Indicators for Oil Pollution Processes of Bottom Sediments in Natural Water Bodies According to Model Experiments

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Abstract

The paper reports experimental results for oil pollution of bottom sediments modelling in closed natural water bodies conditions. In order to identify possible oil pollution of bottom sediments, geochemical indicators, which identify the contribution of oil fluids into organic compounds of recent sediment were used in oil areas. Tri- and tetramethyl-substituted naphthalene and dibenzothiophene compounds, and also fluorene, dimethylbenzanthracene, chrysene, sterane, and hopane derivatives may serve as indicators of oil pollution of bottom sediments in natural water bodies.

Key words: hydrocarbons, natural water bodies, bottom sediments, oil pollution, gas chromatography-mass spectrometry

INTRODUCTION

The key feature of natural environmental systems in oil and gas production regions of Western Siberia is the presence of numerous water bodies with low rates of water exchange and the bogginess of large areas combined with objective risks of oil spillages. The enhanced recovery of oil and consequently, increased scales of its transportation, processing, and consumption leads to the Global environment degradation. Oil and its refinery products have an adverse effect on each and every link in the biological chain. Hydrocarbons (HC) are the major components of oil and oil products that are detected when environmental monitoring is carried out. However, it would not be correct to associate HC only with anthropogenic processes. This is due to the fact that some of them do not only migrate from concentration sites, *i.e.* oil and gas fields, but are also synthesized by aqueous and terrestrial organisms, as well as are transformed from organic matter (OM) of soils and rocks upon its decomposition. As a rule, standard techniques that are used to assess pollu-tion enable to find the content of oil products in total [1–3] but not to determine their structure and source, and also to reliably reveal the technogenic or natural genesis of HC detected. The complexity of the research on bottom sediments (BS) polluted by oil is linked to the fact that they contain native HC animal and plant origin, which are similar to oil components (fats, waxes, resins, steroids, and terpenoids). For the purpose of environmental monitoring, it is required to identify the technogenic component in the total amount of OM [4].

To achieve this goal the modern effective analytical method such as chromatomass spectrometry should be used (GC-MS). This approach enables to determine not only the total amount of HC but also identify organic compounds, their isomeric and homologic composition, and to detect more reliably the presence of anthropogenic oil pollution.

RESEARCH MATERIALS AND METHODS

In order to carry out the model experiment, oil from the Fedorovskiy field (Khanty-Mansiysk Autonomous District) and the bottom sediment of

Tomskoye Lake located outside the area of direct anthropogenic impact were sampled. Two beakers with a capacity of 800 mL were filled with 50 g of the sediment, 500 mL of water, and 1 mL of oil. The samples were left for 3 and 6 months, respectively. Conditions of each performed experiment were maximally close to natural. After the end of the experiment, the sediment was separated from water and dried. The isolation and separation of organic components, and also the analysis of the investigated compounds were performed according to the common technique.

