Contrasting seasons and land uses alter riverine dissolved organic matter composition

Stéphanie Shousha · Roxane Maranger · Jean-François Lapierre

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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. DOM pools considered bio- (microbial-like) and photo-labile (Peak C), along with reactive nutrient forms (ammonium, dissolved phosphorus) tended to accumulate during the winter compared to summer. This implied higher processing during summer as microbial-humic-like DOM and nitrate dominated. DOM composition remained relatively stable under typical spring high 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 DOM. Overall, we found that despite relatively small changes in the quantity of DOM along the axis of flow in this north temperate river, there were major spatial and temporal shifts in its composition, associated with different nutrient forms. These changes inferred contrasting loading and processing potential 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 and Likens 1973; Wetzel 1995), and protects aquatic organisms by reducing exposure to UV radiation (Morris and Hargreaves 1997). Depending on its origin, hence concentration and composition, however, DOM modulates these functions differently. For example, while humic substances may protect organisms from UV radiation (Morris and Hargreaves 1997), smaller, protein-like molecules are preferred energy sources for heterotrophic bacteria (Massicotte and Frenette 2011). DOM sampled in urban streams tended to reduce metal toxicity through greater binding affinity (Baken et al. 2011), but decreased microbial functional diversity in agricultural streams (Fasching et al. 2020). As changes in DOM composition result in shifts in bacterial community structure (Findlay et al. 2003) and functions (Judd et al. 2006), 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 et al. 2011), altering soil organic matter properties and its connectivity with land (Lambert et al. 2017 and references therein). Anthropogenic land uses alter DOM concentration and composition in varying magnitude and direction, and these changes are often context dependent (Xenopoulos et al. 2021). Overall, most studies that consider DOM composition have found that smaller, microbial, protein-like components are more abundant in human-dominated catchments (Wilson and 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. 2013). 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 depend 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 and Zepp 1997) or oxidised 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 can stimulate 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; Bengtsson et al. 2018). 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 in regions with ice and snow cover. The dominance of different nutrient forms among seasons is suggestive of differential processing potential (Shousha et al. 2021), but how this could alter DOM composition remains underexplored. In higher flow conditions, which occur in spring in temperate regions, 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 moments of contrasting loading and processing potential may drive riverine DOM composition.
Nutrient concentrations 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 nitrogen (N) and phosphorus (P) forms 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. This study builds on the findings of Shousha et al. (2021) who found relatively constant DOC concentrations, i.e. DOM quantity, along the mainstem of a temperate river across seasons despite strong land use changes. Here we further quantify where and how DOM composition, i.e. quality, changed along the same river with its 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 (140 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 characterised 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 and snow covered winter (January). The *Rivière du Nord* watershed has been described in more detail in Shousha et al. (2021) and Galantini et al. (2021).

**Geographical and hydrological analyses**

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

Sampling design

We sampled 13 sites along the mainstem of Rivière du Nord once every season from summer 2017 to winter 2020, resulting in 11 campaigns. Sampling was conducted over a two-day window to reduce hydraulic variability, but targeted hydraulic extremes within each year to capture contrasting moments of flow, light availability and temperature. Summer and winter both represented seasons of low flow but had contrasting temperatures and light availability (winter season being ice and snow-covered). Spring sampling was conducted during yearly maximal flow, which was on average up to 11-fold summer baseflow. To characterise forest and agriculture endmember signatures of DOM components and nutrient pools, we also targeted contrasting headwater tributary sites, five draining >90%
forest cover and five draining >90% agriculture in summer 2018. As such, when we refer to end-member sites, we refer to the sites in the tributaries draining mostly forested land cover or agriculture land use. In summer 2021, we sampled the effluent of the wastewater treatment plant (WWTP) serving the largest town in the urban region, Saint-Jérôme (population of just over 77 000) as an additional urban endmember. This WWTP discharges just downstream of RKm 70 (Fig. 1; effluent discharge coordinates 45.53, −74.33). Human and industrial activities as well as the types of wastewater treatments are assumed to have remained similar throughout the study period, suggesting that DOM composition in the WWTP intake and effluent at the measured time point represents characteristic loadings. However, it is possible that this composition is more variable and certain interpretations related to this topic should be made with caution.

