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Abstract

Rapid changes in the volume and sources of discharge during the spring freshet lead to pronounced variations in biogeochemical properties in snowmelt-dominated river basins. We used daily sampling during the onset of the freshet in the Fraser River (southwestern Canada) in 2013 to identify rapid changes in the flux and composition of dissolved material, with a focus on dissolved organic matter (DOM) and mercury (Hg) dynamics. Previous time series sampling (at twice monthly frequency) of dissolved inorganic species in the Fraser River has revealed smooth seasonal transitions in concentrations of major elements and tracers of water and dissolved load sources between freshet and base flow periods. In contrast, daily sampling reveals a significant increase in dissolved organic carbon (DOC) concentration (200 to 550 $\mu\text{mol L}^{-1}$) occurring over a matter of days, accompanied by a shift in DOM optical properties, indicating a transition towards higher molecular weight, more aromatic DOM composition. Comparable changes in DOM composition, but not concentration, occur at other times of year, underscoring the role of seasonal climatology in DOM cycling. Concentrations of total and dissolved Hg also varied during the spring freshet period, although dissolved Hg dynamics appear to be driven by factors beyond DOM as characterized here. The time series records of DOC and particulate organic carbon (POC) concentrations indicate that the Fraser River exports 0.25–0.35 % of its annual basin net primary productivity.

1 Introduction

Export of riverine organic matter (OM) to the coastal ocean contributes significantly to heterotrophic metabolism in coastal marine ecosystems, supplying approximately 0.5 Pg of organic carbon (OC) per year, approximately half in dissolved and half in particulate form (e.g., Cai, 2011). A significant portion of terrestrial OC is metabolized and transformed by biological activity within terrestrial aquatic ecosystems (Cole and Caraco, 2001; Battin et al., 2009; Aufdenkampe et al., 2011), and the molecular

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composition of OM is thought to exert controls on its bioavailability to in situ microbial communities (e.g., Sun et al., 1997; Fellman et al., 2009; Stepanauskas et al., 2005). The concentration and composition of OM in freshwater systems also has implications for mobilization and speciation of mercury (Hg), an important element for its potential toxicity, particularly when converted to monomethyl Hg and biomagnified within food webs (Fleck et al., 2014; Zheng et al., 2012). Comprehensive time-series datasets for fluvial systems, including nutrients, dissolved major elements, water isotopes, and suspended sediments in addition to DOM properties are rare (e.g. Dornblaser and Striegl, 2007, 2009; Spencer et al., 2012; Walling and Foster, 1975; Bagard et al., 2011), yet are necessary to establish a robust foundation for distinguishing biogeochemical from hydrologic and physical processes.

Rapid changes in riverine DOC concentrations are often associated with variations in discharge on timescales of hours to weeks. Such hydrologic effects on DOC concentration have been observed in large Arctic rivers during the spring freshet (Holmes et al., 2012; Mann et al., 2012; Wickland et al., 2012), as well as in tropical catchments experiencing wet-season flushing of surface soils (Spencer et al., 2010; Laraque et al., 2013), and in small streams and headwater catchments dominated by episodic rain or snowmelt events (Sandford et al., 2013; Raymond and Saiers, 2010; Lloret et al., 2013; Fellman et al., 2009; Battin, 1998). In these scenarios, the composition of DOM is often observed to change significantly, as changing hydrologic flow paths draw upon different DOM pools (Striegl et al., 2005; Mann et al., 2012; Spencer et al., 2010). The bulk concentration of DOC in the Fraser River has been investigated through water quality monitoring by Environment Canada (Swain, 2004); however, more detailed information about the composition of Fraser River DOM and its controlling processes are lacking. DOC constitutes the larger pool of OC delivered to the coastal ocean by the Fraser River, at concentrations ~ 5 times higher than POC during the spring freshet when suspended sediment concentrations peak, and ~ 30 times higher during low discharge conditions. This ratio is high compared to the median DOC/POC ratio of 2.3 for 30 rivers compiled by Ludwig et al. (1996).

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The residence time of OC derived from fresh litterfall in soils depends on its initial composition and environmental conditions, and varies between one year or less to hundreds or thousands of years (Mills et al., 2014). DOM that enters stream channels under base flow conditions generally originates from deeper soil layers, where organic matter has been exposed to microbial degradation and potential sorption surfaces for a long time relative to fresh litter leachates in shallow soil layers (Hope et al., 1994; Easthouse et al., 1992; Michalzik et al., 2003). Freshet DOM, which derives largely from overland flow and more extensive soil inundation, is composed of organic matter that has been exposed to soil microbial communities for a shorter time than deep soil DOM (Wickland et al., 2007; O'Donnell et al., 2010). This distinction is evident in the increase in DOC radiocarbon content across the freshet transition in large Arctic rivers, as shallow soil DOC containing bomb ^{14}C is released during spring thaw (Raymond et al., 2007). This relatively fresh DOM has also been identified as more susceptible to microbial degradation (Holmes et al., 2008; Mann et al., 2012), and is therefore a more potent source of metabolic fuel to coastal ocean ecosystems and thus a potential flux of CO_2 to the atmosphere.

