Fluorescence fingerprinting of dissolved organic matter in the Attawapiskat River Watershed – Towards the development of *in situ* proxies for mercury in northern waters

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Introduction

The peatlands of the Hudson Bay Lowlands (HBL) occupy most of Ontario's Far North, contributing substantial freshwater and solute inputs to downstream aquatic ecosystems, notably the James/Hudson Bay. Despite concerns over present and future impacts of climate and land-use changes in the region, comprehensive surface water quality monitoring programs are sparse, largely due to the high costs and logistical constraints associated with implementation in such a vast and remote landscape. Spectroscopic measurements of dissolved organic matter (DOM) have been effective proxies for dissolved organic carbon (DOC) and mercury in many environments (*e.g.,* Bergamaschi et al., 2011), however, to our knowledge, these have yet to be implemented in surface waters that drain northern peatland complexes. Laboratory-based fluorescence measurements of surface waters have also been conducive to resolving seasonal changes in DOM sources and quality that result from variation in hydrological connectivity of a watershed over time, and have been successfully used in arctic and subarctic watersheds (*e.g.*, Spencer et al., 2008), and elsewhere (*e.g.,* Singh et al., 2013). The main objective of this study is to assess the viability of *in situ* optical measurements for widespread use in the HBL to improve the resolution and breadth of water quality data and monitoring in the region. Additionally, we aimed to evaluate temporal changes in DOM optical properties as a reflection of watershed contributors throughout the ice-free season to help elucidate the hydrological behaviour and functioning of peatlands in the HBL.

Study Site and Methods

The study focused on the surface waters of North Granny Creek (NGC; catchment size 30 km^2), a first order peatland stream, and the Nayshkootayaow River (NR; catchment size 1721 km^2), a fourth order river with a substantial groundwater component and a large outlet of peatland chemistry to the Attawapiskat River, into which it flows. The sites are located in the Attawapiskat River Watershed near the De Beers Victor Diamond Mine (52.83 °N, 83.93 °W), approximately 90 km west of the James Bay coastline in the HBL. The landscape is comprised of a mosaic of peatland landforms (*e.g.,* bogs, fens, and ponds) with an average peat thickness of 2 m, thinning noticeably near riparian areas.

In situ RBRmaestro loggers were deployed in the two rivers, collecting continuous measurements of chromophoric DOM fluorescence (FDOM) and other standard water quality parameters during the ice-free season. Discrete samples were collected every 1-2 days for DOC, total mercury (THg) and methylmercury (MeHg) analysis and ancillary chemistry (stable water isotopes and major ions) over the course of three ~two-week long sampling campaigns (*i.e.,* spring freshet, summer, and fall). Excitation-emission matrices were generated and used in combination with parallel factor (PARAFAC) analysis to derive fluorescence indices for each surface water and additional terrestrial samples collected (Cory and McKnight, 2005).

Results

Peak discharge in both rivers occurred during spring freshet. The lowest flows of the ice-free season occurred in the summer months (late-July to early-August). The highest DOC concentrations occurred during the peak flows of spring freshet in the NR and NGC, although water sampling began after peak freshet flows in the NR.

Linear regression yielded several significant relationships between *in situ* and PARAFAC-derived fluorescence indices, DOC and THg (Figure 1), although no such relationships existed for MeHg. The strongest correlation was observed between *in situ* FDOM measurements and DOC in the NR only ($r^2 = 0.93$, $p < 0.0001$), with no apparent link with THg. In the NGC, there was no observable relationship between *in situ* FDOM and DOC or THg. Conversely, relationships between specific UV absorbance (SUVA) and fluorescence index (FI) and THg were significant and comparable in both streams, while the correlation with DOC was only present for the NGC. However, when fall data from the NR were excluded from the regressions of FI and SUVA with DOC, relationships emerged that resembled their counterparts in the NGC, in both strength and direction. A strong correlation also materialized between THg and *in situ* FDOM when only freshet and summer data were analyzed from this site.

