Regional variability in stream DOM characteristics across forested regions of Canada, and its implications for drinking water treatability

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INTRODUCTION

Rationale:

Forested catchments are important sources of drinking water for communities across Canada. Dissolved organic matter (DOM) has the ability to negatively affect drinking water quality and treatability. The amount and characteristics of DOM in surface waters depend on the biogeochemical processes within the surrounding terrestrial and aquatic environments. The quality and quantity of DOM exported to lakes and streams is affected by climate, soils, geology, hydrologic connectivity and flow paths, and may change seasonally.

DOM, and in particular large molecular weight organic compounds, are known as precursors of disinfection by-products (DBPs), potentially harmful compounds formed during water disinfection. Studies observed correlations between the DBP formation potential (DBPs-FP) and SUVA as well as molecular weight distribution.

Our goal is to understand the variation in stream DOM across Canada's ecozones, and what it means for drinking water treatability.

Research Questions:

1) What are the main differences in DOM chemical composition in stream water among ecozones?
2) How does climate, surficial geology, and dominant soils/ecosystems influence DOM composition among ecozones?
3) Does DOM composition influence drinking water treatability, in particular DBPs-FP?

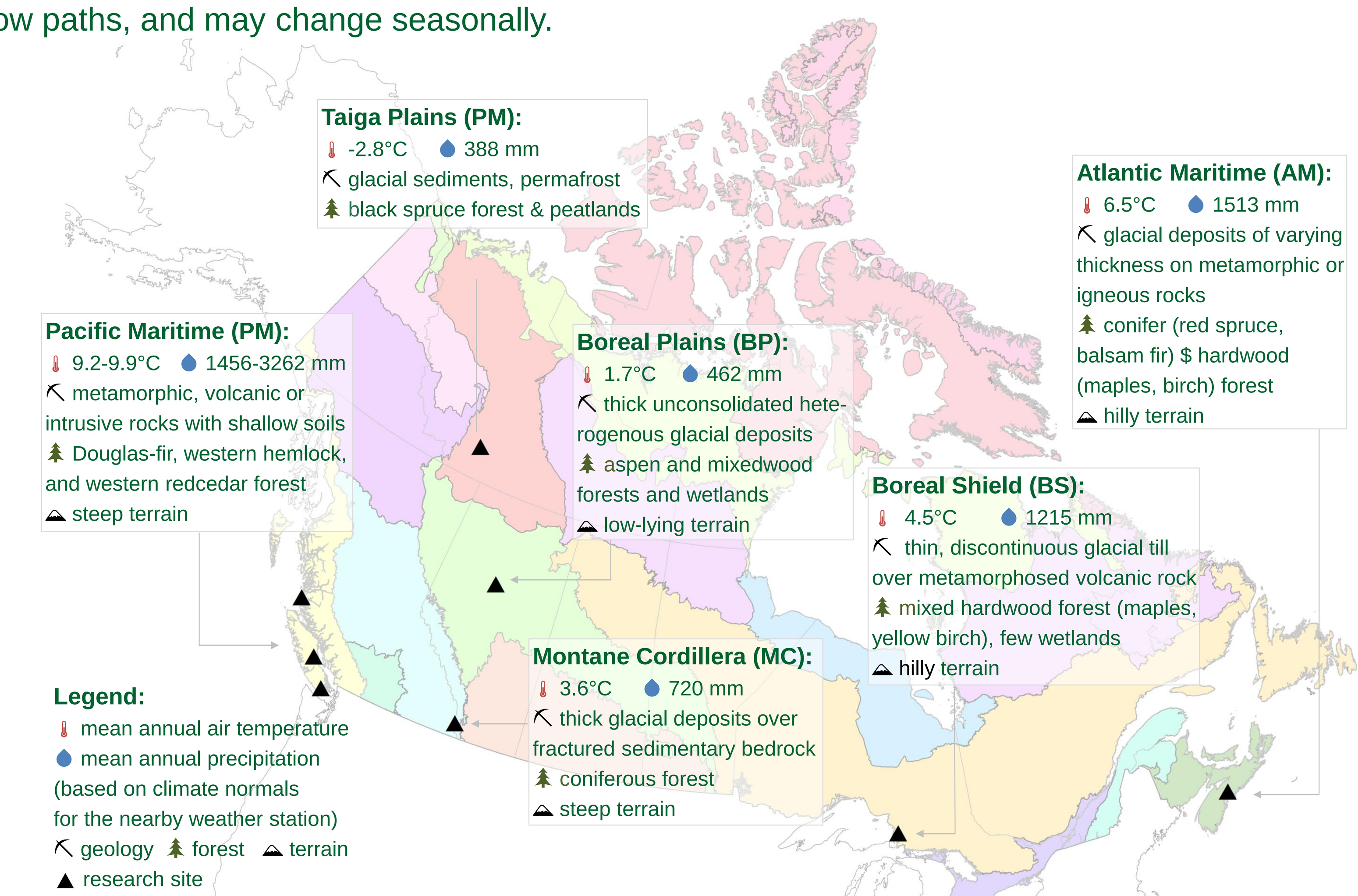


