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## Composition of Organic Components of Snow Pack in Areas of Tomsk Region with Diverse Technogenic Load

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### Abstract

Using gas chromatography-mass spectrometry (GC-MS), there was explored the composition of organic compounds in snow samples collected in the territory of Tomsk region in areas with diverse technogenic load: at the oilfield, in the forest-park area of the city of Tomsk (Academgorodok), and in wetlands remote from anthropogenic sources. In snow pack samples, the following components were determined: alicyclic and aromatic hydrocarbons, normal aliphatic acids and their esters, acyclic and aromatic ketones, aldehydes, terpenes, phenols, orthophosphoric acid esters, furans, and thiophenes. According to the results of analysis of the composition of the organic compounds identified, sources of their entry to snow pack (biogenic and anthropogenic) were revealed.

**Keywords:** lipids, GC-MS, biogenic structures, compounds of anthropogenic origin

### INTRODUCTION

Due to the ability to accumulate chemicals, snow pack is an important indicator of environmental condition. Accumulation may proceed both at the time of snowflake formation and snowfall and directly during substance deposition from the atmosphere, and also from underlying soils and rocks [1].

The componential composition of aerosols is very diverse. It includes substances of natural biogenic, geological, and anthropogenic origin. Their distribution in snow pack has captured increased attention of researchers. This also applies to organic compounds, among which carcinogenic pollutants, *i.e.* polycyclic aromatic hydrocarbons (PAH) [2–4] and dioxins [5], stand out. At the same time, natural substances have not been fully explored, though they are significant components of the global organic carbon cycle.

The objective of this work was to explore the componential composition of organic compounds in snow pack of three areas of Tomsk region that were exposed in varying degrees to technogenic impact.

### EXPERIMENTAL

Sampling areas are found in the West Siberian southern taiga subzone. To quantitatively extract organic components, sampling was carried out late in March, during the maximum height of snow pack for the territory. In March of 2016, snow samples were collected in Bakchar bog, in March 2017 – in the territory of an oil field located in the Parabel district and in the Park area of Tomsk Akademgorodok (Fig. 1).

Bakchar bog (sampling work, SW 1) is located in the interstream area of Bakchar and

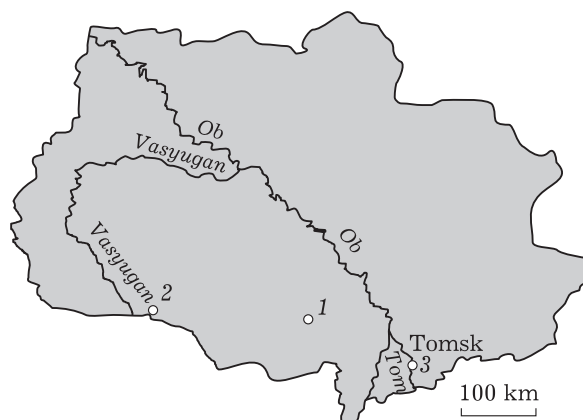


Fig. 1. Location of objects of research: 1 – Bakchar swamp; 2 – oil field (Parabel district); 3 – Tomsk, Akademgorodok.

Iksa rivers (Chaya river basin) in an area remote from anthropogenic impact sources, with poorly developed transport infrastructure. Sampling was carried out within the limits of pine-shrub-sphagnum phytocenosis with low pine. The type of peat deposit at a sampling point is upstream, power of 3 m.

In the oil field (SW 2), there is oil and fuel gas production. The nearest town is about 50 km away. There is no road network and

communication is by air transport, in winter on winter roads.

Academgorodok (SW 3) is located in the south-east part of Tomsk city. According to the data of the Department of Natural Resources and Environmental Protection of Tomsk region for 2015, the Atmosphere Pollution Index (API) in Tomsk, calculated by the priority pollutants, points to increased air pollution [6]. The total volume of pollutant emissions in the Tomsk region in 2015 is 293.081 thousand t, of which 35.71 % falls on the territory of Parabel district, 11.67 % – Tomsk, 0.15 % of the total – on the Bakchar district.

