

HYDROCARBONS IN SURFACE SEDIMENTS FROM THE NORTHERN AEGEAN SEA

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Abstract

Aliphatic and polycyclic aromatic hydrocarbon (PAH) concentrations were determined in 15 superficial sediments collected from northern Aegean Sea, during 1996. The values found varied from 10.5 to 57.3 $\mu\text{g/g}$ for total aliphatic hydrocarbons and from 31.0 to 176.3 ng/g for total PAH. Several diagnostic criteria used to identify the origin of the hydrocarbons indicated in most cases a major contribution of petroleum inputs.

Key-words: sediments, PAH, Aegean Sea

Introduction

In the last decades the development of sophisticated analytical techniques such as gas chromatography/mass spectrometry has enabled the identification of organic compounds which are present at very low concentrations and in complex mixtures in the marine environment. In this context, the analysis of the hydrocarbons has become an issue of major importance for marine research. The origin of hydrocarbons in sediments can be either natural or anthropogenic. Natural hydrocarbons derive mainly from terrestrial plants and marine algae, while the main sources of the man-made hydrocarbons are the various petroleum inputs into the ocean, the industrial discharges and the atmospheric fallout [1]. In this work, the study of aliphatic and aromatic hydrocarbons in surface sediments of northern Aegean Sea was performed. In fact, no other references concerning hydrocarbon contents in the sediments of this area are available in the literature. Therefore, this study provides baseline information for hydrocarbon distribution and origin in the sediments of Aegean Sea.

Experimental details

Surface sediment samples (the upper 2 cm) were collected from 15 stations in the northern Aegean during October 1996 using a Smith-McIntyre type grab sampler. The sampling locations are shown in Fig. 1.

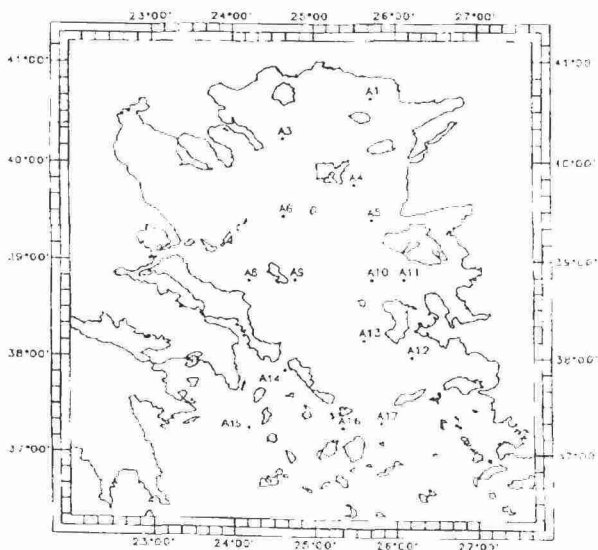


Fig. 1. The sampling locations of surface sediments from the northern Aegean Sea.

The analysis was performed according the methods suggested by IOC [2]. After oven drying at 40°C, the sediment samples were pulverized, spiked with internal standards (androstane and pyrene-D10) and extracted in a Soxhlet apparatus for 24 h with a mixture of dichloromethane-methanol 2:1. The extract was saponified with a methanolic solution of KOH and the hydrocarbons were extracted with hexane. The clean-up and fractionation step was performed by silica gel and alumina column chromatography and resulted in the collection of two hydrocarbon fractions. The first fraction contained the aliphatic compounds and the second the aromatic ones. The final determination was carried out by gas chromatography-mass spectrometry (Hewlett Packard 6890 GC-MS).

Results and discussion.

The results of the hydrocarbon analysis and some other compositional parameters are given in Table 1. The total hydrocarbon concen-

Table 1. Organic carbon content (Corg), concentrations of total hydrocarbons (THC), unresolved complex mixture (UCM), total aliphatic hydrocarbons (ALIPH), total n-alkanes (n-ALK) and polycyclic aromatic hydrocarbons (PAH), the ratio unresolved/resolved compounds (U/R), the carbon preference index (CPI) calculated from C23 to C34 and the ratio pristane/phytane (Pr/Ph) in the sediments of the Aegean Sea (See Fig. 1 for station location).

