

Surface Active Substances in the Eastern Mediterranean*

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During the EGAMES expedition in the Eastern Mediterranean in July 1993, surface active substances (SAS) were determined in seawater samples from the Ionian and Aegean Seas using a.c. voltammetry. Measurements were made on unfiltered samples on board of the excursion ship and concentrations of SAS were estimated using a calibration graph prepared with an arbitrary standard surfactant, Triton-X-100. The concentrations of SAS in the Aegean Sea ranged from 0.07 to 0.21 mg/L in surface waters (0.5 m), and from 0.07 to 0.35 mg/L at a 5 m depth. In the Ionean Sea, samples were collected only at a 0.5 m depth and the concentrations of SAS were from 0.08 to 0.18 mg/L. Qualitatively, more hydrophobic organic material was present in the Aegean Sea, while in the more turbulent waters of the Eastern Mediterranean and in the open waters of the Ionian Sea more hydrophilic and/or conditionally hydrophobic substances were present.

INTRODUCTION

The Eastern Mediterranean Sea lies east of the straits of Sicily and is made up of the Ionian and Levantine basins and the adjacent Adriatic and Aegean Seas. The Eastern Mediterranean is an open, but isolated, basin of interest as a laboratory basin for global ocean general circulation processes, including oceanic climate dynamical processes. The recent international collaborative program POEM (Physical Oceanography of the Eastern Mediter-

* Dedicated to Marko Branica on the occasion of his 65th birthday.

anean) has provided new and important information about the water mass properties and general circulation of the basin.^{1,2}

In July 1993, the EGAMES (Evasion of gases from the Mediterranean Sea) expedition was organized to study the fluxes of climatic relevant gases to the atmosphere in the Ionian and Aegean Seas.³ A number of physical and chemical parameters necessary for the calculation of these fluxes were measured. Within the framework of the EGAMES cruise, organic surface active substances (SAS) were measured on board by an electrochemical method in seawater samples taken at 0.5 and 5 m depths. Much of the naturally occurring organic matter in the sea are surface active, *i.e.* consisting of structural groups that have very little attraction for the water phase (hydrophobic), together with groups that have strong attraction for water (hydrophilic groups).^{4,5} Surface active substances modify the structure and properties of natural phase boundaries and affect their exchange properties.⁶⁻⁸ Electrochemical study of surface active substances in the sea is based on measurement of their adsorption on the mercury electrode surface. Two electrochemical methods have been widely used in the research on organic matter in the Adriatic Sea: the first is based on measurement of adsorption effects on the suppression of polarographic maxima of oxygen and Hg(II) ions added to the sample,^{9,10} and the second is based on the measurement of the capacity current using the Kalousek device¹¹ and/or a.c. polarography.¹² The capacity current measurements are very sensitive to hydrophobic molecules. The adsorption effect at the mercury electrode of saturated fatty acids of different chain lengths is proportional to the logarithmic value of their octanol-water partition coefficient ($\log K_{ow}$).¹³ Organic surface active substances in natural seawater samples can be characterized by comparing the shape and intensity of the electrochemical signal to those of selected representative model substances. A number of compounds such as proteins, carbohydrates, lipids and humic substances, as well as various synthetic surfactants have been studied.¹⁴

Dissolved organic carbon, including the colloidal fraction and comprising a variety of organic compounds of different physico-chemical properties, is important to both the supply of nutrients for primary production in surface waters of the oceans, and to the global cycle of organic carbon.¹⁵⁻¹⁷ To the best of our knowledge, there are no published data on the content and chemical composition of organic matter in the Ionian and Aegean Seas. Here, we report on the determination of organic surface active substances in surface waters of the Ionian and Aegean Seas in July 1993 and compare our results to the relevant data for the Adriatic Sea.