The isolation of bituminous components from rocks was carried out with a 7 % methanol solution in chloroform with a Tecator Coxtec HT system [5]. Hydrocarbons, and also dibenzothiophene (DBT) and dibenzofuran (DBF) compounds were partitioned by adsorption chromatography using a IV activity grade alumina column. Hexane was used as a mobile phase. The detailed analysis of the hexane fraction containing HC, DBT, and DBF was carried out using a DFS ThermoElectron high resolution mass-spectrometer in the Tomsk Regional Centre for Collective Usage, TSC RAS. The gas chromatograph is equipped with a "ThermoScientific" quartz capillary column with an inner diameter of 0.25 mm, a length of 30 m, and a film thickness of 0.25 μm, TR-5MS stationary phase and helium as carrier gas. Evaporator and interface temperature is 250 °C. Thermostat heating program is as follows: t_{init} = 80 °C, an isotherm for 2 min, then heating at a rate of 4 °C/min to t_{max} of 300 °C. The ionisation method is electron impact, ionizing electrons energy of 70 eV; ionization chamber temperature of 250 °C; the range of recorded masses of 50−500 amu, and a spectrum sweep time of 1 s. Chromatograms were recorded according to the total ion current (TIC) and characteristic fragment ion (SIM). The content of individual groups of HC was calculated according to the total area of individual peaks considering adjustment factors determined for characteristic ions for each group of compounds: di- (m/z 128, 142, 156, 170, and 184), tri- (m/z 178, 192, 206, and 220), tetra-(m/z 202, 216, 230, and 242) and pentacyclic (m/z 252 and 266), and also aromatic HC, cadalene, and retene (m/z 198 and 234, correspondingly), dibenzothiophene compounds (m/z 184 and 198) and dibenzofuran (m/z 168 and 182), for fragment ions of tri-, tetra - and pentacyclic terpane (m/z 191), bicyclic tarpane and secohopane (m/z 123), alkane (m/z 57), alkylcyclohexane (m/z 83 and 97), sterane (m/z 217 and 218), n-alkylbenzene, alkyltoluene, and arylisoprenoid (m/z 92, 105 and 133, correspondingly) species [6].

In order to consider the effect of the specifics of mass-spectral equipment on the intensity of fragment ions and scale all peaks of mass-fragmentograms with chromatograms according to the total ion current for each group of compounds, adjustment factors were determined on the basis of the research on pure mixtures of the latter. Adjustment factors are a ratio of the area of peaks according to the total ion current to peak areas of fragment ions for this group of compounds. To determine the relative content of a specific compound, the area of its peak according to the characteristic fragment ion was multiplied onto the adjustment factor and the percentage of individual compound was calculated in the total amount of all determined moieties.

RESULTS AND DISCUSSION

The distribution of n-alkanes of Fedorovskiy field oil is unimodal. The distribution maximum in a series of $C_{11}-C_{33}$ falls on C_{17} (Fig. 1, a).

Among aromatic HC, bicyclic structures presented naphthalene and biphenyl compounds are prevailing. Dimethyl substituted naphthalene derivatives are prevalent among the latter. Triaromatic hydrocarbon compounds are present as phenanthrene, its methyl-, dimethyl-, and trimethyl-substituted homologues, and also retene. Monoaromatic compounds are presented by unsubstituted and methyl-substuted alkylbenzene derivatives and their methyl homologues (n-AB and MAB, respectively). Fluoranthene, pyrene, benzanthracene, chrysene, and their methyl- and dimethyl-substituted homologues were detected among tetraaromatic HC. There are no pentaaromatic HC. Sterane derivatives are mainly presented by compounds with regular structures, such as cholestane (C_{27}) species. Terpanes are presented by tri- and pentacyclic compounds. There are no di- and tetracyclic terpane compounds. Among hopane compounds, C_{30} homologue, 17α(H)-trisnorhopane, is prevalent; C_{27} (Tm) compound is prevailing over 18α(H)-trisnorhopane. There are heterocyclic compounds, such as DBT and DBF, and also their methyl- and dimethyl-substituted homologues (Table 1).

The hydrocarbon composition of the initial BS of Tomskoye Lake (deposit 1) is characterised by the presence of alkanes in $C_{14}-C_{33}$ series with the prevalence of odd homologues over even ones.

