Title: Hydrologic Compartments are More Important than Ecozone in Size-Based Characterization of Freshwater Dissolved Organic Matter across Canada

Running Head: DOM Composition across Canadian Ecozones

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ABSTRACT

Dissolved Organic Matter (DOM) represents a mixture of organic molecules that vary due to different source materials and degree of processing. Characterizing how DOM composition evolves along the aquatic continuum can be difficult. Using a size-exclusion chromatography technique (LC-OCD), we assessed the variability in DOM composition from both surface and groundwaters across a number of Canadian ecozones (mean annual temperature spanning -10 to +6 C). A range in DOM concentration was found from 0.2 to 120 mg C/L. Proportions of different size-based groupings across ecozones were variable, yet similarities between specific hydrologic compartments, regardless of location, suggest commonality in the processes dictating the evolution of DOM composition. A principal-component analysis identified 70% of the variation in LC-OCD derived DOM compositions could be explained by the hydrological compartment. We find that hydrologic compartment has a greater influence on DOM composition than differences in climate or surrounding vegetation.

Keywords:
Dissolved organic matter, size-exclusion chromatography, DOM composition, hydrologic compartment, Canadian ecozones

1 INTRODUCTION

Dissolved organic matter (DOM) is a ubiquitous component of terrestrial and aquatic ecosystems. DOM influences light penetration within lakes (Schindler et al. 1996) and provides an energy source for microbial metabolism (Biddanda and Cotner 2002). Comprised of thousands of molecules with differing structures and properties, DOM concentration and composition can vary greatly among environments due to different physical, chemical, and biological processes. Future drinking water treatment options may be significantly impacted as climate change is predicted to alter the quantity and quality of DOM in surface waters (Ritson et al. 2014). Harmful disinfection by-products (DBP), formed by reactions between DOM and chlorine, are increasingly found in most municipal drinking water supplies (Krasner et al. 2006). Further, DBP formation is more strongly correlated with DOM composition than overall DOM concentration (Awad et al. 2016). Increased terrestrial DOM contributions observed among northern surface waters are thought to result in the 'brownification' of these systems, affecting lake characteristics and food webs (Creed et al. 2018; Wauthy et al. 2018). Hence, the evolution of DOM composition across the aquatic continuum has important implications for downstream ecosystems, and must be monitored or observed to better understand its impact on water treatment effectiveness and downstream ecosystems.

Watershed characteristics, such as terrestrial land cover or number of upstream lakes, can dictate the concentration and composition of DOM that is transported through the aquatic continuum (Mueller et al. 2012; Jaffé et al. 2012). The persistence of DOM within freshwaters has been linked to its initial composition (Kellerman et al. 2015). Determination to the variability in DOM composition across the aquatic continuum can indicate potential avenues of change, allowing us to better anticipate water treatment requirements and costs related to future DOM changes. However, the inherent complexity and heterogeneity of DOM makes it difficult to rely on a single method to quantify compositional differences.

Characterizing DOM can involve a number of different techniques, yet many measure either bulk characteristics or only a subset of all DOM by capturing specific components. A comprehensive chemical characterization of DOM would involve the identification and quantification of thousands of individual compounds, would be computationally and economically intensive, and may not actually be possible with current technologies. Fortunately, this level of analysis is not required to make useful predictions on how DOM will behave in the environment. DOM composition has been assessed via molecular ratio assays (Hunt et al. 2000), light absorption (Weishaar et al. 2003), fluorescence (Jaffé et al. 2008), resin fractionation (Kent et al. 2014), and mass spectrometry (Kellerman et al. 2014; Hutchins et al. 2017). Generally, the need for enhanced information on DOM composition and molecular moieties results in increased cost and complexity to implement (McCallister et al. 2018). Bulk optical indices, although common due to the relative ease of analysis, only respond to compounds that absorb or fluoresce in a specific range of wavelengths and can include non-organic components in the matrix (Weishaar et al. 2003) or miss non-absorbing DOM components (Her et al. 2002). The ideal DOM characterization method, or combination of methods, would provide sufficient detail on the key aspects of DOM composition that control its fate and function, yet be analytically simple enough to be cost effective and practical for environmental applications.

Size exclusion chromatography (SEC) has been used to characterize DOM in a variety of settings including marine systems (Ogawa et al. 2001), lakes (Kent et al. 2014), rivers or streams (He et al. 2016), and groundwaters (Szabo and Tuhkanen 2010). Liquid Chromatography – Organic Carbon Detection (LC-OCD) is a simple and quantitative SEC method that separates DOM based upon hydrodynamic radii and electrostatic properties (Huber et al. 2011). This technique is relatively fast (<120 minutes per sample) and characterizes both absorbing and non-absorbing DOM components. Studies using LC-OCD have focussed on wastewater and water treatment applications (Ciputra et al. 2010). Some LC-OCD environmental data exists from agricultural and forested catchments in Germany (Heinz et al. 2015) and rivers in South Korea (He et al. 2016) and Spain (Catalán et al. 2017). LC-OCD-based DOM groupings provide a relatively easy measure of DOM size-based composition across a large suite of environments.

