Seasonal variability of *n*-alkanes and polycyclic aromatic hydrocarbons in the atmosphere of Novosibirsk and its suburbs

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We present the results of determination of saturated hydrocarbons and polycyclic aromatic hydrocarbons in the atmospheric aerosol of Novosibirsk and one of its suburbs in winter and summer. Possible sources of inflow of *n*-alkenes into the atmosphere were determined by the CPI-index and C_{max}. Total content of saturated hydrocarbons in the aerosol of the city and suburb is 25—38 ng/m³. Total concentrations of polycyclic aromatic hydrocarbons in the aerosol of Novosibirsk and Klyuchi in winter are 37 and 96 ng/m³, respectively. The organic compounds were determined by the method of chromatography—mass spectrometry.

Introduction

Atmospheric aerosol (AA) is a complex heterogeneous system in its chemical and dispersion composition. In addition to its mineral[1] and water-soluble[2] fractions, there are various aliphatic and aromatic compounds of natural and anthropogenic origin (C_{org}) among the most important types of aerosol. Primary sources of aerosol are motor transport; dust, which is produced due to attrition of pavement and tires; heat and electric power plants; integrated iron-and-steel, chemical, or building plants; consumption of mineral fuel and biomass, etc. Woody plants releasing a lot of phytoorganic compounds into the environment create a specific ecological background.[3] Besides, organic substances arrive into the atmosphere with injured plant tissues, especially, leaves.[4] Secondary C_{org} can be produced in catalytic and photochemical reactions of different gaseous hydrocarbons.

Qualitative and quantitative content of organic substances of aerosol is an important criterion for estimating atmospheric pollution. Some organic compounds, such as *n*-alkanes, can serve as markers for a certain sources, which cannot be identified, for instance, by its multi-element composition.[5] Besides, aerosol can consist many noxious organic substances, for instance, polycyclic aromatic hydrocarbons (PAH), therefore, it is important to know their composition and concentration levels. Rather many works are devoted to investigations of the PAH content in aerosol of different cities of the world.[6–8] The study of PAH in the environment of the Baikal region is presented in Refs. 9 and 10.

In this paper, we present the results of determination of the individual composition of *n*-alkanes and PAH at a distant continental territory in the south of Western Siberia in winter and in summer.

To investigate seasonal variability of *n*-alkanes and PAH in aerosol and determine possible sources of their inflow into the atmosphere, AA samples of Novosibirsk city and one of its suburbs were taken.

Materials and methods

The samples of atmospheric aerosol were taken in the city of Novosibirsk and Klyuchi settlement situated at a distance of 30 km to the southwest from the city. Novosibirsk is a megalopolis (its population is more than 1 500 000) with a high traffic and other anthropogenic sources. Samples of the suburb aerosol were taken at a distance of 300 m from Klyuchi at the ionospheric station of the Institute of Geology and Mineralogy (IGM), Siberian Branch of the Russian Academy of Sciences. It should be noted that, although Klyuchi is rather far from large anthropogenic sources, atmospheric pollution in this sampling point can be caused by transfer of noxious contaminants both from the city and other local sources.[11] In the analysis, we have used AA samples taken in June and July, 2006 and in January and February, 2007.

Samples of AA were drawn onto filters with the use of a filter-ventilating unit, operating at a rate of 13 m³/h. To identify organic compounds in the aerosol and determine them quantitatively, three AA samples were used from each of the sampling points with maximal overweight. Preparation of samples included the extraction of the filtered residue by an organic solvent. To obtain the extract, a half or a quarter of the filter was placed in a glass jar with 1 ml of ethyl ether for 24 h. Analysis of the samples was performed with a chromatomass spectrometer HP 6890N/5973N, Agilent Technologies (USA).

A capillary column HP-5MS ((5%)-diphenyl-(95%)-dimethylsiloxane) of a 30 m length and an

internal diameter of 0.25 mm with a film thickness of 0.25 μm was used for chromatographic separation of a sample. The column temperature was programmed from 50°C (3 min) at a rate of 10 grad/min to 250°C (25 min). The temperature of the evaporator was 250°C. The flow rate of the carrier gas (helium) was 1 ml/min. The sample was injected without division of the flow. Mass spectra were obtained by the method of electron shock at electron ionization energy of 70 eV. The compounds were identified with the electron library of mass spectra NIST-98. Solution of benz(a)pyrene in hexane was used as the external standard.

