Contrasting Seasons and Land Uses Alter Riverine Dissolved Organic Matter Composition

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1 CONTRASTING SEASONS AND LAND USES ALTER RIVERINE DISSOLVED ORGANIC 2 MATTER COMPOSITION

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ABSTRACT

Different sources and fates control riverine dissolved organic matter (DOM) composition in catchments of contrasting land use, and climate. However, assessing the changes in DOM composition together with nutrient forms along rivers exposed to these gradients remains rare. Here we quantified the spatial and temporal patterns in DOM components and nutrient forms along the mainstem of a 5th order river through sequential forested, urban, and agricultural reaches during low flow moments in summer and winter, and two contrasting springs, one with a historically rare flooding event. There were widespread abrupt shifts in the composition of DOM in low flow seasons that coincided with changes in land use whose sources could be inferred by endmember samples and nutrient changes. Compared to summer, DOM pools considered bio- (microbial-like) and photo-labile (Peak C) tended to dominate during the winter, along with reactive nutrient forms (ammonium, dissolved phosphorus). This implied higher processing potentials during summer, where microbial-humic-like DOM and nitrate dominated, and accumulation of reactive forms during winter. DOM composition remained relatively stable under typical flow conditions with reduced retention time and processing, but major shifts were observed during an extreme flood year, pointing to unusual loadings of highly labile sources of DOM. Overall we found that, despite relatively small changes in the quantity of DOM flowing in this north temperate river, there were major spatial and temporal shifts in its composition and associated nutrients that reflected contrasting loading and processing potentials depending on land use and seasonal patterns in temperature and hydrology.

Keywords: dissolved organic matter, nutrients, composition, rivers, seasons, land use

INTRODUCTION

Rivers are dynamic ecosystems that receive, transform, and export dissolved organic matter (DOM), inorganic nutrients, and other materials from their watersheds, with impacts on ecosystem processes and communities within the river and beyond. Riverine DOM contributes to the global carbon budget (Cole et al., 2007), is a source of energy to food webs (Fisher & Likens, 1973; Wetzel, 1995), and protects aquatic organisms by reducing UV radiation (Morris & Hargreaves, 1997). Depending on its origin, however, DOM modulates these functions differently depending on its concentration and composition. For example, while humic substances may protect organisms from UV radiation (Morris & Hargreaves, 1997), smaller, protein-like molecules are preferred energy sources for heterotrophic bacteria (Massicotte & Frenette, 2011). Furthermore, anthropogenic DOM sources differ from natural ones. They tend to reduce metal toxicity through greater binding affinity (Baken et al., 2011), but have also been found to decrease microbial functional diversity, at least in agricultural streams (Fasching et al., 2020). Indeed, changes in DOM composition results in shifts in bacterial community structure (Findlay et al., 2003) and functions (Judd et al., 2006). Therefore, evaluating the sources and fate of different riverine DOM components may help better determine how rivers are responding to environmental change.

The amount and nature of DOM loaded from land to rivers depend, in part, on the land use and land cover (LULC) of the surrounding catchment. Increasing human populations have extensively converted pristine forested watersheds into more urbanised and agricultural ones (Pielke Sr. et al., 2011), altering soil organic matter properties and connectivity with land (Lambert et al., 2017 and references therein). Although there is no clear trend in how these anthropogenic changes influence the overall amount of DOM loaded to rivers (Stanley et al.,

2012), most studies that consider DOM composition have found that smaller, microbial, protein-like components dominate in human-dominated catchments (Wilson & Xenopoulos, 2009; Hosen et al., 2014; Lambert et al., 2017; Chai et al., 2019, including others). By comparison, larger, more aromatic molecules appear to dominate in streams draining forested ones (Lu et al., 2015). Along the same line, in the Yangtze River, a catchment home to 430 million people, both DOC and low molecular weight, protein-like DOM concentrations increased along the mainstem, proportional to human population increases (Zhou et al., 2021). While recent studies suggest an effect of LULC on DOM composition, the direction and size of this effect in the context of other environmental changes remain poorly understood.

Once in the water, DOM transformation and removal depends largely on photochemical and microbial reactions, which selectively target specific DOM components. Aromatic and highly unsaturated polyphenols (Riedel et al., 2016) tend to be photodegraded through the cleaving of larger molecular weight molecules into smaller ones (Moran & Zepp, 1997) or oxidized into CO₂ (Cory et al., 2014). By comparison, algal-derived DOM is more easily consumed by heterotrophic bacteria (Benner, 2003). The presence of high inorganic nutrient concentrations stimulates the degradation of DOM, either because autochthonously produced DOM is more labile or recalcitrant forms are more easily accessed (Farjalla et al., 2009; Wickland et al., 2012). As different degradation processes vary over time and favour the removal of different DOM pools, their rates are not only influenced by LULC (Lu et al., 2013) but also by seasonal patterns in temperature, irradiation, and hydrology. In temperate streams and rivers, summer baseflow represents a period of high water residence time, temperature, and sunlight, which result in conditions of high processing potential. But winter also represents another low flow season, albeit with colder temperatures and reduced light availability, particularly where there is ice

cover. The dominance of different nutrient forms between the seasons is suggestive of differential processing potential (Shousha et al., 2021), but how this could alter DOM composition remains underexplored. Between these low flow seasons, rivers alternate with high flow ones. In higher flow conditions, DOC concentrations may be proportionally (Zarnetske et al., 2018), inversely, or even un-correlated with flow, presumably due to greater dilution (Winterdahl et al., 2014). In all cases, higher flows that reduce water retention times within the river will likely lower DOM transformation along the continuum, reducing compositional changes (Weyhenmeyer et al., 2012; Lambert et al., 2016; Raymond et al., 2016). Seasonal sampling of riverine DOM thus offers an opportunity to assess how times and moments of contrasting loading and processing potential may drive riverine DOM composition.