The time series record of DOC concentration in the Fraser River from Environment Canada (Swain, 2004) has not been analyzed and published in peer-reviewed literature, and we are not aware of any published studies of DOM composition in the Fraser River. The hydrology of the Fraser River basin is controlled by its distinctive geographic and climatic features. The annual hydrograph is dominated by a relatively protracted annual spring freshet, which commences in late March to early May, when air temperatures rise to the point that snow accumulated over the winter months begins to melt, and lasts from one to three months in the main stem Fraser. The mountainous headwaters of tributary basins which supply most of the freshet discharge lie to the north of the river mouth, and consequently, as spring warming migrates to higher latitudes, tributaries progressively reach their melting thresholds over a period of weeks. The elevations of the major mountain ranges in the Fraser basin peak at 3000–4000 m.

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A consequence of variability in DOM concentration and composition in freshwaters is the potential for dynamic behavior of dissolved Hg. Due to the strong affinity of dissolved Hg for DOM, especially reduced organosulfur moieties (Haitzer et al., 2003, 2002; Gerbig et al., 2011), concentrations of DOC and total dissolved Hg are typically positively correlated in natural waters (Schuster et al., 2011; Dittman et al., 2010; Burns et al., 2012a). We are not aware of any Hg observations in the main stem Fraser River by federal or provincial government agencies, although Hg monitoring has been recommended (MacDonald et al., 2011). Mercury concentrations in water and fish tissue are not presently found at levels deemed unfit for human consumption; however, it is a health concern for the Fraser River fisheries and individuals who subsist on diets rich in fish (Cohen Commission, 2012; Kelly et al., 2008). Potential sources of Hg within the Fraser basin include urban and industrial point sources (e.g. sewage effluent, paper pulp mills), atmospheric deposition (particularly aerosols derived from coal combustion in east Asia), and mobilization of legacy Hg contamination from placer gold mining (including hydraulic mining in some areas), which was widespread in the central portion of the basin in the 1850s–1910s. Given the major role of rivers in global surface cycling of Hg (Amos et al., 2014), it is important to constrain the flux of Hg from this regionally-significant river basin.

In this study we examine how: (1) rapid changes in discharge impact DOC load during the early stages of the spring freshet, (2) hydrology influences changes in DOC flux and composition throughout the year; and (3) DOM and suspended sediment dynamics influence the Hg load of the Fraser River. The spring freshet is a critical period to quantify, as it is responsible for the bulk of total annual fluxes of many constituents, including DOC and suspended sediment (Swain, 2004). Given the anticipated changes in hydrological conditions in the Fraser basin under a warming climate – particularly an increase in net annual and winter precipitation, a shift towards more rain-dominated relative to snow-dominated precipitation, and a corresponding decrease in snowpack, and an earlier onset to the spring freshet (Morrison et al., 2002; Déry et al., 2012; Shrestha

et al., 2012) – understanding freshet biogeochemical dynamics under present conditions is critical to detecting future changes and anticipating their consequences.

2 Methods

2.1 Discharge and historical data

Continuous discharge and water temperature information (5 min frequency) were obtained from the Environment Canada Water Office online real-time hydrologic data source (<http://www.wateroffice.ec.gc.ca>). The record used was the station at Hope (08MF005; 49.381° N, -121.451° E), which is ~ 100 km upstream of our sampling location at Fort Langley (49.172° N, -122.577° E; Fig. 1), and the farthest downstream station for which gauge height is not influenced by tides. Discharge at Fort Langley is 10–20 % higher than at Hope (due mainly to input from the Harrison River), and water temperature is ~ 1.5 °C higher. The discharge and water temperature records for the study year 2013 are shown in Fig. 2.

Historical Fraser River DOC concentration data at Hope (1997–2014, station BC08MF0001) were obtained from Environment Canada Pacific Yukon Freshwater Quality Monitoring and Surveillance online data repository (<http://aquatic.pyr.ec.gc.ca/>). A portion of this record is presented with sampling and analytical information by Swain (2004). Average DOC loads and discharge-weighted average DOC concentrations were calculated from time series records using the LoadEst program (Runkel et al., 2004) as described previously by Voss et al. (2014).