Moreover, the molecular mass distribution maximum falls on C_{23} (see Fig. 1, b). Among aromatic HC, mono, di-, tri-, and tetraarenes were
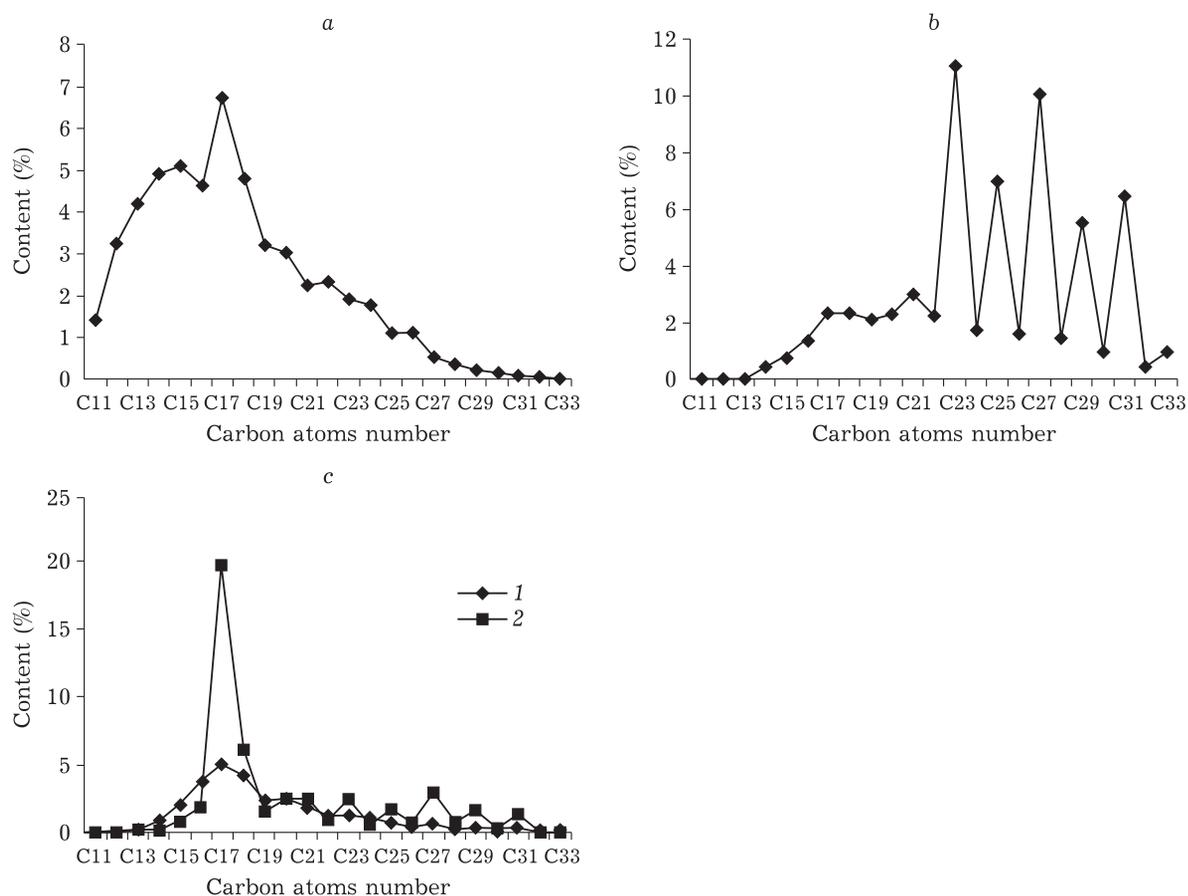
Fig. 1. Molecular mass distribution of *n*-alkanes: *a* − Fedorovskoe field oil; *b* − initial BS of Tomskoye Lake, *c* − in BS after 3 (*1*) and 6 (*2*) months.

detected; monoaromatic hydrocarbons are prevailing among them (see Table 1).