Light absorbing and fluorescing components of DOM vary in the environment (Jaffé et al. 2008, 2012) but few studies examine how non-light absorbing DOM components differ across areas with different climate and vegetation. Here we determine the effectiveness of using size-based groupings of DOM to quantify differences in DOM composition and, to our knowledge, present one of few studies that pairs DOM characterization of both groundwater and surface water across a gradient of climate and vegetation regimes. The objectives of this study are: 1) to determine whether differences in DOM composition across a gradient of ecozones can be identified by LC-OCD alone, and 2) to quantify the degree of similarity in DOM composition among hydrological compartments in different ecozones.

2 METHODS

2.1 Site Descriptions

Samples were collected in the summer months (June to August) across various Canadian ecozones (Marshall et al. 1999) that span a mean annual temperature from -9.8 to 6.5°C, precipitation from 313 to 940 mm, and overlie continuous to no permafrost (Figure 1; Suppl. Table 1). Surface water samples were collected from the Boreal Shield (IISD Experimental Lakes Area (ELA)), Mixedwood Plains (agriculturally-impacted Grand River (GR)), Taiga Shield (Yellowknife (YW) and Wekweètì (WK)), and Southern Arctic ecozones (Daring Lake (DL); Suppl. Info Table 1). Groundwater, defined here as water collected beneath the ground surface, was sampled from various depths from the Boreal Shield (Turkey Lakes Watershed (TLW)) Mixedwood Plains (Nottawasaga River Watershed (NRW)), Atlantic Maritime (Black Brook Watershed (BBW)), Taiga Shield (YK, WK), and Southern Arctic (DL). Both NRW and BBW are areas of extensive agriculture. Shallow subsurface samples were collected from the Northwest Territories (deepest extent of active-layer in July or August, ~0.1 to 0.5 meters below surface) and TLW (between 0 to 7 m.b.s), while samples from NRW and BBW were collected at depths ranging between 1 and 30 m.b.s.

2.2 DOM Characterization

All samples were filtered to 0.45µm (Whatman GD/X) into acid-washed and pre-rinsed glass vials. Samples were immediately stored cool (<4°C) and dark until analyses (within two weeks). DOM composition was quantitatively assessed using LC-OCD (DOC-Labor, Karlsruhe, Germany; Huber et al. 2011) at the University of Waterloo. The sample is injected through a size-exclusion column (Toyopearl HW-50S, Tosoh Bioscience) that separates DOM based on hydrodynamic radii into five hydrophilic fractions (from largest to smallest): biopolymers (BP; polysaccharides or proteins), humic substances fraction (HSF; humic and fulvic acids), building blocks (BB; lower weight humic substances), low molecular weight neutrals (LMWN; aldehydes, small organic materials), and LMW-acids (LMWA; saturated mono-protic acids). A portion of the sample bypasses the column for measurement of total dissolved organic carbon concentration. The difference between the overall DOM concentration and the sum of the five eluted fractions is used to quantify a 'hydrophobic parameter'. As hydrophobics are not a measured parameter from the LC-OCD, and that the hydrophilic component comprised 90±9% across all DOM samples, group percentages were normalized to the sum of the eluted components (total hydrophilic fraction, herein referred to as DOM_{hyphl}). Duplicates run at six concentrations yield a precision for the LC-OCD of ±0.09 mg C/L or better. Samples also pass through a UV-Detector (Smartline UV Detector 200, Germany) for determination of the specific ultra-violet absorbance at 254 nm (SUVA), calculated by normalizing the absorbance at this wavelength to the concentration of DOM.

2.3 Statistical Analyses

Multiple sampling events from the same site have been averaged into one value per site (Suppl. Fig S1) and can be viewed in the online data repository (Aukes et al. 2020). Principal component analyses (PCA) was performed using R (R Core Team 2019).

3 RESULTS

3.1 DOM Quantity

Highest DOM concentrations were found in groundwater samples in organic-rich peats from Yellowknife (mean: 97 mg C/L, 1σ: ±40 mg C/L) and ELA (48±22 mg C /L; Figure 2a, Table 1). Lowest concentrations were found in organic-poor groundwater sites (BBW: 0.6±0.4 mg C/L; NRW: 2.1±0.5 mg C /L). The agriculturally-impacted river (GR: 6.1±1.0 mg C /L) contained similar DOM concentrations to Canadian Shield subarctic rivers (YW: 6.6±3.1 mg C /L). Groundwater DOM concentration exhibited greater difference between ecozones than surface water DOM, and were lower in southern than northern areas. In general, a larger range in DOM concentration was found across groundwater than surface water sites.

3.2 DOM UV-Absorbance

The UV-absorbing capability of DOM can be compared across samples using SUVA values. Lowest SUVA values were measured in agriculturally-impacted groundwater DOM and highest in northern groundwater and boreal stream DOM (Figure 2b; Table 1). Unlike samples from ELA, northern ecozone groundwaters (DL, WK, and YW) had higher SUVA values than surface water. Highest SUVA values were encountered in three Boreal Shield lakes at depth (~5-10 m below surface) and may represent samples with iron interference (Weishaar et al. 2003) and are not included in subsequent discussion. Overall, SUVA values were generally similar across ecozones and hydrologic compartments.

