Characterization of dissolved and colloidal organic matter in Lake Michigan using flow field-flow fractionation coupled with fluorescence EEMs

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Water samples were collected from southwestern Lake Michigan along a trophic gradient from the Milwaukee River estuary to open lake stations to examine variations in the abundance, composition and size spectra of dissolved organic matter (DOM) across the river-lake interface. Ultrafiltration, UV- and fluorescence-spectroscopy, and flow field-flow fractionation (FlFFF) coupled online with UV-absorbance and fluorescence detectors and offline with EEMs were used for the characterization of DOM. Similar to absorption coefficient, concentrations of DOC decreased from 767±219 μM in mesotrophic Milwaukee River harbor to 152±6 μM-C in oligotrophic open lake water. Within the bulk DOC pool, the >1 kDa colloidal organic carbon comprised up to 71% in river water and decreased to 52% in open lake water. Four major fluorescent DOM components were identified, including three humic-like (C1, C3, C4) and one protein-like (C2) DOM components, with increasing C2/C1 ratio from river to open lake. Chromophoric and humic-like DOM were mostly (>70%) partitioned in the 0.5-4 nm size range, while the protein-like DOM was partitioned not only at the 0.5-4 nm size range but also at the 4-8 and >30 nm size ranges. Similar to the bulk DOM, the relative abundance of fluorescent humic-like colloidal organic matter decreased from river to lake waters and from surface to deep waters, while the abundance of protein-like COM increased slightly from river to lake waters. The relative abundance of larger sized protein-like DOM increased from surface to deep waters, likely resulting from the preferential degradation of smaller sized DOM or the production of larger sized DOM from benthic biogeochemical processes. Overall, there existed a dynamic change in the abundance, composition and size spectra of DOM across the rive-lake interface and from surface to deep waters in Lake Michigan.