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OPTICAL MODELS AND DATABASES

Hydrocarbon Composition of Tropospheric Aerosol in the South of Western Siberia

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Abstract—We considered the methodological questions: aerosol sampling on board research aircraft, extraction of an organic component, and identification of its constituent compounds. It is verified how aviation materials (kerosene, oil, hydraulic fluid) can influence the measurement data. We analyzed the composition of organic components of atmospheric aerosol, sampled in the winter—spring period of 2013 at altitudes of 500–7000 m over the southern part of the Novosibirsk reservoir. In the samples, we identified the normal-structure alkanes, cyclanes, and alkyl arenes. Cyclic saturated and alkyl aromatic hydrocarbons were detected in the composition of atmospheric aerosols of Western Siberia for the first time.

Keywords: atmospheric aerosol, composition, hydrocarbons, *n*-alkanes, cyclanes, alkylnaphthalenes, alkylphenanthrenes

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INTRODUCTION

Aerosol particles play a key role in the process of formation of the atmospheric radiation field and weather, participate in different physical-chemical reactions and, in particular, those associated with air pollution products of human activity. The significance of aerosol is now widely recognized and a great many studies have been recently performed; nonetheless, considerable gaps still remain in describing and modeling the behavior of aerosols in the atmosphere and, in particular, the carbon component of aerosol [1].

It has long been thought [2, 3] that the inorganic component mainly contributes to the chemical composition of atmospheric aerosols, while the fraction of the organic component does not exceed a few percent. Possible global climate change and the Intergovernmental Panel on Climate Change (IPCC) first report provided an impetus for new aerosol studies since the largest uncertainty in estimates of the radiation budget of the Earth is due to the contribution of aerosol particles.

Studies showed that the contribution of the organic component to the composition of ultrafine (nanoparticles) and fine aerosol fractions may vary strongly. The authors of works [4, 5] noted that organic carbon may account for 25-35% of the particle content. The

authors of work [6] give an average value changing from 40 to 65%. A close value, i.e., 57.3-71.2%, was found in [7]. Moreover, experiments revealed that the fraction of the organic component may reach 90-92% in the microdispersed fraction [8, 9].

The relationship between the contents of organic (OC) and elemental carbons (EC) in aerosol was studied in a number of works. Authors of works [10, 11] indicated that this relationship lies in the range 0.3-0.4. However, Perrone et al. [12] present data showing that the ratio of OC to EC is equal to two for the coarse aerosol fraction and is equal to four for the ultrafine fraction.

It was found that the organic part of the aerosol consists, to a considerable degree, of water-soluble compounds. For instance, the authors of work [13] showed that the degree of aerosol solubility in water is proportional to content of organic substance in aerosol. The authors of work [14, 15] found that the amount of water-soluble organics ranges from 56 to 61% in the fine fraction and attains 79% in the ultrafine fraction. Unsurprisingly, the organic component of aerosol plays an important role in the processes of cloud formation [16–18]. As a result, organic substances account for up to 40% of all compounds found in cloud water [19].

Usually, every publication on the analysis of the organic aerosol composition lists the detectable compounds often with nonoverlapping names. For instance, 150 amines only had been identified in the aerosol composition in work [20]. The authors of work [21] indicate that they detected from 186 organic ions to 494 radicals in different samples. Seemingly, the list of compounds in the composition of the organic component of aerosol will further increase. This means that there are considerable deviations from the commonly accepted theory of binary and ternary nucleation in the atmosphere [22, 23], and so due attention should be paid to nanoparticle formation in the atmosphere.

It was found that a significant portion of the aerosol may form in the course of chemical or photochemical processes directly in the atmosphere from precursor gases [24–27]. This may proceed via reactions of oxidation involving interaction with ozone [28–30], hydroxyl [31, 32], nitrogen oxides [33–35], or acids [36]. The progress of the processes depends on the air temperature or the presence of catalysts [37–39]. It is noteworthy that many of these processes were predicted as early as the work of V. A. Isidorov [40], but were experimentally confirmed only in recent decades.