3.3 LC-OCD Characterization

Proportions of BP were similar across ecozones, yet different hydrological compartments within an ecozone contained different proportions of BP. Biopolymers ranged from 1-45% of DOM_{hyphl} but generally contributed less than 15% to DOM_{hyphl} (Figure 3a; Table 1). Streams and lakes contained higher BP proportions than groundwaters. Further, groundwater samples from agricultural sites contained the lowest BP proportions (0.4 and 1.3%, respectively). High BP proportions were found in Boreal and Arctic lakes, while moderate BP proportions were found in rivers, close to values found in similar hydrological environments in other studies using LC-OCD (He et al. 2016; Catalán et al. 2017) (Figure 3). The BP fraction of DOM_{hyphl} is more similar across hydrological compartments than comparing different compartments within an ecozone, and high BP proportions are indicative of surface water DOM.

The HSF comprised the largest proportion, representing up to 85% of DOM_{hyphl} in some environments (Figure 3b). Overall, the HSF proportion ranged from 15-85% with the highest proportions found in Taiga Shield groundwater and Boreal streams (Figure 3). Taiga Shield and Southern Arctic lakes and ponds contained higher HSF proportions than Boreal lakes (Table 1). Taiga Shield rivers had slightly lower proportions than an agriculturally-impacted river. Boreal and agriculturally-impacted groundwaters had the lowest HSF proportions, as well as Boreal wetland groundwater (Table 1; Figure 3).

Smaller molecular weight humics, defined as building blocks (BB), ranged from 5 to 37% of DOM_{hyphl}. High BB proportions were found from southern agricultural groundwater samples, while lowest proportions were observed among groundwater samples in organic rich peats in YW and ELA (<10%; Figure 3c). Across ecozones, surface waters had comparable proportions of BB between 10-30% of DOM_{hyphl}.

Proportions of LMWN ranged from 3-76% and were much lower than HSF except among groundwater samples (Figure 3d). DOM from Boreal wetland groundwater sites contained higher LMWN proportions than any other environment (Table 1). Groundwater environments with the lowest HSF proportion had higher LMWN proportions, specifically the agriculturally-impacted sites. Lowest proportions were found from Boreal streams and Arctic groundwater and pond samples. LMWA generally comprised a minor component of total DOM (Figure 3e).

The variability across different sites in LC-OCD defined DOM composition was assessed using PCA. Initially, two principal axes accounted for 60% of the variability within the dataset (Suppl. Fig S2). However, high LMWN proportions from Boreal wetland groundwaters did not allow for a good resolution of other components. For this reason, wetland groundwater samples were omitted (n=28) and the PCA was recalculated based on the remaining samples (n=122; Figure 4). Two principal axes now account for 71% of the variability and illustrates a similarity in DOM composition when comparing hydrologic compartments across ecozones. Distinct compositions are observed comparing lake and groundwater DOM, while rivers and streams contain intermediary compositions between these.

Differences in groundwater DOM composition were identified by HSF and LMWN or BB proportions, while higher BP proportions were common for surface waters. Groundwater DOM from Arctic ecozones (for organic soils) grouped separately from other groundwater samples (from mineral substrate), but were similar in composition to Boreal streams. Lakes can be identified by higher BB and LMWN, lower HS, and occasionally high BP.

4 DISCUSSION

4.1 Can LC-OCD Analyses Differentiate DOM Composition?

This study provided a comprehensive dataset to examine how size-based groupings of DOM can be used to quantify DOM heterogeneity across a range of environmental conditions that spans the Southern Arctic, with long-cold winters and short-cool summers, to the Mixedwood Plains with warm-wet climates and productive soils. Differences in both the absorbing and non-absorbing DOM fractions are apparent (Figure 2, 3) and result from differences in organic matter sources, catchment characteristics, residence times, and processing history (Curtis and Schindler 1997; Jaffé et al. 2008; Mueller et al. 2012). We find that size-based groupings can identify differences in DOM composition not observed measuring optical properties alone. For instance, ELA and TLW wetland groundwater samples contained similar SUVA values (Figure 2b) but different LC-OCD compositions: a greater proportion of degraded humics at TLW than ELA (Figure 3c; Table 1**)**. The use of various characterization techniques would provide different information on DOM and may be the best way to holistically quantify DOM. Differences in size-based groupings of DOM provide additional information suited to identifying differences in DOM composition that is not provided by UV-based techniques alone.