To estimate the presence of possible contamin ants in AA samples, we measured the extract of the pure filter and samples of ethyl ether at the same analytical conditions. Regular contaminants of ethyl ether are 1,1-diethoxyethane, 2-methylpentanone-3, 1-methyl-3-phenoxybenzene; the extract of the pure filter is trichloracetaldehyde.

Results and discussion

Combustion of mineral fuels and gases in household conditions is the main channel by which n-alkanes $< C_{27}$ arrive into the atmosphere.[12] Cigarette smoke[13] or injured surface of leaves[4] are sources of n-alkanes $> C_{27}$. To determine the type of the source of inflow of the saturated hydrocarbons into the atmosphere, the so-called CPI-index (carbon preference index) is used.[5] This index is the ratio of hydrocarbons with an odd number of carbon atoms in molecule to the "even" hydrocarbons ($C_{odd/even}$) and is calculated by division of the sum of C_{odd} concentrations identified in a sample by the sum of C_{even}. As is shown in Refs. 4 and 14, concentrations of C_{odd} predominate in plant leaves, whereas concentrations of even homologs predominate in motor exhausts. If CPI is higher than 3, then the source of hydrocarbons is some biological material. If CPI is close to 1, then the presence of n-alkanes in the atmosphere is caused by processes of incomplete combustion of fuels.[5]

Table 1 shows the range of the measured hydrocarbons, their total and individual concentrations, and the CPI-index. Note that the range of the measured n-alkanes in the aerosol is $C_{19}-C_{27}$. A distinct seasonal variability of the identified substances in the city aerosol is observed. For instance, the range of the measured n-alkanes in summer is $C_{23}-C_{27}$ with predomination of C_{odd} concentrations. In winter, there are no sharp variations of concentration in the range $C_{19}-C_{26}$. We note only a higher content of $C_{20}-C_{23}$ in aerosol. A similar situation occurs for winter AA samples from Klyuchi. In particular, higher concentrations of $C_{21}-C_{23}$ as compared to C_{19}, C_{20}, and C_{24} content are also observed. In summer, the presence of only eicosane in rather large amount (25 ng/m³) probably indicates a local short-time anthropogenic emission, or this is connected with air mass transfer from other regions. There are no sufficient reasons to say about non-typical presence of n-alkanes in Klyuchi aerosol in summer by the results of three samplings. The CPI magnitude is extremely high for the city aerosol,[5,6] which probably indicates a considerable contribution of the biological material. In winter samples taken in Novosibirsk and Klyuchi, the CPI value is close to 1, which says about predomination of local anthropogenic sources. As is seen from Table 1, total concentrations of n-alkanes in the city and suburb aerosols have no visible fluctuation (25–38 ng/m³), that is probably connected with the influence of the city aerosol. Low concentrations and individual appearance of tetradecane and hexadecane in AA samples is probably caused by a loss from the aerosol phase due to volatilization from the filter surface during storage.

Table 1. Daily average concentrations of n-alkanes (ng/m³) in the atmospheric aerosol

n-alkane	Novosibirsk		Klyuchi		Algiers [7]	Pasadena [15]
	summer	winter	summer	winter		
Tetradecane (C_{14})	n. d.*	n. d.	n. d.	0.4	—	—
Hexadecane (C_{16})	n. d.	2.2	n. d.	n. d.	—	—
Nonadecane (C_{19})	n. d.	3.2	n. d.	1.1	2.3	—
Eicosane (C_{20})	n. d.	7.1	25.2	3.3	3.5	—
Heneicosane (C_{21})	n. d.	5.5	n. d.	4.6	5.6	—
Docosane (C_{22})	n. d.	5.3	n. d.	8.2	8.5	—
Tricosane (C_{23})	3.5	6.1	n. d.	9.4	10.1	5.4
Tetracosane (C_{24})	1.9	2.6	n. d.	3.1	7.8	4.7
Pentacosane (C_{25})	9.3	3.6	n. d.	n. d.	5.1	9.5
Hexacosane (C_{26})	1.6	2.3	n. d.	n. d.	4.0	4.3
Heptacosane (C_{27})	16.5	n. d.	n. d.	n. d.	3.8	5.6
Total	32.8	37.9	25.2	30.1	50.7	29.5
CPI	5.6	1.2	—	1.3	0.9	1.7

*Not detected in the samples.

