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Modelling the Contact of Oil Systems with Natural Water Bodies

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Abstract

Laboratory modelling of oil pollution of water bodies was carried out using the diesel fuel – water – mineral phase system. The content and composition of organic compounds in each of the parts making up the system were studied using gas chromatography-mass spectrometry. The trends of changes in the composition of *n*-alkanes, polycyclic aromatic and naphthenic hydrocarbons, cyclohexanes, alkylbenzenes and trimethylalkylbenzenes present in diesel fuel during the transition from diesel fuel to the aqueous and mineral phases have been revealed.

Keywords: water pollution, composition of organic compounds, diesel fuel, natural waters, bottom sediments

INTRODUCTION

Enhancement of oil production, the scale of its transportation, processing, and consumption cause substantial aggravation of local environmental situation in the cases of oil spillage. Therefore, a highly relevant issue arises to determine the boundaries of pollution propagation for subsequent development of the concept of territory clean-up and efficient environmental protection. Organic compounds in oil and in the products of its processing drastically affect all links of the biological chain, cause substantial disorders in major vital ecosystem functioning, so it is important to monitor the concentrations of these compounds in aquatic environment. Various approaches are applied to solve the problem, including development of the methods to diagnose the extent to which the environmental objects are polluted with various kinds of oil pollutants and to identify pollution sources [1, 2]. Various technogenic sources produce combinations of compounds specific for each source [3], which are transformed and differentiated under the action of different conditions. Changes in the composition of some oil components in aquatic environment have been studied in [4, 5], but further studies are necessary to achieve a more complete notion of oil compound differentiation in water bodies.

The goal of the work was to optimise the parameters of oil pollution monitoring for the aquatic environment. For this purpose, the regularities of pollutant propagation were analysed by modelling various conditions of contact with water and bottom sediments, and the features of changes in

the composition of a broad range of oil compounds entering natural water bodies were investigated.

EXPERIMENTAL

The oil pollution of water objects was modelled using a ternary system pollutant – water – mineral phase exposed under laboratory conditions for different time intervals. Diesel fuel (DF) was chosen as the pollutant in this system.

The model natural system was composed of spring water in the amount of 3 dm^3, diesel fuel – 15 cm^3, and bottom sediments (BS) sampled in the amount of 40 g from an uncontaminated riverbed region. Experiments were carried out in a glass vessel at a temperature of 25 °C, with protection from direct sunlight for 3 and 6 months (Table 1). The terms of experiment were chosen to rely on actual periods of active elimination of the consequences of technology-driven disasters.

In parallel, an experiment with the introduction of additional factor (layer mixing) reproducing the motion of water mass was arranged. Mixing stage was performed for 3 h, and then the system was settled for 3 days.

Diesel fuel was removed from the system with the help of a separating funnel after 3 h, 3 or 6 months, depending on experimental conditions. Organic components were extracted from water with chloroform. Bottom sediments were dried preliminarily, and then extracted with the solution (7 vol% methanol in chloroform) under heating on a water bath. Thus obtained extracts from the aqueous and mineral phases were distilled until dry using a vacuum rotary evaporator. In the experiment with mixing, BS were separated into two parts. One of them was extracted with a chloroform-methanol mixture, while the other part was washed with a fresh portion of water. Water extract from the sediment was extracted with chloroform.

All extracts, as well as DF, were analysed by gas chromatography – mass spectrometry (GC-MS) with the help of a Thermo Fisher Scientific DFS instrument (Germany) at the Tomsk Regional Multi-access Centre, TSC SB RAS. The components of extracts were separated in a quartz capillary column of Agilent company, with the inner diameter equal to 0.25 mm, 30 m long, with TR-5MS immobile phase 0.25 μm thick. Analysis conditions: helium as carrier gas, evaporator temperature 250 °C, interface temperature 250 °C, electron impact ionisation, the energy of ionising electrons 70 eV; temperature of ionisation chamber 250 °C; the range of recorded masses 50–500 Da, sweep duration 1 s. The programme of thermostat heating was: T_{in} = 80 °C, isothermal exposure for 2 min, then heating at a rate of 4 °C/min to T_{max} = 300 °C, isothermal exposure for 35 min.