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 collecting 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 24 h 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. Water temperature 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 for ammonium (NH$_4^+$) and nitrate (NO$_3^-$), in 250 mL bottles for total dissolved N (TDN) and P (TDP), and in 40 mL pre-combusted amber vials for dissolved organic matter (DOM) absorbance and fluorescence measurements. Nitrogen and P samples were stored in the dark at −20 °C, and DOM in the dark at 4 °C.

Nutrient analyses

Detailed methods for the measurement of N and P forms have been described in Shousha et al. (2021). Briefly, N forms (NO$_3^-$, NH$_4^+$, TDN, TN) were measured using a Latchat QuickChem 8000 flow injection analyser (Latchat Instruments, Loveland, United States; USEPA-350.1 1993; USEPA-352.3 1993). Dissolved inorganic N (DIN) was calculated as the sum of NO$_3^-$ and NH$_4^+$. Dissolved organic N (DON) was calculated as the subtraction of DIN from TDN. Particulate N, as the difference between TN and TDN, accounted for less than 3% of TN and was henceforth disregarded. Phosphorus forms (TP, TDP) were analysed with a segmented flow analyser (Astoria-Pacific, Clackamas, United States; USEPA-365.1 1993). Total particulate P (TPP) was estimated as the subtraction of TDP from TP.

DOM optical properties

The coloured fraction of DOM (CDOM) absorbance was measured with a Shimadzu UV-1800 spectrophotometer (Agilent Technologies) using a 1 cm optical path length in a quartz cuvette from 190 to 900 nm (1 nm increments). Concentrations of CDOM are reported as the pathlength-corrected absorbance at 440 nm. The DOM aromaticity proxy, SUVA$_{254}$, was calculated as the pathlength-corrected absorbance at 254 nm divided by DOC concentration (Weishaar et al. 2003). We measured the fluorescent fraction of CDOM, FDOM, with a Cary Eclipse Fluorescence spectrophotometer (Agilent Technologies) in 1 cm quartz cuvettes across excitation and emission wavelengths of 230 to 450 (5 nm increments) and 240 to 600 (2 nm 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 $F_{\text{max}}$. EEMs were then analysed using the parallel factor analysis (PARAFAC) model (Stedmon et al. 2003) in MATLAB 8.2 (MathWorks, Natick, MA, USA) with the DOMFluor toolbox (Stedmon and Bro 2008). The model was based on 1,078 samples originating from various Québec aquatic ecosystems from temperate and boreal climates. The model validated 5 distinct components (De Bonville et al. 2020; Supplementary Table 1

| $\lambda_{\text{Ex}}/\lambda_{\text{Em}}$ | Description                                                                 | OpenFluor TCC > 0.95 references* | References other than OpenFluor, with associated $\lambda_{\text{Ex}}/\lambda_{\text{Em}}$ |
|--------------------------------------|-----------------------------------------------------------------------------|-----------------------------------|-------------------------------------------------|
| C1 245 / 490                         | Terrestrial humic, rivers draining peatlands                               | Zhou et al. (2019)                |                                                 |
|                                      | Peak A, humic-like fluorophores                                            | Kothawala et al. (2014)           |                                                 |
|                                      | Ubiquitously terrestrial, UVC-humic, photoresistant, smaller molecular size | Ishii and Boyer (2012)            | <230–260 / 400–500                               |
| C2 285 / 512                         | Reoccurring humic-like FDOM                                               | Wünsch et al. (2017)              |                                                 |
|                                      | Ubiquitous humic-like, photolabile                                       | Murphy et al. (2018)              |                                                 |
| C3 <245 (310) / 414                   | Humic-like, found in leaf and soil leachates                               | Derrien et al. (2020)             |                                                 |
|                                      | Microbial humic-like                                                      | Retelletti Brogi et al. (2020)    |                                                 |
|                                      | Peak M found in leaf litter of deciduous forests (ML)                     | Garcia et al. (2018)              | 240 (305) / 404 310 / 436                       |
|                                      | Peak A + M, unrelated to environmental variables, microbial activity or DOM optical indices | Williams et al. (2010)            | <250 (310) / 416                                |
| C4 345 / 452                         | Widespread terrestrial, humic-like, susceptible to photodegradation       | Lambert et al. (2017)             |                                                 |
|                                      | Traditional Peak C                                                        | Lambert et al. (2016)             |                                                 |
|                                      | Peak C, probable autochthonous origin                                     | Søndergaard et al. (2003)         |                                                 |
|                                      | Peak C, photolabile                                                       | Chen et al. (2018)                |                                                 |
|                                      | Peak W, detergents and whitening agents                                   | Zhou et al. (2019)                |                                                 |
| C5 270 / 300                         | Protein-like, soil and litter from temperate mixed forest                  | Wu et al. (2021)                  |                                                 |
|                                      | Protein-like                                                              | Gonçalves-Araujo et al. (2015)    |                                                 |
|                                      | Amino acid-like                                                           | Osburn et al. (2016)              |                                                 |
|                                      | Free protein-like, in riverine sediment pore water                        | Chen et al. (2017)                | 270 / 302                                       |

