Sulfide ligands in natural organic matter (NOM)

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Group B metals, such as Hg, Cu, Ag, Pb and Cd bind strongly to reduced inorganic and organic S(II-) ligands [1]. Most trace metal speciation studies until recently have been at elevated (micro-molar) metal concentrations and have blurred the effect of M-S binding for natural occurrences (pico- to nano-molar). S(II-) ligands in oxic waters are shown to exist at the 10-100s nM concentrations [2], and these ligands suppress the toxicity of Group B metals significantly [3].

We have developed a procedure for the determination of metal bound sulfides by use of Cr(II) and a purge/trap method [2]. The resulting chromium reducible sulfide (CRS) does not detect those thiolates found in nature. CRS has been shown to be equivalent to strong total ligand, L_T, that has been determined by competitive ligand titration scheme using Ag as the probe metal [4]., for waste water plant effluent.

S(II-) ligands are associated with organic matter. There is a linear correlation of CRS (nM) with organic C (mg C/L) (OC). The slope of CRS-OC is 14.9nM CRS/mg C (r^2=0.75), reflecting about 0.02 % S ligand in NOM. The scatter of the slope is quite large, however, suggesting direct measure of CRS is needed for accurate and specific results. The CRS is postulated to reflect an M-S coordination (M = Cu(I)?) in NOM.

We used Ag as a metal titrant in a competitive ligand setup to determine the conditional binding constant, Log K', for Ag and strong ligand. Log K' values decreased linearly with fraction of L_T filled from 12 to 8.8 for rivers, but were nearly constant for waste water treatment effluent (log K' = 11.3).

References

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Stochastic synthesis of DOM: Predicting Cu(II) complexation from precursor structures

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Equilibrium models of metal complexation by dissolved organic matter (DOM) typically are calibrated using experimental measurements from metal-DOM solutions. These models can represent the binding data quite well, but the model parameters are not easily interpreted on a molecular level. In addition, DOM from different sources with significantly different binding properties must calibrated separately.

A stochastic, agent-based model of DOM synthesis from precursor molecules has been devised which treats DOM as a complex mixture of interacting molecules, each with a (potentially) unique structure. A quantitative structure-activity relationship (QSAR) using the same data model predicts the log K_{Cu} of well-defined ligands with r^2 of 0.89 for a calibration data set which ranges over 14 orders of magnitude. This QSAR is used to predict log K_{Cu} of the molecules in simulated DOM samples, and these values are then used to predict Cu(II) complexation. Simulations beginning with small organic precursors (tannins, terpenes and flavonoids) produce N-poor DOM with Cu(II)-binding behavior similar to Suwannee River fulvic acid. Simulations beginning with biopolymers (protein, lignin) produce N-rich DOM with stronger Cu-binding behavior similar to that observed in the field. In the former simulation, but not the latter, log K_{Cu} correlates with molecular weight.

This agent-based model calibrated on known ligands currently fits experimental data less well than empirical models calibrated on NOM-metal equilibrium data, but has the advantages that 1) specific binding sites have structural properties which can be interpreted on a molecular level and 2) different ecosystems and DOM treatments produce distinct Cu-binding behaviors without separate calibration.