Nutrient concentration and composition are known to vary along gradients of land uses (Merseburger et al., 2005; Shousha et al., 2021). Seasons of contrasting temperature, hydrology and light availability can lead to a disproportionate accumulation of certain forms of nitrogen (N) and phosphorus (P) along a river's axis of flow (Shousha et al., 2021). The presence of such forms can inform on the loadings and transformation processes responsible for potential changes in DOM composition. For example, if photo- or bio-labile DOM is associated with high concentrations of inorganic nutrients such as nitrate (NO_3^-), which are predominantly loaded from agricultural watersheds, this could point to either reduced mineralisation within the ecosystem or high flow conditions (Wiegner et al., 2009; Wu et al., 2019). In contrast, when relatively higher algal-derived DOM is observed with lower concentrations of inorganic nutrients and photo-resistant DOM, a river is likely an active reactor (Casas-Ruiz et al., 2017). As such, a river mainstem of consistent Strahler Order that drains a gradient of land uses and undergoes seasonal extremes may offer a unique opportunity to study DOM composition and its association

to certain nutrient forms. Assessing how DOM components, along with N and P forms, change with these conditions may provide greater insight as to when, where, and how a river receives, transforms, and exports different DOM types to downstream ecosystems, but such studies remain rare. Here we aim to determine how seasonal and land use gradients influence how a temperate river acts as a receiver, processor, and exporter of different DOM components. Specifically, we quantify where and how DOM composition changed along the mainstem of a temperate river with a gradient of LULC during moments of seasonal extremes for three consecutive years. By considering the association of DOM composition with changing nutrient pools along a river mainstem across contrasting conditions of low, high, and extreme flows as well as high versus low temperatures and light availability, we determined which DOM pools were associated with differential loading and processing potentials.

METHODS

Site description

Work was conducted in the *Rivière du Nord* watershed located ~100 km north-west of Montreal, QC, Canada, in the Laurentians region. The watershed mainstem (146.6 km-long Strahler order 5) consecutively drains forested, urban, and agricultural regions (Fig. 1). Sites along the mainstem are numbered by River Kilometer (RKm), as the distance estimated from the river mouth. The forested (RKm 140 to 92) and urban (RKm 92 to 70) portions of the watershed are found in the Canadian Shield, a geographical province with strong topography, abundant lakes, temperate forest, and little topsoil. The forested subwatersheds are covered by < 5% impervious area and < 5% agriculture. The urban reach of the mainstem is characterized by impervious areas covering up to 37%. Agriculture (RKm 70 to outlet) in the lower half of the watershed is supported by rich fertile soils, covers 74% of the area, and is located in the rather flat

geographical province of the St. Lawrence Lowlands. The river is situated in temperate climate and undergoes marked differences in hydrology, with high flows occurring in spring (April) and low flows occurring in summer (August) and ice covered winter (January). The *Rivière du Nord* watershed has been described in more detail in Shousha et al. (2021) and Galantini et al. (2021).

Fig. 1 The Rivière du Nord watershed overlays two geological provinces, the Canadian Shield and the St. Lawrence Lowlands. Its mainstem drains a gradient of landscapes starting from mostly forested regions, to urban, then to agricultural reaches. The sites sampled during the snapshot campaigns are circled in white, while the forested and agricultural tributary

144 *endmembers sampled once in summer 2018 are represented by green and red squares,*
145 *respectively*

146 Geographical and hydrological analyses

147 We delineated the *Rivière du Nord* watershed and its subwatersheds using 1x1 meter digital
148 LiDAR elevation data (Gouvernement du Québec, 2016) in the ArcHydro Toolbox of the ESRI
149 ArcGIS version 10.5.1 193 (ESRI, 2017). Land use and land cover data (Natural Resources
150 Canada, 2009) were intersected with the subwatershed layer to estimate %forest, %urban and
151 %agriculture. Daily discharge data was downloaded from the *Saint-Jérôme*'s gauging station just
152 above RKm 70 (MDDELCC, 2018). Discharge at every site was estimated using the relationship
153 between discharge at the gauging station and proportion of subwatershed surface area. Spring
154 flood recurrences were calculated following $recurrence = (N + 1) / r$, where N is the number of
155 full years with available discharge data (here, 1930 to 2021) and r is the rank of the maximum
156 annual value of mean daily flows. For spring 2018, the maximum annual value at the *Saint-*
157 *Jérôme* gauging station ($218 \text{ m}^3 \text{ s}^{-1}$) ranked the year 27th with a recurrence of 3.41 years. Spring
158 2019 ranked 3rd with a maximum annual value of $303 \text{ m}^3 \text{ s}^{-1}$ and a recurrence of 30.7 years,
159 indicating this magnitude of flood has a ~3% chance of occurring every year. As such, we refer
160 to 2019 as a historically rare flood year.

161 Sampling design

162 We sampled 13 sites once every season from summer 2017 to winter 2020, resulting in 11
163 campaigns. Sampling was conducted over a two-day window to reduce hydraulic variability, but
164 targeted hydraulic extremes within each year to capture contrasting moments of flow, light
165 availability and temperature. Summer and winter both represented seasons of low flow but had

contrasting temperatures and light availability (winter season being ice-covered). Spring sampling was conducted during yearly maximal flow, which was on average up to 11-fold summer baseflow. In summer 2018, we also targeted contrasting tributary sites, five draining > 90% forest cover and five draining > 90% agriculture to characterize forest and agriculture end member signatures of DOM components and nutrient pools. In summer 2021, we sampled the effluent of the wastewater treatment plant serving the largest town in the urban region, *Saint-Jérôme* (population of just over 77 000) as an additional urban end member.

Field measurements

For the 13 mainstem sites, we collected water samples in the middle of the river, just below the surface. This was done by lowering a Van Dorn sampler from a bridge or from a boat, or when neither option was feasible, walking out as far as possible without disturbing sediments and collected water facing the current. In winter, holes in the ice were drilled with an ice-auger. Prior to sampling, bottles for nutrient sampling were soaked in a 10% HCl solution for 24h and rinsed with Milli-Q water multiple times. During sampling, we conditioned the bottles with river water three times before filling them and stored them in coolers. Physical and chemical variables such as water temperature, dissolved oxygen, pH, and conductivity were measured with a hand-held meter (Yellow Springs Instrument, Ohio, United States).

Sample preparation

We stored unfiltered water collected in opaque 0.5L bottles in the dark at -20°C for total N (TN) and total P (TP) analyses. The remaining water was filtered through 0.45 µm Filtropur S 155 polycarbonate filters using a syringe (Sarstedt, Nümbrecht, Germany). Filtrate was collected in 125mL HDPE bottles for ammonium (NH_4^+) and nitrate (NO_3^-), in 250mL bottles for total

188 dissolved N (TDN) and P (TDP), and in 40mL pre-combusted amber vials for dissolved organic
189 carbon (DOC) concentration and dissolved organic matter (DOM) absorbance and fluorescence
190 measurements. Nitrogen and P samples were stored in the dark at -20°C and C, in the dark at
191 4°C.