4.2 The Similarity in Groundwater DOM

Groupings of similar hydrologic comparments in the PCA indicates a commonality of DOM composition across spatial scales. The general conception, especially in groundwater environments, is that processing of DOM results in a loss of heterogeneity. For instance, leachate degradation resulted in a convergence towards similar DOM optical properties and degradation kinetics (Harfmann et al. 2019), while physiochemical and biological processes conformed South Carolina soil DOM composition (Shen et al. 2015). The grouping of groundwater DOM in the PCA supports these observations as various ecozones contain similar mixtures of LC-OCD defined components. Groundwater DOM is differentiated from surface water DOM by the proportion of BP, but can be even further separated by HS and LMWN to compare organic-rich contributions (ELA and TLW) to agriculturally-impacted sites (BBW and NRW; Figure 3a; Figure 4). Biodegradation and accumulation of DOM in porewaters (Chin et al. 1998) may be responsible for wetland subsurface DOM from Boreal shield sites being easily identified by high proportions of LMWN. Hence, size-based groupings of groundwater DOM indicates that, while composition can differ among groundwater environments, groundwater contains much different DOM than in surface waters.

4.3 Trends in DOM Composition across Hydrological Compartments

Photolysis and *in-situ* production are two processes that occur among surface waters that alter the composition of DOM, and can be identified in changes to size-based groupings of DOM along the aquatic continuum. Exposure of DOM to sunlight and photochemical transformations of humics results in smaller molecules and increased proportions of BB (Tercero Espinoza et al. 2009; He et al. 2016). This is observed in the dataset by a shift in PCA groupings towards higher BB and LMWN among surface water DOM (Figure 4). High BP in lakes and streams indicate the presence of high molecular weight polysaccharides or proteins that form during *in-situ* production of autochthonous DOM or microbial processing of DOM (Ciputra et al. 2010; Huber et al. 2011; Catalán et al. 2017).

Rivers and streams can act as conduits of DOM transport and internal producers and processors of DOM (Creed et al. 2015), producing a DOM composition intermediary between lake and groundwater end-members. Further, stream DOM composition can identify DOM source as some samples plot closely with either groundwater or lake DOM (Figure 4). Thus, size-based DOM groupings can be used to evaluate the importance of autochthonous versus groundwater sources of DOM in rivers and streams.

Along a hypothetical flow path, terrestrial subsurface DOM is mobilized into surrounding ponds and lakes, and eventually exported from the watershed via rivers or streams. Changes to LC-

OCD components, concurrent with decreases to overall DOM concentration, are found along this hypothetical flow with high-HSF from the subsurface being lost as LMW and BP proportions increase (Figure 3, 4). These changes are in agreement with watershed-scale observations of DOM composition change along a continuum, shifting from relatively high-molecular weight subsurface components to smaller, more degraded, and more aliphatic components (Kellerman et al. 2014; Hutchins et al. 2017). The similarity in DOM composition within hydrological compartments across different ecoregions (Figure 4) represents how intrinsic properties of DOM may be similarly processed regardless of surrounding vegetation or climate.

4.4 Implications of Different Size-Based Groupings of DOM

Differences in DOM composition are linked to its hydrologic compartment, hence shifts or changes to the hydrological regime, such as recent increases to terrestrial-derived DOM, can alter DOM composition, reactivity, and its effect upon the surrounding environment (Creed et al. 2018). Size-based groupings of DOM composition can quantify changes that may help identify lakes experiencing stronger terrestrial influences, such as higher HSF and lower BP. In particular, a shift towards heavier fall rains in the Northwest Territories, Canada (Spence et al. 2011), can enhance terrestrial DOM contributions to surrounding surface waters, which may result in increased pre-treatment costs (Ritson et al. 2014) and higher DBP concentrations (Awad et al. 2016). The ability to characterize and compare specific DOM compositions is important to better predict, plan, and adapt water treatment methods for these climate-induced changes.

5 CONCLUSION

Size exclusion DOM analyses provides a quantitative measure of DOM composition variability across aquatic environments. In some cases, LC-OCD alone identified differences in DOM among hydrologic compartments rather than SUVA. Overall, PCA analyses indicates similar size-based mixtures of DOM among hydrologic compartments regardless of ecozone. Certain characteristics can be used to identify specific hydrologic compartments; namely, proportions of BP and LMWN differentiate surface from groundwater DOM. Groundwater DOM evolves with enhanced processing time and sorption to mineral surfaces into a composition dominated by smaller components. Surface water DOM is much different than groundwater DOM and contains high proportions of processed humics and microbial-like DOM. Implementation of this size-based grouping scheme provides a quantitative tool to measure DOM composition while acknowledging the inherent heterogeneity when attempting to characterize DOM.

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TABLES

Table 1: Dissolved organic matter concentration, specific UV-absorbance at 254 nm (SUVA), and LC-OCD characterization for different sites and hydrological compartments across a range of Canadian ecozones. The LC-OCD percentages are relative to the total hydrophilic fraction of the samples and include biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight neutrals (LMW-N), and LMWN acids (LMWA).