The maximal concentration of hydrocarbon (C_{max}) is a criterion for estimation of some source intensity. As shown in Ref. 5, C_{max} is a marker for C_{27}, C_{29}, C_{31}, and C_{33} of mechanical injury of leave surfaces; for C_{29} and C_{31} — a sign of natural forest fires; for C_{23} and C_{25} — of vegetation combustion; for C_{21} and C_{22} — of motor exhaust; for C_{10} — of oil products; for C_{19} — of lubricating oil and diesel fuel. Thus, the homologs with the distribution $C_{max} \geq 27$ are of biogenic origin, $23 < C_{max} < 26$ represent the mixed group of biogenic and anthropogenic sources, and the distribution $C_{max} \leq 23$ is characteristic for anthropogenic sources. Figure 1 shows that motor exhausts are the main sources of n-alkanes in the city and suburb atmosphere in winter. In summer, the main source is a mixed group, namely, the biological material and the combustion of vegetation.

Thus, the comparison with literature data indicates that n-alkanes are general class of continental aerosol (see Table 1) and, in addition, the data on qualitative composition and quantitative content can serve as information about the type and intensity of one or another source.

Polycyclic aromatic hydrocarbons are commonly spread in the biosphere both in the gaseous and aerosol phases. Much attention is given to the study of PAH content in the atmosphere due to mutagenic and carcinogenic properties of these compounds. Light PAH were detected mainly in the gaseous phase, whereas PAH with more than three rings in the aerosol phase. Light PAH have weak toxic properties, but they can react with other contaminants and form more toxic derivatives. PAHs, whose molecular weight is more than 252, are chemically stable in the aerosol phase. Low-molecular PAHs (less than 252) leave the aerosol phase due to volatilization or chemical decomposition.

PAHs were detected only in winter samples, and their total concentrations in aerosol of Novosibirsk and Klyuchi reach 37 and 96 ng/m^3, respectively (Table 2).

Figure 2 shows that about 70% of the total content of PAH consist of phenanthrene, fluoranthene, and pyrene.

As is seen from Table 2, a similar situation can be observed in the series of other measurements.
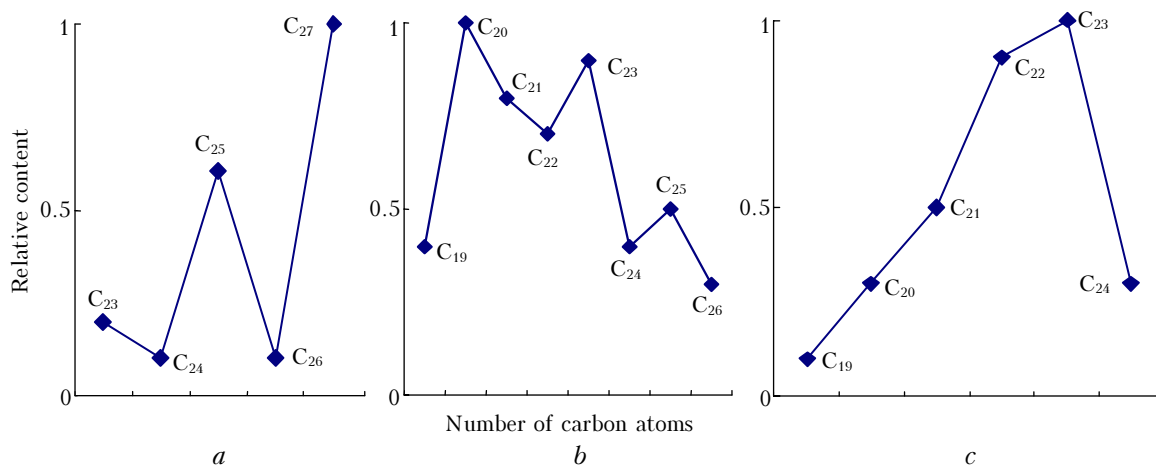

Fig. 1. Distribution of n-alkanes in the atmospheric aerosol: Novosibirsk, summer, 2006 (*a*); Novosibirsk, winter, 2007 (*b*); Klyuchi, winter, 2007 (*c*).

