

Investigation of Surfactants in North Adriatic in the Period of 1974 to 1978. Evaluation of Natural Variations and Pollution Effects

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Dissolved organic compounds in the sea originate from several internal and external sources, including excretion by plants and animals, bacterial decomposition, autolysis of dead organisms, inputs by rivers and effluents and from the atmosphere. The concentrations in the "open sea" vary between 0.3 - 3 mg/l with higher values in surface layers than in deep water¹. In coastal waters the concentration may be significantly elevated because of increased primary production and of pollution.

A part of organic compounds in seawater is surface active and thus adsorbed and accumulated at interfaces (sea-water boundaries with atmosphere, sediment and dispersed particulate material and biota^{2,3}). Surface active substances modify the structure of interboundary layers and effect the processes of mass and energy transfer through them. Surfactants, natural and synthetic, change the solubility and physicochemical state of other microconstituents (heavy metals, hydrocarbons, etc.) in sea water, and influence their accumulation and spreading at phase boundaries.

Surfactant content have been analyzed in the large number of different seawater samples from the North Adriatic in the period of 1974 to 1978 with the aim to evaluate their natural

seasonal variations and pollution effects.

Total surface active substances have been determined by using recently developed direct electrochemical methods.^{4,5,6} The content of anionic detergents has been measured spectrophotometrically.⁷

Simultaneous measurements of total surfactant content and of anionic detergents at a given locality provides useful informations on organic content of seawater and characterization of direct pollution effects and biogenic components. Some typical examples will be presented and discussed in detail.

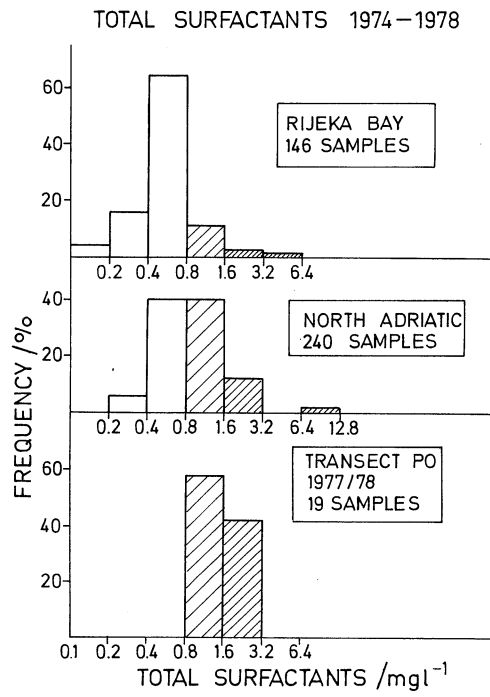
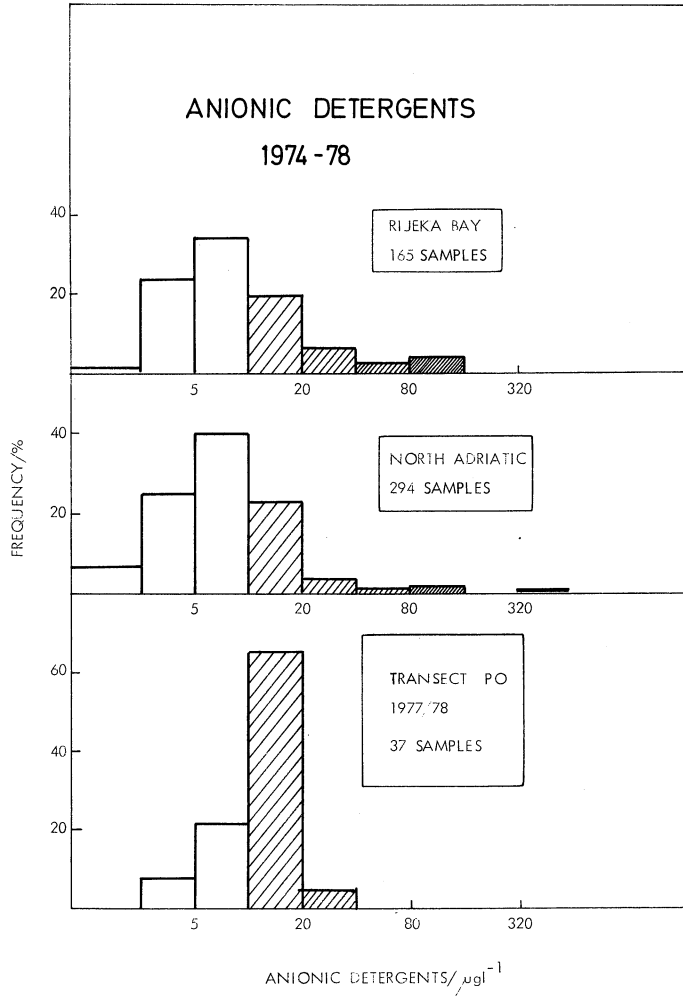
High seasonal increase of total surface active substances observed during phytoplankton blooms will be compared with surfactant content of various phytoplankton culture media and of sea surface microlayer.