$\lambda_{\text{Ex}}/\lambda_{\text{Em}}$ refers to the maximum fluorescence in excitation and emission for every component

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

Table 1 Description of the 5 DOM PARAFAC components with associated literature

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Fig. 1), described in Table 1 as the excitation and emission fluorescence peaks. The change in DOM reported here refers only to the coloured fraction of organic matter that fluoresces (Stubbins et al. 2014), and can be compared with the rich literature using the OpenFluor website interface (Murphy et al. 2014). C1 has been associated with terrestrially derived DOM and thought to be photo-resistant (Ishii and 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 correlated strongly with a protein-like component in summer (Retelletti Brogi et al. 2020). Its M-peak has also been found in stream water, soil leachates, and leaf leachates (Garcia et al. 2018). C4 matched with a large number of OpenFluor studies, ranging from large rivers with often high land-use to shallow or saline lakes, and peatlands. In large rivers, such as the Meuse and Congo Rivers, authors characterised the equivalent component as widespread, terrestrial, humic-like, and susceptible to photodegradation, where its contribution decreased in urban and agricultural subcatchments (Lambert et al. 2017) or under conditions of lower flow (Lambert et al. 2016). C5 matched with the widely reported protein-like component thought to be freshly produced or imported in a variety of riverine ecosystems (Lapierrre and del Giorgio, 2014; Gonçalves-Araujo et al. 2015; Osburn et al. 2016; Chen et al. 2017), and has been found in water extracted organic matter from soils and litter in temperate forests (Wu et al. 2021).

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

All analyses were carried out at the Université de Montréal's GRIL (Groupe de recherche interuniversitaire en limnologie) analytical lab. The composition of the C, N, and P pools was estimated as the percent that each elemental form contributed to total C, N, or P concentrations. For example, $\% \text{NH}_4^+ = [\text{NH}_4^+] / [\text{Total N}]$.

Statistical analyses

Potential shifts in composition were determined with linear and piecewise regressions using the relative contribution of C1–C5 to total fluorescence (expressed as $\%$C1–$\%$C5) as a function of river kilometer. A significant linear relationship would represent a gradual shift in composition, while a significant breakpoint relationship would represent an abrupt shift in composition. For the breakpoint model, the potential breakpoint as well as the intercepts and slopes of each regression line (before and after the breakpoint) were free parameters in the model. We fit both linear and piecewise models in a Bayesian framework using Stan and rstan (Stan Development Team 2019a, 2019b). Minimally informative regularising priors on the intercepts, slopes, and 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.

From these analyses, numerous breakpoints were identified with regards to chemical composition around the heavily urbanised areas of Saint-Jérôme between the geological provinces, suggesting chemically distinctive reaches upstream and downstream from that area. As such, we quantified the differences between forms of C, N, and P (in $\%$) as the arithmetic difference between the two reach segments, after having centered and scaled the values. Using $\%\text{NH}_4^+$ as an example, the formula was the following:
A positive resulting value would suggest a greater contribution of NH$_4^+$ to the total N pool in the downstream reach. These differences are the values plotted in Fig. 4 (x-axis), Fig. 5b (y-axis) and Fig. 5c (x-axis), and labelled “Difference in composition between mainstem reaches”. The same calculation was performed to quantify the difference between seasons (winter averages minus summer averages, Fig. 4 y-axis labelled “Difference in composition between seasons”), and between endmembers (agricultural endmembers minus forested endmembers, Fig. 5a y-axis labelled “Difference in composition between endmembers”). To elucidate whether mainstem C, N, and P pools could be explained by forested or agricultural inputs (as represented by the sampled endmembers), we calculated:

\[
\text{Contrast between endmember and mainstem (Fig. 5c y-axis)} = \text{Difference in composition between endmembers (Fig. 5a y-axis)} - \text{Difference in composition between mainstem reaches (Fig. 5b y-axis)}
\]

A positive resulting value would suggest that the variable represents a higher proportion of the C, N, and P pools in the endmembers (whether agricultural or forested) than in the mainstem (whether upstream or downstream). This would infer that the endmember is an important source of that variable. A negative value would suggest that the source of the variable to the mainstem is other than agricultural or forested (ex: groundwater, in situ production, urban).