Snow samples were collected at the entire depth of snow pack in 5–6 points at a distance of 1–2 m from each other. The research procedure involved the following steps: 1) the heating of combined snow samples in enameled ware at room temperature; 2) preservation of melt water with chloroform in glass bottles and delivery to the laboratory of the Institute of Petroleum Chemistry SB RAS; 3) triple extraction of organic substance with chloroform from the entire sample of melt water in a separating funnel. The combined lipid extract was concentrated using a rotary evaporator at reduced pressure and the residue was dissolved

TABLE 1

Characteristic ions and conversion factors for organic components

Components	Characteristic ions ( $m/z$ )	Conversion factors
<i>n</i> -Alkanes	57	4
<i>n</i> -Alkylbenzenes	91, 105, 119, 133, 134	2.2, 2.2, 2.2, 3.3, 3.3
Naphthalene, its methyl-, dimethyl, and tetramethyl derivatives	128, 142, 156, 170, 184	2, 2.7, 3.2, 4.1, 6
Fenanthrene, its methyl-, dimethyl derivatives	178, 192, 206	2.2, 3.5, 7
Fluoranthene, pyrene, and their methyl substituted derivatives	202, 202, 216	3.4, 3.4, 4
Fatty acids	60	7
Methyl esters of fatty acids	74	5.5
Alkanones	58	7
Aldehydes	82	9
Tocopherols	402	3
Cyclohexane derivatives	83	4
Dibenzofurane and its methyl substituted derivatives	168, 182	2, 3.5
Dibenzothiophene and its methyl substituted derivatives	184, 198	2, 3.5
Fluorenone	152, 180	3
Antron	165, 194	3
Trimethyl phosphate and and its methyl substituted derivatives	326, 340, 354	5, 5, 5
Tributylphosphate	99	2.5

in 1 mL chloroform. Lipids were investigated by gas chromatography-mass spectrometry (GC-MS) using Thermo Scientific DFS magnetic chromatography-mass spectrometer (Germany) provided by the Tomsk Regional Collective Use Center, Tomsk Science Center SB RAS.

The separation was carried out using an Agilent DB-5MS quartz capillary chromatographic column with a size of  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ; helium carrier gas, the volume of the sample introduced is  $1\text{ }\mu\text{L}$ . The samples under study were heated stepwise in helium flow according to the temperature program: initial temperature of  $80\text{ }^\circ\text{C}$ , the isotherm of 2 min, then heated at a rate of  $4\text{ }^\circ\text{C}/\text{min}$  to  $300\text{ }^\circ\text{C}$  followed by 30 min at the same temperature. Mass spectrometer: electron impact ionization; ionizing electron energy of 70 eV; the temperature of ionization chamber and interface of  $270\text{ }^\circ\text{C}$ . Chromatograms of lipids were recorded at the total ion current, herewith, mass spectrum scanning time is 1 s in the 50–550 Da range.

The identification of individual organic compounds was carried out using the data library of the National Institute of Standards NIST-05 and literary sources. When processing data, there were utilised chromatograms reconstructed according to characteristic fragmentary ions. The content of components was determined according to the area of the corresponding peaks in the chromatograms using deuterio-acenaphtene ( $\text{C}_{12}\text{D}_{10}$ ) as an internal standard. Calculations of the content of identifiable compounds are of semi-quantitative nature, therefore standard compounds for different classes of the analysed components were not used in the work and current factors for sensibility (response factor) were not determined. The content of individual compounds was computed according to the total area of individual peaks considering the conversion factors in the transition from fragmentograms to chromatograms for the total ion current (Table 1). The limit of detection of the determined component per water volume is  $10\text{ ng}/\text{dm}^3$ .

## RESULTS AND DISCUSSION

In snow pack samples, there were determined the following components: alicyclic and aromatic hydrocarbons (HC), normal aliphatic acids and their esters, acyclic and aromatic ke-

tones, aldehydes, terpenes, phenols, orthophosphoric acid esters, furans, and thiophenes (Table 2). The volume of melt water in the analyzed samples,  $\text{dm}^3$ : SW 1 – 5.26, SW 2 – 1.65, and SW 3 – 3.63.

