Organic speciation of copper in the Mediterranean Sea in relationship with natural organic matter.

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In the modern ocean, copper (Cu) speciation is mostly driven by its complexation to natural organic matter (NOM), which regulates inorganic Cu concentrations to levels enough high to sustain biological uptake and enough low to not inhibit phytoplankton growth and reproduction [1].

We explored the speciation of Cu using a pseudo-polarographic method on a vibrating gold micro-wire electrode in Mediterranean seawater samples. This method previously used in coastal seawater, demonstrated its robustness at trace levels through an intercalibration exercise and allows it use for the first time in open seawater samples. Then we combined these results to NOM distribution with the aim to present the first comprehensive dataset of the Cu organic complexation in the Mediterranean Sea.

We identified 4 different Cu complexes, determined their thermodynamic constants ($9 < \log K_{Cu\text{-}L} < 23$) and found that Cu binding ligands (L_{Cu}) have both a marine and a terrestrial origin. While the extremely stable complexes seem to dominate the Cu speciation in the euphotic zone, it gradually shifts to weaker complexes in the mesopelagic layer (200 - 1000m). Combined to the vertical distribution of NOM this shift might be related to the degradation of the strong L_{Cu} by heterotrophic bacteria. Differently, the weaker ligands ($\log K \sim 10$) occurred all along the water column and were associated to the Humic substances. Bottom depth enrichment of strong L_{Cu} was also recorded.

[1] Moffett and Dupont Deep Sea Res. Part I, 54 (4) (2007), pp. 586–595