192 Nutrient analyses

193 Nitrogen forms (NO_3^- , NH_4^+ , TDN, TN) were measured using a Lachat QuickChem 8000 flow
194 injection analyzer (Lachat Instruments, Loveland, United States; USEPA-350.1, 1993; USEPA-
195 352.3, 1993). Dissolved inorganic N (DIN) was calculated as the sum of NO_3^- and NH_4^+ .
196 Dissolved organic N (DON) was calculated as the subtraction of DIN from TDN. Particulate N,
197 as the difference between TN and TDN, accounted for less than 3% of TN and was henceforth
198 disregarded. P forms (TP, TDP) were analyzed with a segmented flow analyzer (Astoria-Pacific,
199 Clackamas, United States; USEPA-365.1, 1993). Total particulate P (TPP) was estimated as the
200 subtraction of TDP from TP.

201 DOM optical properties

202 DOC concentrations were analyzed (USEPA-415.1, 1974) using a TOC analyzer (Aurora 1030,
203 IO Analytical Instruments, Texas, United States). The coloured fraction of DOM (CDOM)
204 absorbance was measured with a Shimadzu UV-1800 spectrophotometer (Agilent Technologies)
205 using a 1cm optical path length in a quartz cuvette from 190 to 900nm (1nm increments).
206 Concentrations of CDOM are reported as the pathlength-corrected absorbance at 440nm. The
207 DOM aromaticity proxy, SUVA_{254} , was calculated as the pathlength-corrected absorbance at
208 254nm divided by DOC concentration (Weishaar et al., 2003). We measured the fluorescent
209 fraction of CDOM, FDOM, with a Cary Eclipse Fluorescence spectrophotometer (Agilent

Technologies) in 1cm quartz cuvettes across excitation and emission wavelengths of 230 to 450 (5nm increments) and 240 to 600 (2nm increments), respectively. FDOM emission and excitation matrices (EEMs) were corrected using the paRafac.correction R library (LaBrie et al., 2017; R Core Team, 2019). This package corrected all the EEMs simultaneously for the inner filter effect and for minor deviations in the light path of the lamp, removed the Raman and Raleigh scattering, and transformed the intensity of the fluorescence which is measured at the peak of the component in Raman units (RU), and referred to as $F_{\max}$. EEMs were then analyzed using the parallel factor analysis (PARAFAC) model (Stedmon et al., 2003) in MATLAB 8.2 (MathWorks, Natick, MA, USA) with the DOMFluor toolbox (Stedmon & Bro, 2008). The model was based on 1078 samples originating from various Québec aquatic ecosystems from temperate and boreal climates. The model validated 5 distinct components (De Bonville et al., 2020; Supplementary Fig. 1), described in Table 1 as the excitation and emission fluorescence peaks. The DOM diversity thus determined is limited to the coloured fraction of organic matter that fluoresces. Our PARAFAC model components were compared with those previously reported in the literature using the OpenFluor website interface (Murphy et al., 2014). C1 has been associated with terrestrially derived DOM, thought to be photo-resistant (Ishii & Boyer, 2012; Kothawala et al., 2014; Zhou et al., 2019). C2 has also been associated with terrestrial humic-like components but is considered more photo-labile and has been found in a number of ecosystems, such as saline lakes (Osburn et al., 2011), thermokarst ponds (Wauthy et al., 2018), and large rivers (Wünsch et al., 2017). C3, often characterized as “microbial humic-like”, has been found in particulate organic matter of summer storms in two South Korean rivers (Derrien et al., 2020), in oligotrophic shallow lakes where it was more photo-resistant than other components (Soto Cárdenas et al., 2017), and in a medium-high impacted Italian river, where it

233 correlated strongly with a protein-like component in summer (Retelletti Brogi et al., 2020). Its
 234 M-peak has also been found in stream water, soil leachates, and leaf leachates (Garcia et al.,
 235 2018). C4 matched with a large number of OpenFluor studies, ranging from large rivers with
 236 often high land-use to shallow or saline lakes, and peatlands. In large rivers, such as the Meuse
 237 and Congo Rivers, authors characterized the equivalent component as widespread, terrestrial,
 238 humic-like, and susceptible to photodegradation, where its contribution decreased in urban and
 239 agricultural subcatchments (Lambert et al., 2017) or under conditions of lower flow (Lambert et
 240 al., 2016). C5 matched with the widely reported protein-like component thought to be freshly
 241 produced or imported in a variety of riverine ecosystems (Lapierre & del Giorgio, 2014;
 242 Gonçalves-Araujo et al., 2015; Osburn et al., 2016; Chen et al., 2017), and has been found in
 243 water extracted organic matter from soils and litter in temperate forests (Wu et al., 2021).

244 Using the FDOMIndices function from the paRafac.correction R library (LaBrie et al., 2017), we
 245 calculated the fluorescence index (FI), the freshness index ($\beta:\alpha$), and the humification index
 246 (HIX). FI is used to differentiate between microbial and terrestrial sources of DOM (McKnight
 247 et al., 2001), $\beta:\alpha$ indicates the contribution of freshly released DOM (Wilson & Xenopoulos,
 248 2009), and HIX increases with greater humicity (Ohno, 2002).

Table 1 Description of the 5 DOM PARAFAC components with associated literature. $\lambda_{Ex}/\lambda_{Em}$ refers to the maximum fluorescence in excitation and emission for every component

	$\lambda_{Ex}/\lambda_{Em}$	Description	OpenFluor TCC >0.95 references*	References not from OpenFluor and their maximum $\lambda_{Ex}/\lambda_{Em}$
C1	245 / 490	Terrestrial humic, rivers draining peatlands Peak A, humic-like fluorophores Ubiquitously terrestrial, UVC-humic, photoresistant, smaller molecular size	Zhou et al. (2019) Kothawala et al. (2014)	Ishii & Boyer (2012) < 230-260 / 400-500
C2	285 / 512	Reoccurring humic-like FDOM Ubiquitous humic-like, photolabile	Wünsch et al. (2017) Murphy et al. (2018)	
C3	< 245 (310) / 414	Humic-like, found in leaf and soil leachates Microbial humic-like	Derrien et al. (2020) Retelletti Brogi et al. (2020)	