2.2 Sample collection and basic water chemistry

Basic water properties were determined with a handheld multiparameter probe (YSI Professional Plus). The probe was equipped with sensors for water temperature (°C), conductivity ($\mu\text{S cm}^{-1}$), pH, and dissolved oxygen (DO, $\text{mg O}_2 \text{L}^{-1}$). DO and pH probes were calibrated according to manufacturer specifications approximately every 5 days.

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Samples were collected from a floating dock, ~ 5 m from the river bank, where the water depth is ~ 6 m. All samples for concentrations of dissolved species were collected by in-line filtration (Pall AcroPak 500 Supor Membrane, 0.2 μm pore size with 0.8 μm pre-filter) of surface water directly into pre-cleaned vials, which were rinsed three times with filtered sample water before filling. Sampling and analytical methods for most types of samples are described in detail by Voss et al. (2014), therefore the following methods descriptions are abbreviated.

Nutrient samples were collected in pre-cleaned 20 mL polyethylene scintillation vials and stored frozen until analysis. Analyses for dissolved $\text{NO}_3 + \text{NO}_2$, NH_4 , PO_4 , and SiO_2 were performed on an AutoAnalyzer (Lachat QuickChem 8000) with standard U.S. Environmental Protection Agency-certified spectrophotometric methods and calibrated using standard reference material MOOS-2 (National Research Council Canada).

Samples for dissolved major cations (Ca, Mg, Na, K) and anions (Cl, SO_4) were collected in pre-cleaned 125 mL high-density polyethylene bottles. Cation concentrations were determined using a Thermo Scientific Element2 single collector inductively-coupled plasma mass spectrometer, based on a standard curve of natural river water standard reference material SLRS-5 (National Research Council Canada). Anion concentrations were determined using a Dionex ion chromatograph with an anion column (AS15, 4 mm, with ASRS suppressor), based on a standard curve of a mixture of SpecPure ion chromatography standards (Alfa Aesar). No preservative was added to major cation and anion samples after collection, and samples were stored at room temperature until analysis.

Samples for stable isotope compositions of water were collected by filling 4 mL glass vials with filtered water without head space. Hydrogen (δD) and oxygen ($\delta^{18}\text{O}$) isotope compositions were measured on a Picarro L2120-I cavity ring-down spectrometer. Measured values were calibrated using secondary standards (mean \pm 1 SD: Mediterranean Sea water, δD 8.12 ± 0.30 ‰, $\delta^{18}\text{O}$ 0.95 ± 0.05 ‰; Jungfrau water, δD -160.28 ± 0.21 ‰, $\delta^{18}\text{O}$ -22.50 ± 0.06 ‰; Zürich water, δD -75.57 ± 0.19 ‰, $\delta^{18}\text{O}$

–10.62 ± 0.04 ‰), which were calibrated against standard reference materials SLAP2, GISP, and VSMOW2 (International Atomic Energy Agency).

2.2.1 Turbidity and suspended sediment concentration

An optical nephelometer (LaMotte, 2020-WE) was used to determine turbidity (measured in normalized turbidity units, NTU). The nephelometer was calibrated before each measurement with solutions of known turbidity (0, 1.0, and 10.0 NTU). A 20 mL surface water grab sample was collected in a glass vial and allowed to equilibrate to ambient air temperature. Vial walls were dried and wiped thoroughly with a Kimwipe and the vial was rolled and gently inverted to resuspend particles before analysis. At least 6 readings were averaged for each sample to account for measurement variability.

To transform turbidity measurements into concentrations of suspended particulate matter (SPM), nephelometer readings were complemented with weighed sediment masses from filtered water samples. Large volume surface water grab samples (4–20 L) were filtered with specially designed filtration units onto 90 mm polyethersulfone membrane filters (Millipore, pore size 0.22 µm). The resulting sediment was rinsed from filters with purified water (Millipore, 18.2 MΩ cm⁻¹), freeze dried, and weighed. As there is some loss of sediment in sample processing due to retention of a small amount of sediment within the filters, rather than use these measured concentrations directly, we have used the linear correlation between turbidity and filtered-mass sediment concentration (Fig. 3) to calculate SPM concentration based on nephelometer measurements. The SPM concentration values presented throughout the text are turbidity measurements converted to SPM concentration using this relationship.