The total content of the compounds identified by the GC-MS method in snow samples from different sites is almost the same, while the amount and intensity of precipitation at each of sampling points may significantly vary. In this regard, it is not correct to compare absolute values of concentrations. In addition, there are still no standards for the content of organic impurities in snow pack. In our opinion, for comparative analysis it is advisable to use the relative content of compounds of different origin in each object, which allows determining sample pollution degree with greater certainty.

### *Compounds of biogenic origin*

Biogenic compounds directly produced by biological systems mainly include oxygen structures, such as fatty acids and their esters, alkanones, aldehydes, alcohols, tocopherols, steroids and terpenoids, as well as amines and other nitrogen compounds. They are found in high concentrations in plants and recent sediments and herewith, are absent or present in trace amounts in geological systems [7, 8].

Fatty acids composition in the examined snow samples is typical for biological systems: even structures of  $\text{C}_{10}$ – $\text{C}_{18}$  series prevail, and palmitic ( $\text{C}_{16}$ ) acid is prevalent among them (Fig. 2, a). Palmitic and stearic ( $\text{C}_{18}$ ) acid derivatives are the only representatives of methyl esters in snow samples collected near the oil field (SW 2) and within the city (SW 3), while high molecular mass acid methyl esters, mainly  $\text{C}_{24}$  and  $\text{C}_{26}$ , are also found in sample SW 1 (see Fig. 2, b). Their presence points to the contribution of terrestrial and aquatic plants to the lipid composition [9]. Wax esters, *i.e.* higher fatty acid long-chain esters and alcohols presented by even homologues  $\text{C}_{28}$ – $\text{C}_{34}$ , which are formed, apparently, by even alcohols and acids  $\text{C}_{14}$ – $\text{C}_{18}$  are also found in sample SW 1. These compounds are synthesized by various organisms (bacteria, plants, and animals) [10]. *n*-Aldehydes presented by even structures  $\text{C}_{22}$ – $\text{C}_{30}$  are second (after *n*-alkanes) in the prevalence of components in snow collected from the upper swamp (SW 1); in sample SW 3, their con-

TABLE 2

Content of individual groups of organic compounds in snow samples,  $\mu\text{g}/\text{dm}^3$ 

Components	SW 1	SW 2	SW 3
<i>Biogenic structures</i>			
Alkanes*	13.38	b.d.l	6.39
Fatty acids	1.25	0.91	4.20
Esters of fatty acids	0.79	0.05	0.27
Alkanones	0.29	0.03	0.18
Aldehydes	6.10	b.d.l	0.31
Diterpenes	0.81	b.d.l	Traces
Tocopherols	0.03	0.01	Traces
<i>Compounds of anthropogenic origin</i>			
Alkanes*	b.d.l	2.55	b.d.l
Cyclohexanes	b.d.l	0.35	0.86
Isoalkylbenzenes (trimethyl alkyl)	b.d.l	0.02	0.03
Dibenzofurans	b.d.l	0.14	b.d.l
Dibenzothiophenes	0.01	0.47	0.01
Bi- and triarenes	0.24	1.73	0.06
Tetraarenes	0.03	0.04	0.05
Fluorenone and antron	b.d.l	0.07	0.12
$\alpha$ -Tocopherol acetate	b.d.l	b.d.l	0.04
Triphenyl phosphates	0.10	0.05	0.39
Tributyl phosphate	b.d.l	0.44	b.d.l
<i>Sum of identified compounds</i>	23.03	6.86	12.91
CPI-2**	10.28	1.12	9.96

Note. B.d.l. signifies below the detection limit.

\* Composition determines origin of *n*-alkanes.

\*\* Oddness coefficient of *n*-alkanes.

tent is significantly lower, and in sample SW 2, there are no compounds this class. For samples SW 2 and SW 3, distribution of *n*-alkan-2-ones, typical for peats and plants: odd-numbered homologues  $C_{19}$ – $C_{31}$  are prevailing and the maximum falls on  $C_{25}$ – $C_{29}$  (see Fig. 2, c). The composition of a now sample from the oil field is notable for a low content and a specific set of *n*-alkane-2-ones: homologues  $C_{19}$  and  $C_{21}$  are prevailing among odd structures  $C_{19}$ – $C_{31}$ .