		Peak M found in leaf litter of deciduous forests (M _L)	Garcia et al. (2018)	240 (305) / 404
		Peak A+M, unrelated to environmental variables, microbial activity or DOM optical indices	Williams et al. (2010)	310 / 436 < 250 (310) / 416
C4	345 / 452	Widespread terrestrial, humic-like, susceptible to photodegradation Traditional Peak C	Lambert et al. (2017) Lambert et al. (2016) Søndergaard et al. (2003) Chen et al. (2018) Osburn et al. (2011) Zhou et al. (2019)	
		Peak C, probable autochthonous origin Peak C, photolabile Peak W, detergents and whitening agents	Mostofa et al. (2010) Niloy et al. (2021)	≈ 340 / 445
C5	270 / 300	Protein-like, soil and litter from temperate mixed forest Protein-like	Wu et al. (2021) Gonçalves-Araujo et al. (2015) Osburn et al. (2016)	
		Amino acid-like Free protein-like, in riverine sediment pore water	Chen et al. (2017)	270 / 302

* There were only two OpenFluor references for C1, and they matched with a Tucker congruence coefficient (TCC) of > 0.90.
249

250 All analyses were carried out at the *Université de Montréal's* GRIL (*Groupe de recherche*
251 *interuniversitaire en limnologie*) analytical lab. The composition of the C, N, and P pools was
252 estimated as the percent that each elemental form contributed to total C, N, or P concentrations.

253 Statistical analyses

254 Potential shifts in composition were determined with linear and piecewise regressions using the
255 relative contribution of C1-C5 to total fluorescence (expressed as %C1-%C5) as a function of
256 river kilometer. A significant linear relationship would represent a gradual shift in composition,
257 while a significant breakpoint relationship would represent an abrupt shift in composition. For
258 the breakpoint model, the potential breakpoint as well as the intercepts and slopes of each
259 regression line (before and after the breakpoint) were free parameters in the model. We fit both
260 linear and piecewise models in a Bayesian framework using Stan and rstan (Stan Development
261 Team, 2019a, 2019b). Minimally informative regularising priors on the intercepts, slopes, and
262 residual standard deviation parameters, as well as a boundary avoiding prior on the breakpoint

were used to avoid the trivial cases where the breakpoint snaps to the outlet or headwater of the river network. In the case of an abrupt shift (piecewise model), the most probable river kilometer where the shift occurs was noted. These river kilometers (RKm) were then compared among components and seasons.

RESULTS

Climatic conditions

There were large differences in environmental and climatic conditions among seasons (Table 2), except for fall which was similar to summer in terms of discharge, although typically colder. Fall was excluded from further analyses to focus on the most contrasting conditions to assess DOM component and nutrient loading and processing potentials. To do that, we considered average summer and winter conditions as well as the two different springs, the more typical high flow of 2018 and the historical flood of 2019, which had the third highest ever recorded flow since 1931. During the 2-day campaigns, air and water temperatures were highest in summer (mean of 23.5°C and 21.5°C respectively) and lowest in winter (mean of -0.5°C and -0.6°C respectively). Discharge during those campaigns at the *Saint-Jérôme* gauging station (between RKms 70 and 82) was lowest for winter (11.1 m³ s⁻¹) and highest during spring, reaching 143.6 m³ s⁻¹ (2018, normal spring thaw) and 246.3 m³ s⁻¹ (2019, major flood). For both spring flows, we sampled within one day of peak flow.

Table 2 Climatic conditions are shown by season. These include air and water temperatures, discharge averages of the 2-day snapshot campaigns recorded at the *Saint-Jérôme* gauging station, three-month seasonal discharge averages recorded at the *Saint-Jérôme* gauging station, yearly peak flow for both spring campaigns, and some river description. Data represent the average of the variable $\pm$ standard deviation

Variables	Summer (average of 3 campaigns)	Winter (average of 3 campaigns)	Springs	
			2018	2019
Air temperature (°C)	23.5 $\pm$ 3.4	-0.5 $\pm$ 5.2	15.9 $\pm$ 4.2	6.5 $\pm$ 1.5
Water temperature (°C)	21.5 $\pm$ 2.3	-0.6 $\pm$ 1.0	4.0 $\pm$ 2.1	2.0 $\pm$ 0.7

Snapshot discharge ($\text{m}^3 \text{s}^{-1}$)	17.8 ± 7.1	11.1 ± 1.1	143.6 ± 23.8	246.3 ± 18.3
Campaign dates			(May 6 and 7)	(April 25 and 26)
Three-month seasonal average ($\text{m}^3 \text{s}^{-1}$)	11.2 ± 8.3 (July – September)	18.1 ± 12.1 (January – March)	49.26 ± 51.0 (April – June)	81.65 ± 73.9 (April – June)
River particularities	Low-flow, light, warm	Ice cover in 10 out of 13 sites	Typical high flow year	Historical rare flood year

281

282 Non-linear changes in DOM composition

283 The composition of the DOM pool, expressed as the percent contribution of each PARAFAC
284 component to the total fluorescence, tended to shift non-linearly from upstream to downstream.
285 In particular, for most relationships of %C1-5 versus river kilometer, the piecewise relationship
286 with one breakpoint better explained the shift in composition than the no-breakpoint linear model
287 (Fig. 2, example of model output in Supplementary Fig. 2). For summer and winter, 7 out of 10
288 relationships resulted in a significant breakpoint. For these two low-flow seasons, breakpoints
289 were situated between RKm 82 and 69 with a mean at RKm 74, suggesting that the shift in DOM
290 composition changed in terms of strength or direction almost immediately following the urban
291 reach. This also coincided with the transition to the more anthropogenically impacted region of
292 the St. Lawrence Lowlands, a different geological province. For either summer or winter, %C5
293 had no abrupt shift in composition, but there was a slight linear increase from upstream to
294 downstream during winter (from 2.2% to 5.9%, $R^2 = 0.33$, p-value < 0.001). In the typical high-
295 flow spring of 2018, there was no abrupt shift in composition for 4 out of 5 components: %C1,
296 %C3, and %C5 had no relationship with RKm, and both linear and breakpoint models performed
297 equally well to quantify the change in %C4 which appeared to decrease gradually along the
298 continuum (Fig. 2). Contrary to spring 2018, the piecewise model best represented the abrupt
299 change in composition for 4 out of 5 components in spring 2019. On average, the breakpoints
300 were estimated at RKm 84.5, which is situated at the end of the forested region and the

301 beginning of the major urban one. Based on the widespread shift in DOM composition following
 302 the transition from the Canadian Shield to the St. Lawrence Lowlands, we then treated the river
 303 as two different functional units: the pristine upstream reach (sites at RKm 140 to 82), and the
 304 anthropogenic reach altered by urban and agricultural land use changes (sites at RKm 70 to the
 305 outlet). Following a slightly different breakpoint for spring 2019, the pristine reach in this season
 306 included sites from RKm 140 to 92, and the downstream impacted reach included sites from
 307 RKm 82 to the outlet.