Ecozone	**Location**	**Hydrological Compartment**		**DOM (mg C/L)**		**SUVA (L / (mg m))**		**BP (%)**		**HS (%)**		**BB (%)**		**LMWN (%)**		**LMWA (%)**	
		Type	n	Mean	σ (±)	Mean	σ (±)	Mean	σ (±)	Mean	σ (±)	Mean	σ (±)	Mean	σ (±)	Mean	σ (±)
Southern Arctic	Daring Lake	Subsurface	4	21.0	*9.35*	5.3	*0.5*	5.39	*3.95*	73.1	*4.52*	14.8	*2.75*	6.39	*2.37*	0.30	*0.35*
		Pond	1	4.00		2.2		33.5		39.8		15.3		11.3		0.00	
		Lake	8	5.64	*2.95*	3.4	*1.2*	14.6	*14.4*	58.5	*15.8*	15.6	*3.41*	10.8	*1.93*	0.54	*0.42*
		Stream	10	7.96	*3.44*	3.8	*0.8*	13.3	*9.50*	57.4	*10.4*	17.4	*3.30*	11.0	*1.15*	0.95	*0.48*
Taiga Shield	Wekweètì	Subsurface	1	10.2		4.7		2.09		70.1		14.8		6.91		6.18	
		Lake	6	11.0	*5.05*	3.4	*1.1*	7.24	*4.07*	59.9	*10.3*	20.7	*4.75*	10.3	*2.90*	1.91	*2.36*
		Stream	1	6.24		2.6		12.3		57.2		19.6		9.94		0.91	
Taiga Shield	Yellowknife	Subsurface	17	94.1	*41.4*	4.4	*0.8*	5.79	*3.90*	75.8	*5.93*	10.3	*2.91*	7.15	*1.61*	1.02	*1.75*
		Pond	2	31.9	*2.97*	3.6	*0.4*	5.08	*1.89*	70.5	*1.70*	14.8	*0.53*	8.56	*0.65*	1.04	*0.31*
		Lake	1	27.8		1.5		21.9		52.0		15.8		9.84		0.60	
		Stream	1	16.0		2.0		19.5		55.4		15.8		8.67		0.64	
		River	3	6.49	*1.25*	2.0	*0.2*	10.7	*3.10*	59.8	*2.36*	17.0	*1.27*	10.7	*0.56*	1.76	*2.08*
Boreal Shield	IISD-Experimental Lakes Area	Wetland Subsurface	17	47.8	*22.3*	2.9	*0.9*	7.21	*2.76*	37.2	*13.6*	7.82	*2.65*	46.9	*15.0*	0.81	*1.60*
		Lake	21	7.53	*2.80*	3.2	*1.7*	14.8	*6.21*	49.2	*6.95*	23.0	*3.74*	12.2	*1.82*	0.79	*0.57*
		Wetland Complex	2	12.2	*3.00*	4.3	*0.2*	11.8	*0.71*	58.7	*4.41*	18.1	*2.85*	10.7	*0.54*	0.83	*0.30*
		Stream	11	20.4	*6.77*	5.3	*0.6*	2.50	*2.66*	80.7	*2.85*	9.40	*3.60*	7.27	*1.62*	0.17	*0.27*
	Turkey Lakes Watershed	Wetland Subsurface	9	1.83	*0.69*	3.2	*1.4*	3.20	*4.22*	43.5	*17.7*	21.5	*5.05*	28.0	*18.8*	6.49	*15.8*
		Subsurface	7	4.20	*5.56*	3.4	*1.0*	0.51	*0.40*	58.3	*12.2*	23.5	*7.20*	17.3	*11.5*	0.68	*1.13*
Mixedwood Plains	Nottawasaga Valley	Subsurface	6	2.07	*0.53*	3.6	*0.1*	0.42	*0.26*	54.9	*8.02*	28.8	*5.30*	15.9	*3.24*	0.03	*0.08*
	Grand River	River	7	6.07	*0.73*	2.6	*0.6*	9.54	*0.77*	65.9	*1.78*	14.6	*0.93*	9.60	*0.79*	0.28	*0.45*

Atlantic Maritime	Black Brook	Subsurface	15	0.67	*0.47*	2.3	*0.9*	1.32	*1.39*	53.6	*10.2*	27.3	*7.87*	17.7	*6.66*	0.12	*0.47*