The chromatograms of organic components were recorded over total ion current (TIC) and characteristic fragment ions (SIM). Individual compounds were identified using the mass spectral library NIST-5. The qualitative and quantitative determinations were carried out over the corresponding peaks in chromatograms and their areas using deuterated acenaphthene ($C_{12}D_{10}$) as the internal standard [5].

TABLE 1

Characterisation of the conditions of model experiments with the system diesel fuel – spring water – sediment

Sample code	Experimental conditions	Contact time	Sample description
		Experiment 1	
1Water	Stationary contact	3 months	Extract from the aqueous part
2BS	Stationary contact	3 months	Extract from BS
		Experiment 2	
3Water	Stationary contact	6 months	Extract from the aqueous part
4BS	Stationary contact	6 months	Extract from BS
		Experiment 3	
5Water	Mixing for 3 h, settling	3 days	Extract from the aqueous part
6BS	Mixing for 3 h, settling	3 days	Extract from a part of BS
		Experiment 4	
7Water	Mixing for 3 h, settling	3 days	Extract of the second water extract from a part of BS

Note. BS – bottom sediment (mineral phase).

RESULTS AND DISCUSSION

To assess the transition of DF components into the aqueous and mineral phases by GC-MS (TIC), the initial composition of fuel was determined (Fig. 1).

The groups of compounds identified in the chromatograms (SIM) of DF are: *n*-alkanes C_{11}–C_{33} (*n*-Alk, *m/z* 57, where *m/z* is the mass to charge ratio in the mass spectra); isoprenoid alkanes C_{14}–C_{21} (i-Alk, *m/z* 57); cyclohexane homologues C_{11}–C_{25} (CH, *m/z* 83); homologues of phenanthrene (P, *m/z* 178), represented by mono-, bi-, and trimethylphenanthrenes (*m/z* 192, 206, 220, respectively); homologues of naphthalene (Np), including mono-, bi-, and trimethylnaphthalenes; tetracyclic aromatic hydrocarbons (TeC, *m/z* 202), in particular fluoranthene and pyrene; *n*-alkylbenzenes C_{12}–C_{25} (*n*-AB, *m/z* 92), and trimethylalkylbenzenes with alkyl substituent of isoprenoid structure – C_{13}–C_{16}, C_{18}–C_{21} (TMAB, *m/z* 133). Sesquiterpanes (ST, *m/z* 123) were detected in small amounts, including drimanes C_{15}, and homodrimanes C_{16}, with homodrimanes prevailing; polycyclic naphthenes (PCN), including steranes C_{27}–C_{29} (C, *m/z* 217), and hopanes C_{27}, C_{29}–C_{33} (H, *m/z* 191). Relative concentrations of the components are shown in Fig. 2.

The major compounds in DF are *n*-alkanes; their molecular mass distribution (MMD) is shown in Fig. 3. They are characterised by the unimodal distribution with maximum at C_{11}–C_{12}. About 80 % of the sum of identified *n*-alkanes are within C_{11}–C_{23} range.

The distribution of alkylbenzenes and cyclohexanes is similar, with the maxima at C_{11}, C_{15}, C_{16} (Fig. 4).

Distinguishing features of TMAB are the absence of C_{17} homologue in their composition and non-uniform retention during chromatographic separation, characteristic of isoprenoid structures (Fig. 5).

The ratio of the sum of isoprenoid alkanes (pristane (Pr) and phytane (Ph)) to *n*-alkanes (K_i) was calculated using the equation:

$K_i = (Pr + Ph)/(n\text{-}C_{17} + n\text{-}C_{18})$

The value of K_i is equal to 0.93, and the ratio Pr / Ph is 1.17. The average molecular mass (M_{av}) was calculated using equation:

$$M_{av} = \frac{\Sigma(M_i \cdot \Sigma C_i)}{\Sigma C_i}$$

where M_i is the molecular mass of a homologue, and C_i is its content.

In diesel fuel, M_{av} for *n*-alkanes is 193, cyclohexanes – 186, alkylbenzenes – 201, trimethylalkylbenzenes – 215.

Identification of a source of oil pollution entering water bodies is a problem related to changes in its composition, due to differences in the chemical properties of separate compounds. A model experiment under laboratory conditions was carried out to verify and identify the possible processes of DT component transition into the aquatic medium, and then into BS, and to clarify the changes of DF composition in the system pollutant – water – mineral phase.