Fig. 1. Terrestrial ecozones of Canada are the largest ecological classes characterized by distinct abiotic and biotic factors. Research sites in this study are located in 6 different ecozones.

DATA COLLECTION

- Two to six streams were sampled at each research site in 2019-2020. Each stream was sampled between two and four times under different hydrologic conditions.
- 91 samples were analyzed for general water chemistry (major ions, nutrients), DOC concentration. Indicators of DOM chemical composition determined with absorbance and fluorescence spectroscopy included SUVA (specific UV absorbance at 254 nm), S_R (slope ratio), $S_{275-295}$ (absorbance slope), E2:E3 (250/365 nm absorption ratio), BIX (freshness index), HIX (humification index).
- 41 samples were analyzed using Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). The following metrics were used to differentiate between samples: aliphatic and condensed aromatic compounds, polyphenols, oxygen-rich and oxygen-poor unsaturated compounds; H/C and O/C ratios.
- Zeta potential, and true formation potential for nine DBPs, including four trihalomethanes (THMs: TCM, BDCM, DBCM, TBM) and five haloacetic acids (HAAs: MCAA, DCAA, TCAA, MBAA, DBAA), were measured in 72 samples.

RESEARCH SITES

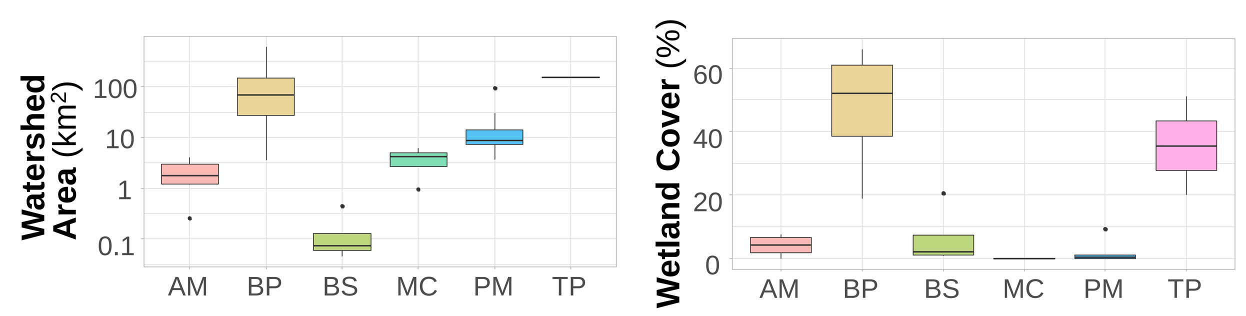


Fig. 2. Catchment characteristics (area and proportion of wetlands) of sampled streams by ecozone.

Sampled streams differed in size, runoff and catchment characteristics (e.g., proportions of wetlands, open water, slope etc.; Fig. 2).