METHODS

Seawater samples were collected with a Pyrex/Teflon sampler¹⁸ at 42 stations in the Ionian and Aegean Seas (Figure 1) from July 4 to July 14,

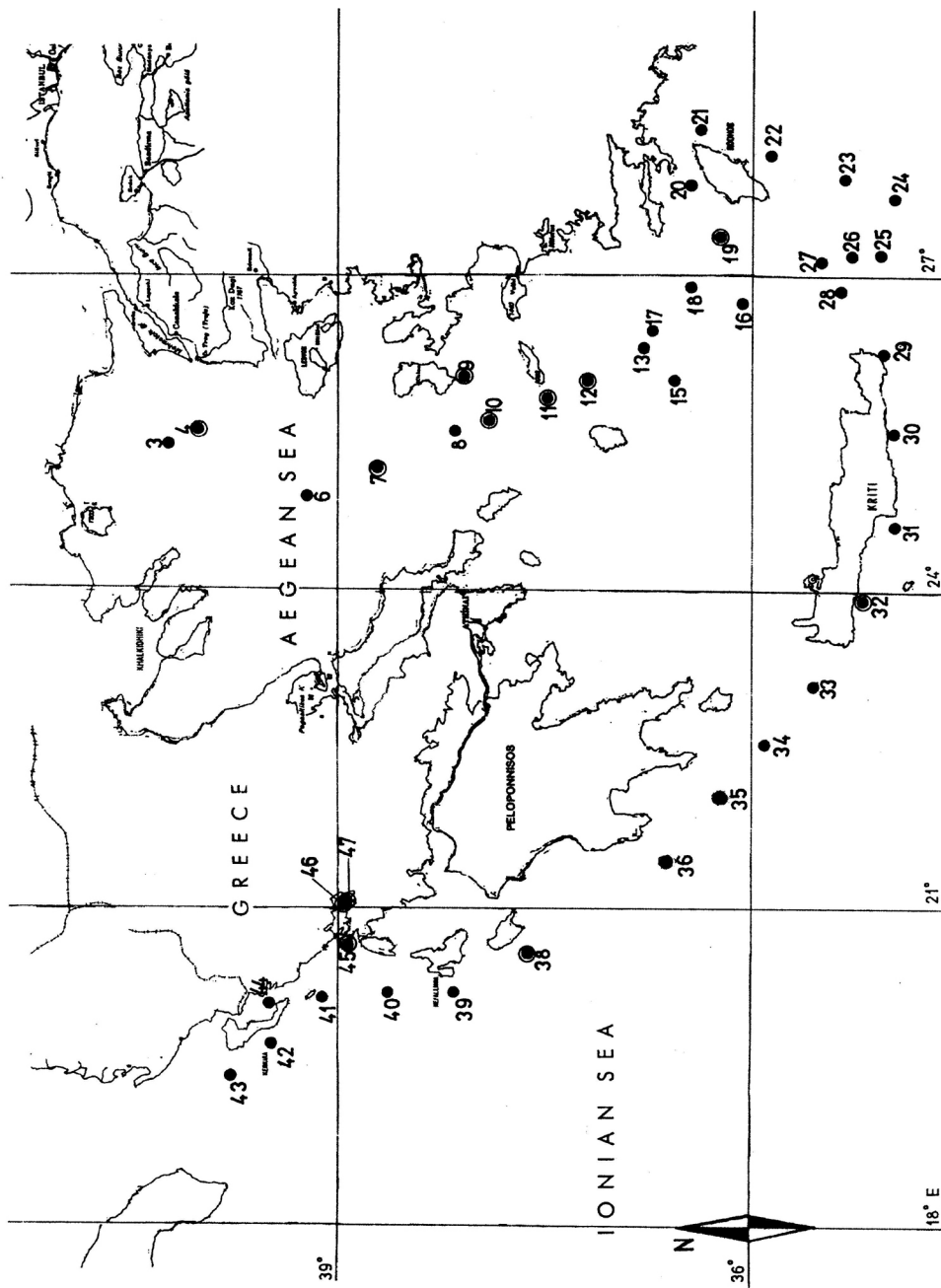


Figure 1. Oceanographic map with sampling stations. Closed circles indicate stations where mainly the hydrophobic type (I) SAS were present in surface waters, and open circles where more hydrophilic type (II) SAS were prevalent.