The conditions of model experiments and description of the extracts of organic matter after

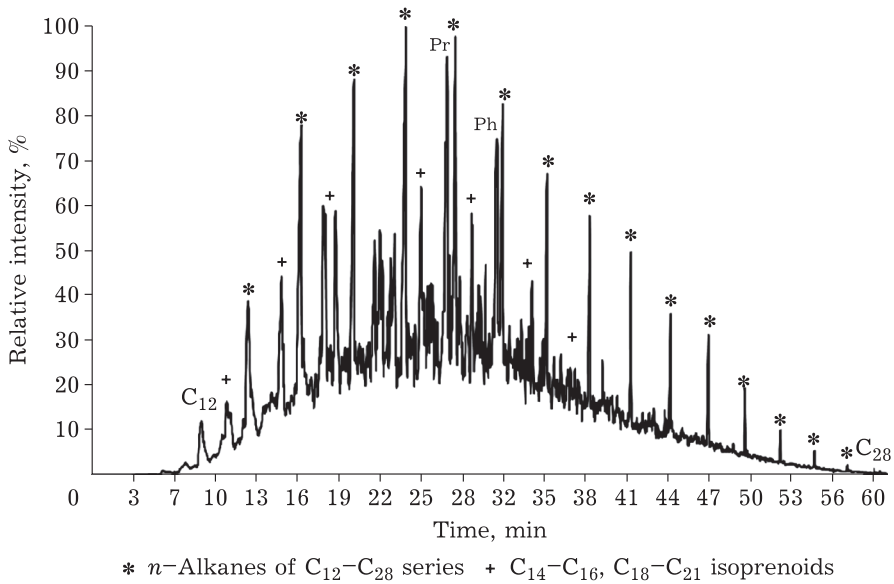

Fig. 1. Chromatogram of diesel fuel over total ion current (TIC). Pr – pristane; Ph – phytane.

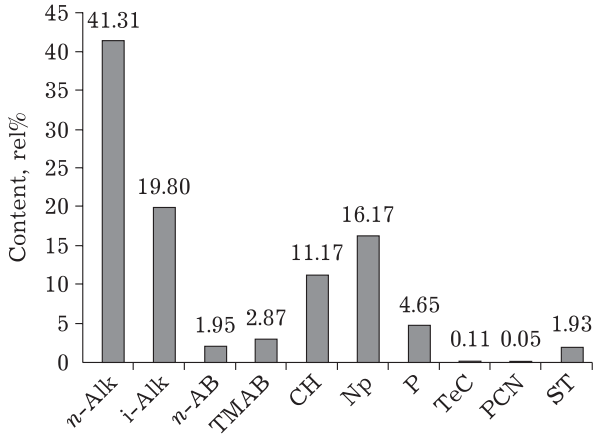

Fig. 2. Group composition of diesel fuel. *n*-Alk – normal alkanes; i-Alk – isoprenoid alkanes; *n*-AB – *n*-alkylbenzenes; TMAB – trimethylalkylbenzenes; CH – cyclohexane homologues; Np – naphthalene homologues; P – phenanthrene homologues; TeC – tetracyclic aromatic hydrocarbons; PCN – polycyclic naphthenes; ST – sesquiterpanes.

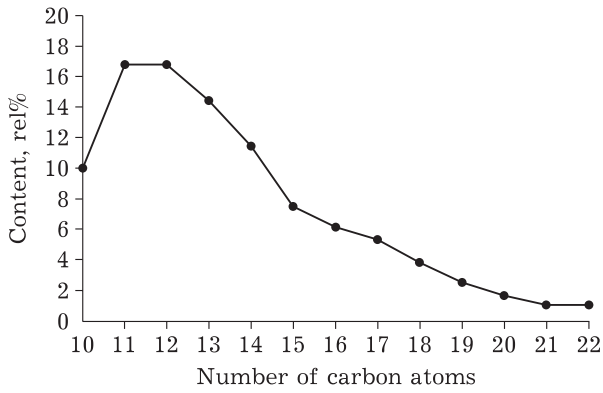

Fig. 3. Molecular mass distribution of *n*-alkanes in diesel fuel.

contact with DF for 3 and 6 months that have been sampled for analysis are presented in Table 1. In the experiments under consideration, the model of DF transformation in water is substantially simplified in comparison with natural conditions. Evaporation, emulsification and dispersion, photochemical oxidation processes are minimised. Nevertheless, the model allows us to assess the trends of changes in DF composition caused by the interaction with the aqueous phase and then, through water, with the mineral phase.

