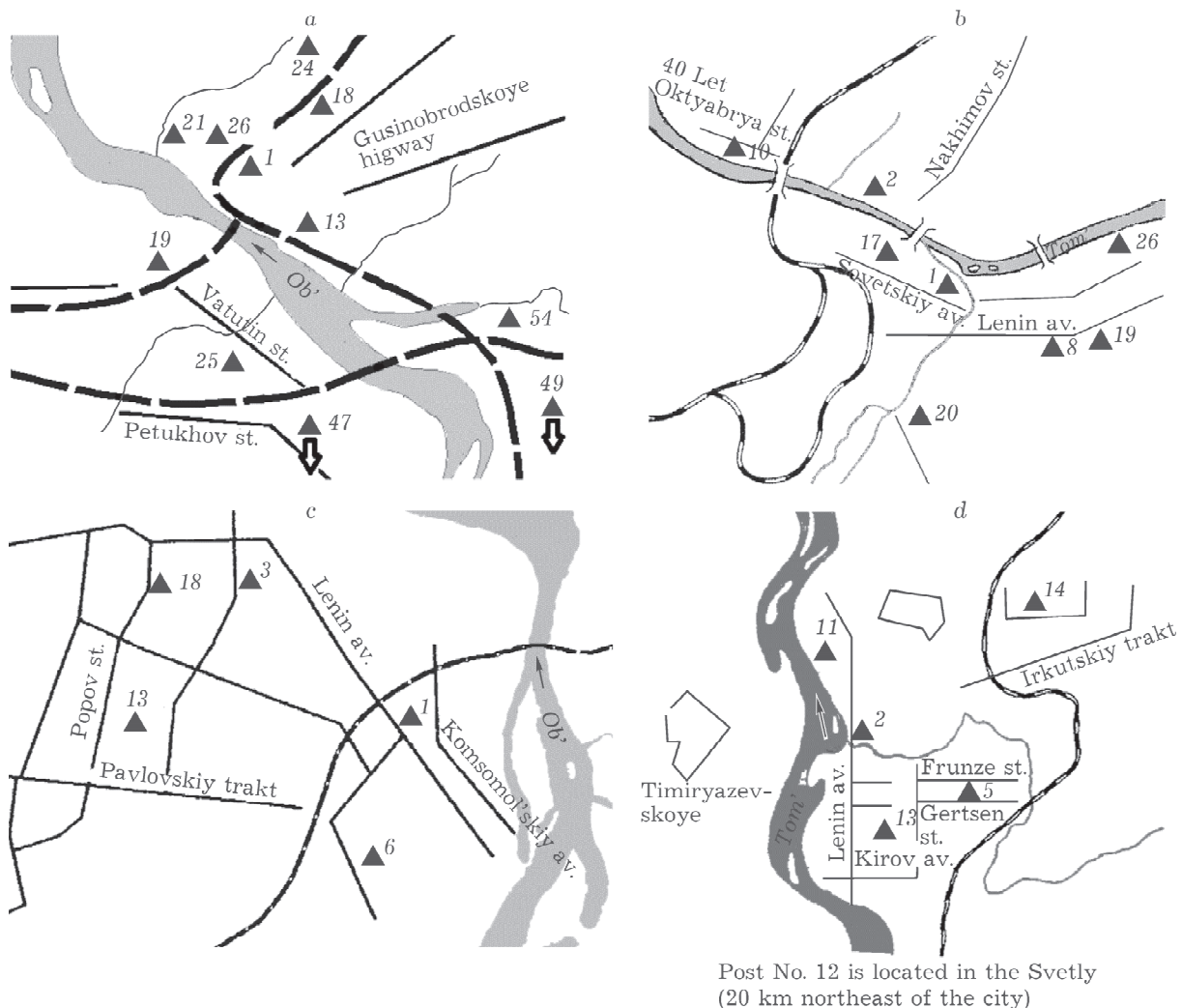

Fig. 1. Schemes of snow sampling at the territories of Novosibirsk (*a*), Kemerovo (*b*), Barnaul (*c*), and Tomsk (*d*).

snow and the atmospheric air on territories of large cities of the south of West Siberia. In this regard, during a number of winter seasons field works on sampling of snow on the territories considered, the chemical analysis of samples from on the major PAH, numerical analysis of observational data. An important work stage is the comparison of ground observations with the results of processing corresponding space images by tones of gray colour. It should be noted that this study was conducted in a close cooperation with territorial hydrometeorological services (Novosibirsk, Kemerovo, Tomsk Regions and Altai Territory) within the framework of Integration project SB RAS No. 84 in the period of 2009−2011 [15, 16, 21].