Clear differences in DOC concentrations were seen across ecozones, and the three Pacific Maritimes research sites (PM1, PM2, PM3) show that there can be substantial variability within an ecozone.

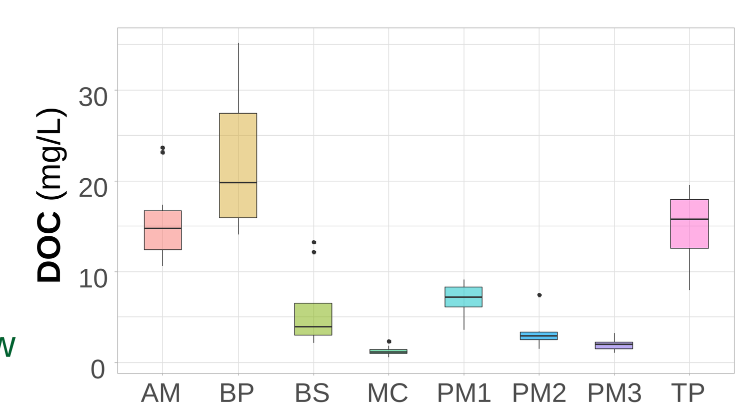
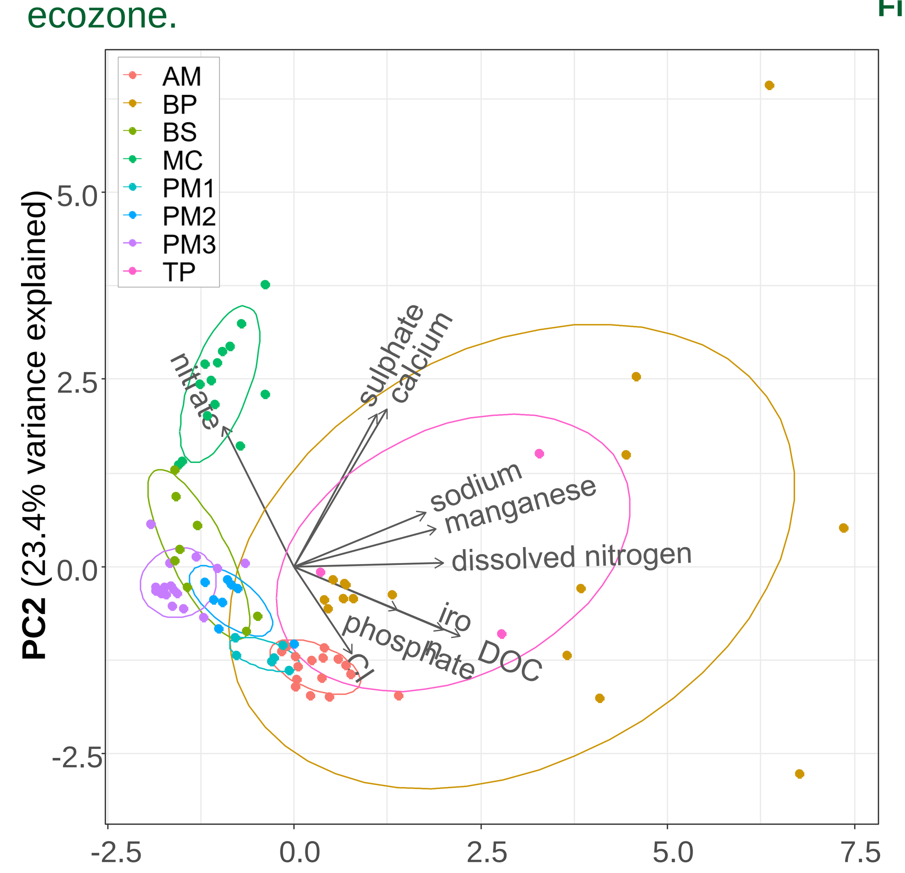


Fig. 3. DOC concentrations by research site (above).