After phase separation and BS drying, the DF components that passed into water and got sorbed on the mineral component were extracted using proper solvents. The extracts were studied by GC-MS.

Analysis of results obtained in the experiments modelling the distribution of DF components in a stagnant (back-water type) stationary system pollutant – water – mineral phase shows that after contact with pollutant for 3 months 0.16 wt% of DF pass into stagnant water (1Water), while 0.19 wt% is accumulated in the mineral phase (2BS). Further interaction (for 3 months more) has only an insignificant effect on the percentage of DF components in water (0.19 wt%), while the corresponding fraction in the mineral component of the system has increased substantially to 0.91 wt%. The content of major groups of organic compounds in the aqueous and mineral phases is shown in Table 2.

The total content of *n*-alkanes (*n*-Alk), polycyclic aromatic hydrocarbons (PAH), alkylbenzenes

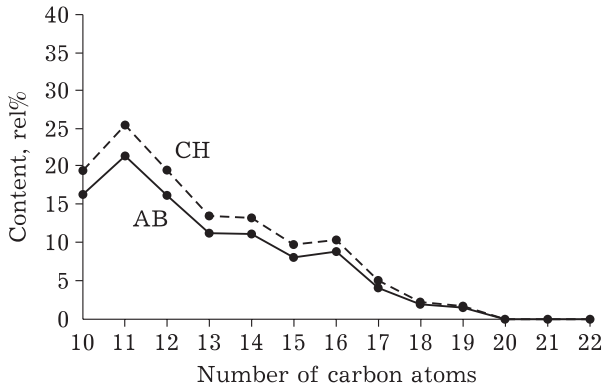

Fig. 4. Distribution of alkylbenzenes (AB) and cyclohexane homologues (CH) in diesel fuel.

(AB), trimethylalkylbenzenes (TMAB), cyclohexanes (CH) and hopanes extracted from the aqueous and mineral phases after contact with DF for 3 months is 4444.00 μg/dm^3 from water (1Water) and 666.39 μg/g from the mineral component (2BS), while after contact for 6 months the corresponding values are 9313.76 μg/dm^3 (3Water) and 1853.15 μg/g (4BS), respectively. So, an increase in the time of DF contact with water causes an increase in DF component content both in the aqueous and mineral phases of the system (Table 3). With an increase in the time of interaction with DF, the fraction of *n*-alkanes in the aqueous phase increases from 55 to 67 rel%, while for the mineral phase an increase in relatively smaller: from 68 to 72 rel%. With an increase in contact time, the percentage of isoprenoid alkanes also increases in the DF part that passed

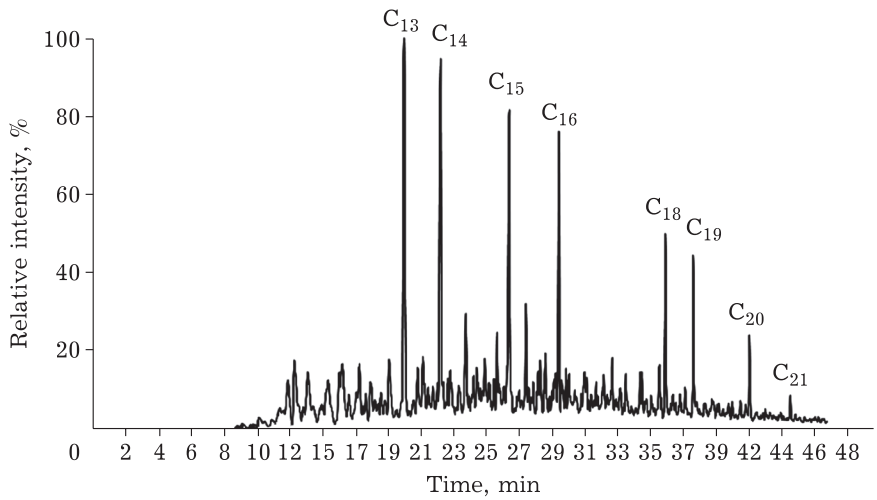

Fig. 5. Mass fragmentogram of trimethylalkylbenzenes (m/z 133) in diesel fuel.