EXPERIMENTAL STUDY

Regular snow sampling was carried in the end of winter seasons of 2009−2011 on the territories of Novosibirsk, Kemerovo, Barnaul and Tomsk near the stationary posts of air contamination monitoring (PCMs) of Roshydromet. The location scheme of PCM is shown in Fig. 1. Note that in Novosibirsk and Barnaul, these studies were continued and in the subsequent years.

The samples were taken using a plastic or titanium tube at open areas of undamaged snow cover in it full depth. It should be noted, that in some cases, the selection of places for sampling had certain difficulties: the absence of the fence of PCM, close location of local sources in the form of parking lots, highways, construction works, etc.

In big cities, the control for the air quality at the posts of Roshydromet is conducted on the following basic parameters: suspended substances, soot, sulphur and nitrogen dioxides, carbon monoxide, and specific parameters: nitrogen oxide, hydrogen chloride, ammonia, hydrogen fluoride, formaldehyde, benzo(a)pyrene, etc. The conditional division of the posts on certain groups related to the nature of city territory contamination source is accepted. In particular, for Novosibirsk, the posts are divided into "regional background" (PCM 47), "urban background" (PCMs 13, 24, 26) located in residential areas, "industrial" − near plants (PCMs 18, 19, 25), and "auto" −

near highways or areas with heavy transport traffic (PCMs 1, 21, 49, 54).

Many cities in Siberia are characterized by increased content of suspended substances, benzo(a)pyrene, soot. The highest concentrations of benzo(a)pyrene and soot in atmosphere are marked for the cold season of the year. The measurements of soot in the cities are performed practically at all posts several times a day. Benzo(a)pyrene is measured less frequently and at 1−3 city posts. Only since 2011, the number of posts in Novosibirsk and Tomsk, where benzo(a)pyrene is measured, was substantially increased.

CHEMICOANALYTICAL STUDY

For determining 19 basic PAHs, the method of [22] was used. The starting snow sample was melted at room temperature, substances-witnesses, which allow assessing the completeness of PAHs extraction, were introduced into the sample; hereafter, extraction concentrating PAH into dichloromethane was performed. After separation, the extract was dried by anhydrous sodium sulphate. The dry residue after evaporation at a rotary evaporator was dissolved in acetone. The solution obtained was analysed by method of gas chromatography mass spectrometry (GC-MS) using Agilent Technologies (AT) 6890 N gas chromatographer with a capillary column HP-5MS and quadrupole mass spectrometer detector AT 5975 N working in the detection mode of characteristic ions for determined compounds. The calibration of GC-MS was done using a standard mixture of PAH (Hewlett Packard No. 8500-6035). The error of PAH determination was not higher than ±20 %. The additives of standard bromine and deuterated PAH derivatives introduced in the samples allowed to evaluate the correctness of the result definition.

Tables 1−4 present the basic results of PAHs determination in snow samples taken at the posts of Novosibirsk, Kemerovo, Barnaul, and Tomsk in the end of the winter season of 2010−2011. They include the sum of PAHs, the content of benzo(a)pyrene as most toxic, and phenanthrene, which in samples was represented by the largest concentrations between.