308 **Fig. 2** Upstream-downstream changes in DOM components for summer, winter, typical spring of
 309 2018, and extreme flood spring of 2019. The circles on the slopes show whether and where the
 310 model estimated a breakpoint. Y-axes are proportion of variable from 0 to 40 (%). X-axes are
 311 River Kilometer (RKm). All linear relationships were significantly different from 0 (p -value <
 312 0.1), otherwise we plotted a horizontal slope that represented no change

Compositional changes in high flow seasons

DOM composition (%C1-5) appeared virtually unchanged during the typical high flow season of spring 2018 as most upstream-downstream variations were small (Fig. 2). However, there were pronounced changes in composition in spring 2019 and we wanted to determine if these changes were related to shifts in concentrations. Indeed, shifts were mostly driven by the unusually high C5 concentration found upstream (mean = 0.47 Raman Units (RU), sd = 0.31, with a wide range of 0.17 to 1.07 RU; Fig. 3), which were on average 5-fold higher than those downstream (mean = 0.09 RU, sd = 0.04). Spring 2019 upstream C5 concentrations were also on average 8-fold higher than those of spring 2018 (mean = 0.059 RU). The spring 2019 C3 concentrations followed a similar trend (Fig. 3). These sharp shifts in DOM components in 2019 were coherent with the patterns in HIX and BIX, which showed the lowest (least humified) and highest (freshest) values during the major flood year (Table 3).

Fig. 3 Upstream-downstream changes in DOM concentration for the typical high flow spring of 2018 and the extreme high flow spring of 2019. The circles on the slopes show where our model estimated a breakpoint. Y-axes are component concentrations measured as Raman Units (RU) from 0 to 1.2. X-axes are River Kilometer (RKm). All linear relationships were significantly

330 *different from 0 ($p\text{-value} < 0.1$), otherwise we plotted a horizontal slope that represented no*
331 *change*

332 Compositional changes in low flow seasons

333 Winter vs summer

334 There were less pronounced, but consistent changes in the DOM components and associated
335 nutrient forms in the two low flow seasons of summer and winter, and these changes differed
336 depending on LULC and season. The biggest spatial changes were for %C4 and %NH₄⁺, which
337 showed the highest relative increase from upstream to downstream, and conversely for %C1-2
338 and %DON, which showed the highest decrease (Fig. 4 x-axis). The biggest seasonal differences
339 were for %NH₄⁺, %TDP, and %C4, which were relatively more abundant in winter, and for
340 %C3, %DON, and %TPP which were relatively more abundant in summer (Fig. 4 y-axis). Thus,
341 %C1, %DON and %TPP found in the bottom-left quadrant (c) were more dominant in moments
342 of high processing potential and areas of pristine sources of terrestrial material, whereas %C4-5,
343 %TDP and %NH₄⁺ found in the top-right quadrant (b) were more dominant in moments of low
344 processing potential and areas of urban or agricultural sources (Fig. 4).

Fig. 4 Changes in the composition of DOM components and nutrient forms from upstream to downstream (x-axis from left to right) and between winter and summer (y axis top or bottom). Values represent the delta of the z-scores of the different components and forms % contribution to total concentrations between seasons (y-axis) versus land use changes on the x-axis as the delta between pristine versus anthropogenic reaches. Colours match colours used in Figs. 2 and 3, and grey is used for N and P forms

Forest, urban, and agricultural endmembers

Tributaries draining primarily forested or agricultural catchments (i.e., “endmembers”), as well as the effluent of a wastewater treatment plant (WWTP), had contrasting composition in DOM components and in nutrients forms. Percent DOM components 1, 2 and 4 were on average higher in the forested endmembers (Table 3). Percent C3 was higher in the agricultural endmembers and highest in the WWTP effluent. C5 was found in almost identical, low proportions in both

forested and agricultural endmembers (mean of 2.9% of total fluorescence, Table 3), but reached a high of 11.4% in the effluent. This DOM anthropogenic signature co-occurred with change in relative nutrient composition, with NO_3^- representing most (81.5%) of the N pool in agricultural endmembers and NH_4^+ (93.2%) and TDP (88.0%) representing most of the N and P pools in the WWTP. Most (94.3%) of the N in the forested endmembers consisted of DON, and P was in majority (61.5%) composed of TDP.

Upstream-downstream shifts in DOM as a function of endmember sources

We then determined how the upstream to downstream shifts in DOM components and nutrient forms in summer were coherent with the composition of predominant sources along the mainstem. DOM components C1 and C2 were relatively more abundant upstream (Fig. 5a) as well as in the forested endmembers (Fig. 5b), suggesting that a relative decrease in these components along the mainstem was coherent with a change in the inputs going downstream. There were no significant changes in protein-like C5 among endmembers nor along the mainstem, suggesting that it was not predominantly driven by changes in loadings. C3, TPP and NO_3^- were relatively more abundant in the agricultural endmembers compared to the upstream to downstream patterns (Fig. 5c). This suggests that agricultural loadings are important sources of these DOM and nutrient forms for downstream sites, but that they are under-represented in the mainstem. In contrast, DON, NH_4^+ , TDP and C4 were relatively more abundant in the mainstem than in the endmembers of the corresponding river sections (Fig. 5c). This suggests that sources other than forested loadings support concentrations of DON in upstream sites, and that sources other than agricultural loadings support concentrations of NH_4^+ , TDP and C4 in downstream sites. WWTP effluent could plausibly account for NH_4^+ and TDP (Supplementary Fig. 3), but apparently did not account for proportional increase in C4 (Table 3).