**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 m$^3$ s$^{-1}$) and highest during spring, reaching 143.6 m$^3$ s$^{-1}$ (2018, normal spring thaw) and 246.3 m$^3$ 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

| Variables                  | Summer (average of 3 campaigns) | Winter (average of 3 campaigns) | Springs 2018 | Springs 2019 |
|----------------------------|---------------------------------|---------------------------------|--------------|--------------|
| Air temperature (°C)       | 23.5 ± 3.4                      | − 0.5 ± 5.2                     | 15.9 ± 4.2   | 6.5 ± 1.5    |
| Water temperature (°C)     | 21.5 ± 2.3                      | − 0.6 ± 1.0                     | 4.0 ± 2.1    | 2.0 ± 0.7    |
| Snapshot discharge (m$^3$ 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 (m$^3$ 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 properties           | Low-flow, high light availability, warm | Ice and snow cover in 10 out of 13 sites | Typical high flow year | Historical rare flood year |

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 ± standard deviation.
Non-linear changes in DOM composition

The composition of the fluorescent DOM pool, expressed as the percent contribution of each PAR-AFAC component to the total fluorescence, shifted non-linearly from upstream to downstream for a little more than half the cases. In particular, for most relationships of %C1-5 versus river kilometer, the piecewise relationship with one breakpoint better explained the shift in composition than the no-breakpoint linear model (Fig. 2; example of model output in Supplementary Fig. S2). For summer and winter, 6 out of 10 relationships resulted in significant breakpoints between RKm 74 and 76 with a mean at RKm 75. This suggests a shift in DOM composition, that changed in terms of strength or direction almost immediately following the urban reach, which also coincided with the transition to the more anthropogenically impacted region of the St. Lawrence Lowlands. For either summer or winter, %C5 had no abrupt shift in composition, but there was a slight linear increase from upstream to downstream during winter (from 2.2% to 5.9%, R² = 0.33, p-value < 0.001). In the typical high-flow spring of 2018, there was no abrupt shift in composition for any component: %C1, %C3, %C4, and %C5 had no relationship with RKm, and both linear and breakpoint models performed equally well to quantify the change in %C2 which appeared to decrease gradually along the continuum along with %C4 (Fig. 2). Contrary to spring 2018, the piecewise model best represented the abrupt change in composition for all components in spring 2019. On average, the breakpoints were estimated at RKm 85, which is situated at the end of the forested region and the beginning of the major urban one. Based on the widespread shift in DOM composition following the transition from the Canadian Shield to the St. Lawrence Lowlands, we then treated the river as two different functional units: the pristine upstream reach (sites at RKm 140 to 82), and the anthropogenic reach altered by urban and agricultural land use changes (sites at RKm 70 to the outlet). Following a slightly different breakpoint for spring 2019, the pristine reach in this season included sites from RKm 140 to 92, and the downstream impacted reach included sites from RKm 82 to the outlet.

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 fivefold higher than those downstream (mean = 0.09 RU, sd = 0.04). Spring 2019 upstream C5 concentrations were also on average eightfold 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 β:α (Supplementary Figs. S5-S8), which showed the lowest (least humified) and highest (freshest) values during the major flood year (Table 3).