Heterocyclic hydrocarbons are presented by DBT and DBF, and also by their methyl- and dimethyl-substituted homologues. Steranes and hopanes were not detected. There are no fluorine derivatives and their methyl-substituted homologues, methyl derivatives of benzanthra-

TABLE 1

Content of individual groups of hydrocarbons in the investigated samples, % of the total amount of identified ones according to GC-MS

| Components	Fedorovskoe oil field	Deposit 1, (Tomskoye Lake initial BS)	Deposit 2, (BS in 3 months)	Deposit 2, (BS in 6 months)
Alkanes	53.11	64.41	29.43	49.00
Monoaromatic HC	13.23	14.50	21.97	20.65
Biphenyl species	0.20	1.12	0	0
Naphthalene derivatives	17.26	5.50	20.90	1.89
Triaromatic HC	7.26	7.58	12.51	13.71
Fluorene compounds	1.72	0	3.79	0.30
Fluoranthene + pyrene	0.64	1.02	0.66	2.55
Benzanthracene + chrysene	0.31	0.75	0.17	0.56
DBT	3.03	0.91	4.83	4.19
DBF	1.51	1.88	3.24	1.74
Hopane homologues	0.54	0	0.79	1.58
Sterane compounds	0.90	0	1.14	2.55
Retene and cadalene	0.29	2.33	0.56	1.28
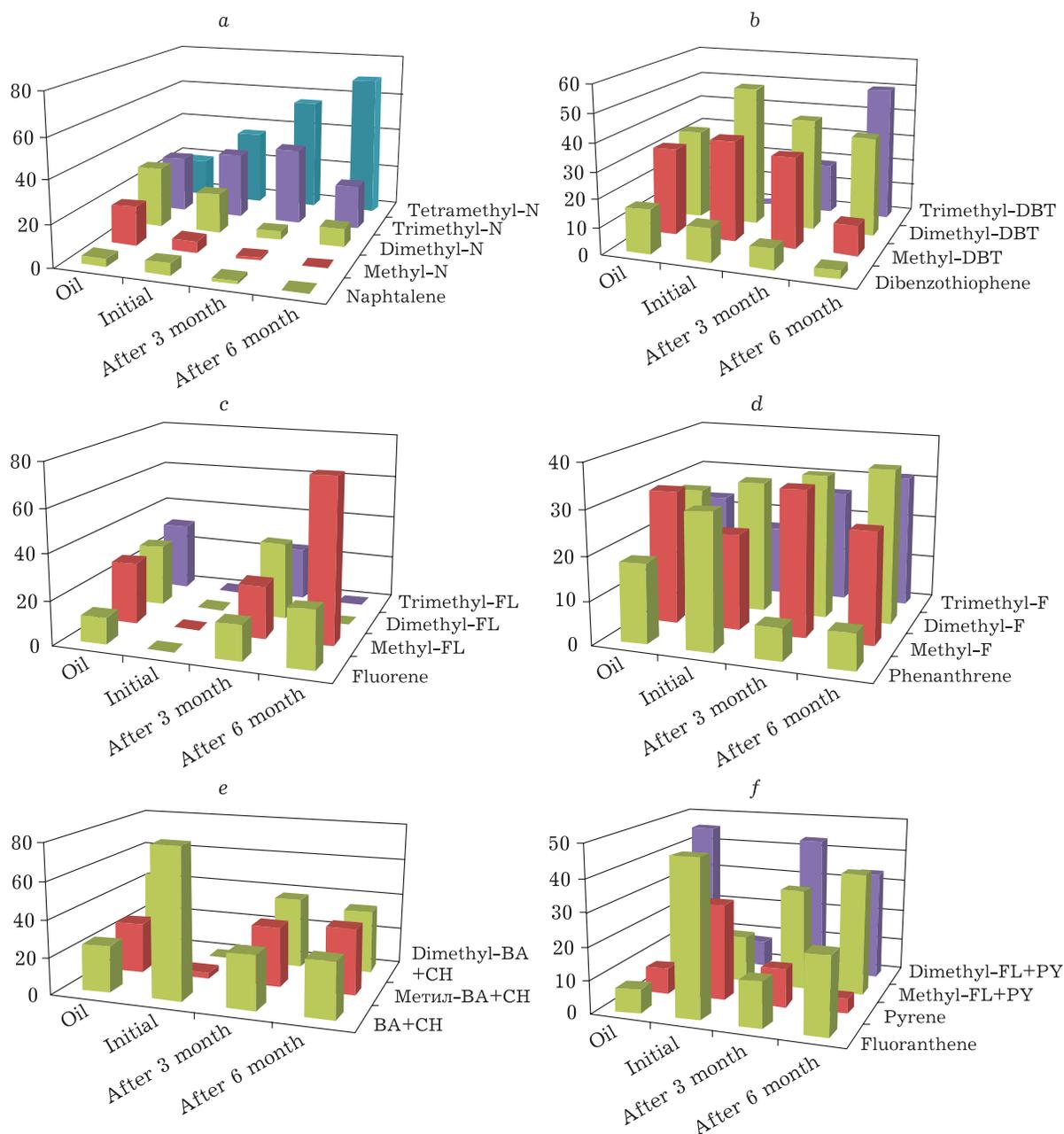
Fig. 2. Change in the composition of individual groups of hydrocarbon compounds in the investigated objects: *a* − homologues of naphtalene (N), *b* − dibenzothiophene (DBT), *c* − fluorene (FL), *d* − phenanthrene (PHN), *e* − benzanthracene (BA) and chrysene (CH), *f* − fluoranthene and pyrene.

