

## The impact of chemical heterogeneity on the binding of trace metals by marine dissolved organic matter

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Bioavailability and toxicity of trace metals in the global ocean depend on their chemical speciation, which is the result of environmental conditions and interactions between trace elements and organic matter. Understanding the interdependencies between marine dissolved organic matter (DOM) binding properties, and trace metal biogeochemical cycling is therefore of high relevance for the contemporary ocean and future climate change scenarios [1].

There is a tendency to describe the binding of trace metals to marine organic ligands using simple conditional stability constants. Nevertheless, for a better understanding of trace element biogeochemistry it is essential to untangle the main drivers that influences chemical speciation (e.g. pH, salinity and temperature), and determine a complete set of intrinsic binding parameters for marine DOM, which are thermodynamically consistent and independent from the specific conditions of the seawater sample.

Competitive adsorption effects and the overall DOM binding capacity are related to the acid-base properties (i.e., proton binding) of DOM. Here we present experimental results, based on the solid-phase extractable fraction of DOM, of proton binding titrations from surface (ca. 2m depth) and deep (500m depth) waters of the North Atlantic. We determine the main chemical functional groups potentially involved in the trace metal-binding properties of oceanic DOM using a combination of the non-ideal competitive adsorption (NICA) isotherm and the Donnan electrostatic model [2].

We identify DOM chemical heterogeneity as a key parameter to properly understand the underlying mechanism controlling trace metal binding. We critically compare calculated intrinsic binding parameters of North Atlantic DOM with values from the semi-enclosed Baltic Sea and from generic freshwater organic matter [3].

We discuss our results within the context of understanding how binding properties of marine DOM could change in a less oxygenated, warmer, more acidic, and more stratified global ocean.

### *References*

[1] Toward a Quality-Controlled and Accessible Pitzer Model for Seawater and Related Systems. Turner, D. et al. (2016), *Front. Mar. Sci.*

[2] Acid-base properties of dissolved organic matter extracted from the marine environment. Lodeiro, P. et al. (2020), *Sci. Total Environ.*