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Physicochemical signatures of natural surfactant sea films from coastal Middle Adriatic stations

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Boundary layers between different environmental compartments represent critical interfaces for biological, chemical and physical processes. The sea surface microlayer (SSM) as a top layer of the sea surface represents natural interface between the atmosphere and ocean. Although < 1 mm in thickness the SML plays a key role in the global biogeochemical cycling because all gaseous, liquid and particulate materials must pass through this interface when exchanging between the ocean and the atmosphere. The SSM thus represents a very important driver enhancing air–water exchange processes. A variety of natural and anthropogenic organic compounds, particularly those which are surface active (SA) are generally enriched in the SML. It is widely acknowledged that the SSM is complex matrix of SA organics as carbohydrates, proteins, lipids and humic substances. Although lipid material is much less abundant than carbohydrates and proteins in the SML, their contribution to surface activity may be disproportionately large. The surfactant films at the air–sea interface change its physicochemical properties reducing air–sea exchange possesses by impeding molecular diffusion across the interface and influencing the hydrodynamic characteristics of water motion at the interface. Various biological, chemical and physical processes lead to the alteration of the film chemical composition, surface physical properties, surface concentration and spatial distribution of film-forming components. Instead of analyzing its chemical composition, it should be possible to scale the SML surface pressure-area (π-A) isotherms in terms of structural parameters which appear to be a sensitive and quantitative measure of the film physicochemical composition, surface concentration and miscibility of its film-forming components.

We will present a large data set obtained by electrochemical and monolayer techniques, accompanied with the novel scaling approach for physicochemical characterization of SA substances of the natural microlayers from coastal Middle Adriatic stations including saline Rogoznica Lake and Krka river estuarine station. Higher primary production during late spring-early autumn is reflected in the presence of microlayers of higher surfactant activity containing on average molecules of lower molecular masses (Mw=0.65$\pm$0.27 kDa) and higher miscibility (y=6.46$\pm$1.33) and elasticity (E=18.33$\pm$2.02 mN/m) modulus in comparison to structural parameters (average Mw=2.15$\pm$1.58 kDa; y=3.51$\pm$1.46; E=6.41$\pm$1.97 mN/m) obtained for microlayers from period of lower organic matter production. Higher inhibition effect on the reduction process of cadmium ions is observed for natural microlayers abundant with SA material from more productive period. This kind of distribution is explained as the consequence of competitive adsorption of hydrophobic lipid-like substances of lower Mw which highly influence the surface structural properties of natural air-water interface forming there segregated surface films during more productive period. This study will offer different perspective on contemporary SML concept taking into account the lipids that act as end-members highly influencing seasonal change of SA concentration and surface structural properties of natural films at the air-water interface.