Biogenic Hydrocarbons and Their Effect on Oil Pollution Estimates of the Sea of Azov

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Abstract—The results of studies on the efficiency of identification criteria for the origin of hydrocarbons in the ecosystem of the Sea of Azov. Their amount in the cells of major planktonic and benthic organisms of the Sea of Azov. The share of biogenic hydrocarbons in their total amount determined by monitoring the oil pollution of the sea is also evaluated.

Keywords: ecology, monitoring, aquatic ecosystem, oil pollution, biogenic hydrocarbons.

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INTRODUCTION

Hydrocarbons (HC) are the main components of oil and oil products. They enter the Sea of Azov during oil spills and oil-containing wastewater discharge. However, HC present in the sea can originate not only from human activity but have natural origin. The hydrocarbons with natural origin are commonly referred to as natural or biogenic hydrocarbons.

The diversity of the composition of biogenic HC is due to the wide variety of natural biochemical processes. Studies of the bituminosity of sediments in the Pacific and Indian oceans and the Caspian and Bering seas have shown that the main role in the formation of bitumens in nonpolluted regions belong to planktonic organisms. In coastal regions, the amount of bituminous substances increases, which is in good agreement with an increase hundreds times and more in phytoplankton production near shores [3].

The amount of HC in the sea can increase in the places of accumulation of algae or in the periods of their blooming; this may result in imitation of seawater pollution by oil and oil products [8]. Therefore, the issues of concentration and distribution of natural HC are of interest not only in the solution of the complex problem of studying organic compounds in natural waters, but also in the search for criteria for taking into account their effect in assessing water pollution by oil hydrocarbons.

The effect of biogenic HC on oil pollution of water bodies depends on the biological production of the water body and the volume of oil products that are discharged into it or have accumulated in the elements of aquatic ecosystems. In the recent years, this question has gained in importance for the Sea of Azov because of the growing biomass of phytoplankton and bacteria, which are assumed to accumulate the majority of biogenic HC.

Oil pollution is commonly evaluated by the total concentration of HC of different classes and resinous substances. Considering that oil HC are in principle of natural origin as well, the terms oil and biogenic used in this paper in the former case imply HC in the composition of crude oil, which has formed thousands of years ago, and in the latter case, HC occurring in water bodies as the result of vital activity and postmortem degradation of aquatic organisms.

HC is difficult to differentiate in terms of their origin, since individual HC are components of both different oil samples and planktonic and benthic organisms and other aquatic animals.

However, there still exists difference between “biogenic” and “oil” HC:

- oil contains approximately equal amounts of HC with even and odd numbers of C atoms; aquatic organisms and higher aquatic plants mostly contain HC with an odd number of C atoms, primarily, C_{15}, C_{17}, C_{19} and C_{27}, C_{29}, C_{31};
- oil contains a large amount of aromatic HC; organisms contain no homological series of mono-, di-, tri-, and tetramethylbenzol and mono-, di-, tri-, and tetramethylnaphthalenes;
- oil contains some naphtheno-aromatic HC and heterocompounds, containing S, N, O, metals, and heavy asphaltelic substances, which do not occur in organisms.

Based on these distinctions, some authors suggest criteria allowing one to establish the presence of biogenic HC in the total sum of detected HC [4]:

- pristane to phytane ratio Pr/Ph;
- heptadecane to pristane ratio C_{17}/Pr;
- pentadecane to hexadecane ratio C_{15}/C_{16}.

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the ratio of peak areas of separated compounds $S_{sep}$ to the “hump” area $S_{hump}$; in the case of separation of a complex multicomponent mixture, especially, transformed petroleum HC, the so-called unresolved background envelope will form;

the ratio of HC with even and odd numbers of C atoms (carbon petroleum index (CPI)).

The CPI criterion is calculated as

$$\text{CPI} = \frac{\sum C_{25-31} - 1}{\sum C_{25-31} + \sum C_{26-32} + \sum C_{24-30}},$$

where $C_{24-32}$ are the concentrations of HC with appropriate number of C atoms.

MATERIALS AND METHODS

The share of biogenic HC in oil pollution of the Sea of Azov was estimated by using the results of HC determination and data on hydrobiological characteristics collected during many-year comprehensive environmental monitoring 1985–2006 carried out in AzRIF in different vegetation periods.