TABLE 1

PAHs content in the snow samples at Novosibirsk posts, ng/kg

PAHs	Post No.										
	1	13	18	19	21	24	25	26	47	49	54
Benzo(a)pyrene	62	24	89	48	216	34	24	66	13	24	52
Phenanthrene	914	425	757	971	968	498	479	485	69	206	556
PAHs sum	2756	1252	3378	2672	4918	1601	1270	1927	325	815	3100

TABLE 2

PAHs content in the snow samples at Kemerovo posts, ng/kg

PAHs	Post No.							
	1	2	8	10	17	19	20	26
Benzo(a)pyrene	77	174	43	167	81	16	39	15
Phenanthrene	545	741	1025	1150	769	164	663	142
PAHs sum	2000	3670	2700	5030	2830	582	2000	544

Analysis of the tables and sampling schemes shows that high PAH concentrations are reached near the highways, in areas of intensive influence of coal power stations, industrial plants. The residential areas of the cities are characterized by the lowest PAH concentrations. Generally, one can conclude from the data presented that Barnaul, Kemerovo, and Novosibirsk are contaminated by PAH in some greater extent, than Tomsk which is in less.

ANALYSIS OF CORRELATIONS

It is reasonable to compare the parameters of the chemical composition obtained for air and snow on the assumption of their nature by the following groups: benzo(a)pyrene in air and snow; soot in air and benzo(a)pyrene and PAHs sum in snow; suspended particles (dust) in air and precipitates in snow. The calculation of mid-winter concentrations of impurities measured in the atmosphere was performed over a period of mid-November to mid-March, which approximately corresponds to the period of sustainable snowpack bedding in the city.

Analysis of the experimental results was carried out within the framework of linear correlation dependences. On the vertical axis (Fig. 2), the mean air winter-impurity concentration is presented, on the horizontal axis, the data for snow samples. From the figure, one can see the linear correlations between the concentrations of the snow sample PAHs sum and mean air winter-impurity concentration for Novosibirsk and Barnaul posts, as well as for benzo(a)pyrene concentrations in both environments in Novosibirsk, Tomsk for the winter seasons of 2009−2012.

Analysis of Fig. 2 shows that the values of the considered parameters from post to post change quite consistently in large concentration ranges for the both environments. In Novosibirsk, for example, the maximum value of the compared impurity concentrations in atmosphere and snow is achieved for the post No. 21; mini-

TABLE 3

PAHs content in the snow samples at Barnaul posts, ng/kg

PAHs	Post No.				
	1	3	6	13	18
Benzo(a)pyrene	181	127	188	128	65
Phenanthrene	2080	1350	1940	976	443
PAHs sum	7740	5220	6910	3760	1750

TABLE 4

PAHs content in the snow samples at Tomsk posts, ng/kg

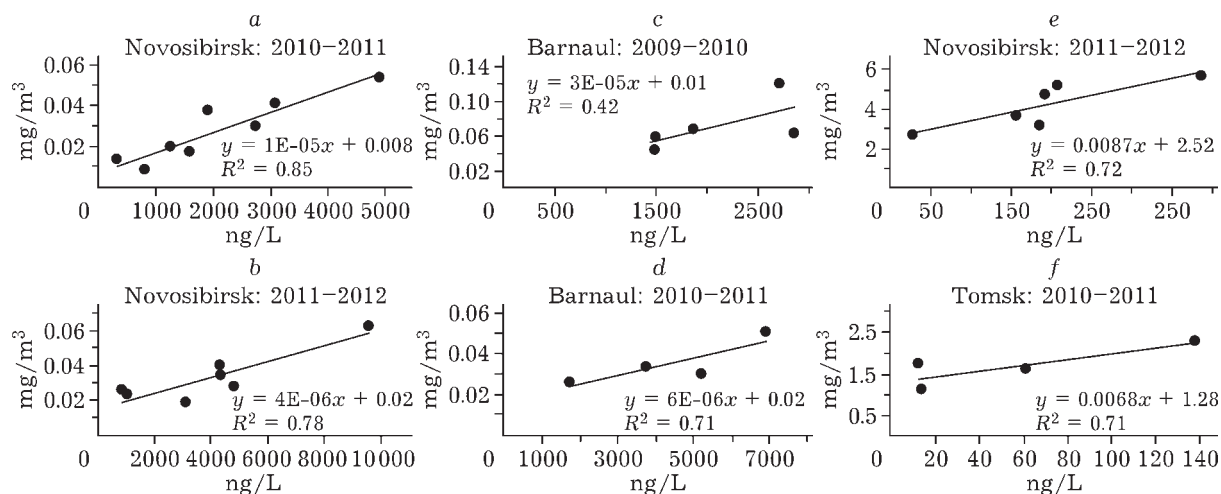| PAHs	Post No.					
	1	3	6	13	18	
Benzo(a)pyrene	138	8.5	61.5	9.61	4.2	12.6
Phenanthrene	471	100	411	76.8	237	313
PAHs sum	2440	431	1910	306	729	780