Still another mechanism, which may prove to be an efficient source of organic particles, had been found recently. It is caused by the exceptional reactivity of Criegee radicals, i.e., compounds of oxygen and hydrocarbon radicals [41]. It is predicted to be more efficient than hydroxyl or ozone. Although still remaining within the laboratory, the research has already given results confirming the predictable characteristics [42, 43].

Aerosols contribute to the radiation budget of the Earth via the processes of absorption, reflection, and scattering of solar radiation. However, as recent publications show, the optical characteristics of organic aerosols have not yet been sufficiently studied, from the refractive index of the particle substance and to the absorption and scattering coefficients [44, 45].

In the aerosol material there are many dangerous organic compounds such as aromatic hydrocarbons and chlorine-, sulfur-, and nitrogen-containing species [46, 47]. This determines their ecological significance. Changes in concentration of many organic components under the influence of human activities may cause hard to predict changes in the entire structure of atmospheric processes [48]. Nonetheless, the scales of the contribution of anthropogenic organic compounds to the atmosphere have not yet been determined.

Intensive studies, which followed the first IPCC report and aimed at ascertaining the role of aerosols in the atmospheric and radiation processes, revealed that the contribution of organic components to the composition of aerosol particles is currently completely underestimated. At present, organic aerosols are intensely studied around the world. An exception is the territory of Russia, for which information on the amount, composition, and spatiotemporal variations in the organic component of the atmospheric aerosol is totally absent. For this reason, the authors of the present paper initiated in 2012 the interdisciplinary project of the Siberian Branch of the Russian Academy of Sciences aimed at studying the conditions for the formation and behavior of the organic component of aerosols in the atmosphere over the Siberian region. The present paper contains the first data obtained within this project.

METHODS OF SAMPLING AND ANALYSIS

Studies are performed on board the research aircraft, a TU-134 "Optik", which in the base variant was described in [49]. A new sampler based on a standard airspeed pitot was fabricated to collect the samples of organic aerosol from the atmosphere. It is extruded forward and mounted in the window of the cockpit door. The inner cross section of the sampler is increased to 10 mm, and the canal is made of Teflon with a cylindrical cross section of 8×10 mm and equipped with vacuum auick-split iunctions (Kamozzi, Italy). We purchased and mounted a new high-volume dry-running vacuum pump V-VTN 26 (Elmo Rietschle, Germany) with a capacity of up to $25 \text{ m}^3/\text{h}$. A drainage hole in the cabin below the ventilator window of the second pilot is isolated to drain the condensate; it is located in the direction of sampler and may be an internal source of hydrocarbon (lubricant) pollution. To identify the possible influence on measurements, the technical flight personnel were employed to select and analyze the specimens of consumables used to service the aircraft (the hydraulic fluid Hydraunycoil FH 51, oil MS-8, kerosene, diesel fuel for auxiliary power unit).

Data obtained in analysis of aviation consumables are considered below in the discussion of the results. The placement of the sampler is shown in Fig. 1.

In the winter-spring period of 2013, atmospheric aerosol samples were taken on board the research aircraft TU-134 "Optik" in the region of the Karakan Pine Forest on the right-hand coast of the southern part of the Novosibirsk Reservoir. The samples were collected in the tropospheric layer of 500–7000 m on reinforced Teflon filtering membranes Grimm 1.113A with a mean pore diameter of $0.8-1.2 \mu m$. The volume of air pumped through the filter was 7.2 m³ in January, 7.5 m³ in February, and 12.0 m³ in April, 2013.

The collected aerosol samples were treated as follows: the organic part was extracted from the filter, using chromatographic acetone (1.5 cm³) in an ultrasonic bath; then, it was concentrated in vacuum up to 50 μ L,with the subsequent analysis using a chromatography-mass spectrometer.



Fig. 1. Placement of the aerosol sampler on board the research aircraft TU-134 "Optik".

Chromatography-mass spectrometers Agilent 6890N (Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences) and Shimadzu QP 5050A (Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences) were used for the analysis.