into water (from 8.5 to 12.1 rel%), but in BS, in contrast to *n*-alkanes, the content of isoprenoid alkanes decreases from 20.3 to 14.5 rel%. An inverse situation is observed in the case of polycyclic aromatic hydrocarbons (PAH), formed by the sum of naphthalene, phenanthrene homologues and tetracyclic compounds, which are present in the extracts in substantially higher percentage than in DF: their amount decreases in the aqueous phase with time from 25 to 11 rel%, while in BS it increases from 2.4 to 7.4 rel%. This may be caused by the preferential sorption of PAH by the mineral component and the accumulation of these compounds, which are more polar in comparison with other compounds. The change of relative content of CH, AB and TMAB in the aqueous phase and in BS with an increase in the time of contact with DF does not exceed 1 %.

Hopanes appear in water (3Water) after 6 months and account for 0.01 rel% of the sum of all identified compounds. Hopanes were detected among the rock-sorbed components as early as after 3 months (2BS), but their percentage sharply decreased after 6 months (4BS) from 0.18 to 0.002 rel%.

The introduction of additional factor (mixing) into the system pollutant – water – mineral phase demonstrated a higher portion of DF components passing into the aqueous (5Water) and mineral (6BS) phases in comparison with the stationary system: 0.93 and 1.68 wt%, respectively. The ratio of major groups of compounds does not change: *n*-alkanes are prevailing. The fraction of AB is 2 rel%, TMAB – 3 rel%, CH fraction is somewhat higher in water – 8 rel%, while hopane content is higher in bottom sediments (0.006 rel%).

TABLE 2

Group composition of organic matter in the aqueous (μg/dm^3) and mineral (μg/g) phases

Hydrocarbons	Exposure for 3 months		Exposure for 6 months		Mixing		
	1Water	2BS	3Water	4BS	5Water	6BS	7Water
n-Alkanes	2474.12	450.48	6275.60	1341.36	8192.62	862.64	4542.18
i-Alkanes	377.03	135.38	1130.86	268.63	964.40	182.92	1336.22
CH	355.80	44.93	670.43	52.85	1111.24	95.59	500.42
n-AB	57.43	8.28	104.81	23.32	192.12	19.67	84.31
TMAB	82.61	10.38	147.86	29.81	253.68	28.59	100.80
PAH*	1097.01	15.74	983.28	137.15	2630.64	278.42	1032.52
Hopanes	0	1.20	0.93	0.03	0.23	0.06	0.60
Total	**4444.00**	**666.39**	**9313.76**	**1853.15**	**13344.94**	**1467.89**	**7597.06**

Notes. 1. i-Alkanes – isoprenoid alkanes; CH – cyclohexanes; AB – alkylbenzenes; TMAB – trimethylalkylbenzenes; PAH – polycyclic aromatic hydrocarbons (the sum of homologues of naphthalene, phenanthrene and tetracyclic aromatic hydrocarbons). 2. For designations of model systems, see Table 1.

Considering mixing as an approximate model of a river, which is a labile system, one may assume that pollutants sorbed previously on BS can be washed out of the BS. To model water flowage through a part of the bottom sediments polluted with DF (6DO), a portion of spring water (7Water) was passed to extract a part of the sorbed components.

It is shown that a fresh portion of water (7Water), washing the sorbed components of DF out of bottom sediments, contains a smaller amount of these components than water (5Water) after contact with DF (see Table 1 for experimental conditions). The total content of *n*-alkanes, AB, TMAB, CH and hopanes detected in this portion of water is 7597.06 μg/dm^3. The percent ratio of these components in the mixture is: *n*-alkanes / PAH / CH / AB / TMAB / hopanes = 59.8 : 13.6 : 6.6 : 1.1 : 1.3 : 0.01, which is almost the same as the fractions of most of these compounds in BS. Hopanes and PAH are exceptions. The fraction of the former in water extract (7Water) is 2 times higher, while the fraction of the latter is 1.4 times lower than those among the compounds sorbed by the mineral phase (6BS). This is in agreement with the data demonstrating a decrease in the relative content of hopanes in BS with an increase in experiment duration under stationary conditions. Desorption of the pentacyclic naphthenic hopane structures is likely to be activated with an increase in the time of water – sediment interaction, while the sorption and desorption of cyclic compounds with long alkyl chains (CH, AB, TMAB) in water – sediment system are in equilibrium, and desorption rate in the case of PAH is minimal.

