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What's in an EEM? : Molecular signatures associated with dissolved organic fluorophores

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## ABSTRACT

Excitation emission matrix fluorescence spectra are now widely used to provide a rapid, inexpensive assessment of dissolved organic matter quality. Yet little is known about the molecules that track these fluorophores in the environment. Here we present patterns of correlations between fluorescent components and the thousands of dissolved organic molecular formulas resolved by Fourier transform ion cyclotron mass spectrometry from a suite of boreal river samples. The mass spectral peaks correlating with specific fluorophores have distinct, organized elemental stoichiometries. For instance, the group or cohort of molecular peaks correlating with protein-like fluorophores was enriched in nitrogen, whereas the cohort correlating with humic-like fluorescence was overwhelmingly comprised of CHO-only molecules. Not all mass spectral peaks correlating with a fluorophore were fluorescent, i.e. not all were aromatic, indicating that EEM peaks also track molecules beyond the fluorescent DOM pool. Therefore the correlations between mass spectral and fluorescent peaks are presumably driven by similarities in the sources and sinks of the molecular peaks that track a specific fluorophore in the environment.