383 **Fig. 5** Differences in DOM components and associated nutrient forms between forested and
384 agricultural endmembers (panel b) help explain differences in composition between the two
385 mainstem reaches (panel a). Panel c shows the difference between panels b and a on the y-axis
386 and the difference between the mainstem reaches on the x-axis (also the y-axis of panel a).
387 Variables plotting above the horizontal 0 are richer in the forested or agricultural endmembers
388 than in the mainstem; variables plotting below the horizontal 0 are richer in the mainstem. Values
389 were taken from the summer seasons only

Table 3 Averages of % C1-C5, % elemental nutrient form, and certain proxies for summer, winter, and springs in both pristine and impacted regions, extreme forested and agricultural endmembers sampled in summer 2018, and the <i>Saint-Jérôme</i> WWTP intake and effluent sampled in summer 2021.												
Variable	Canadian Shield				Saint-Lawrence Lowlands				Endmembers		WWTP ^c	
	Summer	Winter	Spring 2018	Spring 2019	Summer	Winter	Spring 2018	Spring 2019	Forest (n=5) ^a	Agric. (n=5) ^b	Intake (n=1)	Effluent (n=1)
% C1	34.7	35.1	34.5	24.4	32.2	31.1	34.2	35.0	35.5	33.6	9.4	25.2

% C2	8.6	9.4	9.7	8.7	7.0	7.0	8.9	9.6	9.4	8.1	4.2	5.5
% C3	34.0	30.8	31.8	34.9	35.0	32.2	32.7	29.9	31.6	35.9	50.1	42.0
% C4	18.6	20.7	21.3	15.5	21.9	23.5	20.9	21.2	20.5	19.5	9.8	15.8
% C5	4.2	4.0	2.8	16.4	3.9	6.2	3.3	4.3	2.9	2.9	26.4	11.4
% NH ₄ ⁺	8.9	25.2	8.1	7.1	15.6	45.4	8.7	9.0	1.3	1.4	-	93.2
% NO ₃ ⁻	32.7	43.9	46.4	62.6	54.8	37.2	50.5	57.9	12.7	81.5	-	3.6
% DON	54.6	31.3	45.6	28.0	25.4	14.7	35.3	29.8	94.3	15.0	-	3.2
% TDP	45.5	70.0	39.5	30.4	54.4	71.0	25.2	22.2	61.5	55.0	-	88.0
% TPP	54.5	30.0	60.5	69.6	45.6	29.0	74.8	77.8	38.5	45.0	-	12.0
DOC (mg/L)	5.9	4.5	5.0	5.6	6.4	4.9	5.3	5.2	8.2	9.8	26.1	11.6
DOC:DON	37	28	31	51	29	29	31	33	25	12	-	17
Sum/DOC	0.39	0.36	0.42	0.49	0.48	0.41	0.42	0.40	0.46	0.54	0.30	0.42
SUVA ₂₅₄	4.6	4.7	5.6	5.0	4.4	4.2	5.0	5.0	5.0	3.1	0.99	2.0
CDOM	4.4	3.4	3.7	3.9	4.6	3.4	3.9	3.9	6.2	4.8	1.8	1.4
FI	1.20	1.24	1.21	1.22	1.45	1.52	1.22	1.19	1.20	1.37	1.66	1.62
β:α	0.51	0.50	0.46	0.90	0.50	0.51	0.49	0.47	0.49	0.62	0.89	0.81
HIX	0.92	0.93	0.94	0.79	0.92	0.91	0.93	0.92	0.94	0.94	0.65	0.84

^a These are the forested endmembers sampled in summer 2018, represented as green squares in Fig. 1.

^b These are the agricultural endmembers sampled in summer 2018, represented as red squares in Fig. 1.

^c These refer to the wastewater treatment plant intake and effluent sampled in summer 2021.

390

391 DISCUSSION

392 To empirically assess the origin and fate of DOM in a north temperate river, we targeted areas
393 and moments of contrasting potential in terms of loadings and processing. We found that despite
394 relatively low quantitative changes in the concentrations of dissolved organic carbon (Shousha et
395 al., 2021), there were consistent changes in the composition of DOM that were modulated by
396 seasons and land use, and that were informed by patterns observed for nutrient composition. In
397 moments or areas of low processing, the observed shifts in DOM composition would be
398 predominantly due to compositional differences in the inputs from varying land use and land
399 cover. Conversely, in a scenario where all inputs are qualitatively equal, changes in DOM
400 composition would be due to the preferential removal of certain pools via photochemical or
401 microbial degradation, flocculation, or sedimentation. Realistically, both loading and processing
402 mechanisms interact to control DOM composition, and considering joint patterns with nitrogen

(N) and phosphorus (P) forms allowed us to determine how the *Rivière du Nord* receives, transforms and exports different pools of DOM across land uses and seasons.

DOM composition under contrasting loading potentials: low flow conditions

During low flow seasons we observed widespread, sharp breakpoints in the upstream-downstream patterns of DOM and nutrient concentrations and composition, suggesting qualitative changes in the loadings from land. These were typically found at the boundary of the Canadian Shield and the St. Lawrence Lowlands geological provinces (Figs. 2, 3). Across this boundary, the upstream DOM and nutrient pools shifted from being dominated by higher %C1-2, and %dissolved organic nitrogen (DON), to being dominated by higher %C3-4-5, %ammonium (NH_4^+), and %nitrate (NO_3^- , x-axis on Fig. 4); P forms varied the least. Mechanisms that may explain this shift include groundwater or subsurface inputs from forested or agricultural landscapes, urban inputs, and autochthonous production, but not all mechanisms may affect all forms equally. For example, C1 and C2 are widely recognized as DOM pools of terrestrial, forested origins (Ishii & Boyer, 2012; Wünsch et al., 2017), and DON has been found to contribute ~80% of total N in streams draining unimpacted forested watersheds (Hedin, 1995; McGroddy et al., 2008). This supports the higher relative abundance of C1-2 and DON in the upstream mainstem reach which is dominated by forest cover.

Moving downstream, C3 and C4 became increasingly dominant relative to the total FDOM pool, coherent with presumed agricultural and urban sources. The increasing dominance in C4 concurred with higher proportions of NH_4^+ in the downstream mainstem reach, coherent with an urban source for both pools that may originate from WWTP inputs (Gücker et al., 2006; Waiser et al., 2011; Shousha et al., 2021). In particular, we measured high concentrations and

proportions of NH_4^+ and TDP in the *Saint-Jérôme* WWTP effluent (22.7 mg L^{-1} and 0.28 mg L^{-1} , respectively), which accounted for 9.9 and 7.4% of the total river discharge in winter and summer, respectively (Shousha et al., 2021). C4, NH_4^+ and TDP were all more relatively abundant in the mainstem than in the agricultural endmembers (Fig. 5c), suggesting that the sharp increase of these forms downstream is explained by a non-agricultural, but rather urban, source. A component similar to our C4 ($\lambda_{\text{Ex}}/\lambda_{\text{Em}} = 345/452$), Peak W, has previously been identified in detergents and whitening agents (Mostofa et al., 2010; Niloy et al., 2021), which is coherent with an urban point source. However, C4 was not particularly dominant in the WWTP effluent (15.8% in effluent vs 21.9% in the downstream mainstem), suggesting that if the source of C4 is urban in our study, it may originate from overland flow rather than from the WWTP point source.