In the composition of tocopherols (vitamin E),  $\alpha$ - and  $\beta$ -tocopherols were determined in samples SW 1 and SW 2; the  $\alpha$ -form was prevailing. The  $\beta$ -isomer was not detected in a snow sample from Akademgorodok,  $\alpha$ -tocopherol acetate, *i.e.* a synthetic derivative of tocopherol, was prevailing.

Diterpenes common in coniferous plants are presented in sample SW 1 by oxygen-contain-

ing tricyclic structures with acid, ether, aldehyde or alcohol substituents. Dehydroabietic acid is prevailing among them. Abietic and dehydroabietic acid methyl esters are present in the composition of sample SW 3 in minor amounts, and diterpenes were not detected in sample SW 2.

#### *Compounds of antropogenic origin*

Compounds of this type are widely common in the composition of a sample collected in the territory of the oilfield (SW 2). Derivatives of cyclohexane, alkyl-substituted trimethylbenzene, dibenzofuran, and dibenzothiophene refer to oil structures [7]. Obviously, compounds distribution nature in sample SW 2 is due to the arrival of oil components when hydrocarbon raw materials extracting. A considerable content of cyclohexane derivatives included in

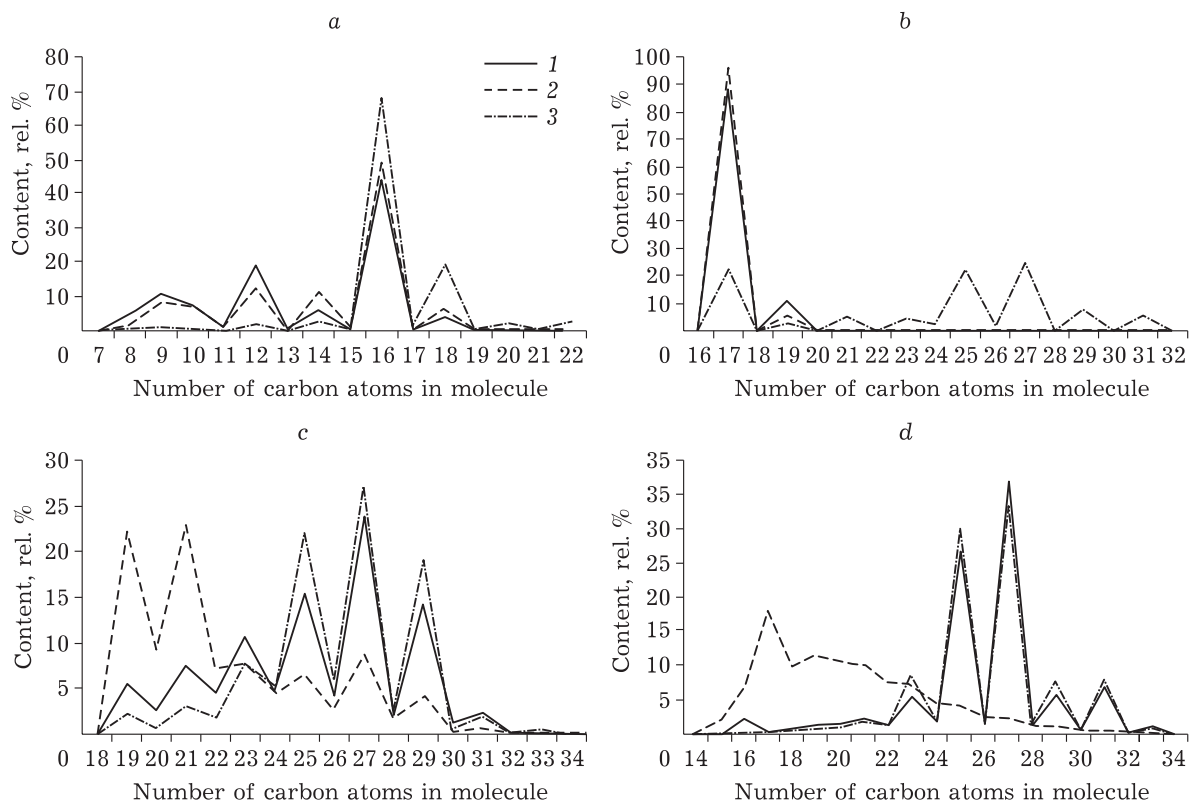


Fig. 2. Molecular mass distribution of fatty acids (a) and their methyl esters (b), *n*-alkane-2-ones (c) and *n*-alkanes (d) in snow samples: sampling works (SW) 1-3 (1-3).

motor fuel composition, and alky trimethyl benzene derivatives is also typical for sample SW 3, while dibenzofurans are absent, and there are little dibenzothiophenes. Only small amounts of dibenzothiophenes that are probably formed by the transformation of thiophene structures of aquatic plants are recorded in sample SW 1 [11].