1993. The samples were collected below the surface (0.5 m) and at a 5 m depth. Measurements were made on unfiltered samples immediately after sampling, without any pretreatment. Surface active substances were analyzed in 100 mL aliquots using the phase sensitive a.c. voltammetry, as described in our previous papers.^{10,12} For quantitative determination, the calibration curve of the nonionic surfactant, polyoxyethylene *t*-octylphenol, (Triton-X-100, Mw 600, Rohm and Haas, Milano, Italy) was used. Electrochemical measurements were performed with a Metrohm E-506 polarecord (Metrohm, Switzerland) using a hanging mercury drop electrode, and Ag/AgCl as the reference electrode. All potentials are expressed *vs.* Ag/AgCl reference electrode.

Salinity and temperature were measured in the near surface waters by CTD.

RESULTS AND DISCUSSION

In the Aegean Sea, the concentrations of SAS ranged from 0.07 to 0.21 mg/L in surface waters and from 0.07 to 0.35 mg/L at a 5 m depth (Table I). In the Ionian Sea surface waters, the concentrations of SAS ranged from 0.08 to 0.18 mg/L. The mean value of surfactant concentrations for the whole investigated area at a 0.5 m depth was 0.124 mg/L equiv. Triton-X-100, or similar to the Adriatic Sea samples. For example, the mean value for the

TABLE I

Station <i>n</i>	Date	Time	Depth (m)	Salinity	Temp. (°C)	SAS*	
3	40°13.47'N, 25°21.26'E	July 4	13:00	5		0.22	
4	40°00.38'N, 25°32.83'E	July 4	17:00	0.5	38.0	26.3	0.09
				5			0.07
6	39°15.02'N, 24°50.84'E	July 5	05:30	0.5	38.0	26.3	0.09
				5			0.07
7	38°40.33'N, 25°10.44'E	July 5	09:30	0.5	38.1	26.2	0.08
				5			0.12
8	38°09.00'N, 25°29.54'E	July 5	13:00	0.5	38.1	26.3	0.10
				5			0.10
9	38°06.73'N, 25°05.02'E	July 6	01:00	0.5	38.4	25.2	0.07
				5			0.30
10	37°56.13'N, 25°38.83'E	July 6	05:00	0.5	37.9	26.7	0.13
				5			0.09
11	37°35.39'N, 25°52.84'E	July 6	08:30	0.5	38.4	26.2	0.19
				5			0.13

* Surface active substances, equiv. T-X-100 (mg/L)

TABLE I (continuing)