Agricultural inputs appeared as important sources of C3, which was relatively higher in the agricultural tributary endmembers than in the downstream mainstem reach (1.9 vs 1.05 RU , Fig. 5). This further suggests that there may be processing or dilution from upstream flow of this DOM pool in the river that prevents it from reaching proportions representative of agricultural sources. A similar pattern was observed for NO_3^- (downstream mainstem: 713 ug L^{-1} or 55%, agricultural endmembers: 5861 ug L^{-1} or 82%), which we have attributed to an agricultural source (Shousha et al., 2021), coherent with the wide use of tile drainage in the region (MRC d'Argenteuil, 2011) and the high mobility of NO_3^- in the soil matrix (Caraco & Cole, 1999). A recent study conducted in a river of similar size, land use, and geology found a DOM component similar to our microbial humic-like C3 and associated it autochthonously produced DOM (Retelletti Brogi et al., 2020), and other studies conducted in a variety of aquatic ecosystems support that this component may have some non-terrestrial origins (Asmala et al., 2014;

Retelletti Brogi et al., 2021). In the *Rivière du Nord* watershed, the higher C3 concentrations found in the agricultural tributaries could be due to direct in situ autochthonous production supported by the higher N and P concentrations or recent production of this component in agricultural soils and its subsequent leaching to the mainstem. Finally, protein-like C5 was generally the least variable from upstream to downstream during low-flow moments (Fig. 2, Supplementary Fig. 4), suggesting an ubiquitous behaviour that may be explained by a tight balance between input or production and processing in the river of this labile component (Lapierre & del Giorgio, 2014). It was dominant in the WWTP effluent (sampled during the summer; Supplementary Fig. 5), yet we did not measure a significant breakpoint going downstream in low flow conditions (Fig. 2, Supplementary Fig. 4), suggesting rapid uptake. Under very high land use, a similar DOM component has been shown to increase with human population in the 6 000km long Yangtze River (Zhou et al., 2021), but in the *Rivière du Nord*, land use appeared insufficient to break the balance between input and removal. It is only under extreme flow conditions that unusually high concentrations and proportions of this component have been measured (Figs. 2, 3), suggesting contrasted loading and processing potential under different hydrological settings.

DOM composition under contrasting loading potentials: extreme flow conditions

The observed behaviour of DOM and its coupling with nutrients provide evidence of distinct loading scenarios occurring as a function of land use and hydrological events. High flows would typically lead to low transformation of DOM (Weyhenmeyer et al., 2012; Lambert et al., 2016; Raymond et al., 2016), and this was indeed the pattern observed for spring 2018 in the *Rivière du Nord* (Figs. 2, 3). In this context, however, the major shifts observed during the historical flood of 2019 were surprising, with very high concentrations and proportions of the protein-like C5

471 and microbial humic-like C3 in the upstream portion of the river (Fig. 3). Two lines of evidence
472 may explain this pattern. As the upper forested region of the watershed is mainly covered with
473 deciduous trees (Abrinord, 2015), fresh litter decomposition that accumulated in top soils and
474 rich in protein-like (Wu et al., 2021) or microbial humic-like (Garcia et al., 2018) organic matter
475 may have been temporarily transported to the mainstem during the flood. Another possible
476 source could be sewage overflows from several small sewerred villages upstream of *Saint-Jérôme*
477 during the flood in 2019 (4 villages in sequence, total population ~30 200). The WWTP intake
478 sampled in summer 2021 was enriched in C3 and C5 (Table 3, Supplementary Fig. 5) and should
479 largely represent other sewer intakes in the region. DOM indices may also help support this
480 provenance. Although SUVA₂₅₄ and FI stayed relatively constant at $4.65 \pm 0.73 \text{ L mg}^{-1} \text{ m}^{-1}$ and
481 1.3 ± 0.16 , respectively, throughout the mainstem and among seasons, suggesting a strong
482 overall aromatic content of the DOM pool flowing in *Rivière du Nord*, other indices varied
483 between periods of low and high flow, and LULC changes. The freshness index ($\beta:\alpha$) was
484 highest (0.90) in the spring 2019 upstream mainstem reach compared to any other moment or
485 place, forested (0.49) and agricultural (0.62) endmembers included, but very close to the WWTP
486 intake (0.89) and effluent (0.81; Table 3). $\beta:\alpha$ values close to 1 are indicative of strong microbial
487 activity and have been measured in several other WWTPs (Li et al., 2020). The humification
488 index (HIX) in the spring upstream mainstem reach (0.79) resembled the WWTP intake HIX
489 (0.65), which could also point towards potential, somewhat diluted, sewage overflow sources.
490 Similarly, low HIX values were indeed found in other WWTP intakes or effluents (Li et al.,
491 2020). Another study with a strong urban gradient found a positive relationship between their
492 tyrosine and tryptophan components and discharge at their most downstream site gauging
493 discharge (Zhou et al., 2021), which they hypothesised came from treated and untreated sewage

flushing over impervious areas. However, in the *Rivière du Nord*, there were no obvious signs of higher overflow frequency or magnitude in 2019 vs 2018 (MDDELCC, 2021). Furthermore, in terms of a nutrient response, the NO_3^- concentration was almost 1.5 times higher in the upstream mainstem reach during the extreme flood year (368 ug L^{-1}) compared to the more normal 2018 year (287 ug L^{-1}), whereas NH_4^+ remained the same (2018 = 50 ug L^{-1} , 2019 = 57 ug L^{-1}). This suggests that overflows should not be the main source of DOM during the extreme flood, as we would have captured a strong NH_4^+ signal. Higher NO_3^- combined with the C3 and C5 however may be a function of a stronger leaching from septic beds, along with higher inputs from subsurface flow after winter N processing (Creed & Band, 1998). Approximately 70% of the population in the northern reaches of the river's wastewater is treated through septic and even modest urbanization in the area can impact the NO_3^- signal in surface waters (Charrier Tremblay et al., 2020). While it is not possible to assess whether decomposed leaf litter, overflows, septic leaching or subsurface inputs contributed more to the changes in C3 and C5, these changes combined with higher NO_3^- suggests that these likely co-occurred, and it was clear that extreme flow events led to unusually high loadings toward the end of the pristine reach of the river (Figs. 2, 3) resulting in major breakpoints in the DOM composition of certain components along the river at high flow.