2.3 Organic matter analyses

Fluorescent dissolved organic matter (FDOM) was measured in the field using a handheld probe (TurnerDesigns Cyclops-7 with DataBank). The probe was blank-calibrated with deionized water every 5 days and values are reported as blanked relative fluores-

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cence units (RFUB). In situ FDOM was measured by lowering the probe from the dock at least 3 m below the river surface to eliminate possible interference from sunlight. Because changes in sediment concentration can significantly impact FDOM measurements (Saraceno et al., 2009), for each sample, a second FDOM measurement (“ex situ FDOM”) was performed on filtered water (filtered with 0.2 μm pore size membrane filters as described above) in a shaded vessel. Since fluorescence is temperature-sensitive, ex situ FDOM samples were filtered and analyzed as quickly as possible, with the FDOM measurement typically completed within 30 min of sample collection. The probe measurement frequency was 30 s, and a minimum of 20 values were averaged to account for measurement variability. Filtered FDOM values (539–1856 RFUB) correlated strongly with measured DOC concentrations, with an apparent approach towards a plateau in FDOM (~ 1800 RFUB) at high DOC ($> \sim 500 \mu\text{mol L}^{-1}$; Fig. 4a), likely due to light attenuation from increasing chromophoric DOM (Downing et al., 2012; Pereira et al., 2014). The suspended sediment concentration was found to account for most of the difference between in situ and filtered ex situ FDOM measurements (Fig. 4b).

Samples for the determination of DOC concentration were collected in pre-combusted 40 mL amber glass vials. Concentrated HCl was added immediately to achieve a pH of 2 and hinder biological activity. Samples were stored in the dark at 4 °C until analysis. DOC concentrations were determined by high-temperature catalytic oxidation on a Shimadzu TOC/TN-V instrument combined with a nitrogen chemiluminescence detection unit (TNM-1). Concentrations are reported as the mean of 3–5 replicate injections with a coefficient of variation $< 2\%$ (Mann et al., 2012).

Samples for the determination of DOM optical properties were collected in 20 mL polyethylene scintillation vials. Samples were stored at 4 °C in the dark until analysis. UV-visible absorbance spectra were measured at room temperature on a Shimadzu UV1800 dual-beam spectrophotometer using a 10 mm path length quartz cuvette. All samples were analyzed in triplicate and referenced to purified laboratory water (MilliQ, $18.2 \text{ M}\Omega \text{ cm}^{-1}$; Mann et al., 2012). Napierian absorption coefficients ($a(\lambda)$) were calcu-

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a clean laboratory, samples were oxidized on the day before analysis with 100 μL saturated BrCl solution to convert all Hg species to Hg^{2+} , then reduced with 100 μL each $\text{NH}_2\text{OH}\cdot\text{HCl}$ and SnCl_2 immediately before analysis to convert all species to elemental gaseous Hg^0 . Mercury concentrations were determined using a purge and trap/cold vapor atomic fluorescence spectrometry total mercury analyzer (Tekran 2600). A MilliQ water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) blank was analyzed at the beginning of each day of analysis to ensure that background signal was sufficiently low ($\sim 0.5 \text{ pmol}$). A standard curve was generated from analyses of varying quantities of aqueous standard (NIST SRM-3133), which was checked against a vapor Hg^0 saturated air standard held at 15°C (Tekran 2505) and introduced to the detection system using a gas-tight syringe. Samples were analyzed at least three times until SD were $< 10\%$ of the measured value, or until sample material was exhausted.

Total Hg concentration in suspended particulate matter (SPM THg) was analyzed on material recovered from membrane filters. SPM samples were analyzed on a Milestone Direct Mercury Analyzer (DMA-80) following established methods (U.S. EPA, 2007). Concentrations were calibrated using standards MESS-3 and PACS-2 (marine sediments; National Research Council Canada) and IAEA-SL-1 (lake sediment; International Atomic Energy Agency). Samples were analyzed in pre-combusted (500°C , 1 h) nickel boats; empty boats were analyzed to determine the analytical blank. The total amount of Hg analyzed in samples ranged from 1.2–4.9 ng. The very low amounts of Hg reported here are above the detection limit ($3 \times \text{SD}$ of blank = 0.6 ng), but in two of six samples were not quantifiable ($10 \times \text{SD}$ of blank = 2.0 ng). This limitation does not affect the conclusions drawn from the data.

3 Results

3.1 Early freshet water quality trends

The data presented here include Fraser River samples collected during the early portion of the 2013 spring freshet (Table 1), and a DOM-specific dataset for samples collected between June 2011 and September 2013 (Table 2). During the period 26 March–22 April 2013, hereafter referred to as the “early freshet,” discharge (at Hope) increased from 950 to 3000 m³ s⁻¹. SPM concentrations were very low (3–9 mg L⁻¹) for the first ~ 10 days, then increased rapidly to higher, but variable values (40–150 mg L⁻¹; Fig. 3c).