cene and chrysene, and also trimethyldibenzo-
thiophene.

    As demonstrated by the research on the hy-
drocarbon composition of bituminous components
of BS of lake water bodies and oil field located
near them [7], alkane composition and distribu-
tion cannot be the indicator when the oil back-
ground is assessed, as aliphatic compounds are
exposed to decomposition upon biodegradation
faster than aromatic HC. At the same time, aro-
matic compounds that are found both in oil and

sediments of lake water bodies may be used as
pollution indicators. The distinguishing feature of
these species consists in the fact that they are
characterised by better solubility in water and
the greater resistance towards oxidation com-
pared to alkanes.

    Unlike the initial deposit, molecular mass dis-
tribution maxima in compositions of model depos-
its (2 and 3) fall on C_{17}, just as in oil (see Fig. 1, c).
The fractions of monoaromatic HC for oil and the
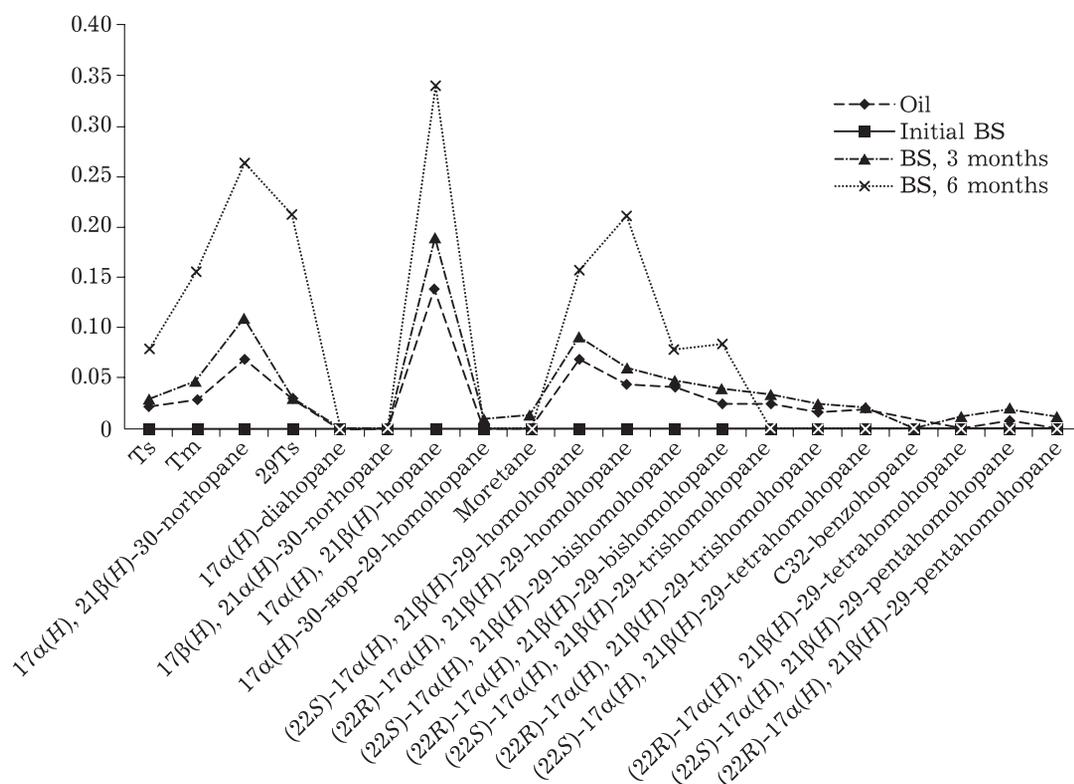initial BS are comparable (13.23 and 14.50 %),

