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Dynamics of trace elements and dissolved organic matter in estuarine surface microlayer

SAŠA MARCINEK, ANA-MARIJA CINDRIC AND DARIO OMANOVIC

Ruder Boskovic Institute

Presenting Author: smarcin@irb.hr

Dynamics of various trace elements (Cu, Zn, Pb, Cd, Ni, Co, Cr, Fe, Mn, Al, As, V, U) and dissolved organic matter, including the ambient Cu speciation, was studied at the sea-atmosphere phase boundary in the Krka River estuary. The study was performed in order to determine the levels of total and dissolved concentrations of various trace elements, to evaluate their diel variability in the surface microlayer and their enrichment with respect to underlaying water (ULW). The influence of wind speed and direction, as well the organic matter quantity and composition were examined. The SML was collected using an in-house constructed rotating drum sampler. In order to test the importance of bubble scavenging on SML enrichment, the SML samples were also collected after generating the air bubbles ~ 0.5 m in front of the drum sampler (at ~ 0.2 m depth).

The intensive SML samplings (every 2 hours during 16-hour period) in two sampling campaigns (July and September 2020) provided several insights into the factors influencing trace element dynamics at the microlayer. Pronounced diel variability of trace elements (Figure_1 and Figure_2) and the dissolved organic carbon (DOC) was observed within the SML, highlighting the flaws of discrete sampling and emphasizing the importance of carefully designed sampling campaigns. A strong influence of suspended particulate matter on the accumulation and variability of trace metals in SML was observed, primarily on Fe, Al, Mn and Pb. The results indicated that the enrichment of dissolved Fe, Cu, Pb, Mn, Zn and Al in the estuarine SML is driven by complexation with organic ligands, primarily Fe, Cu and Pb. These metals also showed the highest enrichment as a result of bubble scavenging. Analysis of Cu-binding ligands in SML showed higher enrichment of strong L_1 ligands (average $\log K'_{CuL1}$ = 13.2), although Cu speciation in SML was controlled by the abundance of weaker L_2 ligands (average $\log K'_{CuL2}$ = 11.1). Finally, a day-night variations in trace element enrichment and organic matter concentration and composition in the SML indicated the importance of bacterioneuston activity in the cycling of organic matter and associated trace metals in the SML.