The extracted organic part of atmospheric aerosol was chromatographically separated in a universal-type capillary column (HP-5MS) with an inner diameter of 0.25 mm and length 30 m when the temperature of thermostat of the column in the course of the analysis linearly rose from 50 to 250° C at a heating rate of 5°C/min. The isotherm at the initial and final temperatures was 3 and 45 min, respectively.

Hydrocarbons were identified using mass spectral library databases NIST, Wiley, as well as by comparing retention times of reference compounds in model mixtures.

Two model mixtures and hydrocarbon petroleum concentrate were analyzed in the same regimes to ensure confident identification. The first model mixture comprised only *n*-alkanes C_6-C_{22} ; and the second model mixture mainly comprised aromatic hydrocarbons: *n*-hexyl benzene, naphthalene, 1.6-dimethylnaphthalene, 4-methylbiphenyl, phenanthrene, 9-methylphenanthrene, chrysene, as well as *n*-hexadecane. This allowed us to use the retention times of hydrocarbons to confirm the reliability of identification, because the expert appraisal of results of identification with respect to mass spectra with the use of library databases turns out to be difficult in some cases since the mass spectra of different hydrocarbon classes bear a considerable resemblance to those of other organic compounds.

The samples were analyzed in two modes with the Shimadzu QP 5050A chromatography-mass spectrometer: scan (total scanning of all ratios of mass to charge m/z) and SIM (scanning with selecting ion monitoring m/z).

A total of 49 ratios m/z, corresponding to the main hydrocarbon classes (Table 1), were introduced in the program to record mass spectra in the SIM mode.

RESULTS AND DISCUSSION

Alkanes

Normal- (linear-) structure alkanes were identified in all samples of atmospheric aerosols. Homologous series of alkanes includes the compounds from $C_{10}H_{22}$ to $C_{26}H_{54}$ (Fig. 2a, Table 2).

In the low-molecular weight region, all samples exhibit the "naphthene hump", indicating the presence of a mixture of naphthene hydrocarbons nonseparable under the chromatographic conditions. The elution time of "naphthene hump" varies in the range 15–25 min.

The maximum in the distribution of *n*-alkanes in all aerosol samples is accounted for *n*- hexadecane (C_{16}). It is hypothesized that the high content of hexadecane and the presence of "naphthene hump" in

Table 1. Th	e ratio of the	mass to charge	(m/z)	for the basi	c hydrocarbon c	classes
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Compound	m/z
Alkenes	55
Normal-structure alkenes	57
Isoprene-structure alkenes	183
Cyclopentanes	69
Cyclohexanes	83
Bicyclanes	123
Tricyclanes	191
Steranes (tetracyclanes)	217
Hopanes (pentacyclanes)	191, 177
Alkyl benzenes	91, 105, 119, 133
Diphenyls	154, 168
Acenaphthenes	153
Fluorenes	165
Alkyl naphthalenes	128, 142, 156, 170, 184
Alkyl phenanthrenes	178, 192, 206, 220, 234
Trinaphthenes (monoaromatic steranes)	253
Mononaphthene phenanthrenes (triaromatic steranes)	231
Simmonelites	237, 252
Thiophenes	112, 126, 140, 134, 147, 161
Benzothiophenes	175, 189
Dibenzothiophenes	184, 198
Oxygen-containing compounds (spirits, ethers)	31, 45, 59, 72
Normal and branched fatty acids	74, 87, 88, 101
Aliphatic acids	60
Phenols	107

aerosol samples is a consequence of pollution by aviation consumables. In this regard, we analyzed the samples of aviation kerosene, hydraulic fluid FH-51, and oil MC-8.

It was found that aviation kerosene could not be the reason for increased hexadecane concentration in aerosol samples because the content of *n*-alkanes in aviation kerosene is confined to pentadecane $C_{15}H_{32}$ (Fig. 2c).

