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Amino acid-rich, very high molecular weight river DOM supports flocculation of C and Fe and carries signatures tracking these processes in a boreal estuary

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The fate of terrestrial dissolved organic matter (DOM) delivered to coastal zones is critical to global carbon (C) budgeting, particularly in boreal regions where mobilization of terrestrial DOM is predicted to increase with climate change. C-rich, small-to-medium sized boreal rivers are experiencing hydrologic changes impacting the delivery of DOM. However, much of our understanding of DOM dynamics across salinity gradients comes from very large and urbanized rivers. To address this gap, we investigated the composition of DOM across three size fractions (10kD-0.3µm VHMW; 1-10kD HMW; <1kD LMW) and along a salinity gradient within a small boreal estuary. We assessed salinity-induced DOM flocculation by comparing size fraction results to the composition of DOM in situ across the salinity gradient and following artificial seawater additions. The largest losses in Fe, DOC, DON and total hydrolysable amino acids (THAA) occurred at 15 psu and coincided with an increase in the C:N ratio. However, little change in the optical properties (e.g. specific UV absorbance at 254nm ($SUVA_{254}$)) of DOM was observed. The VHMW fraction represented only 11% of the river DOC but contained 91% of the Fe and 60% of the THAA of the isolated river water. The THAA content and composition best explained differences among size fractions with the VHMW exhibiting a unique THAA composition distinct from the other two fractions. This fraction also exhibited significant losses of DOC, DON, THAA, $SUVA_{254}$ and Fe at 15 psu which were not observed in the other fractions. Flocculation of the river DOM, by mixing with 30 psu estuarine water or with artificial seawater, resulted in decreases in VHMW-THAA and increases in LMW-THAA composition consistent with the salinity gradient observations. Our results indicate that THAA-rich VHMW riverine DOM plays a major role in Fe transport and flocculation in this estuary. This study demonstrates the potential of THAA composition as a means to track “floc reactive” DOM in high latitude estuaries by distinguishing between vascular-plant derived DOM and microbial sources. Future investigation into controls on riverine DOM THAA composition and its relationship to flocculation should aid in evaluating potential DOM and Fe flocculation and burial.