Fig. 1. Frequency distribution of values for total surfactants content in seawater samples.

Fig. 2. Frequency distribution of values for anionic detergents content in seawater samples.

REFERENCES

1. Riley, J.B. and Chester, R., (1971), *Introduction to Marine Chemistry*, Academic Press, 465 pp.
2. Jarvis, N.L., Garret, W.D., Scheiman, M.A. and Timmons, C.O., (1967), *Surface Chemical Characterization of Surface Active Material in Seawater*, *Limnol. Oceanogr.*, 12, 88-96.
3. Liss, P.S., (1975), *Chemistry of the Sea Surface Microlayer*, in *Chemical Oceanography*, Vol. 2, Ed. J.P. Riley and G. Skirrow.



4. Zvonarić, T., (1975), Electrochemical Determination of Surface Active Substances in Seawater. M. Sc. Thesis, University of Zagreb.
5. Zvonarić, T., and Žutić, V., (1978), Cruises of RV "Vila Velebita" in the Kvarner Region of the Adriatic Sea. VI. Electrochemical Determination of Dissolved Surfactants. *Thalassia Jugosl.*, in press.
6. Kozarac, Z., Čosović, B., and Branica, M., (1976), Estimation of Surfactant Activity of Polluted Seawater by Kalousek Commutator Technique, *J. Electroanal Chem.*, 68, 75-83.
7. Kozarac, Z., Čosović, B., and Branica, M., (1975), Spectrophotometric Determination of Anionic Surfactants in Sea Water, *Marine Science Communications*, 1, 147-163.

DISCUSSION

Questions and comments:

1. In what extent the biodegradation of surfactants and anionic detergents influence the distribution of these compounds in seawater? (A. BALLESTER, Spain)
 - Seawater samples have been analyzed fresh or within 24 hours from sampling, so that it could be supposed that the biodegradation of organic matter is not significant. For anionic detergents this was checked by parallel measurement of anionic detergents in samples preserved by addition of HgCl_2 solution. Generally, the biodegradation of organic matter would decrease the measured effect of surfactant activity, because smaller and simpler

organic molecules are less adsorbed at the electrode.

2. Did you make total dissolved organic carbon determinations?
(G. CAUWET, France)

- So far we didn't make total dissolved organic carbon determinations. It will be the subject of our further investigations to compare surfactant activity of seawater samples with the corresponding total dissolved organic carbon content.

3. On what basis have you concluded that some values correspond to unpolluted waters? (M.L.El - HEHYAMI, Egypt)

- On the basis of the frequency distribution of values for total surfactant content of large number of samples taken at locations distant from direct pollution sources we concluded that total surfactant content of $0.2-0.8 \text{ mg l}^{-1}$ (polarographic measurement, calibration curve for Triton-X-100) correspond to naturally occurring organic substances of unpolluted seawater in the Adriatic.

4. Have you an explanation for the high values in the offshore waters in the Adriatic? (M.L.El-HEHYAMI, Egypt)

- Offshore waters of the North Adriatic are under great influence of river Po fresh waters, specially during stratification period in summer. One of the consequences is that the content of anionic detergents and total surfactants is increased in surface waters. Very high values of total surfactants observed in the offshore waters of the North Adriatic, specially in summer 1977 are in close relation with the phytoplankton bloom.

5. Pouvez-vous me préciser si, dans le cas des surfactants totaux, une concentration inférieure à $500 \mu\text{g l}^{-1}$ permet de définir un échantillon comme nonpollué (sous réserve bien sûr que les anioniques MBAS soient $\sim 10 \mu\text{g l}^{-1}$)? Quelle peut être la part des tensio-actifs cationiques dans ces $500 \mu\text{g}$? (R. PUCCI, Monaco)
- The answer on the first part of the question as regards total surfactants content in unpolluted seawater is given in the previous discussion. In addition it is to mention that total surfactants in seawater comprise a mixture of different organic substances, nonionic, anionic and cationic. The direct electrochemical measurements can not distinguish contribution of particular substances. However, if we compare adsorption behaviour of seawater samples at the positively and negatively charged surface of the mercury electrode, it seems very probably that anionic surfactants predominate in seawater, what is in agreement with general findings.