FIGURES

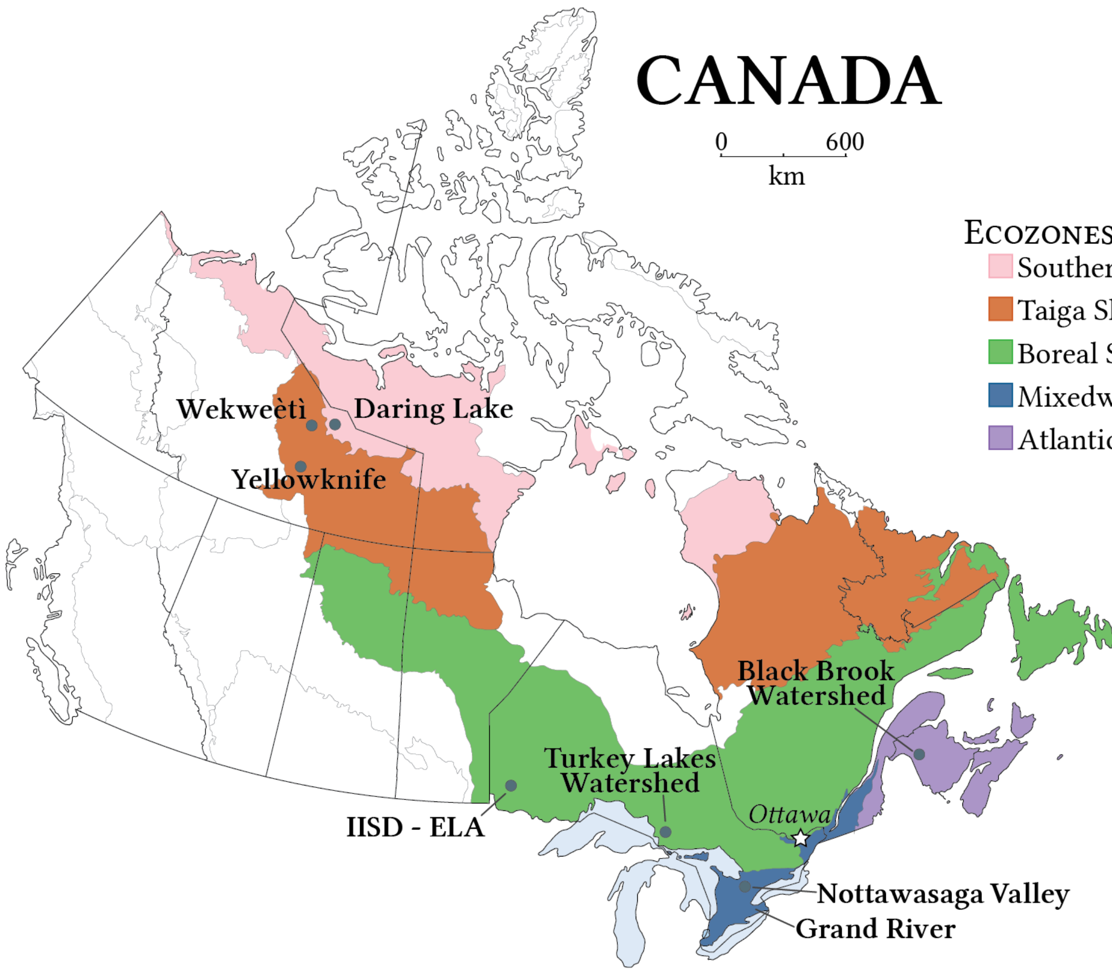

Figure 1: Ecozones (Marshall et al. 1999) and DOM collection sites: Daring Lake (DL; Southern Arctic ecozone), Wekweeti (WK; Taiga Shield ecozone), Yellowknife (YW; Taiga Shield ecozone), International Institute for Sustainable Development - Experimental Lakes Area (IISD-ELA; Boreal Shield ecozone), Turkey Lakes Watershed (TLW; Boreal Shield ecozone), Nottawasaga Valley (NW; Mixedwood Plains ecozone), Grand River Watershed (GR; Mixedwood Plains ecozone), and Black Brook Watershed (BBK; Atlantic Maritime ecozone).