The stable isotope composition of water (δD , $\delta^{18}O$) showed a steady shift to more depleted compositions over the 2013 early freshet (Fig. 5). The change ($> 15\%$ in δD over 27 days) is large and rapid in the context of the total annual variability in this parameter ($\sim 40\%$ in δD ; Voss et al., 2014). Deuterium excess ($\delta D - 8 \cdot \delta^{18}O$; values not shown) decreased during this period from ~ 8.4 to $\sim 4.7\%$.

3.2 Seasonal changes in OC concentration and OM composition

In both 2011 and 2013, DOC concentrations rose rapidly during the early freshet period from fall/winter levels of $\sim 200 \mu\text{mol L}^{-1}$ to a peak of 700–900 $\mu\text{mol L}^{-1}$ (Fig. 6). This “pulse” of DOC occurs at the very onset of the rise in discharge, with peak DOC concentrations achieved when discharge had only reached 40% of its maximum. DOC concentration is highly correlated with wavelength-specific absorption coefficients (Fig. 7).

Optical properties of DOM reveal changes in the composition of the DOM pool during the early freshet period, as well as at other times of the year (Fig. 8). Absorbance at specific wavelengths can be diagnostic of certain DOM properties. Normalizing DOC concentrations to wavelength-specific absorbance (e.g. $SUVA_{254} = \text{absorbance at } 254 \text{ nm divided by DOC concentration in } \text{mg L}^{-1}$) allows the chromophoric character

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of DOM in different settings to be compared, and the value of $SUVA_{254}$ has been previously shown to be positively correlated with bulk aromaticity (Weishaar et al., 2003). The absorbance ratio (a_{250}/a_{365}) represents the ratio of absorbance coefficients at two wavelengths (250 and 365 nm), and has previously been shown to be negatively correlated with molecular weight and aromaticity of DOM (Peuravuori and Pihlaja, 1997). The slope ratio (S_R) represents the ratio of the slopes of the absorbance-wavelength curve over two wavelength ranges (275–295 and 350–400 nm) and is also negatively correlated with DOM molecular weight and aromaticity, as well as relative vascular plant content (cf. Spencer et al., 2012 and sources therein). The use of multiple optical proxies provides support from multiple metrics for interpretations of the data.

During the early freshet of the Fraser River in 2013, values of a_{250}/a_{365} and S_R decrease, while $SUVA_{254}$ increases. These early freshet changes are part of a larger seasonal cycle, shown in Fig. 8 for a_{250}/a_{365} and S_R . While the values of these parameters decrease during the early freshet DOC pulse, they gradually rise throughout the summer, peaking in early fall. In winter, values drop again before rising rather abruptly prior to the early freshet. For the ~ 2 year record of these DOM optical properties, both S_R and a_{250}/a_{365} show a consistent twice-yearly cycle between higher values in fall and early spring and lower values in winter and during the early freshet (and the reversed trends for $SUVA_{254}$), exhibiting a hysteresis cycle with discharge similar to DOC concentration.

In addition to DOC concentration, the POC concentration and particulate organic matter (POM) composition change rapidly during the early freshet (Fig. 9). Although the OC content of suspended sediments decreases during this time (from 4.5 to 0.8%), the increase in SPM concentration is so large that the POC concentration rises by an order of magnitude (from 9 to 89 $\mu\text{mol L}^{-1}$). The relative change in POC concentration is greater than that of DOC concentration, as the DOC : POC ratio decreases from a value of 30 on 26 March to a minimum of 4.6 on 8 April, followed by values of ~ 10 over the following two weeks. The C : N composition of POM also changes, with values before 6 April varying between 8.5 and 9.9 (excepting the values of 10.5 on 27 March and

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10.3 on 31 March), and then rising to values between 10–11 for the remainder of the sampling period. The $\delta^{13}\text{C}$ of POC also varied (–27.7 to –26.1‰); however, no clear trends are apparent. A negative exponential relationship between SPM concentration and POC concentration (Fig. 9f) is a common feature of rivers globally, due to the tendency for sediment mobilization events (such as those associated with the spring freshet) to erode particles from deeper soil horizons which are depleted in OC content by microbial activity (Galy et al., 2015), or coarser mineral particles with lower capacity for OC loading (Mayer, 1994).

3.3 Early freshet changes in mercury concentration

Total dissolved Hg (TDHg) concentrations varied between 5.9 and 15.2 pmol L⁻¹, with no distinct temporal trend during the early freshet period (Fig. 10). In contrast, unfiltered THg concentrations increased significantly in a matter of days during this period, with concentrations before 7 April of ~ 15 pmol L⁻¹ and those on and after this date of ~ 50 pmol L⁻¹. The portion of the total Hg load composed of dissolved Hg correspondingly decreased from ~ 75 % before 7 April to < 25 % afterwards. Concentrations of Hg in SPM were relatively constant, varying between 0.43–0.46 pmol mg⁻¹.