Compositional changes in low flow seasons

Winter vs summer

There were less pronounced, but consistent changes in the DOM components and associated nutrient forms in the two low flow seasons of summer and winter compared to spring, and these changes differed depending on LULC and season. The biggest spatial changes were for %C4 and %NH₄⁺, which showed the highest relative increase from upstream to downstream, and conversely for %C1-2 and %DON, which showed the highest decrease (Fig. 4 x-axis). The biggest seasonal differences were for %NH₄⁺, %TDP, and %C4, which were relatively more abundant in winter, and for %C3, %DON, and %TPP which were relatively more abundant in summer (Fig. 4 y-axis). Thus, %C1, %DON and %TPP found in the bottom-left quadrant (c) were more dominant in moments of high processing potential and areas of pristine sources of terrestrial material (summer, upstream), whereas %C4-5, %TDP and %NH₄⁺ found in the top-right quadrant (b) were more dominant in moments of low processing potential and areas of urban or agricultural sources (winter, downstream; Fig. 4).
Fig. 2 Upstream–downstream changes in DOM components for summer, winter, typical spring of 2018, and extreme flood spring of 2019. The summer and winter slopes include all three years of sampling. Y-axes are proportion of variable from 0 to 40 (%). X-axes are River Kilometer (RKm). The linear relationships significantly different from 0 (p-value < 0.1) are represented by solid lines, and the horizontal slopes that represent no change by dashed lines. The raw data and associated slopes are shown in Supplementary Figs. S3 and S4.

Fig. 3 Upstream–downstream changes in DOM components for the typical high flow spring of 2018 and the extreme high flow spring of 2019. Y-axes are fluorescent intensities reported in Raman Units (RU) from 0 to 1.2. X-axes are River Kilometer (RKm). The linear relationships significantly different from 0 (p-value < 0.1) are represented by solid lines, and the horizontal slopes that represent no change by dashed lines. The raw data and associated slopes are shown in Supplementary Fig. S4.
Table 3  Averages ± standard deviations of % C1–C5, % elemental nutrient form, and certain proxies for summer, winter, and springs in both upstream pristine and downstream impacted regions, extreme forested and agricultural endmembers sampled in summer 2018, and the Saint-Jérôme WWTP intake and effluent sampled in summer 2021