DOM composition under contrasting processing potentials

Differences between summer and winter DOM composition hinted at variations in the preferential removal of certain forms as a function of light and temperature availability. In particular, the DOM pool in the downstream mainstem reach in winter was dominated by C4-5, along with NH_4^+ and TDP nutrient forms (Fig. 4, quadrant b), while in summer it was dominated by C3 and NO_3^- (quadrant d). This illustrates how the DOM and nutrient pools differ at the river

mouth despite flowing along the same watershed in two seasons of contrasting processing potential.

The largest change in DOM components between both seasons was for %C3, which we propose originated in summer from recent production either in the agricultural soil or, more probabilistically, in the water through phototrophic processes. In winter, lower light and temperature would reduce autochthonous production, thus explaining the lower C3 concentrations (Supplementary Fig. 4) and proportions (Fig. 4) compared to summer. The second largest change was for %C4. Relative abundances for the whole river were almost the same (20.1% vs 19.9% in summer and winter, respectively), but concentrations of other components in winter were smaller, leading to a higher dominance of %C4, especially downstream. Following the breakpoint at Rkm 74, winter C4 concentrations also increased from upstream to downstream, a pattern opposite to summer observations (Supplementary Fig. 4). As C4 is thought to be a photolabile component (Dainard et al., 2015; Zhou et al., 2019), ice cover may have protected it from irradiation during the winter. C5 was also more dominant in winter than in summer (Fig. 4), potentially due to lower uptake. While there was no stepwise increase in concentrations in either season, the slow and steady increase in winter C5 (Fig. 2, Supplementary Fig. 4) may be explained by the higher groundwater contribution in this season (Peralta-Tapia et al., 2015). Combined with reduced uptake under the ice, groundwater inputs rich in microbial-like DOM (O'Donnell et al., 2010; Hobara et al., 2014; Shen et al., 2015) could lead to the increase we observed in winter C5 along the continuum. Thus, the forms that dominate the winter pools (C4, C5, NH_4^+ , TDP) highlight not only the inputs of highly reactive or bio-labile forms of C, N, and P from predominantly urban or groundwater sources, but also the lower processing potential during the cold and dark winter season that allow these pools to persist in

the water. The pool of DOM and nutrients measured downstream during summer highlights how the most bio-reactive forms measured during winter have been removed between the urban reach and the river mouth. The summer downstream pool reflects within stream production (dominated by C3) and likely groundwater inputs for NO_3^- from the fertile plains of the St. Lawrence Lowlands.

Hence, through the seasons, the *Rivière du Nord* exports alternating pools of DOM and nutrients that differ in their reactivity and persistence as a function of land use, land cover, and climate. These findings likely transpose well to most temperate rivers, which like *Rivière du Nord* tend to be exposed to large gradients of land uses across their continuum and experience seasonal variations in hydrology, temperature, and light availability. In temperate regions where snowfall is important, both spring precipitation and snowmelt constitute major drivers of riverine peak flow (Berghuijs et al., 2016). Precipitation is predicted to increase in winter and spring in certain regions of North America such as in Québec, Canada (Mailhot et al., 2008, 2012) with more extreme events likely to occur in the future (Trenberth et al., 2003). As such, extreme spring flows may become more frequent and mobilize unusually large amounts of microbial and protein-like sources of DOM from land to water, while summer droughts may be more common and lead to preferential removal of specific pools of DOM and nutrients. Winter temperatures are also predicted to increase (Ouranos, 2015) reducing snow mass, a trend already seen in the last decades in North America (Pulliainen et al., 2020). Combined with urban expansion and agricultural intensification, the predicted changes in seasonal hydrology and ice cover thus have the potential to greatly affect how temperate rivers receive, process and export DOM and nutrients of various sources and fates in the aquatic environments, with impacts on ecosystem processes of the rivers themselves and the downstream receiving environments.

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889

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896 We have no competing interests to disclose.

897 Author Contributions

898 SS, RM and JFL designed the study. SS performed sampling, analyses, and writing of the initial
899 draft. JFL and RM edited subsequent drafts.

900 Data Availability

901 The datasets generated during the current study will be available on the Zenodo repository upon
902 acceptance of the manuscript.

903

CONTRASTING SEASONS AND LAND USES ALTER RIVERINE DISSOLVED ORGANIC MATTER COMPOSITION

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Fig. 1 Five DOM components identified using Parallel Factor Analysis (PARAFAC)

Fig. 2 Bayesian model output showing where the estimated breakpoint would fall along the river. The thick black vertical line represents the breakpoint median of 3000 estimation outputs (RKm 75.2) for the variable “winter %C4”. The thin grey vertical lines represent the 95% credible intervals. The thin dust-coloured vertical lines show an example of 100 of those 3000 estimation outputs. Estimated rates of change in %C4 are also shown with the black dotted line (pristine reach) and the red dotted line (impacted reach). These linear regressions were modelled via the Bayesian breakpoint model and estimated slopes and intercepts are -1.3606 and 0.17, and -0.0003 and 0.23, for the pristine and impacted reaches, respectively

Fig. 3 Difference between the urban and forested endmembers for dissolved organic matter components (C1-5) as identified by PARAFAC, and nutrient forms (ammonium (NH₄⁺), nitrate (NO₃⁻), dissolved organic nitrogen (DON), total particulate phosphorus (TPP), and total dissolved phosphorus (TDP)). Values were calculated as the difference in the z-scores of the urban effluent (August 2021 sampling) and forested tributary endmember average (summer 2018 sampling)

Fig. 4 Upstream-downstream changes in DOM components for summer and winter. The circles on the slopes show where our model estimated a breakpoint. Y-axes are component concentrations measured as Raman Units (RU) from 0 to 1.2. X-axes are River Kilometer (RKm). All linear relationships were significantly different from 0 (p -value < 0.1), otherwise we plotted a horizontal slope that represented no change. The breakpoints are visualized with dots and are situated at RKm

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952 **Fig. 5** DOM components measured in the intake and effluent of the *Saint-Jérôme* wastewater

953 treatment plant in August 2021. Proportions are represented as pie charts (percentage) and

954 concentrations as bar plots (Raman units)