Research sites have distinct stream water chemistry composition based on major ions and nutrients (Fig. 4). in The BP and TP sites show the largest variability, likely due to variable connectivity to groundwater.

The variability in water chemistry as seen in the principal component analysis (PCA) can be explained by connectivity to calcareous or saline groundwater, peatland connectivity, oceanic influence.

Fig. 4. PCA based on major ions and nutrients; select outliers were removed (left).

RESULTS

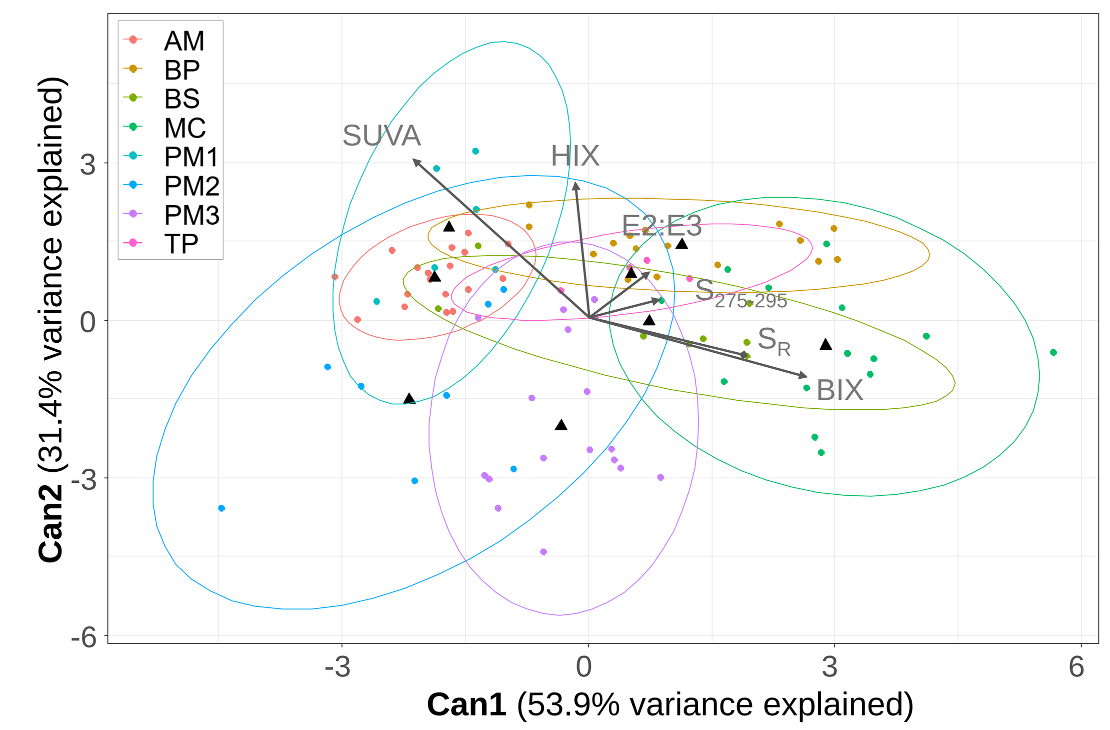
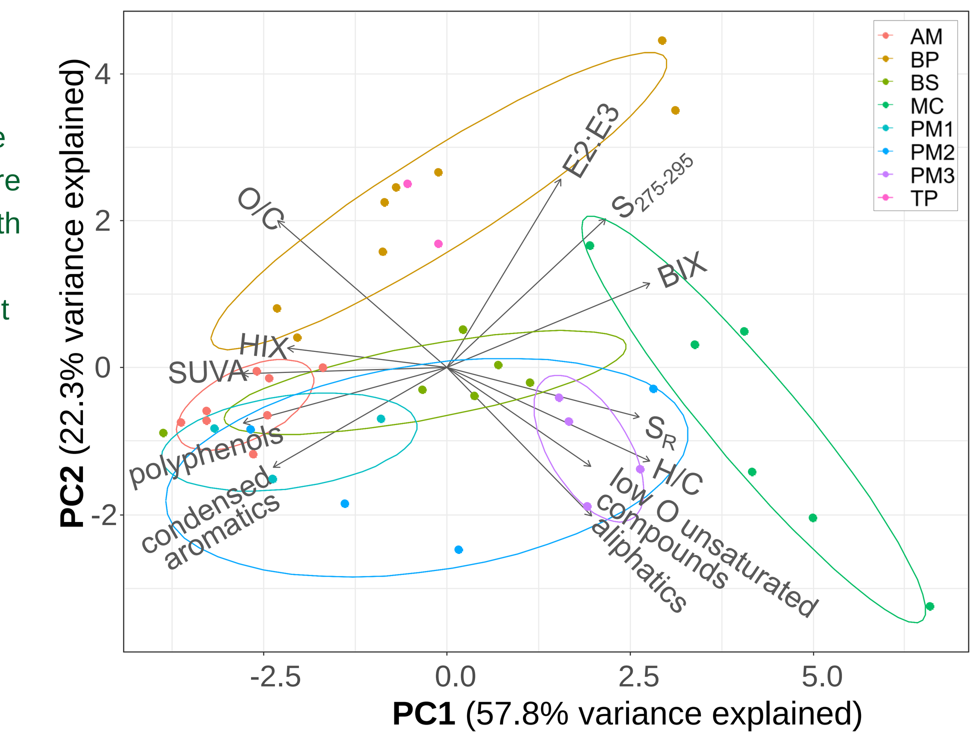