Station <i>n</i>		Date	Time	Depth (m)	Salinity	Temp. (°C)	SAS*
12	37°10.57'N, 26°06.87'E	July 6	13:00	0.5 5	38.4	26.2	0.21 0.35
13	36°47.90'N, 26°20.76'E	July 6	17:00	0.5 5	38.2	25.7	0.11 0.16
15	36°31.00'N, 25°26.01'E	July 7	01:30	0.5 5	38.3	26.2	0.09 0.09
16	36°36.68'N, 26°47.46'E	July 7	21:30	0.5 5	38.4	26.7	0.12 0.19
17	36°39.90'N, 26°31.00'E	July 8	01:00	0.5 5	38.3	25.3	0.09 0.10
18	36°26.50'N, 26°57.10'E	July 8	05:30	0.5 5	38.3	26.6	0.10 0.10
19	36°14.20'N, 27°21.70'E	July 8	09:30	0.5 5	38.3	26.1	0.20 0.12
20	36°23.93'N, 27°52.62'E	July 8	13:00	0.5 5	38.4	28.8	0.09 0.12
21	36°22.50'N, 28°20.24'E	July 9	12:30	0.5 5	38.6	28.8	0.12 0.08
22	35°42.91'N, 28°20.13'E	July 9	17:00	0.5 5	38.6	29.0	0.11 0.16
23	35°20.76'N, 28°06.68'E	July 9	21:00	0.5	38.5	28.7	0.14
24	34°56.73'N, 27°59.46'E	July 10	01:00	0.5	38.4	26.3	0.12
25	35°01.95'N, 27°27.58'E	July 10	09:30	0.5	38.4	25.6	0.14
26	35°15.07'N, 27°24.80'E	July 10	13:00	0.5	38.4	26.2	0.12
28	35°20.83'N, 26°58.28'E	July 11	13:00	0.5	38.4	26.1	0.16
29	35°03.88'N, 26°18.37'E	July 11	17:00	0.5			0.10
30	34°55.74'N, 25°34.40'E	July 11	21:00	0.5	38.4	28.2	0.14
31	34°53.11'N, 24°41.47'E	July 12	01:00	0.5	38.3	29.2	0.11
32	35°07.03'N, 23°52.79'E	July 12	05:00	0.5	38.3	26.2	0.18
33	35°25.00'N, 23°10.00'E	July 12	09:00	0.5	38.1	27.2	0.08
34	35°50.29'N, 22°36.13'E	July 12	13:00	0.5	38.1	27.6	0.12
35	36°10.16'N, 22°03.41'E	July 12	17:00	0.5	38.1	27.6	0.09
36	36°33.23'N, 21°25.44'E	July 12	21:00	0.5	37.5	27.3	0.06
37	37°01.99'N, 20°58.62'E	July 13	01:00	0.5	37.5	26.7	0.10
38	37°34.65'N, 20°38.42'E	July 13	05:00	0.5	37.5	24.4	0.16
39	38°04.12'N, 20°15.01'E	July 13	09:00	0.5	37.2	26.0	0.14
40	38°36.94'N, 20°10.46'E	July 13	13:00	0.5	37.2	26.1	0.14
41	39°05.86'N, 20°09.01'E	July 13	17:00	0.5	37.5	23.6	0.14
42	38°31.03'N, 19°30.04'E	July 13	21:00	0.5	37.5	23.0	0.09
43	39°45.95'N, 19°22.83'E	July 14	01:00	0.5	37.5	24.0	0.14
44	39°30.44'N, 20°04.04'E	July 14	09:00	0.5	37.6	23.7	0.10
45	38°55.79'N, 20°43.20'E	July 14	13:00	0.5			0.11
46	38°58.75'N, 21°01.99'E	July 14	17:00	0.5			0.21
47	38°55.91'N, 21°04.22'E	July 14	21:00	0.5			0.21

* Surface active substances, equiv. T-X-100 (mg/L)

north Adriatic samples in summer 1992 was 0.23 mg/L and that for the middle Adriatic (Split – Gargano) transect samples was 0.136 mg/L (Table II).

The Adriatic Sea is a semiclosed and relatively shallow sea except in its southern part, where the maximum depth is about 1200 m. In the northern Adriatic Sea, the mean depth is about 30 m. Due to the dominant influence of the River Po on the distribution of hydrographic and biological properties of the northern Adriatic, this basin is characterized by a higher biological productivity than the other parts of the Mediterranean Sea.^{19–21} Systematic studies of SAS in the northern Adriatic during the last decade showed that relatively high surfactant concentrations (up to about 0.47 mg/L) occur from spring to autumn, while in winter SAS reach only 0.05 mg/L.¹⁹ Such low concentrations of SAS are similar to those found in the open waters of the western Mediterranean during the PHYCEMED cruise of April 1981.¹⁰

Compared to the Adriatic Sea, the Aegean and Ionian Seas are larger and deeper basins. The distinguishing features of the Aegean are the very irregular coastline and the presence of more than 2000 islands scattered over the area. During the period of high insolation, temperature of the surface seawater are quite high, as shown in Table I for July 1993. At stations near the Rhodos Island, which are under the influence of warm Levantine water masses, seawater temperature up to 29 °C was measured. In the Ionian Sea surface water, the temperature was lower, *i.e.* in the range from 23 to 27 °C, which is in accordance with the fact that through the Sicily Straits the Ionian Sea receives water from the western Mediterranean, which has lower salinity and lower temperature.