| Variable | Canadian Shield (Upstream) | | St. Lawrence Lowlands (Downstream) | | Endmembers | WWTP<sup>c</sup> |
|----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|          | Summer (n = 21) | Winter (n = 21) | Spring 2018 (n = 6) | Spring 2019 (n = 6) | Summer (n = 18) | Winter (n = 18) | Spring 2018 (n = 7) | Spring 2019 (n = 7) | Forest (n = 5)<sup>a</sup> | Agric. (n = 5)<sup>b</sup> | Intake (n = 1) | Effluent (n = 1) |
| % C1 | 34.7 ± 1.1 | 35.2 ± 1.0 | 34.6 ± 1.1 | 24.4 ± 6.8 | 32.2 ± 2.1 | 31.2 ± 1.4 | 34.2 ± 1.4 | 35.0 ± 1.2 | 35.1 ± 0.5 | 33.9 ± 0.9 | 9.4 | 25.2 |
| % C2 | 8.6 ± 0.3 | 9.4 ± 0.4 | 9.7 ± 0.1 | 8.7 ± 0.9 | 7.0 ± 1.2 | 7.0 ± 0.5 | 9.0 ± 0.3 | 9.6 ± 0.2 | 9.2 ± 0.6 | 8.2 ± 0.3 | 4.2 | 5.5 |
| % C3 | 34.0 ± 0.9 | 30.8 ± 0.7 | 31.7 ± 0.7 | 34.9 ± 3.9 | 35.0 ± 1.5 | 32.2 ± 0.5 | 32.7 ± 1.3 | 29.9 ± 0.5 | 32.5 ± 2.1 | 35.7 ± 0.8 | 50.1 | 42.0 |
| % C4 | 18.6 ± 0.9 | 20.7 ± 0.8 | 21.4 ± 0.6 | 15.5 ± 3.6 | 22.0 ± 2.1 | 23.5 ± 1.0 | 21.0 ± 0.5 | 21.2 ± 0.7 | 20.0 ± 1.5 | 19.8 ± 0.1 | 9.8 | 15.8 |
| % C5 | 4.1 ± 1.6 | 3.8 ± 1.4 | 2.6 ± 1.2 | 16.4 ± 7.6 | 3.9 ± 1.4 | 6.1 ± 2.3 | 3.1 ± 0.6 | 4.3 ± 1.8 | 3.8 ± 1.0 | 2.3 ± 0.6 | 26.4 | 11.4 |
| % NH4<sup>+</sup> | 8.9 ± 7.9 | 25.2 ± 9.3 | 6.5 ± 1.4 | 7.1 ± 0.8 | 15.8 ± 11.3 | 44.5 ± 9.3 | 10.0 ± 4.0 | 9.0 ± 1.1 | 1.2 ± 1.1 | 1.7 ± 0.8 | – | 93.2 |
| % NO3<sup>−</sup> | 32.9 ± 18.8 | 43.9 ± 5.6 | 46.0 ± 2.5 | 62.6 ± 3.3 | 53.8 ± 13.6 | 37.4 ± 7.2 | 50.2 ± 3.9 | 57.9 ± 3.6 | 11.9 ± 5.2 | 79.9 ± 7.0 | – | 3.6 |
| % DON | 54.6 ± 24.4 | 31.3 ± 10.0 | 45.9 ± 6.2 | 28.0 ± 5.1 | 26.2 ± 11.3 | 15.0 ± 10.7 | 36.5 ± 4.8 | 29.8 ± 1.9 | 75.5 ± 7.7 | 15.8 ± 7.1 | – | 3.2 |
| % TDP | 45.5 ± 12.1 | 70.0 ± 14.7 | 42.8 ± 16.7 | 30.4 ± 8.2 | 54.9 ± 10.3 | 70.7 ± 7.7 | 24.4 ± 3.3 | 22.2 ± 5.3 | 51.6 ± 17.3 | 51.9 ± 13.7 | – | 88.0 |
| % TPP | 54.5 ± 12.1 | 30.0 ± 14.7 | 57.2 ± 16.7 | 69.6 ± 8.2 | 45.1 ± 10.3 | 29.3 ± 7.7 | 75.6 ± 3.3 | 78.7 ± 5.3 | 48.4 ± 17.3 | 48.1 ± 13.7 | – | 12.0 |
| SUVA<sub>254</sub> | 4.6 ± 0.6 | 4.7 ± 0.7 | 5.7 ± 0.5 | 5.0 ± 0.5 | 4.4 ± 0.8 | 4.2 ± 0.8 | 5.0 ± 0.4 | 5.0 ± 0.4 | 5.0 ± 0.5 | 3.2 ± 0.2 | 0.99 | 2.0 |
| CDOM | 4.4 ± 2.0 | 3.4 ± 1.5 | 6.0 ± 0.5 | 3.9 ± 0.8 | 4.6 ± 2.6 | 3.4 ± 1.7 | 5.49 ± 0.5 | 3.97 ± 0.7 | 6.5 ± 1.3 | 5.7 ± 0.3 | 1.8 | 1.4 |
| FI | 1.20 ± 0.06 | 1.24 ± 0.06 | 1.21 ± 0.04 | 1.22 ± 0.08 | 1.45 ± 0.2 | 1.52 ± 0.1 | 1.21 ± 0.07 | 1.19 ± 0.05 | 1.23 ± 0.05 | 1.38 ± 0.04 | 1.66 | 1.62 |
| β:α | 0.51 ± 0.03 | 0.50 ± 0.02 | 0.46 ± 0.02 | 0.90 ± 0.31 | 0.50 ± 0.04 | 0.51 ± 0.02 | 0.48 ± 0.03 | 0.47 ± 0.02 | 0.50 ± 0.04 | 0.62 ± 0.01 | 0.89 | 0.81 |
| HIX | 0.92 ± 0.02 | 0.93 ± 0.01 | 0.94 ± 0.01 | 0.79 ± 0.08 | 0.92 ± 0.02 | 0.91 ± 0.02 | 0.93 ± 0.01 | 0.92 ± 0.02 | 0.93 ± 0.01 | 0.95 ± 0.01 | 0.65 | 0.84 |

<sup>a</sup>These are the forested endmembers sampled in summer 2018, represented as green squares in Fig. 1.
<sup>b</sup>These are the agricultural endmembers sampled in summer 2018, represented as red squares in Fig. 1.
<sup>c</sup>These refer to the wastewater treatment plant intake and effluent sampled in summer 2021, represented as a light blue X in Fig. 1.
Forest, urban, and agricultural endmembers

Tributaries draining primarily forested or agricultural catchments (i.e., “endmembers”), as well as the effluent of a WWTP, had contrasting composition in DOM components and in nutrient forms (Table 3, Supplementary Figs. S9, S10 for significant differences). Percent DOM components 1, 2 and 4 were on average higher in the forested endmembers. 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 2.8 ± 0.9% of total fluorescence), 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 (79.9 ± 7.0%) 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 effluent. Most (75.5 ± 7.7%) of the N in the forested endmembers consisted of DON. No P form significantly differed in forested or agricultural endmembers.