The chromatogram of MC-8 oil sample contains a "naphthene hump"; however, its elution time differs from that of aerosol samples and is in the interval 30-50 min (Fig. 2b). Against the background of the "naphthene hump", there are chromatographic peaks whose retention times do not coincide with those of *n*-alkanes.

At the same time, in the mass-fragmentogram of the sample of hydraulic fluid there is a "naphthene hump", the retention time of which coincides with that in aerosol samples (Fig. 2d).

Probably, the hexadecane concentration was too high because of the lubrication of the drain port of the condensate in the cabin below the ventilation window of the second pilot, which was isolated later. Therefore, the C_{16} concentration in the composition of *n*-alkanes was not accounted for in order to represent correctly the source of *n*-alkanes in the atmosphere (Table 2).

Tetradecane ($C_{14}H_{30}$) in maximal concentrations, and heptadecane ($C_{17}H_{36}$) in near-maximal concentrations exist among normal-structure alkanes in aerosol samples collected in winter time. The concentration maximum in the April aerosol sample is shifted toward the higher-molecular weight region and corresponds to hydrocarbons $C_{18}-C_{20}$. The absence of *n*-alkanes in aerosols with more than 27 carbon atoms in the molecule may possibly be because the aerosol



Fig. 2. The typical mass-fragmentogram of *n*-alkanes (m/z 57) in (a) atmospheric aerosol and (b–d) aviation consumables.

samples were collected in winter and spring time, when the period of vegetation is in its inactive phase.

It was suggested in [50] to consider *n*-alkanes as markers of a source of a certain type. For instance, *n*-alkanes with 27–33 carbon atoms in the molecule originate in the atmosphere from natural sources, and the *n*-alkanes with less than 23 carbon atoms originate from anthropogenic activities. The *n*-alkanes C_{23} – C_{26} may be of both natural and anthropogenic origins.

Taking this assumption into account, we calculated the ratio of the total content of low-molecular *n*-alkanes $C_{11}-C_{22}$ to the total content of high-molecular *n*-alkanes $C_{23}-C_{26}$ (see Table 2). The high values of this ratio indicate that low-molecular weight homologous series predominate in the composition of *n*-alkanes of aerosols.

Also, the type of the source of n-alkanes in the atmosphere is determined using the carbon preference index (*CPI*), calculated from the formula [50]:

$$CPI = 0.5 \left(\sum_{i}^{z} C_{o} / \sum_{i-1}^{z-1} C_{e} + \sum_{i}^{z} C_{o} / \sum_{i+1}^{z+1} C_{e} \right),$$

where C_o are the concentrations of *n*-alkanes with odd numbers of carbon atoms from *i* to *z*; and C_e are the concentrations of *n*-alkanes with even numbers of carbon atoms.

much less than unity (see Table 2); therefore, it can be concluded that *n*-alkanes originated in the atmosphere from anthropogenic sources.

The CPI values for all samples of aerosol in air are

The authors of works [51, 52] showed that the C_{a} concentrations predominate in the leaves of plants, while the concentrations of even homologous series predominate in vehicular exhausts. The source of hydrocarbons is biological material if the CPI is greater than three; the presence of *n*-alkanes in the atmosphere is determined by the processes of incomplete fuel combustion if the CPI is close to unity [50, 53]. The source intensity is estimated using the concentration of any hydrocarbon as a criterion. Mazurek et al. [50] showed that C_{27} , C_{29} , C_{31} , and C_{33} are the markers of mechanical damage to leaf surfaces; C_{29} and C_{31} are the markers of natural forest fires; C_{23} and C_{25} are the markers of vegetation burning; C_{21} and C_{22} are markers of vehicular exhausts; C_{10} is the marker of petroleum products, and C₁₉ is the marker of lubricating oil and diesel fuel. Thus, n-alkanes with 27 carbon atoms are, probably, biogenic in origin, those with 23-26atoms represent a mixed group of biogenic and anthropogenic sources, and those with 10-19 atoms are characteristic for anthropogenic sources. This classification is, of course, not unique, since light hydrocarbons are also encountered among the prod-