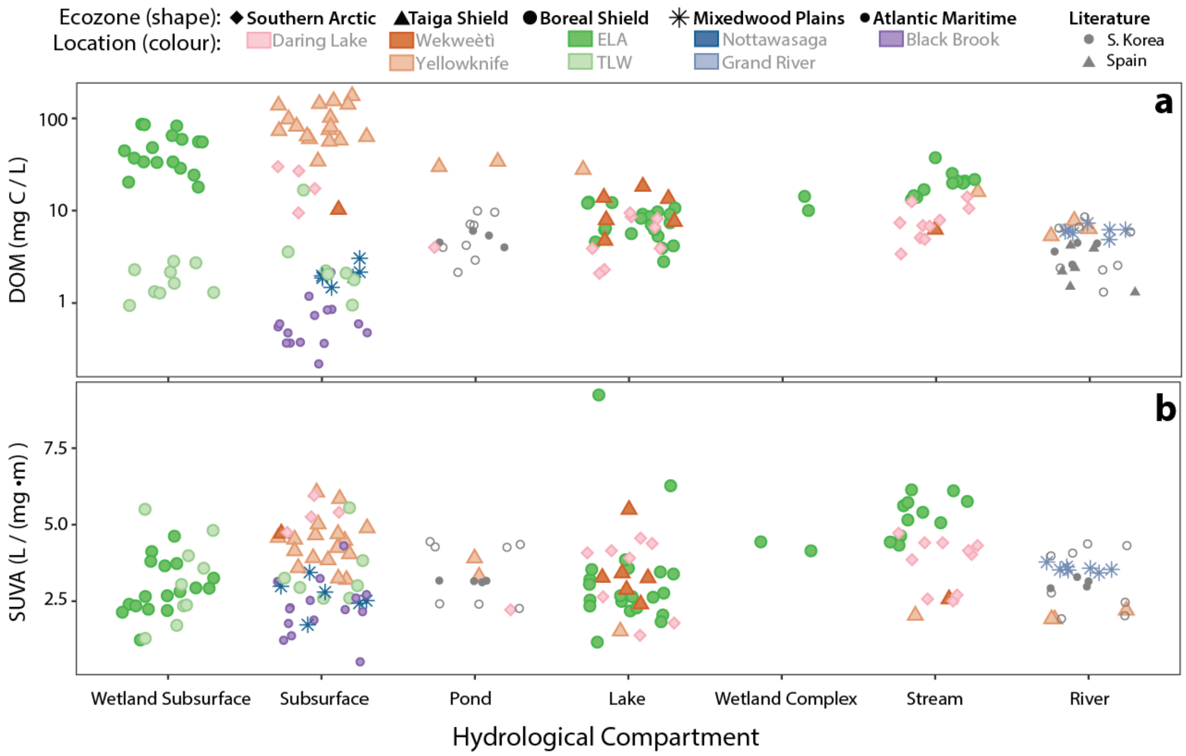

Figure 2: Comparison of dissolved organic matter concentration (DOM; logarithmic y-scale, a) and specific ultra-violet absorbance at 254 nm (SUVA; b) across different hydrological compartments. Different ecozones are denoted by different shapes, and separate locations within each ecozone are differentiated by colour. Included are literature values that use LC-OCD in South Korea (He et al. 2016) and Spain (Catalán et al. 2017), and are denoted by symbols in grey. Literature values from South Korea include a maximum and minimum value found within the study (open circle). Random scatter is introduced in the x-axis for ease of seeing all data points.