4 Discussion

4.1 Rapid geochemical changes in the early freshet

The geochemical data presented here highlight the importance of the very early portion of the spring freshet to biogeochemical dynamics in the Fraser River. While discharge and basic water properties (temperature, DO, pH, conductivity, and major element concentrations) record only modest changes during this interval, the initial melting of snowpack is reflected in a suite of geochemical shifts, including water δD and $\delta^{18}\text{O}$ composition, SPM concentration, and OM concentration and composition.

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The sudden change in water sources from different portions of the basin is demonstrated by the rapid decrease in δD and $\delta^{18}O$ values. As runoff from headwater areas and snowmelt with signatures more depleted in heavy isotopes begins to contribute a greater portion of the total discharge, the lower Fraser main stem quickly records this transition at the whole basin-scale. Quantification of the proportional contributions of various water sources (particular snowpacks and tributaries) based on the observed changes in stable isotope composition is complicated due to insufficient knowledge of source water compositions. The isotope composition of precipitation in the Fraser basin is poorly characterized and the δD and $\delta^{18}O$ values of individual tributaries are highly variable across the year (Voss et al., 2014). Furthermore, the isotope composition of snow and ice likely varies with elevation and water vapor source, causing the composition of the snow within a single tributary basin to vary as seasonal melting progresses. The magnitude of the change in isotope composition of the Fraser main stem, however, is sufficiently large that the transition to greater headwater and snowmelt influence during the early freshet is unequivocal.

Assuming that the deuterium excess of Pacific Ocean source moisture does not change seasonally, the shift towards lower deuterium excess during the early freshet indicates a change in the continental transport pathways and/or evaporation processes affecting spring vs. winter precipitation in the Fraser basin (Froehlich et al., 2008). In the absence of spatially-resolved precipitation isotopic data, we can surmise that the apparently lower deuterium excess of winter snowpack relative to spring rainfall is due to more evaporative recycling over land en route to the site of precipitation for the latter than for winter snowfall. This proposition should be further tested with time series observations of stable isotopes in precipitation, snow and ice, and small streams across the basin.

A pronounced geochemical shift is recorded by the change in concentration of DOC. DOM dynamics are driven by a combination of hydrological and biological processes. When discharge is low at base flow levels, hydrologic flow paths through soil are relatively deep and slow, drawing modest amounts of DOM from deeper soil layers

(Townsend-Small et al., 2011). This DOM is likely older and more degraded from its parent plant source material as a result of preferential remineralization of younger carbon sources by soil microbiota (Gangloff et al., 2014), although a portion of soil DOM may also derive from soil biota. Preferential sorption of DOM to soil particles may also influence soil DOC concentration and DOM composition, enhancing DOM removal during base flow periods. As discharge and overland flow increase and soils become inundated across the basin, hydrologic flow paths draw DOM from greater distances from stream channels and shallower soil horizons. Despite potential dilution from increased discharge, this DOM is likely more concentrated, and exported to stream channels more quickly than base flow DOM (Michalzik et al., 2003, 2001), leading to a pulse of DOM into streams.

Biogeochemical dynamics of DOM have not previously been investigated in the Fraser River, yet several aspects of the basin (e.g., physiographic features, hydrologic regime and climatic setting) suggest it may exhibit somewhat different behavior from established paradigms for large Arctic rivers and small streams. First, the major Arctic rivers (Yenisey, Ob', Lena, Kolyma, Mackenzie) generally have catchments that drain northward and narrow flowing downstream (a "northward funnel" shape), triggering a sudden peak in total basin discharge in the downstream portions of these basins during spring melt. In contrast, the southward-draining orientation of the Fraser basin and northward migration of spring warming mutes the amplitude and prolongs the duration of the freshet. Second, the freshet hydrograph in the Fraser River is often punctuated by pauses in melting due to cold intervals and/or precipitation pulses from spring storms, which, due to the presence of mountain ranges, can exert longitudinal differences across the basin. The resulting stepwise character of the freshet may lead to a more complex transition between base flow and freshet DOC concentrations, and a buffered peak DOC concentration. Third, the smaller size of the Fraser basin relative to large Arctic rivers also means that storm events typically impact large portions of the basin, causing significant short-term increases in total discharge. Fourth, the lack of extensive permafrost in the Fraser basin excludes significant inputs from a poten-

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tial pool of aged soil DOM during late spring and summer months. Finally, in small streams, storm-driven discharge events are short-lived and may deliver fresh DOM to stream channels more efficiently than the long, relatively gradual rising limb of the spring freshet in the Fraser.