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

We determined if the composition, and upstream to downstream shifts in DOM components and nutrient forms could be inferred from the different endmember sources during the summer. As the endmember sites were only sampled in summer, comparisons with the mainstem were only assessed for that season. DOM components C1 and C2 were relatively more abundant upstream (Fig. 5b) as well as in the forested endmembers (Fig. 5a), 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 (Fig. 5a) compared to the mainstem reaches (Fig. 5c). This suggests that agricultural loadings are important sources of these DOM and nutrient forms for downstream sites. In contrast, DON, NH$_4^+$, TDP and C4 were relatively more abundant in the mainstem, independent of river reach, than in the endmembers (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 Figs. S11, S12), but apparently did not account for proportional increase in C4 (Table 3).

Discussion

To empirically assess the origin and fate of DOM in a north temperate river, we targeted river reaches and seasons of contrasting potential in terms of loadings and processing. We found that despite relatively low quantitative changes in the concentrations of dissolved organic carbon (Shousha et al. 2021), there were consistent changes in the fluorescent DOM composition that were modulated by seasons and land use, and that were informed by patterns observed for nutrient composition. This suggests that loading and processing mechanisms of different types of DOM are compensative rather than cumulative in this river. In moments or areas of low processing, the observed shifts in DOM composition would be predominantly
due to compositional differences in the inputs from varying land use and land cover. Conversely, in a scenario where all inputs are qualitatively equal, changes in DOM composition would be due to the preferential removal of certain pools via photochemical or microbial degradation, flocculation, or sedimentation. Realistically, both loading and processing mechanisms interact to control DOM composition, and considering joint patterns with N and 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 (Fig. 2). Across this boundary, the upstream DOM and nutrient pools shifted from a higher %C1–2 and %DON, to being enriched in %C3–4–5, %NH4+, and %NO3− (Fig. 4x-axis); 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 affect all forms or river reaches equally. For example, C1 and C2 are widely recognized as DOM pools of terrestrial, forested origins (Ishii and 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. Interestingly, C1 percent contribution revealed a stepwise decrease across the breakpoint, when other components became more abundant, followed by a linear increase post-breakpoint. This suggests relatively important punctual inputs of other components around the breakpoint, as opposed to a more continuous input of ubiquitous C1. As a result, the accumulation of C1 along the downstream portion of the mainstem was faster than other components.
Moving downstream, C3 and C4 also became dominant relative to the total FDOM pool, but in this case, this is likely due to 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 relatively more 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, 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% or 0.778 RU in effluent vs 21.9% or 0.721 RU in the downstream mainstem). To solely account for the stepwise increase in C4, the WWTP effluent concentration should have been ~3 RU. This suggests that C4 in our study may originate from an urban source other than from the WWTP, but our data do not allow us to identify it.

