

## Metal distribution with different molecular size fractions of dissolved organic matter in stream waters by HPSEC and ICPMS

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The distributions of metals Fe, V, Ce, Th, U, Mo, Cu, Ni, Co, Cr, Zn, Pb and Cd with different molecular size (MS) fractions of dissolved organic matter (DOM) in stream waters from south-central Ontario, Canada were investigated using high-performance size-exclusion chromatography (HPSEC, YMC-Pack Diol-300) coupled with on-line photodiode array detector and high-resolution inductively coupled plasma mass spectrometry (ICPMS, Finnigan MAT ELEMENT2). The MS distribution of metals in DOM fractions was evaluated and compared for reverse osmosis (RO) concentrated DOM samples and XAD-isolated humic substances (HS).

The results show the following decrease order of the average molecular weight in RO-concentrated samples: Cu>Ni>(Co, Zn, Cr)>Pb>Cd for the DOM-bound complexes of transitional metals, which is consistent with Irving-Williams series, and (Fe, V, Ce)>Th>U>Mo for the DOM-bound complexes of the other metals, indicating that the metal distribution among the different MS fractions was mainly related to its binding strength. Metals with high strength were more distributed in the larger MS fractions, and metals with low strength were more distributed in the smaller MS fractions of DOM. The MS distribution of metals in HS was different from that in RO-concentrated samples. The mechanisms for these observations were proposed. This study may have significant implications in the understanding of metal-DOM complexation in aquatic environments.

## Metal binding to NOM determined using component resolution and multiresponse modelling

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Natural organic matter (NOM) has fluorescent components, which can be characterized using excitation versus emission fluorescence scans. Through the application of numerical mixture resolution techniques it is possible to resolve a minimum number of fluorescent components necessary to describe the total fluorescence surface. Types of NOM can be "fingerprinted" in this manner. Fluorescence surfaces for samples of a wide range of NOM isolates were subjected to the SIMPLISMA component resolution technique (Windig and Guilment, 1991). Results show that four major components can be identified, two amino acid like components (tryptophan and tyrosine) and two longer wavelength "fulvic" and "humic" components. Samples where the NOM is algal in origin (e.g., Lake Erie sample) show strong tyrosine-like components, whereas sewage effluent show strong tryptophan-like components. Representative samples of allochthonous organic matter show mainly fulvic and humic-like fluorescence. Samples of mixed origin, such as Lake Ontario organic matter, have contributions from all major components. The fulvic and humic-like components can be further resolved into sub-components and possible molecular analogs for NOM-building blocks proposed (Smith and Kramer, 2000). Once fluorescent components are identified using mixture resolution techniques fluorescence changes for each component can be measured during metal titration (Smith and Kramer, 2000). This resultant multiresponse data can be fit to a chemical equilibrium binding model for metal with multiple sites in NOM. Results for Suwannee River fulvic acid show a mixture of five diprotic/bidentate sites for proton/metal binding with binding constants consistent with salicylic acid – like binding (Smith et al., 1999). Sewage derived organic matter tends to be higher in the amino acid-like components which show relatively large (logK 5) binding sites for silver.

### References

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