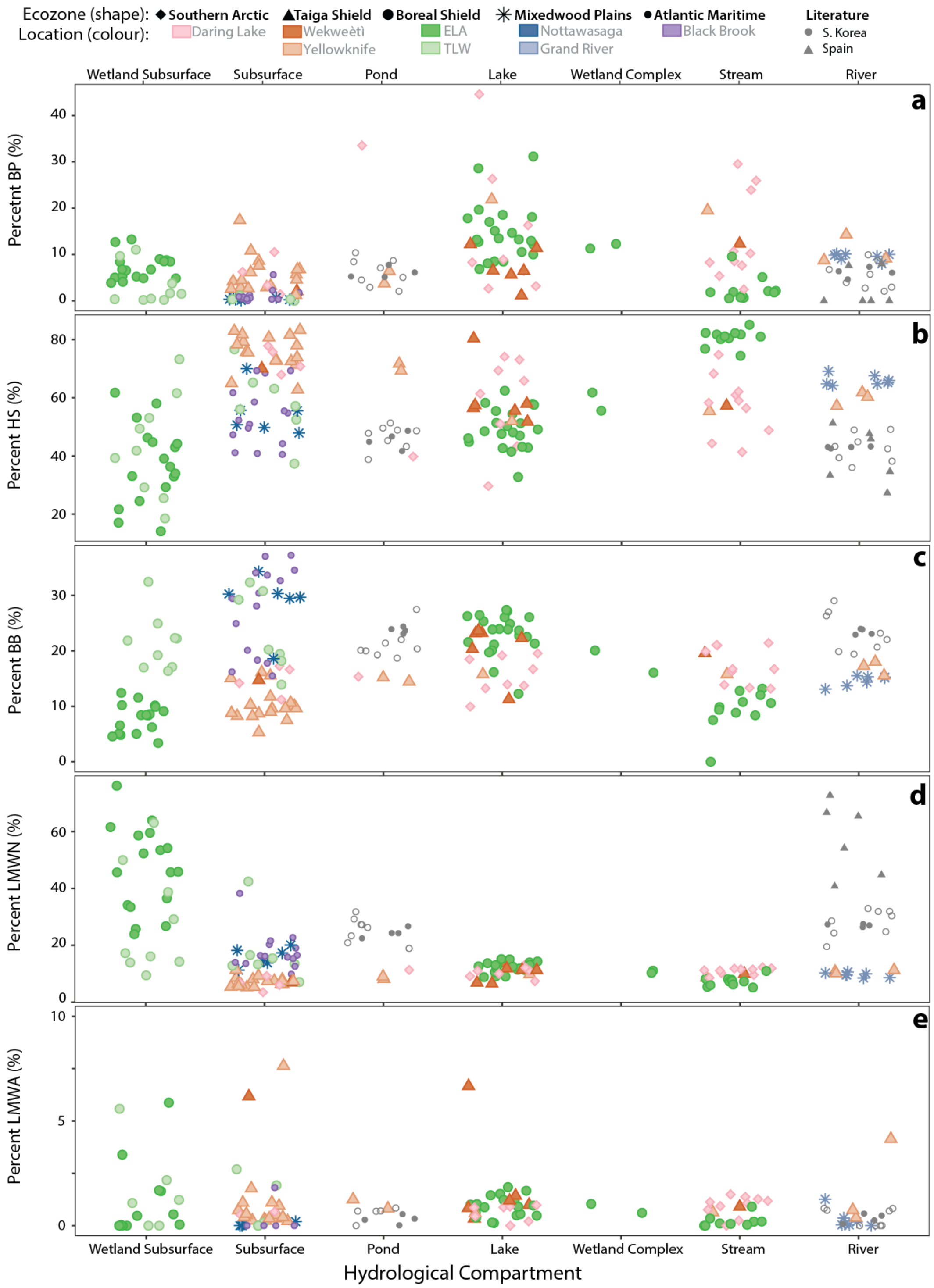

Figure 3: Differences in the composition of DOM based on proportions of LC-OCD groups across hydrological compartments: biopolymers (BP; a), humic substances (HS; b), building blocks (BB; c), low molecular weight neutrals (LMWN; d), and low molecular weight acids (LMWA; e). Different ecozones are denoted by different shapes, and separate locations within each ecozone are differentiated by colour. Included are literature values that use LC-OCD in South Korea (He et al. 2016) and Spain

(Catalán et al. 2017), and are denoted by symbols in grey. South Korea include a maximum and minimum value found within the study (open circle). Random scatter is introduced in the x-axis for ease of seeing all data points.

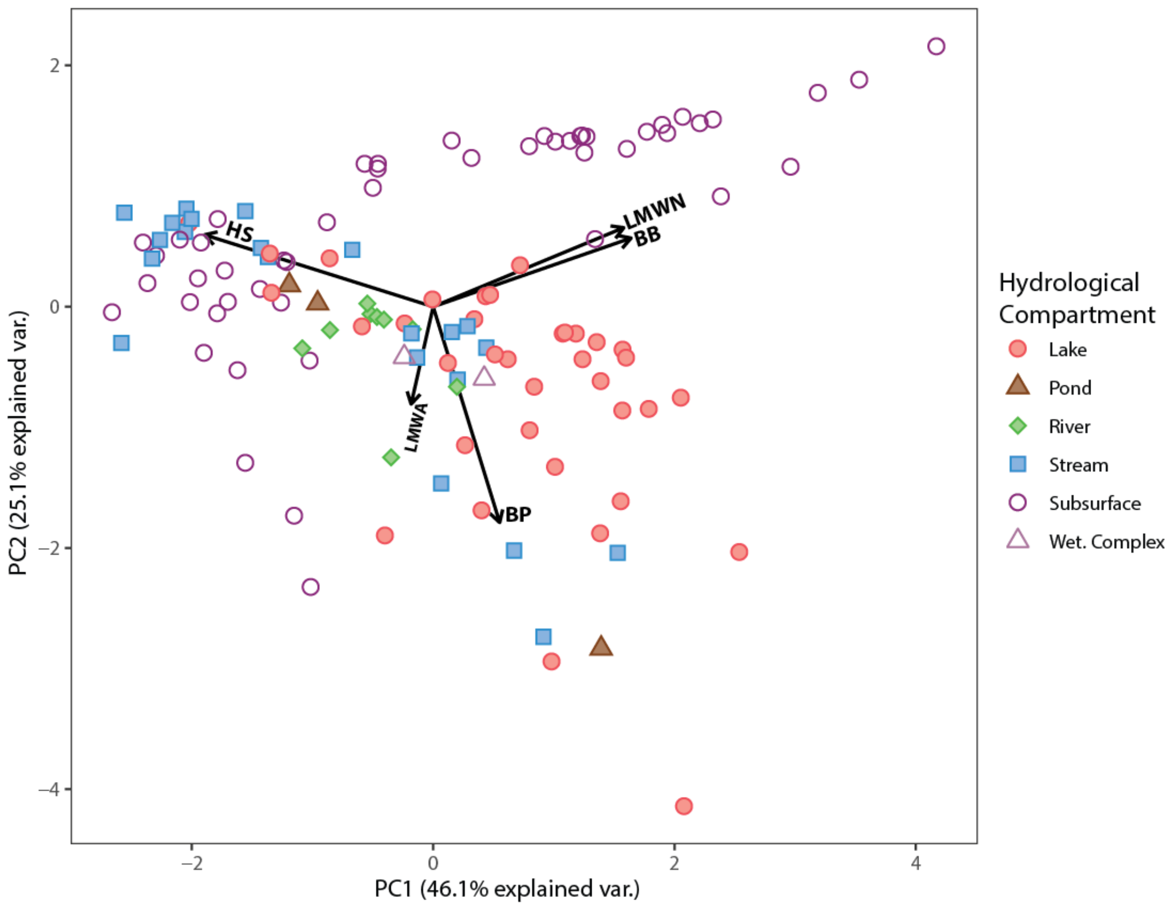

Figure 4: Principal component analyses (PCA) of LC-OCD data (minus wetland groundwater samples) with first and second principal component axes plotted. PCA vectors are included for the proportion of DOM for each LC-OCD group: biopolymers (BP), humic substances fraction (HS), building blocks (BB), low molecular weight neutrals (LMWN), and low molecular weight acids (LMWA).