Fig. 5. Discriminant analysis (candisc). DOC concentration and A_{254} are not included. The differences among ecozones / research sites are statistically significant (p<0.001; permutational MANOVA); ~51% of variance is explained by the site/ecozone differences. Within-ecozone variation in DOM character in different streams can be equally explained by seasonal changes in DOM quality for individual streams and differences among streams.

Fig. 6. PCA with FT-ICR-MS data for 41 samples (right). Some FT-ICR-MS metrics are strongly correlated with other indicators of DOM composition, but allow for additional differentiation among ecozones.



DOM composition

We found large differences in stream water DOM chemical composition between ecozones. Aromaticity, as indicated by SUVA, HIX, and contribution of polyphenols and condensed aromatics, were the best differentiators (Fig 5).

Atlantic Maritime (AM) and Pacific Maritime (PM1) had the highest aromaticity, despite not having the highest DOC concentrations; possibly related to DOM derived from podzolic soils.

Montane Cordillera (MC) and Pacific Maritime (PM3) had the lowest DOC concentration and aromaticity, likely mainly microbially-derived DOM; possibly explained by shallow soils and dominance of deeper flow-paths through mineral soils.

Boreal and Taiga Plains (BP, TP) had the highest DOC concentrations, but with highly variable DOM composition, likely associated with large wetland influences coupled with variable groundwater sources.

Can we predict DBPs-FP using DOM characteristics?

DOC concentration or A_{254} were the strongest individual predictors of DBPs-FP (including THMs-FP and HAAs-FP). Including additional DOM composition indices did not substantially improve the capability to predict DBPs-FP. For example, R^2 for the linear regression to predict THMs-FP varied from 0.76 using DOC, and 0.77 using A_{254}, to 0.79 using DOC and SUVA.