Various oils and oil products obtained from them are usually compared using the coefficients based on the ratios of isoprenoid and normal alkanes, so that these ratios depend on the conditions of formation and transformation of initial oil-source rocks.

Calculation of these coefficients (Pr/Ph and K_i) for model systems showed differences in comparison with the values for DF (Table 3). While K_i for most of aqueous and mineral phases is lower than for DF, the ratio Pr / Ph is increased. The average molecular mass M_{av} and the ratio of low- to high-molecular homologues (LM / HM) for each group of identified compounds also change. Analysis of the individual composition of each of the identified groups of compounds showed higher average molecular mass of *n*-alkanes, AB and TMAB sorbed on BS after contact with DF for 3 months (2BS) in comparison with those present in the aqueous phase (1Water) and in DF itself,

TABLE 3

Calculated ratios for model systems

Calculated ratio	DF	Exposure for 3 months		Exposure for 6 months		Mixing		
		1Water	2BS	3Water	4BS	5Water	6BS	7Water
Pr/Ph	1.17	1.41	1.24	1.42	1.35	1.50	1.40	1.24
K_i	0.93	0.87	0.83	0.82	0.78	0.91	0.84	0.87
Average molecular mass, M_{av}:								
n-Alk	193	222	231	250	233	210	234	248
TMAB	215	199	227	210	213	192	208	232
CH	186	228	228	223	230	231	221	238
AB	201	203	217	200	200	194	213	237
Np	159	151	155	150	154	161	169	173
P	197	193	198	192	191	199	196	201
$\Sigma(C_{13}–C_{15})/\Sigma(C_{16}–C_{25})$:								
n-Alk	2.91	1.25	0.19	0.77	0.62	2.05	1.50	0.20
TMAB	2.71	3.09	0.51	1.75	1.44	4.45	1.97	0.43
CH	5.32	1.42	0.82	0.94	0.92	3.21	1.11	0.29
AB	5.1	1.91	0.79	2.10	1.93	3.25	1.10	0.29

Notes. 1. DF – diesel fuel; Pr – pristane; Ph – phytane; K_i = (Pr + Ph)/(*n*-C_{17} + *n*-C_{18}); i-Alkanes – isoprenoid alkanes; TMAB – trimethylalkylbenzenes; Np, P, CH – homologues of naphthalene, phenanthrene and cyclohexane, respectively; AB – alkylbenzenes. 2. For designations of model systems, see Table 1.

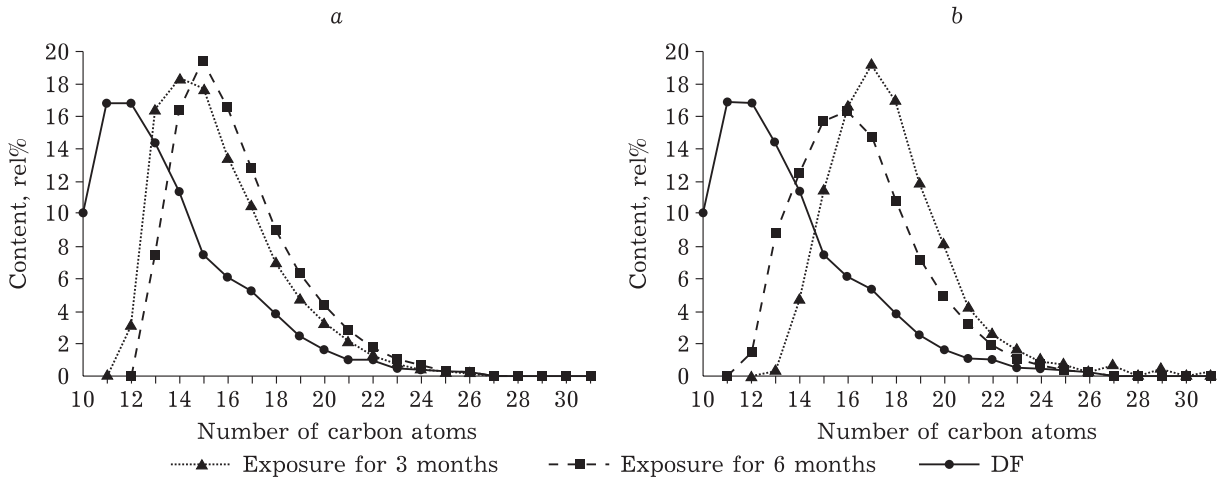

Fig. 6. Typical molecular mass distribution of *n*-alkanes after exposure for 3 and 6 months in the aqueous (*a*) and mineral (*b*) phases after contact with diesel fuel (DF) under stationary conditions.