n Alkana	Content in sample, % rel.				
<i>n</i> -Aikane	Jan. 29	Feb. 27	Apr. 9		
Decane ($C_{10}H_{22}$)	32.8	17.9	9.4		
Undecane ($C_{11}H_{24}$)	3.0	2.2	0.9		
Dodecane ($C_{12}H_{26}$)	3.2	2.0	1.2		
Tridecane ($C_{13}H_{28}$)	4.6	3.4	0.6		
Tetradecane ($C_{14}H_{30}$)	5.6	5.9	1.7		
Pentadecane (C ₁₅ H ₃₂)	2.2	1.9	0.8		
Heptadecane ($C_{17}H_{36}$)	5.0	5.8	4.2		
Octodecane (C ₁₈ H ₃₈)	1.7	3.4	5.9		
Nonadecane ($C_{19}H_{40}$)	1.5	1.6	7.2		
Eicosane ($C_{20}H_{42}$)	1.1	2.5	7.2		
Heneicosane ($C_{21}H_{44}$)	0.8	1.9	4.1		
Docosane ($C_{22}H_{46}$)	1.1	2.0	2.7		
Tricosane ($C_{23}H_{48}$)	1.2	2.2	1.8		
Tetracosane ($C_{24}H_{50}$)	1.1	1.9	1.6		
Pentacosane ($C_{25}H_{52}$)	1.1	3.2	1.1		
Hexacosane (C ₂₆ H ₅₄)	0.5	2.2	0.6		
<i>CPI</i> index	0.2	0.3	0.3		
$\frac{\sum (C_{10} - C_{22})}{\sum (C_{23} - C_{26})}$	13.1	5.0	5.4		

Table 2. The content of *n*-alkanes in samples of atmospheric aerosols (2013)

ucts of plant metabolism [40, 46], while the heavy hydrocarbons are found in the composition of petro-leum products.

Cycloalkanes (Cyclanes)

The January and April aerosol samples comprise homologous series of alkyl cyclohexanes with 16 to 23 carbon atoms in the molecule (Figs. 3 and 4). Only alkyl cyclohexanes C_{20} and C_{21} were identified in the February sample. The cyclohexanes were identified by comparing the retention times of these compounds in the concentrate of petroleum hydrocarbons, which was used as a comparison reference; also, mass spectra libraries were utilized.

The molecular weight distributions of alkyl cyclohexanes in January and April samples are similar in character. The alkyl cyclohexane C_{19} is contained in these samples in maximal concentrations (see Fig. 4).

Pentacyclic alkanes (hopanes) $C_{29}-C_{30}$ are present in the April aerosol sample (Fig. 5). No hopanes were found in January and February samples. They were identified by comparing the retention times between the sample analyzed and a sample concentrate of hydrocarbons extracted from petroleum, as well as by comparing the mass spectra of pentacyclic compounds from library databases against the mass spectra obtained on the chromatogram.

The presence of alkyl cyclohexanes in all aerosol samples and the composition of pentacyclanes in the April aerosol sample, analogous to that in oil, allow us to hypothesize that their presence in the atmosphere, like the presence of *n*-alkanes $C_{11}-C_{22}$, was caused by anthropogenic sources.

Alkyl Biaromatic Hydrocarbons (Alkyl Naphthalenes)

Among the alkyl biaromatic hydrocarbons, in the aerosol samples collected in 2013, we identified (Fig. 6*a*): unbranched naphthalene (peak 1), 2-methyl naphthalene (peak 2), 1-methyl naphthalene (peak 3), 2.7-, 2.6-, 1.7-dimethyl naphthalenes (peak 4), 1.3-dimethyl naphthalene (peak 5), 1.6-dimethyl naphthalene (peak 6), and 2.3-dimethyl naphthalene (peak 7). No trimethyl naphthalenes were found.

These compounds were identified using data on retention times of concentrates of petroleum hydrocarbons and the model mixture, consisting of petroleum hydrocarbons, used as a reference; also, massspectra libraries were utilized.

