Assessment of Cu(I) in marine waters: Evaluating possible impact of antifouling coating on Cu redox cycling

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The antimicrobial properties of copper (Cu) are widely utilized in many different materials as antimicrobial agent. Cu emission from antifouling paints is a worldwide problem with the Cu exceeding acute and chronic water quality concentrations in boat marinas (e.g. 1). Photosynthetic organism counteract the negative effects of high Cu concentration by the production of ligands reducing the concentration of the free Cu ionic form and thereby its toxicity. Nearly all the Cu is in most natural waters is complexed by strong ligands so that Cu it is not instantaneously bioavailable (2). The presence of copper complexation gives rise to extremely low cupric ion activities in surface waters ({Cu²⁺} = 1.4×10^{-14} M).

However, Cu in oxic environments such as oceans is presumably primarily present as Cu(II), leading to speciation models assuming only Cu(II) as significant Cu oxidation state. Rare studies reporting detectable amounts of Cu(I) in water, with Cu(I) ratio ranging from 5-10% of total dissolved copper in oceans and up to 80% of total dissolved copper in estuaries are neglected (e.g. 3). Direct comparison of free ionic forms of Cu(II) versus Cu(I) toxicity with respect to the photosynthetic organisms is virtually almost impossible due to the fast Cu(I) oxidation with molecular O₂ if not complexed.

In this work we present solid phase extraction method for Cu redox speciation in estuarine and marine waters (3). Speciation with respect to the Cu redox state will be conducted on water samples collected marina situated in Krka heavily affected by Cu emission from antifouling boat coating.

References:

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