



Molecular characterization of dissolved organic matter in contrasted freshwater environments by electrospray ionization mass spectrometry and EEM-PARAFAC

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Dissolved organic matter (DOM) is a key parameter in the fate, transport and mobility of inorganic and organic pollutants in natural waters. Excitation emission matrix (EEM) spectra coupled to parallel factor analysis (PARAFAC) provide insights on the main fluorescent DOM constituents. However, the molecular structures associated with PARAFAC DOM remain poorly understood. In this study, DOM from rivers, marshes and algal culture was characterized by EEM-PARAFAC and electrospray ionization Fourier transform mass spectrometry (ESI-FT-MS, Orbitrap Q Exactive). The high resolution of the Orbitrap (i.e. 140,000) allowed us to separate unique molecular species from the complex DOM mixtures. The majority of chemical species were found within the mass to charge ratio (m/z) 200 to 400. Weighted averages of neutral mass were 271.254, 236.480, 213.992Da for river, marsh and algal-derived DOM, respectively, congruent with previous studies. The assigned formula were dominated by CHO in humic-rich river waters whereas N- and S-containing compounds were predominant in marsh and algal samples. Marsh consisted of N and S-containing compounds, which were presumed to be linear alkylbenzene sulfonates. And the double bond equivalent (DBE) was higher in the marsh and in comparison was lower in the algal culture. Kendrick masses, used to identify homologous compounds differing only by a number of base units in high resolution mass spectra, and Van Krevelen diagrams, plot of molar ratio of hydrogen to carbon (H/C) versus oxygen to carbon (O/C), will be discussed in relation to PARAFAC components to further discriminate freshwater systems based on the origin and maturity of DOM. Together, these results showed that ESI-FT-MS has a great potential to distinguish freshwater DOM at the molecular level without any fractionation.