Table 2. Daily average concentrations of PAH (ng/m^3) in aerosol

PAH	Novosibirsk	Klyuchi	Irkutsk[9]	London[6]	Naples[8]
Phenanthrene	9.9	20.1	11.5	23.7	1.3
Fluoranthene	9.1	26.1	46.5	16.1	1.9
Pyrene	8.1	21.9	44.0	16.4	3.1
Phenanthrene, 1-methyl-7-(1-methylethyl)-	4.4	8.1	–	–	–
Benzo(ghi)fluoranthene	1.8	3.9	–	–	–
Naphthalene	2.6	1.1	–	–	–
Benz(a)anthracene/triphenylene	1.8	5.1	–	3.6	3.1
Naphthalene, 1-methyl-/naphthalene, 2-methyl-	n. d.*	0.8	–	–	–
Naphthalene, 1-ethyl-/naphthalene, 2-ethyl-	n. d.	1.1	–	–	–
Naphthalene, 2-phenyl-	n. d.	1.6	–	–	–
Biphenylene/acenaphthylene	n. d.	2.8	–	–	–
4H-Cyclopenta(def)phenanthrene	n. d.	3.5	–	–	–
Total	37.7	96.1	102	59.8	9.4

*Not detected in the samples.

PAH, %

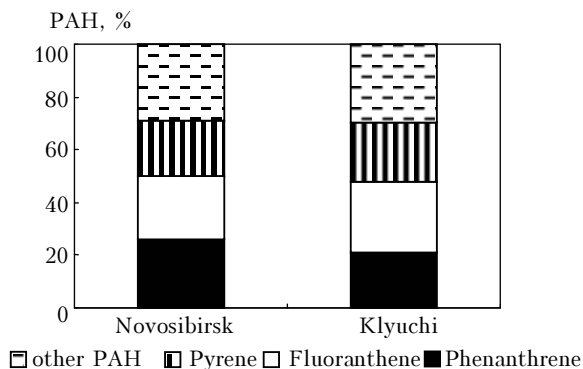□ other PAH   ▥ Pyrene □ Fluoranthene ■ Phenanthrene

Fig. 2. PAH content in aerosol.

In the city aerosols, their daily average concentrations are about 10 ng/m^3, and 2–2.5 times higher in the atmosphere of the suburb. Besides, a wider qualitative range of PAH derivatives was identified in the aerosol of Klyuchi. This is probably connected with the effect of the city aerosol on the suburb, or the potentially higher concentrations of PAH are the result of contaminant transfer from other areas. Thus, PAH concentrations are very high in winter due to emission of motor exhausts and the activity of heat energy plants. In the summer time of a year, PAHs seem to be present in very small amounts (lower than the limit values for detection) due to their washout from the atmosphere.

Conclusion

The results of qualitative and quantitative measurement of saturated hydrocarbons and polycyclic aromatic hydrocarbons in the atmospheric aerosol of Novosibirsk and one of its suburbs in winter and summer demonstrate that the range of the identified n-alkanes in the aerosol is C_{19}–C_{27}. Possible sources, from which n-alkanes fall into the atmosphere of the city and its suburb, were determined by the use of the CPI-index and C_{max}. It was noted that concentrations of C_{even} predominate in the city aerosol in summer, what indicates a considerable contribution

of the biological material. In winter, main sources of n-alkanes in the atmosphere of the city and its suburb are motor exhausts. The total content of the measured PAH in aerosol of Novosibirsk and Klyuchi in winter reaches 37 and 96 ng/m^3, respectively. Phenanthrene, fluoranthene, and pyrene form a considerable part of the total content of PAH. In summer, PAHs seem to be present in very small amounts (lower than the detection limit) and, most likely, they are washed out from the atmosphere.

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