Regardless of a sampling site, *n*-alkanes are prevailing in snow extracts.

Their composition is determined by two different sources (biogenic and anthropogenic), which with a high degree of reliability may be determined by the nature of the molecular mass distribution of individual homologues. In recent sediments and biological structures,  $C_{21}$ - $C_{33}$  homologues with an odd number of carbon atoms prevail over even. The molecular mass distribution in oil and its products is smoothed, and the maximum distribution falls on homologues of smaller molecular mass,  $C_{17}$ - $C_{24}$  [8].

Coefficients of the oddness of *n*-alkanes (ratio of molecules with odd and even numbers of carbon atoms, or CPI-2-carbon preference index) developed to characterize the molecular

mass distribution [12, 13] are close to one for oil *n*-alkanes. Whereas they may reach 6-10 or above for biogenic *n*-alkanes [14].

*n*-Alkane distribution nature in samples SW 1 and SW 3 is typical for biogenic organic matter (see Fig. 2, d): odd-numbered  $C_{23}$ - $C_{31}$  structures are prevailing; the maximum falls on  $C_{25}$ - $C_{27}$  homologues, the CPI-2 index is ~10. *n*-Alkanes in SW 2 snow sample have a different appearance: the maximum is shifted towards the lower molecular mass region, in other words,  $C_{16}$ - $C_{23}$  homologues are prevailing (CPI-2 ~ 1), which points to significant snow pollution with oil components.

Similarly to *n*-alkanes, bi- and triarenes may be of different origin [15-17], nevertheless, it is considered that their content is minor in organic matter. Their total amount in samples SW 1 and SW 3 is 50-100 times lower than the content of *n*-alkanes, and in sample SW 2 - only in 1.5 times. Proceeding from this, one may assume that bi- and triarenes in the snow sample of the oil deposit (SW 2) are mainly of oil genesis.

There are no alkyl aminoarenes in the sample SW 1, while two other samples contain



them in trace amounts. Biaromatic HC presented by naphthalene and its methyl and dimethyl substituted homologues are prevailing in the sample SW 1. Fluorene and its ethyl substituted derivatives prevail among triarenes. It is felt that a source of alkyl naphthalenes is terrestrial plants, *i.e.* cyclic sesquiterpenoids contained in the resin of coniferous plants [18], therefore naphthalene and its methyl-substituted homologues may also have biogenic genesis.

In snow sample SW 2, a homologous series of naphthalenes are supplemented with tri- and tetramethyl substituted compounds; the amounts of di- and trimethyl substituted naphthalenes are by an order of magnitude higher than the content of the methyl substituted homologue and by two orders of magnitude – unsubstituted naphthalene. In addition, phenanthrene, its methyl and alkyl-substituted homologues were found among triarenes.

Sample SW 3 contains only light derivatives of naphthalene and phenanthrene with distribution typical for oil products. Their concentration is 30 times less compared to sample SW 2.

Among other aromatics, heterocyclic aromatic compounds, such as fluorenone and antron derivatives, are present in snow samples collected within the city limits and in the oil field. They are found in oil, bitumen, diesel combustion products, tobacco smoke, *etc.* [19]. Tetracyclic HC, such as pyrene and fluoranthene, are also contained in arenes of all samples, and their methyl derivatives – in sample SW 2. The presence of tetra- and pentaarenes, also called pyrogenic PAH, is usually related to with wind-blown coal combustion products [20]. The amount of bi- and triarenes is much larger than that of tetraarenes in the snow of the oil field and Bakchar bog, and in snow sample within the city limits, their amounts are comparable. A large fraction of tetraarenes probably indicates the main source of these compounds in sample SW 3, *i.e.* combustion products of coal being used in the local CHP located 3.5 km from the sampling site.

