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Impact of specific atmospheric depositions on Cu-organic matter interaction in the sea-surface microlayer of the middle Adriatic

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Atmospheric aerosols supply nutrients and other substances to the ocean and may influence net primary productivity and carbon uptake. The most pronounced influence of atmospheric deposition (AD) on marine biogeochemical processes occurs in oligotrophic seas and it is expected to increase in the future scenarios of a warmer atmosphere with increased atmospheric emissions and deposition rates. The first direct contact of atmospheric substances with seawater occurs at the sea-surface microlayer (SML), a 1-1000 μm top seawater layer placed between the atmosphere and the sea. AD of specific organic substances affects the bioavailability and toxicity of marine trace metals by changing their speciation.

We studied Cu - organic matter interactions in samples of the SML and underlying water (ULW, 0.5 m depth) collected during the period of retrieval of sea surface oligotrophic conditions (February-July 2019) at the coastal central Adriatic sites (Martinska and Jadrija, Šibenik archipelago). During the sampling period, specific intensive atmospheric events in the area such as open field biomass burning (20.2.2019, 2.3.2019, 13.6.2019), pollen (2.4.2019, 17.4.2019), and Saharan dust (22.-23.4.2019) have been identified. We applied the electrochemical method of differential pulse voltammetry (DPV), square-wave voltammetry (SWV) and chronopotentiometric stripping (CPS) to determine the complexation capacity of Cu (CuCC), reduced sulfur species (RSS), and proteinaceous compounds, respectively. CuCC was determined according to the Ružić-van den Berg linearization model with the assumption of Cu : ligand = 1 : 1. Containing functional groups with S, N, and/or O, RSS, and proteinaceous compounds were followed due to their very high affinity toward Cu binding.

CuCC concentrations ranged from 23-654 nM, with corresponding apparent stability constants log K_{app} 7.2-10.0. The highest CuCC values were determined in the SML samples from March and April 2019 at both stations: 654 nM (2.4.2019, Martinska), 336 nM, and 152 nM (2.4.2019 and 17.4.2019, Jadrija), 282 nM (6.3.2019, Jadrija). In those samples, the highest concentrations of RSS (up to 24.6 μg/L equiv. of glutathione) and proteinaceous compounds (up to 19.7 μg/L equiv. of bovine serum albumin) were also detected. Furthermore, selected SML samples were also enriched for CuCC by a factor of : 5.4 (2.4.2019, Martinska), 5.5 (6.3.2019, Jadrija), 5.3 (2.4.2019, Jadrija), and 2.1 (17.4.2019, Jadrija) relative to the corresponding values obtained for ULW samples.

The assessment of specific atmospheric sources and the nature of the enrichments taking place

within the SML will be discussed. For example, intensive pollen deposition in April had the most pronounced impact on the concentration of sea surface proteinaceous compounds, indirectly increasing the CuCC in the SML at the coastal middle Adriatic sites.

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