Contribution ID: **241** Type: **Verbal**

Natural organic matter (NOM) characterization in urban- and nuclear-waste impacted waters using multi-response fluorescence

It is well established that Natural Organic Matter (NOM) plays an important role in metal speciation, in the transport of radioactive contaminants, in the acid-base control of natural waters, etc. NOM originates from various natural and human-impacted processes, and its constituents feature various molecular sizes, functional groups, and other properties which could be important for metal or radionuclide speciation. In this work, NOM impacted by two contrasting human impacts was analyzed using by multiresponse fluorescence, decoupled with the multi-way resolution routine PARAFAC. In the first site at Chalk River, Ontario, Canada, water downstream from a former low-level waste infiltration pit and deep groundwaters were sampled. The second site is surface water from the Grand River in Cambridge, south-central Ontario, Canada, which is impacted by urban activities and agriculture. Our analysis was done on selections of raw water, fractions isolated by ultrafiltration, and solid phase aqueous extracts (SPE). The fluorescence spectra of the NOM, resolved with PARAFAC, showed three common features: humic-like components, at excitation/emission wavelengths 325-350/450-475 nm, fulvic-like components at 325/380-420 nm and protein-like components, at 275/300 nm.

Most of the NOM from the urban-impacted sites and the clean Chalk River site was submitted to ultrafiltration, with >4% of the total in the large fraction (colloidal range, larger than 5000 Da). The proportion of colloidal-sized material in the NOM was substantially higher in the Chalk River contaminated water, with ~18-26% of the total. The protein-like components in the contaminated Chalk River water were largely removed by ultrafiltration, but less so in the clean Chalk River sample and the urban-impacted waters. SPE preferentially removed the protein-like component in the contaminated Chalk River water (typically 89-95% signal decrease), but had a limited effect on humic-like and fulvic-like components. The fulvic-like and humic-like components of the urban-impacted samples and from Chalk River behaved fairly similarly, exhibiting a slight enrichment of humic-like material in the large (colloidal) fraction. Finally, addition of metals (Cu and Co) to Chalk River sample colloidal fractions changed the fluorescence signals for the humic-like and fulvic-like components, but not the protein-like components. In contrast, there was no significant change in signal with addition of Cs. In conclusion, multiresponse fluorescence is a promising technique to determine the origins and dynamics of NOM in field samples, with potential application to metal (Cu) and radionuclide binding (with Co, but not so for Cs). Other new applications will be discussed.

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Track Classification: Separation Methods, Speciation