Triphenyl phosphate, plasticizer and antipyrène, and its homologues have been found in all samples. Herewith, unsubstituted  $(C_6H_5O)_3PO$  is prevailing over its methyl- and dimethyl-substituted derivatives. Like the majority of phosphorus-containing antipyrènes, triphenyl phosphate is met in sediments,

soils, dust, and air. Pollutants of this type are common everywhere, but the highest concentrations are regularly observed in urbanized areas. Nevertheless, antipyrènes are also found in remote regions, for example, in air samples taken at Svalbard in the European Arctic [21]. In our examination, triphenyl phosphate pollution can be said in respect to SW 3 as the most urbanized area, for samples SW 1 and SW 2, the resulting values are probably background ones.

In addition to triphenyl phosphate in sample SW 2, there is also tributyl phosphate, plasticizer and solvent probably used in the oil production process.

Figure 3 gives data on the relative content of organics of diverse origin in snow pack samples. Distribution analysis of *n*-alkanes that compose 37–58 % of the total of identified compounds allowed assessing their origin in all three points of sampling: *n*-alkanes of samples SW 1 and SW 3 are of biogenic nature, and in case of sample SW 2 – anthropogenic.

Pollution by substances of anthropogenic nature is maximum for sample SW 1 (1.6 rel. %) remote from objects of probable technogenic impact. Their fraction is maximum in a sample from the territory of the oil field (85 rel. %) and it is 11.7 rel. % in a snow sample of the parkland of Akademgorodok. Herewith, the composition of compounds of anthropogenic origin at these sites varies significantly. Derivatives of cyclohexane, pyrogenic PAH and aromatic cyclic ketones (products of combustion of motor fuels and/or coal)  $\alpha$ -tokopherol acetate (a widely common component of drugs and cosmetics), and also triphenyl phosphate, plasticizer and antipyrène are prevailing in sample SW 3. Compounds typical for native oils, *i.e.* dibenzofurans, dibenzothiophenes and also bi- and triarenes, prevail in a snow sample from the oil field (SW 2).

## CONCLUSION

As demonstrated by study results, there are components of biogenic and anthropogenic origin in the composition of the identified organic compounds of snow pack in regions of the Tomsk district with diverse antropogenic load.

Biogenic compounds of snow pack of Bakchar bog and parklands of the forest-park area of Akademgorodok comprise of *n*-alkanes, and

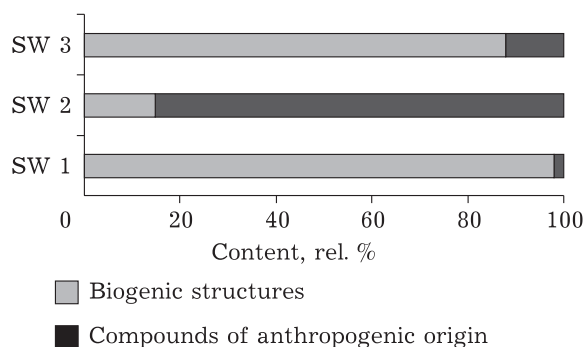


Fig. 3. Distribution of organic compounds of different origin in the snow samples, SW 1–SW 3.

also of aldehydes and diterpenes. Fatty acids and their esters, *n*-alkane-2-ones, and tocopherols of natural origin have been detected in all samples. Snow pack of Bakchar bog is notable for elevated contents of almost all biogenic compounds, except for acids. The concentration of biogenic compounds is minimum in snow samples of the oil field.

Among compounds of anthropogenic origin, bi-, tri-, and tetraarenes, and dibenzothio-phenes have been found in all samples. Moreover, the first two groups of the compounds are present in the maximum amount in a snow sample from the territory of the oil field. Cyclohexane and trimethyl benzene derivatives have been determined in snow pack of the oil field and the forest-park area of Academgorodok. Pyrogenic surfactants, triphenyl phosphate derivatives, aromatic ketones, and  $\alpha$ -tocopherol also prevail therein. There are dibenzofurans only in a snow sample from the oil field. The nature of the molecular mass distribution of *n*-alkanes in this sample points to their anthropogenic origin.

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