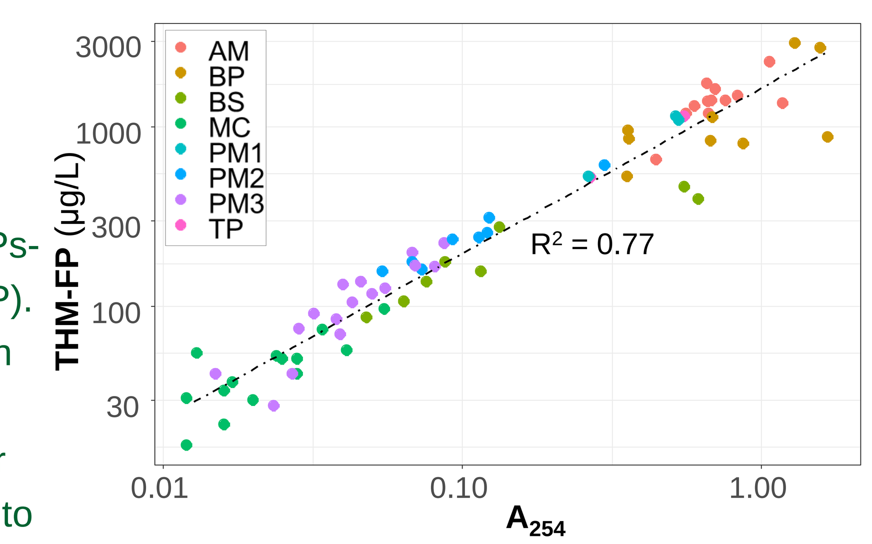


Fig. 7. A_{254} vs. THMs-FP. Note the log scale on both axes. Some sites/ecozones are consistently above the fitted line (e.g., AM) and some are below, suggesting that differences in DOM composition have a marginal influence on DBPs-FP.

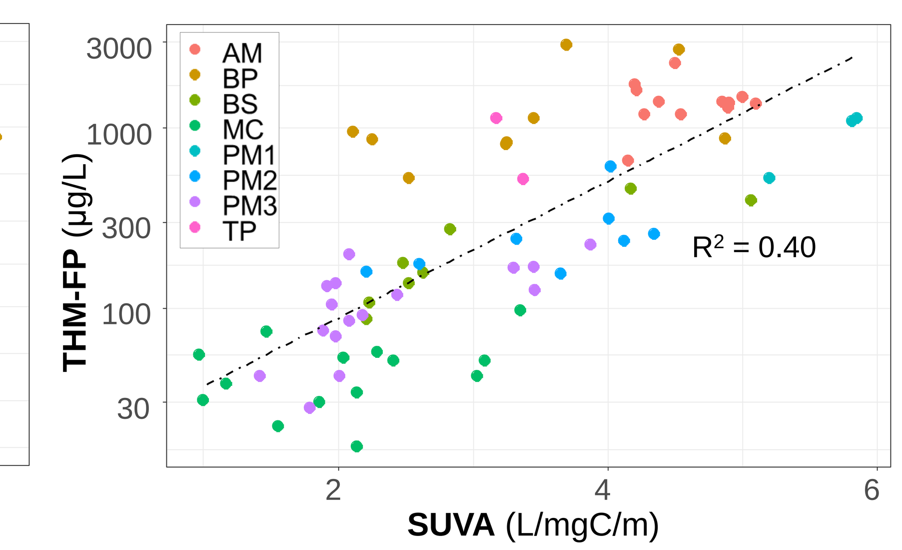


Fig. 8. Higher SUVA is generally associated with higher THMs-FP (R^2 = 0.40). The relationship is similar for other DBPs-FP.

SUMMARY

- Both DOM concentration and molecular composition had ecologically significant differences among ecozones. A majority of the variability in DOM composition between ecozones was captured by simple DOM indices such as SUVA, but information from FT-ICR-MS provided both complementary and additional information.
- Variability in DOM composition between ecozones is consistent with broad differences in landscape characteristics, such as soil types, wetland abundance, and surficial geology.
- DOC concentration and A_{254} were the best predictors for DBP-FP, with only minor improvements to predictive capabilities by further accounting for additional aspects of DOM chemical composition.

Future work: We will further explore the effect of stream catchment characteristics (e.g., watershed size, slope) on DOM composition. We will include PARAFAC analysis to supplement our DOM characterization. Each ecozone included disturbed and undisturbed catchments, hence our analysis will reveal if there are common impacts on DOM composition in disturbed streams across ecozones.

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forWater NSERC Network for Forested Drinking Water Source Protection Technologies

CAWS Catchment And Wetland Sciences Research Group