Fig. 2. Linear correlation dependences between the PAHs concentrations in samples of snow and soot air at PCMs of Novosibirsk (*a*, *b*) and Barnaul (*c*, *d*), benzo(a)pyrene in both environments at PCMs of Novosibirsk (*e*) and Tomsk (*f*) in the winter seasons of 2009−2012.

mum is for the post No. 47. The last is in fact the background post for the city because it locates in the entrance to the dominating winter winds. Note also that the extrapolation of the regression lines to the vertical axis of atmospheric impurities in Fig. 2 passes statistically significant above the origin of coordinates. It can be assumed that a certain part of PAH and soot in air does not settle down on the snow. This assumption requires further experimental studies.
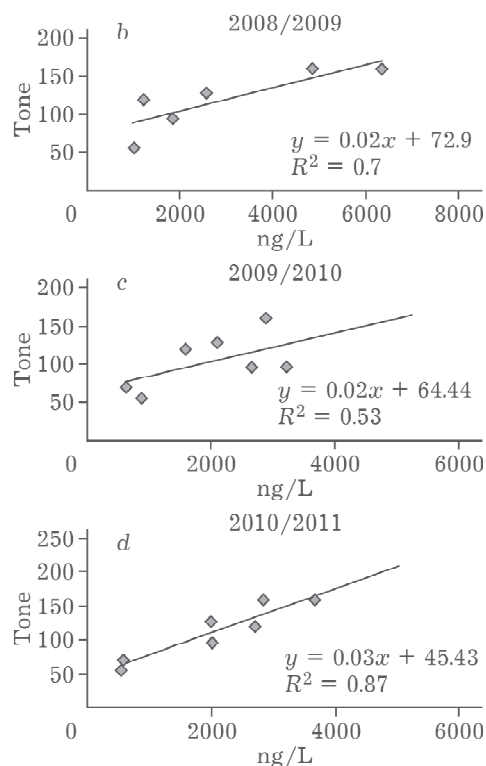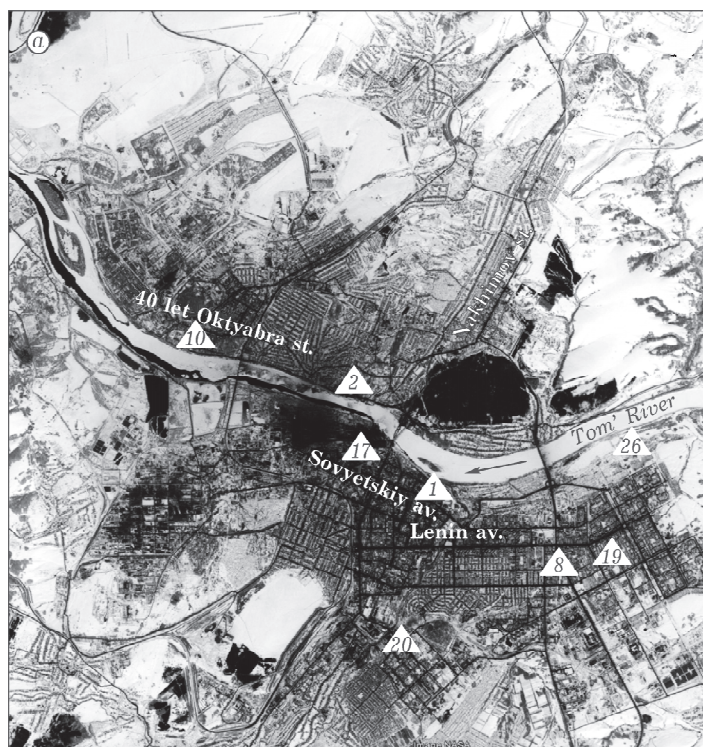

Fig. 3. Satellite image of Kemerovo dated March 26, 2006 (*a*); linear correlations between the shades of gray tones and the PAH concentrations in snow samples for winter seasons: 2008/2009 (*b*), 2009/2010 (*c*), 2010/2011 (*d*).