The average total DOC flux of the Fraser River can be estimated from our three-year record, as well as from the sixteen-year record from Environment Canada at the city of Hope. Hope is ~ 100 km upstream of the sampling site used in our study, and notably excludes a large portion of the agricultural Fraser Valley and a large, DOC-poor Coast Range tributary, the Harrison River. Despite these differences, the estimates of total Fraser River DOC flux based on these two records (Table 3) agree within their uncertainties ($2.8 \pm 1.0 \times 10^{10}$ mol C a⁻¹ for the record in this study, $2.7 \pm 0.4 \times 10^{10}$ mol C a⁻¹ for the Environment Canada record), with the longer Environment Canada record showing smaller uncertainty, as expected. The DOC yield of the Fraser River (1.2×10^5 mol C km⁻² a⁻¹) is significantly greater than that of the nearby Columbia River (0.5×10^5 mol C km⁻² a⁻¹), and comparable to that of the Yukon River to the north (1.4×10^5 mol C km⁻² a⁻¹; Spencer et al., 2013).

4.2 Annual cycles of DOM composition and sources

Considering the full annual records of DOC concentration and DOM composition, it is evident that DOM composition varies at times outside the spring freshet. Throughout the summer, as main stem DOC concentration decreases toward base flow levels, the DOM optical properties gradually return to values similar to those of pre-freshet DOM (higher a_{250}/a_{365} and S_R , lower SUVA₂₅₄). In the late fall, while DOM concentrations remain low, optical properties once again shift to freshet-like compositions (lower a_{250}/a_{365} and S_R , higher SUVA₂₅₄), and then return to pre-freshet composition in late winter/early spring, just before the early freshet DOC pulse. Although daily records of DOC concentration in the Fraser River are not available for the fall period, the Environment Canada record (beginning in 1998, approximately twice monthly sampling)

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indicates that a secondary peak in DOC concentration ($300\text{--}500\ \mu\text{mol L}^{-1}$) often occurs between September and December.

The twice-annual cycle in DOM composition appears to be driven by hydrologic changes. The early freshet shift represents more rapid export of shallow soil DOM driven primarily by melting snowpack across the basin. The compositional change in the fall is likely driven by a similar flushing of shallow soil DOM derived from biomass accumulated over the growth season and mobilized by large rain events, as has been observed in the Yukon River (Wickland et al., 2012), as well as in non-snowmelt-driven systems such as the Mississippi River (Bianchi et al., 2013). The Fraser basin, particularly in areas east of the Coast Range, generally receives very little precipitation in the late summer months, which allows litter from fresh vegetation to accumulate and DOM export to revert to slower, deeper flow paths. Warmer temperatures in late summer relative to spring may also promote more rapid microbial degradation of soil DOM, thus diminishing the potential amount of DOM that can enter streams. In the winter, precipitation in much of the basin falls primarily as snow, which limits surface runoff. Fall precipitation (rain), however, is capable of flushing shallow soil DOM into streams. The more freshet-like composition of this fall DOM suggests that it has a similar soil residence time and limited degradation history.

The amount of DOC mobilized by fall soil flushing is less than that of the spring freshet, presumably because the soil DOC pool has not yet recovered to its pre-freshet size, and the amount of runoff generated by fall rain storms is much less than that from spring snowmelt. The relative magnitude and composition of fall DOC pulses may also be affected by spatial differences in vegetation types (e.g. between coniferous forests which dominate the mountainous portions of the basin and the bunchgrass and dryland vegetation covering significant portions of the interior basin), which also likely exhibit variations in the timing of growing seasons. Growing season varies significantly across the Fraser basin, from > 170 days per year in the Fraser Valley area to < 100 days in the Coast Range and parts of the Rocky Mountains (Agriculture and Agri-Food Canada, 2014). Consequently, this relatively small input of compositionally distinct DOM to the

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initial shift is less clear in the a_{250}/a_{365} and $SUVA_{254}$ records at the onset of the 2013 freshet, thus an initial shift in DOM composition during the freshet DOC pulse requires further investigation. In addition, the magnitude of anthropogenic contributions to the dissolved and particulate OC load of the Fraser basin could potentially be investigated through measurement of tracers such as mammalian fecal markers (e.g., coprostanol) or phenolic flavor compounds (e.g. Writer et al., 1995; Keil et al., 2011).