Fig. 3. Distribution of homologues of hopane (m/z 191) in research samples.

whereas their content in model deposits is increased by 1.5 times.

Biaromatic structures of model **BS** are presented by naphthalene and fluorene derivatives, and also by compounds with sulphur and oxygen atoms, i.e. DBT and DBF. Among naphthalene homologues, there is a significant increase in the quantity of tri- and tetramethyl derivatives. The common portion of these species is higher than 90 % of the total content of all identified homologues (Fig. 2, *a*): after 3 and 6 months − 93.0 and 90.94 %, respectively. Herewith, the content of less substituted methylnaphthalene derivatives is drastically reduced. That may be due to the decomposition of low molecular mass aromatic HC of the native soil microflora. The DBT homologues distribution pattern is also characterised by an increase in the total fraction of di- and trimethyl-substituted derivatives. For example, the latter (in 3 months) is 59.62 % in the model deposit being equal to 86.48 % (after 6 months) in deposit 3 (see Fig. 2, *b*).

There is also a substantial increase in the amount of dimethyl-DBF (about 81 %) in the model sediment sampled after 3 months. As the formation of oxygenated structures is probable

as a result of the secondary biotransformation of oil molecules in aqueous media, the data on the content of such compounds as indicators of anthropogenic pollution should be used with caution [8].

Unlike the initial sediment, model sediments contain fluorene derivatives (see Fig. 2, *c*), which indicates the oil nature of these compounds in BS. Fluorene derivatives and their methyl-, dimethyl-, and trisubstituted homologues are presented in sediment 2 only. On the contrary, there are no dimethyl and trimethyl compounds in sediment 3 (in 6 months).

The composition of triaromatic compounds is characterised by a reduction in the content of unsubstituted phenanthrene as low as 7−8 % against 30.29 % in the initial BS (see Fig. 2, *d*). Furthermore, there is an increase in the fraction of dimethyl- and trimethyl- substituted triarenes. Dimethylbenzanthracene and chrysen derivatives that are absent in the initial BS, appear in sediments 2 and 3 (see. Fig. 2, *f*). Unlike the initial sediment, dimethyl-substituted fluoranthene and pyrene derivatives in model sediments, are present in quantities comparable with oil ones (see Fig. 2, *f*).

Sterane and hopane compounds that are close to the introduced oil according to composition are present in the model sediments only (Fig. 3).

CONCLUSION

Thus, the experiments performed on modelling oil pollution processes of bottom sediments of closed natural water bodies have made it possible to reveal geochemical indicators for the contribution of oil fluids into the organic matter of recent sedimentation, and also to identify a probable oil background in polluted territories. Tri- and tetra-methyl- substituted naphthalene and dibenzo-thiophene compounds, and also fluorene, dimethyl benzanthracene and chrysene derivatives may be indicators of oil pollution. That may also be proven by the presence of sterane and hopane compounds in sediments of natural water bodies.

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