BIOGEOCHEMISTRY OF ORGANIC MATTER IN MEDITERRANEAN SEA SURFACE FILMS

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Abstract

Four representative pairs of microlayer (SML) and underlying water (ULW) samples were collected in the Northern Adriatic Sea in early Spring 1996. DOC, POC, surfactant activity, lipid classes and fatty acids were analysed. Organic matter (OM) was derived mainly from diatoms, bacteria and to a lesser extent from higher plants. OM was generally enriched in the SML compared to ULW waters. The highest surfactant activity occurred on sunny days. Fractionation of organic matter and surface active substances on XAD-8 resin showed a great variability in the distribution of hydrophobic basic and neutral, hydrophobic acid and hydrophilic components as a function of environmental conditions.

Key words : sea-surface microlayer, lipids, organic surfactants, Northern Adriatic

At the boundary between the atmosphere and the ocean, the sea surface microlayer (SML) plays a key role in governing transfer processes between these two major reservoirs such as evaporation, gas exchange, emission of aerosols and cloud condensation nuclei and accumulation of pollutants (1-2). All these processes are influenced by the nature and enrichment of organic material in the SML. To support transfer models, it appears that we do not know enough about the chemical composition of the SML and its variability in space and time. We present here data obtained at sea, using combined analytical approaches to assess the variability of the organic composition of the SML under various environmental conditions: biological productivity, sun, wind, rain, etc.

Material and methods

Four pairs of SML and ULW water samples were collected in early spring in the Bay of Piran (northern Adriatic Sea) under different weather conditions between Julian days 85 and 93. Analysis was performed for dissolved and particulate organic carbon (DOC and POC) and surfactant activity using phase sensitive alternating current voltammetry (3). Fractionation of organic matter and surface active substances (SAS) was achieved by sorption on the XAD-8 resin in hydrophobic neutral and basic, hydrophobic acid, and hydrophilic fractions. Lipids were also analysed as lipid classes by thin layer chromatography with flame ionisation detection and free fatty acids by gas capillary chromatography (4).

Results and Discussion

DOC values vary in a very narrow range for all samples (1.29-1.62 mgl^{1}), indicating low enrichment in the microlayer. Total dissolved lipids show high enrichment in the SML for all samples (4.0 - 28.6). Enrichment factors of SAS are 6.4 and 2.2 for the SML samples 85 and 89, respectively. In the SML samples, POC varies between high enrichment and depletion. POC contributes 33.8 and 16.3 % to total organic carbon of the samples 89 and 93, while in the ULW POC varies between 12.4 – 17.8 % of the total organic carbon. Particulate lipids vary between high enrichment (1.70 and 4.19) and marked depletion (0.60 and 0.34). No correlation was observed between the enrichment of POC and lipids, as would be expected due to the highly hydrophobic nature of lipids. Surfactant activity of the POC was estimated as the difference between the concentrations of SAS (equivalent Triton-X-100) of the nonfiltered and filtered samples. Positive values, such as obtained for SML indicate the presence of surface active particulate organic substances in the range between 20 and 30 % of total surfactant activity. Negative values, as obtained for the ULW imply a strong hydrophilic character of this fraction. A positive correlation (R^2=0.9744) is obtained between total lipids and surfactant activity of nonfiltered samples, indicating a significant contribution of lipids to the surfactant activity of natural samples.

The contributions of hydrophobic basic and neutral, hydrophobic acid and hydrophilic fractions to DOC and surfactant activity shown in Figure 1 were highly varying and suggested possible relationships with weather conditions. For SML in the sample 89, collected on a sunny morning, hydrophobic neutral components are largely responsible for the surfactant activity, whereas hydrophilic components largely predominate in the sample 93, marked by heavy rains and their scavenging effect. Fractionation analysis of ULW shows that the hydrophobic acid fraction predominates. The distribution of fatty acids in the dissolved and particulate phases is shown in Figure 2. The main components of fatty acids are given : polyunsaturated fatty acids (PUFA) indicators of plankton activity, branched fatty acids (BrFA) mostly synthesized by bacteria, and long chain fatty acids in the carbon range 24-30 originating from terrestrial higher plants. PUFA are depleted in the particles of SML, indicating that most of the living organisms move out the SML during day. High values of the ratio of saturated fatty acids with 16 and 18 carbon atoms, in the range 3.4 – 9.1, except in the film at station 87, highlight the predominance of diatoms and diatom-derived material in both SML and ULW. BrFA are enriched in the SML, demonstrating the enrichment of both free and attached bacteria in the SML. Long-chain fatty acids indicate pulsed inputs from terrestrial plants (*e.g.* high at station 87).

Conclusion

The selective accumulation of organic substances in surface films is more pronounced during calm sea conditions, especially during sunny days. Organic matter is mainly derived from diatoms and from bacteria attached to particles, with a minor contribution from higher terrestrial plants. A positive correlation is observed between total lipids and surface active substances. Surface active substances show much higher enrichment than DOC in SML, implying the major role of SAS in ocean/atmosphere exchanges.

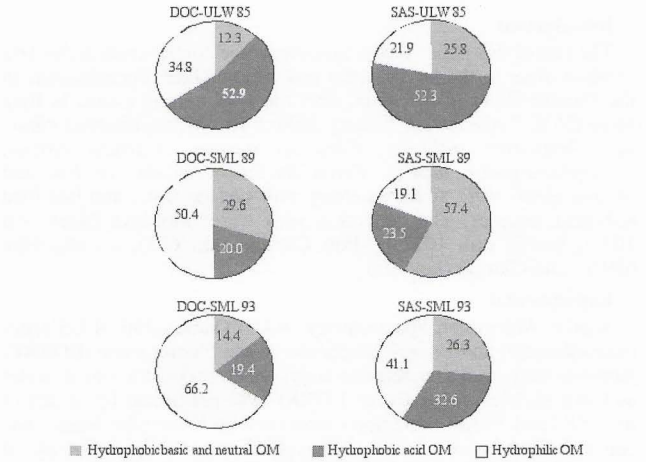

Fig. 1. Fraction of organic matter (OM) by Sportion on the XAD-8resin — SAS = surface active substances

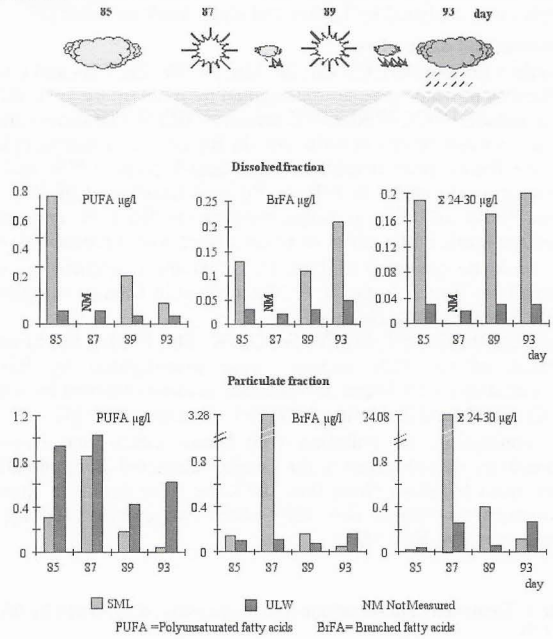

Fig. 2. Distribution of fatty acids in SML and ULW

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