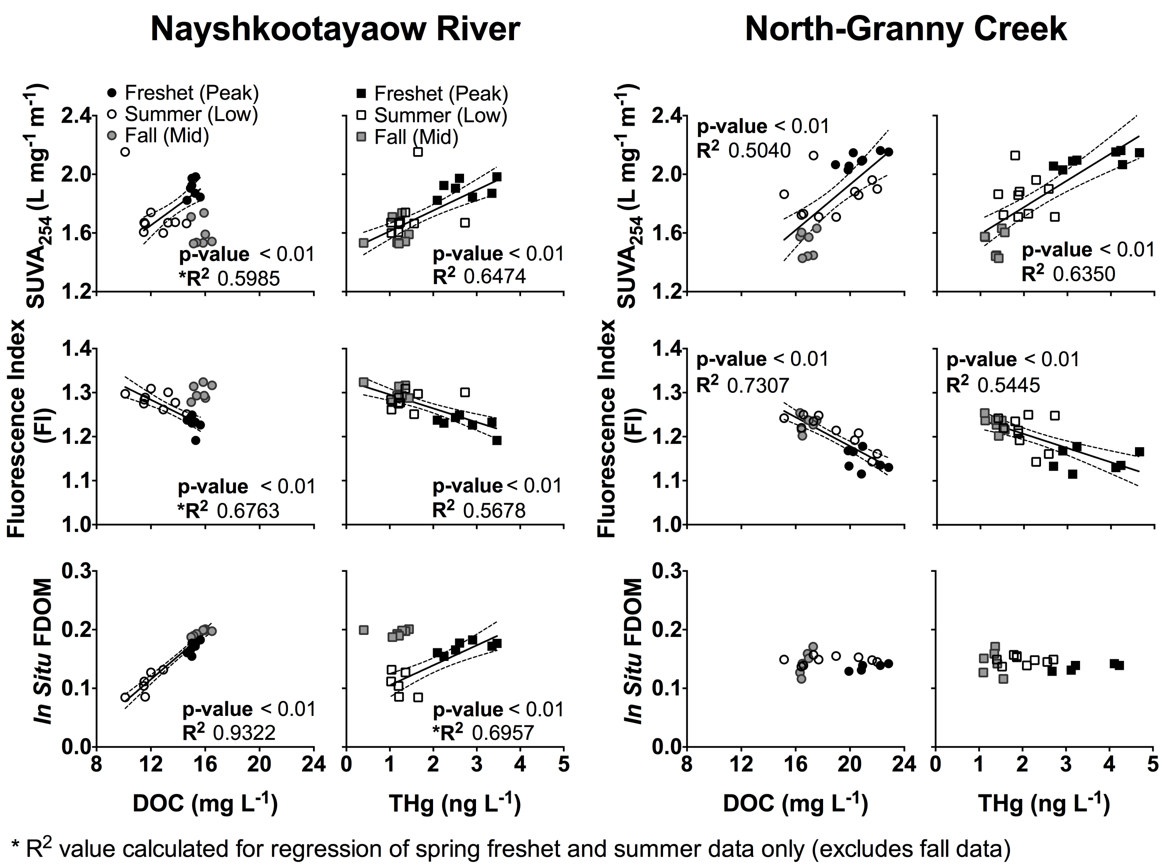

Figure 1. Linear regressions of DOC and THg analytical results with *in situ* and selected laboratory-derived spectroscopic indices showing significant correlations (p-value < 0.01; black lines) and 95% confidence band (dotted black lines). Data are plotted according to season and associated flow condition: spring freshet (peak flow), summer (low flow), and fall (intermediate flow).

Seasonal trends in DOC concentration and DOM quality showed some similarities between sites. SUVA and FI decreased and increased, respectively, with time in both streams, indicating a progressively lessened influence of aromatic terrigenous DOM. Humification index (HIX) at both study sites decreased during summer baseflow conditions, rising again in the fall in the NR, but staying relatively consistent from summer onward in the NGC, similar to FI at this site.

Discussion and Conclusions

Differences in seasonal trends of spectroscopic measurements (*e.g.,* SUVA, FI, HIX) between the NGC and the NR were expected given the dominance of peat sources at the NGC watershed, and the largely groundwater-dominated baseflow of the NR. During spring freshet, litter frozen in place on the peat surface over the winter contributed to the DOM pool during snowmelt in the NR. The increased influence of deeper soil horizons, generally associated with enhanced microbial processing, was observed over the season (especially in the NR) through a slight rise in FI values, indicative of increased mixing of terrigenous and microbial sources. In the NGC, FI values suggested more constant terrigenous sources (< 1.3). The changes in fluorescence during baseflow in the NR suggest that the contributing deep groundwaters underwent preferential removal of humic and aromatic DOM.

An increased breakdown and accumulation of humic DOM during dry summer conditions and subsequent flushing in the fall may have resulted in more labile and humified DOM contributing to the NR in the late portions of the ice-free season. Higher HIX values at this time may also be attributed to fall leaf litter and runoff from the forested riparian areas adjacent to the NR. The relatively unchanging HIX and FI values from late summer to fall in the NGC reflect that DOM source was likely consistent during this time. Around the NGC, the dry summer led to extensive peat drying, thus fall precipitation would have been added to storage, and may not have been sufficient to achieve connectivity between the peatland and stream. Instead, the same peat layers persisted as the dominant sources of water and DOM to the NGC.

The inconsistent nature of correlations in streams of this study suggests that, while *in situ* fluorescence measurements may serve as a valuable proxy for solute monitoring in surface waters of the HBL, the method is site specific. Deviation from relationships in the NR in the fall may have occurred due to interference in the fluorescence signature, likely caused by an unexpected algae bloom that appeared at this time. An assessment of the effectiveness of this monitoring strategy over several distinct flow conditions must therefore be performed prior to deployment in areas where little data exists.

References

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