Analysis of satellite images

Artificial Earth satellite (AES) images obtained in the panchromatic range (Landsat, digitalglobe.com) were used in the work. As a result of processing the image of Kemerovo from March 26, 2006 consisting in the discretization of the scale of gray shades, the digital image of city territories was obtained (Fig. 3, *a*).

This allowed distinguishing out the aureoles of dust precipitation of impurities from pollution focuses of the city (by-product coke plant, CHP, major highways). The dominant impurities removal occurs in the north and northeast directions from the sources [23].

The analysis of Table 2 and Fig. 3 shows that the values of pollution parameters from the post to post change quite consistently in large ranges of concentrations in snow and tone grades of the city territory on the satellite image. For example, the comparison of part of the image with post No. 10 related to the industrial area, and the image fragment with residential area (post No. 26) shows significant contrast in shades of gray. The similar situation is for comparison the snow sample precipitate concentration at the posts.

The numerical processing of the results of ground and satellite studies of snowpack contamination of Kemerovo was carried out in the linear correlation analysis framework. Figure 3 shows the correlation dependences between PAHs concentrations in snow samples and tones of gray on the satellite image for the winter season of 2009−2011 on PCMs of Kemerovo. The vertical axis shows the intensity of the tone near the post, the horizontal axis shows PAH concentration (ng/L) in the snow sample also taken near the post. The maximum values of the tone and concentration of PAH in snow are achieved for PCMs 1, 2, 17, minimum − for PCMs 19, 26. It should be noted that PCM 1 is located in the city centre. Post No. 2 is located relatively not far from the coke-chemical plant and on the direction of the prevailing removal of contaminating impurities across the Tom' River. In general, for all three winter seasons, the level of agreement between the measured PAHs concentrations in the melted water and the data of colour tonality on the satellite image is quite satisfactory.

CONCLUSIONS

The results of conjugated research of contamination of air and snowpack at stationary posts of Roshydromet in a number of major cities of the south of West Siberia the South and numerical analysis of the observation data allowed obtaining qualitative and quantitative regularities between concentrations of soot, benzo(a)pyrene and a sum of PAH in snow and air. The results of these studies can be used for the mutual control of the observation data in snow and the down-to-earth air layer, significantly complement the stationary observation network in the winter time.

The linear correlation analysis of the ground and satellite observation data of the prolonged snowpack contamination has shown for the territories of Kemerovo a fairly high level of agreement. For considered winter seasons, there is certain stability in the location and operational activity of the main sources of PAH atmosphere emissions in the city. The study conducted has shown the creation possibility of mutually complementary monitoring systems and obtaining based on them additional information on the state of long-term snow cover contamination of the city.

The regularities obtained allow creating the cost-effective monitoring system of OC and receiving the detailed condition assessment of the prolonged city atmospheric contamination in the winter time. They can be used for identifying high pollution areas of the city territories and human health risk assessments, serving a basis for establishing regulatory criteria (MPC) of snow contamination.

Acknowledgements

REFERENCES

1 Bezuglaya E. Yu., Monitoring Sostoyaniya Zagryazneniya Atmosphery v Gorodakh, Gidrometeoizdat, Leningrad, 1986. 199 p.

2 Selegey T. S., Formirovaniye Urovnya Zagryazneniya Atmosphernogo Vozdukha v Gorodakh Sibiri, Nauka, Novosibirsk, 2005. 348 p.

3 Bezuglaya E. Yu., Smirnova I. V., Vozdukh Gorodov i Yego Izmeneniya, Asterion, St. Petersburg, 2008.

4 Highwood E. J., Kinnersley R. P., *Environ. Int.*, 32, 4 (2006) 560.

5 Vasilenko V. N., Nazarov I. M., Friedman Sh. D., Monitoring Zagryazneniya Snezhnogo Pokrova, Gidrometeoizdat, Leningrad, 1985.