Both urban and agricultural inputs appeared as important sources of C3. Up to 90% of the stepwise increase at RKm 74 can be explained by the WWTP effluent ([C3]$_{\text{upstream}}=0.81$, [C3]$_{\text{downstream}}=1.006$, [C3]$_{\text{effluent}}=2.072$; assuming a 7.4% contribution of effluent to mainstem discharge). Downstream, agricultural inputs could have sustained C3 concentrations in the rest of the downstream reach, as C3 was relatively higher in the agricultural tributary endmembers than in the downstream mainstem reach (1.9 vs 1.05 RU, Fig. 5), but these inputs are likely largely diluted when they reach the mainstem, as the mainstem’s discharge was over 30×that of the main agricultural tributary. 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), consistent 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 and 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 to autochthonously produced DOM (Retelletti Brogi et al. 2020). 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. S4), 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 and del Giorgio 2014). C5 was dominant in the WWTP effluent (sampled during the summer; Supplementary Fig. S11), yet we did not measure a significant breakpoint going downstream in low flow conditions (Fig. 2, Supplementary Fig. S3), suggesting rapid uptake. Under very urbanised land use, a similar DOM component has been shown to increase with human population in the 6 000 km 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. In contrast to land use, the extreme flow conditions of spring 2019 however, led to unusually high concentrations and proportions of C5 (Figs. 2, 3), suggesting different loadings are possible 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 and microbial humic-like C3 in the upstream portion of the river (Fig. 3). Two lines of evidence may explain this pattern. As the upper forested region of the watershed is mainly covered with deciduous trees (Abrinord 2015), fresh litter decomposition that accumulated in top soils, rich in protein-like (Wu et al. 2021) or microbial humic-like (Garcia et al. 2018) organic matter, may have been temporarily transported to the mainstem during the flood. These inputs would coincide with the most forested RKms along the mainstem (RKms 140 to 92), while the RKms more downstream that are surrounded by less forest would not have received such inputs, thus shifting the breakpoint upstream from RKms ~75 to 84 in spring 2019. Another possible source could be sewage overflows from several small sewered villages upstream of Saint-Jérôme during the flood in 2019 (4 villages in sequence, total population ~30 200). The WWTP intake sampled in summer 2021 was enriched in C3 and C5 (Table 3, Supplementary Fig. S11) and should largely represent other sewer intakes in the region. DOM indices may also help support this provenance. Although SUVA<sub>254</sub> and FI stayed relatively constant at 4.65±0.73 L mg⁻¹ m⁻¹ and 1.3±0.16, respectively, throughout the mainstem and among seasons, suggesting a strong overall aromatic content of the DOM pool flowing in Rivière du Nord, other indices varied between periods of low and high flow, and LULC changes (Supplementary Figs. S5–S8). The freshness index (β:α) was highest (0.90) in the spring 2019 upstream mainstem reach compared to any other moment or place, forested (0.49) and agricultural (0.62) endmembers included, but very close to the WWTP intake (0.89) and effluent (0.81; Table 3). β:α values close to 1 are indicative of strong microbial activity and have been measured in several other WWTPs (Li et al. 2020). The humification index (HIX) in the spring upstream mainstem reach (0.79) resembled the WWTP intake HIX (0.65), which could also point towards potential, somewhat diluted, sewage overflow sources. Similarly, low HIX values were indeed found in other WWTP intakes or effluents (Li et al. 2020). Another study with a strong urban gradient found a positive relationship between tyrosine and tryptophan components and discharge at their most downstream gauging site (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<sub>3</sub>⁻ 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<sub>4</sub>⁺ remained the same (2018 = 50 ug L⁻¹, 2019 = 57 ug L⁻¹). This suggests that overflows were likely not the main source of DOM during the extreme flood, as we would have captured a strong NH<sub>4</sub>⁺ signal. Higher NO<sub>3</sub>⁻ 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 and Band 1998). Approximately 70% of the population in the northern reaches of the river’s wastewater is treated through septs and even modest urbanisation in the area can impact the NO<sub>3</sub>⁻ 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<sub>3</sub>⁻ suggest 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. Both seasons were dominated by %C1 and %C3 (Fig. 2), but the DOM pool in the downstream reach was richer in %C4–5, %NH<sub>4</sub>⁺ and %TDP in winter (Fig. 4, quadrant b), and in %C3 and %NO<sub>3</sub>⁻ in summer (quadrant d). This illustrates how the DOM and nutrient pools differ in some systems under similar flow conditions in two seasons with contrasting processing potential. The largest change in DOM components between both seasons was for %C3, which we propose originated from recent production either in the agricultural soil or, more
probably, in the water through phototrophic processes during the summer. In winter, lower light and temperature would reduce autochthonous production, thus explaining the lower C3 concentrations (Supplementary Fig. S4) 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, but decreased during summer (Supplementary Fig. S3). As C4 is thought to be photolabile (Dainard et al. 2015; Zhou et al. 2019), ice and snow 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 (Supplementary Fig. S3), the slow and steady increase in winter C5 may be explained by reduced uptake under the ice and groundwater inputs rich in microbial-like DOM (O’Donnell et al. 2010; Hobera et al. 2014; Peralta-Tapia et al. 2015; Shen et al. 2015). Thus, the most abundant forms in winter (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 allows 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.

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 snow accumulates, both spring precipitation and snowmelt constitute major drivers of riverine peak flow (Berghuijs et al. 2016). Snowmelt may contribute less to spring flows as winter temperatures increase (Ouranos 2015; Pulliainen et al. 2020) and vernal window lengthens (Grogan et al. 2020), but 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), reducing snow mass, a trend already seen in the last decades in North America. Extreme spring flows may become more frequent and mobilise 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. Combined with urban expansion and agricultural intensification, the predicted changes in seasonal hydrology and ice and snow 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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Author contributions SS, RM and JFL: designed the study. SS: performed sampling, analyses, and writing of the initial draft. JFL and RM: edited subsequent drafts.

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

Declarations

Conflict of interest We have no competing interest to disclose.
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