Although based on measurements taken in only one season, our results indicate only small differences in SAS concentrations between the Ionian and the Aegean waters, as well as between the samples taken at 0.5 m and at 5 m depths. In a number of samples higher concentrations were found at 5 m than at a 0.5 m depth. The highest concentrations of surface active substances (0.30 and 0.35 mg/L) were found at a 5 m depth at stations 9 and 12 in the Aegean in July 1993.

TABLE II

Concentrations of surface active substances in the Eastern Mediterranean. Mean values are given for samples from 0.5 m depth. Standard deviation is in the brackets.

Investigated area	Sampling period	Surface active substances (mg/L) equiv. T-X-100
North Adriatic ¹	August 1992	0.230 (0.018)
Middle Adriatic ¹	August 1992	0.136 (0.013)
EGAMES cruise	July 1993	0.124 (0.039)

¹ Precali and Konrad (1979–1992), Ref. 26

Qualitative differences of surface active substances in seawater samples from different stations are illustrated in Figures 2–5 by presenting typical curves for the capacity current *vs.* potential. In a.c. polarography, desorption processes from the mercury electrode surface produce more or less pronounced peaks. Their features are characteristic of different types of adsorbable substances. Two types of curves were generally observed for samples,

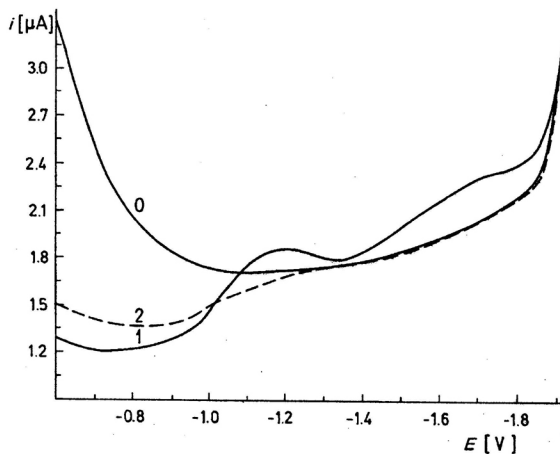


Figure 2. A.c. voltammograms of the seawater sample from station 11, 0.5 m depth (curve 1), 5 m depth (curve 2) and of 0.55 M NaCl (curve 0). Accumulation time 120 s at -0.6 V.

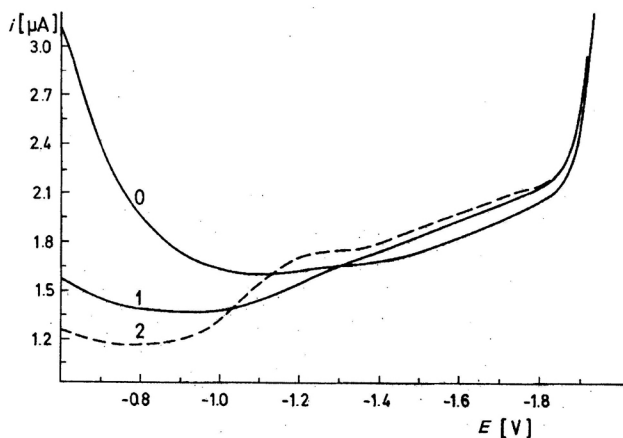


Figure 3. A.c. voltammograms of the seawater samples from station 22, 0.5 m depth (curve 1), 5 m depth (curve 2) and of 0.55 M NaCl (curve 0). Accumulation time 120 s at -0.6 V.