Stations	Depth (m)	Corg (%)	THC ($\mu\text{g/g}$)	UCM ($\mu\text{g/g}$)	ALIPH ($\mu\text{g/g}$)	n-ALK ($\mu\text{g/g}$)	PAH (ng/g)	U/R	CPI	Pr/Ph
A1	45	0.40	43.8	37.3	43.7	4.7	147.8	5.8	1.5	0.6
A3	814	0.75	57.5	45.3	57.3	8.6	159.8	3.7	1.9	0.8
A4	93	0.27	13.8	12.0	13.8	1.2	34.1	7.1	1.8	0.7
A5	300	0.75	32.3	26.2	32.2	4.3	155.7	4.4	2.5	0.9
A6	358	0.62	34.9	28.7	34.8	4.3	149.0	4.8	3.1	0.7
A8	365	0.30	33.5	27.1	33.4	4.2	145.2	4.3	1.7	0.8
A9	254	0.44	29.5	23.5	29.4	4.2	111.8	4.0	2.2	0.5
A10	375	0.56	10.7	7.6	10.6	2.3	176.3	2.6	4.5	1.0
A11	284	0.63	14.5	12.5	14.5	1.3	56.8	6.4	2.5	0.3
A12	770	0.78	20.0	15.8	19.9	3.2	118.7	3.7	2.4	0.6
A13	427	0.39	31.6	24.9	31.5	4.2	119.7	3.8	2.0	0.8
A14	168	0.22	12.1	10.5	12.1	1.1	30.9	6.9	1.5	0.5
A15	476	0.52	12.4	10.3	12.4	1.3	47.9	5.2	2.2	0.8
A16	106	0.40	13.7	11.4	13.7	1.4	43.0	5.1	1.9	0.9
A17	325	0.39	18.2	15.2	18.1	1.9	52.5	5.3	2.4	0.6

trations found ranged between 10.7 and 57.5 $\mu\text{g/g}$ dry sediment (average 25.6 $\mu\text{g/g}$). The highest concentrations were observed at stations A1 and A3, while the lowest values occur at stations A10, A14, A15. These concentrations are generally higher than those reported in unpolluted Mediterranean open sea sediments (<10 $\mu\text{g/g}$) [3].

Aliphatic hydrocarbons. Total aliphatic hydrocarbon concentrations varied from 10.6 to 57.3 $\mu\text{g/g}$ dry weight and accounted for the 98.4-99.8% of the total hydrocarbons. Fig. 2 shows their distribution in the study area. In all samples the gas chromatographic traces of the aliphatic fraction were characterized by two general features: resolved compounds and a unimodal hump corresponding to a mixture of unresolved compounds (UCM) with 15-34 carbon atoms (Fig. 3). The UCM is considered as an elaborate mixture of branched and cyclic hydrocarbons and it is generally well correlated with degraded or weathered petroleum residues [4,5]. In the sediments analyzed the UCM was always the major component representing 72.3-87.4% of the total aliphatics. The ratio unresolved/resolved compounds (U/R) is widely used to identify the origin of the hydrocarbons in marine sediments. Values U/R > 4 are considered as evidence of petroleum residues [6].

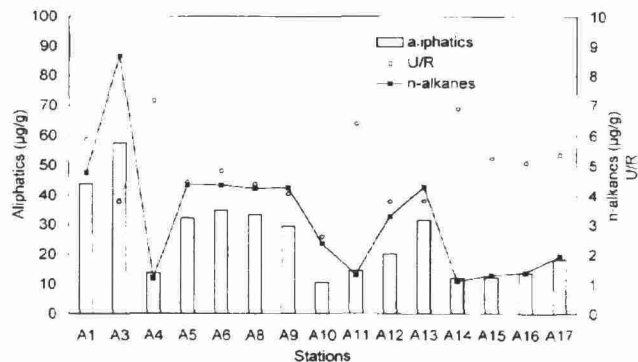


Fig. 2. Distribution of total aliphatic hydrocarbons, n-alkanes and the U/R ratio in the sediments of the Aegean Sea.