Unbranched naphthalene predominates in content over its methyl- and dimethyl-substituted homologous series among alkyl biaromatic hydrocarbons of aerosols (Fig. 7). The amount of methyl naphthalenes is larger than the content of dimethyl naphthalenes among the substituted homologous series.

As in aerosol samples, in kerosene the alkyl naphthalenes are represented by unbranched naphthalene and its substituted homologous series. Kerosene samples differ from aerosol samples in that they contain trimethyl naphthalenes and have another character of the molecular weight distribution of the entire alkyl naphthalene series. No alkyl naphthalenes were detected in samples of MC-8 oil and hydraulic fluid FH 51.

The presence of alkyl naphthalenes in aerosol samples, as well as the presence of saturated cyclic hydrocarbons, is due to anthropogenic sources. The similarity of the type content of alkyl naphthalenes in winter



Fig. 3. The mass-fragmentograms of cyclohexanes (m/z 83) in aerosol samples.

and spring samples suggests that it is constant independent of the season.

Alkyl Triaromatic Hydrocarbons (Alkyl Phenanthrenes)

Compounds of phenanthrene series in collected aerosol samples are represented (Fig. 8*a*) by unbranched phenanthrene (peak 1) and its methylsubstituted isomers: 3-methyl phenanthrene (peak 2), 2-methyl phenanthrene (peak 3), 9-methyl phenanthrene (peak 4), and 1-methyl phenanthrene (peak 5). The alkyl triaromatic hydrocarbons were identified analogously to the identification of alkyl biarenes.

In January and February aerosol samples, the phenanthrene amount exceeds the methyl phenanthrene content by the factors of 1.3 and 1.1, respectively (Fig. 9). The methyl phenanthrenes are a factor of 1.4 more abundant than phenanthrene in the April aerosol sample.

Of the alkyl phenanthrenes, only unbranched phenanthrene is present in the kerosene sample. No alkyl phenanthrenes were found in samples of MC-8 oil and hydraulic fluid.



Fig. 4. The molecular weight distributions of alkyl cyclohexanes in aerosol samples.



Fig. 5. The mass-fragmentograms of pentacyclic alkanes $(m/z \ 191)$ in (a) April aerosol sample and (b) hydrocarbon petroleum concentrate.



Fig. 6. The typical mass-fragmentogram of alkyl naphthalenes (m/z 128, 142, 156, 170) in (a) atmospheric aerosols and (b) hydrocarbon petroleum concentrate.



Fig. 7. The type content of alkyl biaromatic hydrocarbons in aerosol samples (2013).

The presence of alkyl phenanthrenes confirms the hypothesis that organic components in the atmospheric aerosol are anthropogenic in origin. The differences in type content of alkyl phenanthrenes



Fig. 8. The typical mass-fragmentogram of alkyl phenanthrenes (m/z 178, 192, 206, 220) in (a) atmospheric aerosols and (b) hydrocarbon petroleum concentrate.



Fig. 9. The type content of alkyl triaromatic hydrocarbons in aerosol samples (2013).

between winter and spring aerosol samples indicate that these hydrocarbons vary with the season.

The identification of compounds, detected in atmospheric aerosol over the south of Western Siberia,

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coincides, in many respects, with data obtained for other regions [54–56], indicating that particles have a universal character of their formation in the atmosphere. Possibly, we will also be able to identify regional features with more samples taken.

CONCLUSIONS

Studying the composition of organic components of atmospheric aerosols, sampled in the winter-spring period of 2013 at altitudes of 500–7000 m over the southern part of the Novosibirsk Reservoir, showed that the composition and distribution of identified normal-structure alkanes and *CPI* value, calculated on their bases, the relationship of low- and high-molecular weight *n*-alkanes, and also the presence of cyclanes and alkylarenes indicate that these compounds in the composition of atmospheric aerosols are anthropogenic in origin.

Cyclic saturated and alkyl aromatic hydrocarbons are detected for the first time in the composition of atmospheric aerosol in Western Siberia.

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