6 Prokacheva V. G., Usachev V. F., Snezhny Pokrov v Sfere Vliyaniya Goroda, Gidrometeoizdat, Leningrad, 1989.

7 Osipova N. A., Filimonenko K. A., Talovskaya A. V., Yazikov E. G., *Human and Ecol. Risk Assessment: An Int. J.*, 21, 6 (2015) 1664.

8 Barcan V., Sylina A., *Water, Air, and Soil Pollution*, 89 (1996) 49.

9 Rovinskii P. I., Teplitskaya T. A., Alekseeva T. A., Fonovy Monitoring Politsiklicheskikh Aromaticheskikh Uglevodorodov, Gidrometeoizdat, Leningrad, 1988.

10 Zhuravleva N. V., Potokina R. R., Ismagilov Z. R., Khabibulina E. R., *Chem. Sustain. Dev.*, 22, 5 (2014) 445.

11 Tobiszewski M., Namiesnik J., *Environ. Pollution*, 162 (2012) 110.

12 Liu Li-bin, Liu Yan, Lin Jin-ming, Tang Ning, Hayakawa Kazuichi, Maeda Tsuneaki, *J. Environ. Sci.*, 19 (2007) 1.

13 Ravindra K., Sokhi R., Van Grieken R., *Atmos. Environ.*, 42 (2008) 2895.

14 Raputa V. F., Kokovkin V. V., Devyatova A. Yu., *Optika Atmos. i Okeana*, 23, 6 (2010) 499.

15 Raputa V. F., Kokovkin V. V., Devyatova A. Yu., Chirkov V. A., Kazmin O. E., Trudy SibNIGMI, Izd-vo SO RAN, Novosibirsk, 2011, vol. 106, pp. 130–142.

16 Raputa V. F., Romanov A. N., Kokovkin V. V., Morozov S. V., Shutova K. O., VII Int. Sci. Congress "Geo-Siberia 2011" (Proceedings), SCSA, Novosibirsk, 2011, vol. 4, pp. 83–87.

17 Prokacheva V. G., Usachev V. F., *Meteorol. Hydrol.*, 3 (2013) 94.

18 Volkotrub L. P., Egorov I. M., Lazarev A. F. Onkogigiyenicheskaya Situatsiya v Barnaule, Altayblankizdat, Barnaul, 1994.

19 Vasilevich M. I., Shchanov V. M., Vasilevich R. S., *Sovremennye Problemy Distantsionnogo Zondirovanya Zemli iz Kosmosa*, 12, 2 (2015) 50.

20 Dmitriev A. V., Dmitriev V. V., *Sovremennye Problemy Distantsionnogo Zondirovaniya Zemli iz Kosmosa*, 11, 5 (2008) 84.

21 Raputa V. F., Kokovkin V. V., Shuvaeva O. V., Ekologicheskiy Monitoring: Sostoyaniye Okruzhayushchey Sredy Tomskoy Oblasti v 2010 g. (Annual Review), Izd-vo Grafika DTP, Tomsk, 2011, pp. 103–104.

22 Soniyassi P., Sandra P., Schlette K., Analiz Vody: Organicheskiye Mikroprimesi, Teza, St. Petersburg, 1995.

23 Koshinskiy S. D. and Shver Ts. A. (Eds.), Klimat Kemerovo, Gidrometeoizdat, Leningrad, 1987.

Органический углерод на территории городов юга Западной Сибири

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Аннотация

Приведены результаты сопряженных исследований загрязнения снежного покрова и атмосферного воздуха полиароматическими углеводородами (ПАУ) и сажей в ряде крупных городов юга Западной Сибири. Отобранные на стационарных пунктах наблюдения пробы снега анализировали методом хромато-масс-спектрометрии на содержание ПАУ. Полученные результаты сопоставлены с данными Росгидромета по саже и бенз(а)пирену в воздухе. Установлены линейные корреляции между концентрациями рассматриваемых примесей в сопряженных средах. Данные наземного мониторинга загрязнения снежного покрова ПАУ сопоставлены с результатами обработки зимних космоснимков по тонам серого цвета.

Ключевые слова: атмосфера, снежный покров, полиароматические углеводороды, сажа, данные наблюдений, корреляционный анализ