

## Fluorescence spectroscopic analysis of the binding of Cu, Co and Cs to aqueous natural organic matter (NOM).

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Natural Organic Matter (NOM) in aquatic systems originates from the microbial decomposition of existing organic matter plus exudates of biological activities. NOM contains molecular structures (carboxylic, phenolic, sulfidic, etc.) which can interact with metals, and thus change their speciation. In this investigation, we are using fluorescence spectroscopy to study the NOM-metal interactions on samples from three contrasting sites in Northeastern Ontario (Canada): pristine, urban-impacted, and industrial-impacted. The metals of interest were selected based on their industrial (Cu, Co) or radiological impacts (Co, Cs).

The fluorescence spectra recorded with samples from the three sites showed common features when spectrally resolved with a PARAFAC routine: two different humic- (H) regions were resolved, plus a fulvic- (F) and a protein-like (P) regions. The NOM-metal interactions were assessed by making separate metal titrations ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cs}^+$ ) with these samples to record changes in fluorescence signals. Well-established titrations with  $\text{Cu}^{2+}$  [Ryan & Weber, *Anal Chem* 54:986, 1982] served as a benchmark. The observed fluorescence signal changes were interpreted as direct Metal-NOM interactions, upon which metal-NOM conditional stability constants ( $K^c$ ) were calculated.

Our results confirmed the fluorescence signal changes of NOM with additions of  $\text{Cu}^{2+}$ . The signal changes were distinct for the two (H) and the (F) spectral fractions at the three sampling sites. We have obtained (log)  $K^c$  values of 4.5-5.4 for these NOM- $\text{Cu}^{2+}$  fractions. NOM- $\text{Co}^{2+}$  interactions could be determined only for the two (H) fractions at the pristine site (log  $K^c$  ~3.6), whereas only one NOM- $\text{Cs}^+$  interaction was determined for the (P) region (log  $K^c$  ~4.9) at the industrial site. Although these findings appear modest, they are the first ones reported for NOM with  $\text{Cs}^+$  and  $\text{Co}^{2+}$ . These results suggest that metal-NOM binding is specific to classes of NOM, and the origins of NOM from the three sampling sites. Further work should focus on validating these values, because of the impact that NOM could have on metal speciation.