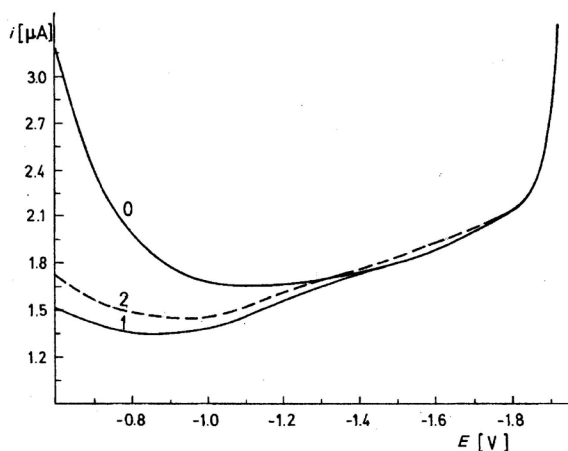


Figure 4. A.c. voltammograms of the seawater sample from station 24, 0.5 m depth (curve 1), station 36, 0 m depth (curve 2), and of 0.55 M NaCl (curve 0). Accumulation time 120 s at -0.6 V.

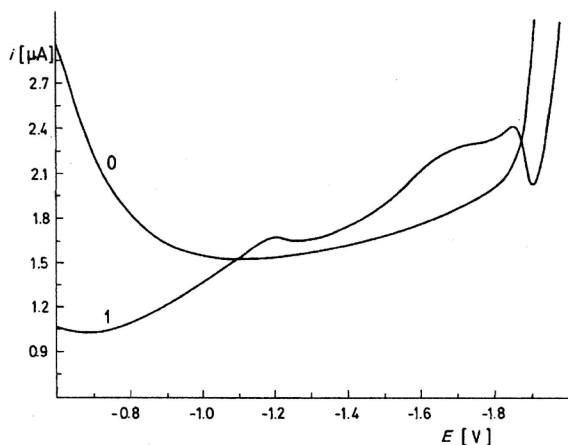


Figure 5. A.c. voltammograms of the seawater sample from station 45, 0.5 m depth (curve 1) and of 0.55 M NaCl (curve 0). Accumulation time 60 s at -0.6 V.

from the Aegean and Ionian Seas. For some samples the shapes of the curves are similar to those presented in Figure 2 (curve 1) and Figure 5, for stations 11 and 45, respectively (type I). These curves exhibit a decrease in the capacity current at the potential -0.6 V in comparison to the value obtained for the SAS-free electrolyte (curve 0). At -0.6 V, the surface of the mercury electrode bears no charge because it is approximately at the potential of the electrocapillary maximum, which is a favourable condition for the

adsorption of organic molecules. The stronger the adsorption, the greater the decrease of the capacity current. Two desorption peaks are visible at potentials of about -1.2 V and -1.7 V, where the electrode surface is negatively charged. The shapes of the current *vs.* potential curves presented in Figures 2 and 5 are characteristic of the presence of organic matter of recent biological origin, usually associated with biological activity. Similar curves have been observed in the north Adriatic Sea,^{12,22} in the Krka River estuary²³ and in a semi-field experiment on a phytoplankton bloom.²⁴ In all cases reported previously,²²⁻²⁴ surface active material that produced such voltammetric curves demonstrated considerable hydrophobicity both at the mercury electrode and by sorption to the XAD-8 resin. The surface active material in those samples was usually composed of both dissolved and small particulate fractions, the latter being removed by filtration or centrifugation. Unfortunately, only untreated seawater samples from the Aegean and Ionian Seas were investigated, so we missed information about the state of surface active substances in these samples.