that is, a change in their individual composition in the system diesel fuel – water – bottom sediments. After 6 months, the molecular mass distribution becomes aligned between these groups of compounds in the aqueous phase and in the solid. A typical shift of the maxima of *n*-alkanes towards higher molecular homologues is presented in Fig. 6 for the aqueous (*a*) and mineral (*b*) phases in comparison with DF.

The PAH compounds of aqueous and mineral phases were determined to contain naphthalene, phenanthrene and their methyl-, dimethyl-, trimethyl-substituted homologues, as well as fluoranthene and pyrene. Similarly to DF, the homologues of naphthalene are prevailing over other PAH. Their fraction in the aqueous phase is higher than in the mineral phase. Di-substituted homologues of naphthalene prevail in water, while tri-substituted ones dominate in BS in all experiments. With an increase in the time of contact with DF, among the homologues of naphthalene (in water and in BS) we observe an increase in the relative content of methylnaphthalenes, and non-substituted naphthalene appears. Among phenanthrenes, which are accumulated in BS to a higher extent than in water, methylphenanthrenes are present in the maximal concentration (in water and in BS), while the fraction of dimethylphenanthrenes and non-substituted phenanthrene is higher in BS. Similarly to the case of naphthalenes, the average molecular mass of phenanthrenes is lower in the aqueous phase than in BS. Quite contrary, it is insignificantly increased in BS. With an increase in the time of contact with DF, trimethyl-substituted compounds disappear in BS, the average molecular mass of phenanthrenes decreases, while the composition of phenanthrenes in the aqueous phase changes only insignificantly, and the average molecular mass approaches the value detected in BS.

Non-substituted and methyl-substituted tetracyclic arenes are present in the aqueous phase in approximately equal concentrations, while non-substituted species prevail in BS. Redistribution of TMAB in BS with time during experiment conducted under stationary conditions and in the experiment with mixing is demonstrated in Fig. 7. With an increase in the time of contact with DF up to 6 months, the amount of low-molecular C_{13}–C_{17} homologues increases, and sorption proceeds much faster in the system with mixing, and the distribution of homologues corresponds to their distribution in DF.

The ratio of the sum of low-molecular TMAB to the sum of high-molecular compounds ($\Sigma(C_{13}–C_{15})/\Sigma(C_{16}–C_{25})$) in BS approaches with time (6 months) to DF composition (Fig. 8). This may be due to the fact that high-molecular homologues are poorly soluble and are faster sorbed on BS, while low-molecular compounds are in the dissolved state in water and get sorbed on BS in the prolonged term.

A similar change of the ratios of low- to high-molecular compounds in BS was also detected for *n*-alkanes, CH, AB. No such change was observed for the aqueous part. So, in order to detect pollution of environmental objects, it is reasonable to study not only the total content of specific groups of hydrocarbons but also the ratios of low- to high-molecular compounds in them.