Petroleum HC were determined by a procedure based on the simultaneous photometry of isolated HC in UV and IR ranges, allowing both the paraffin-naphthene and aromatic fractions of HC to be taken into account, irrespective of their ratio in the sample under examination [9]. The simultaneous photometry in IR and UV ranges allows one to radically reduce the determination errors appearing due to the disagreement between the qualitative composition of the recorded HC and those used for constructing calibration curves. The procedure involves HC extraction by carbon tetrachloride from water and successively by acetone and chloroform from bottom sediments (BS) with chromatographic separation from interfering substances in a thin layer of aluminum oxide in the solvent system hexane : carbon tetrachloride : acetic acid.

The identification criteria for HC origin were constructed with the help of chromatograms obtained by high-performance gas-liquid chromatography with flame-ionization detection.

RESULTS AND DISCUSSION

More than 20-year experience in applying the above criteria in AzRIF shows that the most effective criterion is CPI [12]. The criteria $C_{15}/C_{16}$, $C_{17}/Pr$, and $Pr/Ph$ sometimes give ambiguous responses because of the high volatility and relatively rapid degradation of those HC. Again, the scatter of CPI criterion values for bottom sediments was found to be much wider than for aquatic environment. The $S_{sep}/S_{hump}$ ratio is an informative criterion for water bodies with chronic pollution by petroleum products, especially for BS; it is not considered in this study.

The use of CPI criterion to identify the origin of HC isolated from water and BS of the Kurchanskii Liman, the southeastern part of the sea, which is subject to different degrees of petroleum pollution, confirmed the efficiency of the method [5]. The chromatograms of HC isolated from water and bottom sediments of the sea and limans demonstrated considerable distinctions.

The composition of $n$-alkanes from water of Kurchanskii Liman, where high HC concentrations were recorded (>2 MAC), was found to be considerably dominated by HC in the high-molecular range with odd number of carbon atoms $C_{23}, C_{25}, C_{27}, C_{29}$ (Fig. 1a).

The presence of these compounds clearly correlates with the composition of HC isolated from Potanogeton perfoliatus alga, which is widespread in limans (Fig. 1b).

HC with odd number of C atoms ($C_{23}, C_{25}, C_{27}, C_{29}$, and $C_{31}$) dominate in the composition of $n$-paraffins isolated from Potanogeton perfoliatus alga. The oddness index CPI for paraffins from algae is very high value of 15.1.

The values of the oddness index CPI for HC from BS of Kubanske limans were also high (from 1.7 to 5.5 with a mean of 4.0), suggesting the presence of HC of biogenic origin in appreciable amounts (Fig. 1c).

Additionally, the maximal concentrations of $n$-paraffins in most samples were recorded for hydrocarbons $C_{27}$, $C_{29}$, and $C_{31}$, as is also typical of HC with biogenic origin, when one or more alkanes are present in concentrations far in excess of all other compounds. Hopane (a fragment of HC of many phytoplankton species) was also recorded in most samples (a peak between $C_{28}$ and $C_{29}$). The biogenic origin of HC is also confirmed by the absence in chromatograms of a “hump” of nonseparated substances (Fig. 1c).

At the same time, almost all chromatograms of hydrocarbon fractions isolated from water and BS of the southeastern part of the sea contain a hump (with different size) of nonseparated substances, containing naphthene-aromatic compounds (Figs. 1d and 1e).

The mean value of CPI for water of the southeastern part of the sea was far below that for Kurchanskii Liman—with the range of 0.34–0.94 and the average of 0.61.

The presence in the chromatogram of a hump of nonseparated naphthene-aromatic compounds and the predominance of $C_{20}$, $C_{21}$, $C_{22}$ in the composition of hydrocarbons also suggests the considerable predominance of petroleum HC in the mixture of biogenic and petroleum HC in water of the region (Fig. 1d).

The values of the oddness index CPI for the composition of paraffins isolated from BS of the southeastern part of the sea varied from 0.8 to 2.6 with a mean of 1.5, which is much less (~ 3 times) than that in BS of the Kurchanskii Liman.