<u>Title</u>

Dissolved organic matter dynamics in the Upper Mississippi River Basin

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<u>Abstract</u>

Dissolved organic matter (DOM) in river networks has been rigorously studied for decades because of its importance to food webs, co-transport of metals and other pollutants, effects on light penetration, and role in the global carbon cycle. Despite this, uncertainties remain in DOM sources, transport, and processing in river networks. We conducted a two-year study in the Upper Mississippi River Basin (UMRB) to investigate DOM dynamics across a large river network. Specifically, we examined dissolved organic carbon (DOC) concentration, DOM chemical composition, and DOC biodegradability from headwater streams to large rivers in a basin that has distinct contrasts in land cover and land use. Sampling locations included ten streams and rivers within the Chippewa River (Wisconsin) watershed, a 23,336 km² subbasin in the UMRB. Sampling sites were co-located with USGS stream gaging stations on rivers spanning Strahler stream order 1 to 7. The drainage areas were dominated by forest and wetland land cover (>50% by area) or agricultural land cover (>40% by area). In addition to the Chippewa River watershed, we sampled six large river sites (St. Croix River, Wisconsin; Minnesota River, Minnesota; and three sites on the Mississippi River, Minnesota/Wisconsin) representing Strahler stream orders 6-8 and watersheds with contrasting land use (ranging from 23% to 80% agricultural land cover by area). Again, sampling locations were co-located with USGS stream gaging stations. Sampling occurred over two Water Years (1 Oct. – 30 Sept.), capturing various hydrological and climatic conditions. Most sites were sampled at least twenty times. All samples were analyzed for DOC concentration and specific ultraviolet absorbance (SUVA₂₅₄), a measure of DOM aromaticity. A subset of samples from each site were analyzed for DOM fluorescence to determine Fluorescence Index (FI), which approximates relative contribution of terrestrial versus microbial-derived DOM, and were incubated in the laboratory to determine DOC biodegradability (BDOC). We found that DOC concentrations and SUVA254 values were consistently higher in sites draining predominantly forested land than those draining agricultural land, and that FI values were consistently higher (greater microbial-derived DOM) in streams draining agricultural land across stream order. Overall, DOC was more biodegradable in streams draining agricultural land, with the greatest difference between land covers occurring during spring. Results from this study suggest that accounting for both stream order and land cover/land use effects on DOM sources and processing are important for conceptual and predictive models of river network DOC and DOM.