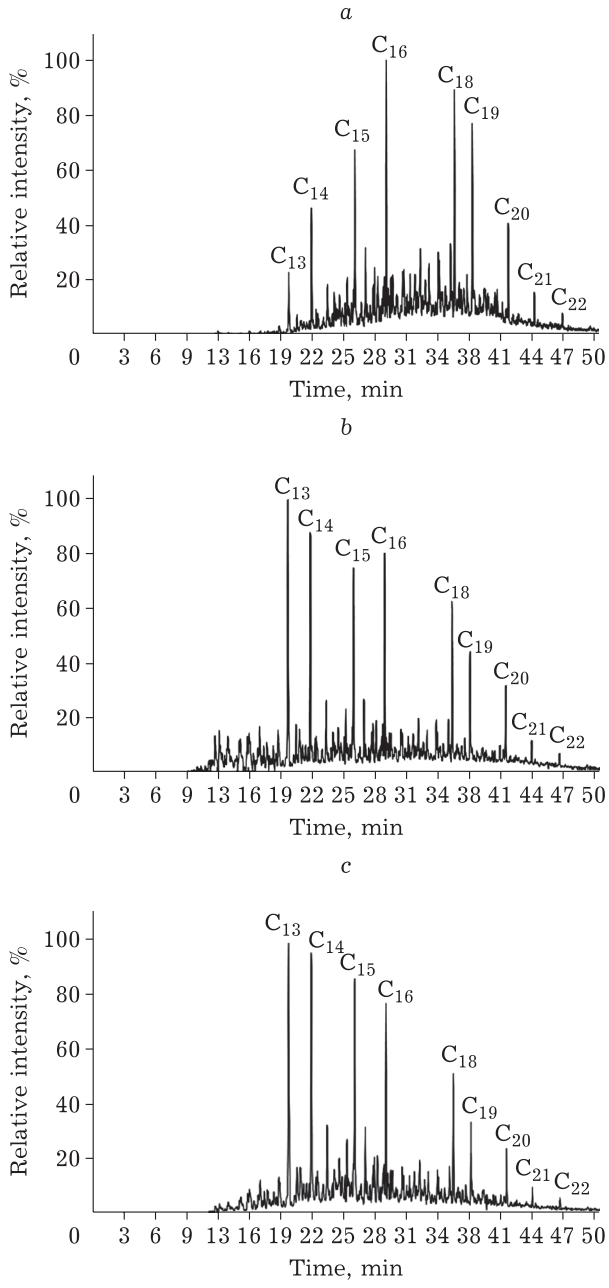

Fig. 7. Mass fragmentograms of trimethylalkylbenzenes (m/z 133) in the mineral phase of model systems: after exposure for 3 (*a*) and 6 months (*b*) under stationary conditions, and after experiment with mixing (*c*).

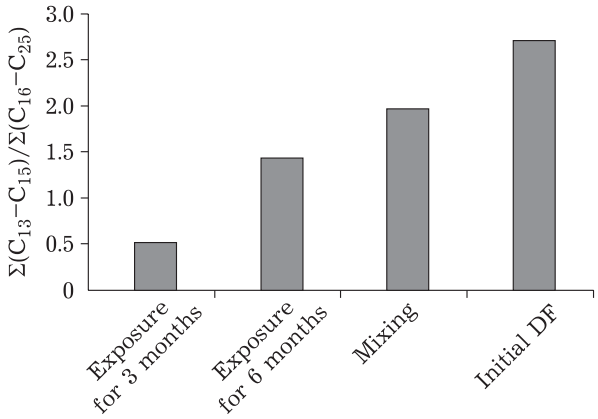

Fig. 8. Ratios of low- to high-molecular trimethylalkylbenzenes ($\Sigma(C_{13}–C_{15})/\Sigma(C_{16}–C_{25})$) in the samples of bottom sediments in model experiments (exposure for 3 and 6 months, mixing) and in initial diesel fuel (DF).

CONCLUSION

Thus, experiments modelling the distribution of organic compounds in the system diesel fuel – water – mineral phase have shown for the first time that *n*-alkanes, PAH, alkylbenzenes, trimethylalkylbenzenes, the homologues of cyclohexane and hopanes that are present in diesel fuel partially pass into the aqueous and mineral phases, so that the fraction of components sorbed in bottom sediments is higher than their content in the aqueous phase. Prevalence of *n*-alkanes, which is characteristic of diesel fuel, is conserved in water and in bottom sediments, though in higher relative content (up to 67 %) than in diesel fuel. The compounds that passed into water and got sorbed by bottom sediments, namely *n*-alkanes, alkylbenzenes, trimethylalkylbenzenes and homologues of cyclohexane are distinguished by higher average molecular mass in comparison with the compounds present in diesel fuel, while hopanes are characterised by a narrower set of homologues and the absence of compounds with carbon chains longer than C_{30}. The ratio Pr/Ph in diesel fuel increases by 15 rel% on average when passing into the aqueous and mineral phases, while K_i decreases by 8 rel% on average.

The results demonstrating the trend of changes in the composition of oil pollutants in the aquatic environment and in bottom sediments allow us to propose an algorithm of investigation, which includes the studies of parameters to evaluate the environmental state of surface water bodies and identification of the sources of their pollution.

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