Another type (type II) of SAS was found in surface samples from stations 24 and 36 (Figure 4) and at a 5 m depth at station 11 (Figure 2, curve 2). On these curves, the desorption peaks are either very small or completely missing. The adsorption effects of the organic molecules, measured as a decrease of the capacity current from the baseline current of the electrolyte, are visible only in the potential range between -0.6 V and -1.2 V. This is a typical adsorption feature of organic polymeric material with a large number of negatively charged functional groups at the natural pH of seawater, which hinder the adsorption at a very negatively charged electrode surface. According to the sorption behaviour on the XAD-8 resin, the negatively charged polymers belong to the groups of hydrophilic and/or hydrophobic acid compounds, *i.e.* conditionally hydrophobic substances.²⁵ Marked differences in the qualitative composition of surface active substances were observed between samples collected below the surface and those collected at a 5 m depth. At station 11, the effect of SAS equivalent to Triton-X-100 was greater in surface water than at the 5 m depth (Figure 2 and Table I). As to qualitative differences, an adsorption curve corresponding to type I was found in the upper layer while at the 5 m depth type II behaviour was rather expressed. A completely different situation was observed at station 22, as illustrated in Figure 3. Stronger adsorption at -0.6 V, accompanied with more visible desorption peaks at very negative electrode potentials, was observed for the sample from the 5 m depth (curve 2) than for the surface water sample (curve 1). It is important to stress that the natural seawater samples contain a mixture of organic substances. The measured adsorption effect at the mercury electrode is influenced by all dissolved and/or dispersed SAS according to their concentration in the solution and adsorbability at the electrode. Small amounts of strongly adsorbable species, particularly those of hydrophobic properties, may have a tremendous influence on the adsorption curves at the mercury electrode.²⁷ On the

other side, recent biological organic substances undergo different transformation and/or elimination processes (especially adsorption on particles and aggregation processes) in the sea, which then influence the composition of SAS at different locations and depths.

The geographic distribution of the predominant types of SAS in surface water at different stations in the Ionian and Aegean Seas in July 1993 are shown in Figure 1. Stations marked with double circles represent SAS mainly of hydrophobic type (I), while stations marked with closed circles, are dominated by more hydrophilic negatively charged surface active substances (type II). Organic substances characterized by the adsorption behaviour of type I were detected mainly in the northern and central Aegean Sea and in a small eutrophic bay (stations 44 and 45) (Figure 1). Since the general circulation of the Eastern Mediterranean in summer is characterized by cyclonic and anticyclonic gyres,^{1,2} it seems likely that organic surface active substances of type II are prevalent in more turbulent water masses. To what extent the qualitative composition of surface active substances depends on their source (e.g. phytoplankton production) or is determined by elimination processes (especially adsorption on particles and aggregation processes) is unknown. Possibly, in turbulent waters, due to physico-chemical processes, the hydrophobic fraction of organic matter undergoes a faster elimination than the hydrophilic fraction. More information is needed about the seasonal variability of surface active substances in the investigated area and about their vertical distribution in the water column.

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SAŽETAK

Površinski aktivne tvari u istočnom Mediteranu

Božena Čosović i Irena Ciglenečki

Tijekom ekspedicije EGAMES u istočnom Mediteranu u srpnju 1993. godine određivane su površinski aktivne tvari (SAS) u uzorcima morske vode iz Jonskog i Egejskog mora s pomoću voltometrije izmjeničnom strujom. Ispitivani su nefiltrirani uzorci morske vode na samom istraživačkom brodu a masene koncentracije SAS određene su iz kalibracijske krivulje za neionski tenzid Triton-X-100. Koncentracije SAS u Egejskom moru bile su između 0.07 i 0.21 mg/L u površinskim vodama (0.5 m), te između 0.07 i 0.35 mg/L na dubini od 5 m. U Jonskom moru uzorci su prikupljeni samo na dubini od 0.5 m, a dobivene koncentracije SAS bile su od 0.08 do 0.18 mg/L. S obzirom na kvalitativni sastav SAS dobiveni rezultati upućuju na prisutnost hidrofobnih organskih tvari u uzorcima iz Egejskog mora, dok su u otvorenim vodama Jonskog mora, te u vodama pod utjecajem vrtložnih strujanja, bile prisutne hidrofilnije ili uvjetno hidrofobne površinski aktivne tvari.