The average depth of the shallow soil horizon responsible for the freshet pulse of DOC can be estimated from the volume of water above base flow discharged during this pulse. In 2013, the freshet DOC pulse – from the point when DOC concentration began to rise rapidly until it returned to nearly pre-freshet values – lasted approximately from 5 April–7 June. The cumulative discharge of the Fraser River during this time was 33 km^3 , or 28 km^3 subtracting a constant base flow of $950 \text{ m}^3 \text{ s}^{-1}$. If this volume of water constitutes the shallow soil end member, we estimate that the maximum shallow soil DOC concentration during this time period is $900\text{--}950 \mu\text{mol L}^{-1}$, assuming a base flow DOC concentration of $100\text{--}200 \mu\text{mol L}^{-1}$. Given an average forest soil porosity of ~ 0.43 in British Columbia (Zhao et al., 2008), the actual soil volume represented by 28 km^3 of water is $\sim 65 \text{ km}^3$. If this volume is distributed equally across the entire basin ($228\,776 \text{ km}^2$), it corresponds to a soil depth of $\sim 28 \text{ cm}$. Given that soil porosity varies considerably across the basin (as low as 0.15 in highly compacted fine-grained and agricultural soils, and as high as 0.70 in coarse-grained soils), depths of ca. 20–80 cm could be flushed in different localities. This estimate represents a basin-wide average soil depth; it is likely that the majority of the DOC pulse derives from soil water in the top centimeters with DOM concentrations much higher than that observed in the river, due to dilution by low-DOM snow melt, low-DOM soil water from deeper layers, and respiration between the point of mobilization into the stream and the sampling location. Total soil depth (above bedrock) is also highly variable across the basin, ranging from $< 0.5 \text{ m}$ in rapidly-eroding mountainous areas to $> 3 \text{ m}$ in flatter areas that have accumulated significant glaciofluvial sediments (Valentine et al., 1978; Vold, 1979). An estimate of a surface horizon of 0.2–0.8 m flushed during the freshet DOC pulse is

therefore a reasonable first-order approximation of the maximum spatial extent of this event.

In addition to hydrologic and soil microbial controls on DOM dynamics, in-stream and lacustrine biological activity may play a role in the observed changes in DOC concentration and DOM composition. Throughout the spring freshet and summer, nutrient concentrations in the Fraser main stem also decrease. Similar to DOC, this trend is likely due in part to changes in the sources of nutrients from soil flushing. However, nutrients are also consumed by autotrophic activity in some portions of the basin, particularly in tributary basins containing lakes. In these basins, such as the Thompson, Nechako, and Quesnel rivers, lakes function as suspended sediment filters, allowing sunlight to penetrate more deeply. Such basins are likely especially depleted in nutrients in spring and summer, and may also contribute some DOM derived from autotrophic production. This DOM would have optical properties reflecting a less aromatic, lower molecular weight composition (Rochelle-Newall and Fisher, 2002). Aquatic autotrophic and heterotrophic DOM input is likely strongest during summer, when water temperatures are higher and discharge and river sediment concentrations are lower than during the peak freshet. More detailed data on seasonal and spatial variability in DOC concentration and DOM composition within these tributary basins would be needed to better constrain this potential source of DOM to the main stem Fraser.

We used the concentrations and optical properties of DOC to estimate the contributions of “shallow” vs. “deep” soil-derived DOC to the total DOC load of the Fraser River (Fig. 11). Assuming that the maximum and minimum values of the optical properties observed in our time series represent these hypothetical end-members, we determined the proportion of deep and shallow soil-derived DOC for each point in the time series, and generated discharge-weighted average values using LoadEst (Table 4). As derived optical properties such as a_{250}/a_{365} and S_R may not vary linearly as a function of end-member inputs (Yang and Hur, 2014; Stedmon and Markager, 2003), the results of this mixing model are intended to show seasonal trends and differences, while the absolute fractions of end-member contributions are necessarily approximate. With this in mind,

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both S_R and a_{250}/a_{365} indicate that, on average, shallow soil-derived DOC constitutes $\sim 60\%$ of the total DOC flux. The estimated fractions of total DOC derived from deep and shallow soils varies non-linearly with DOC concentration (Fig. 11). This may reflect the observation from the time series record that DOM optical properties can change on the basin scale not only during the spring freshet, but also in response to relatively small hydrologic changes while the total DOC load is less variable.

The role of the Fraser River in transferring terrestrial OC to the coastal ocean can be assessed by comparing the fluxes of DOC and POC with total carbon fixation by land plants. The global compilation of riverine OC fluxes of Ludwig et al. (1996) reports net primary productivity (NPP) in the Fraser basin of $585 \text{ g C m}^{-2} \text{ a}^{-1}$ (however no OC fluxes are reported), corresponding to total terrestrial carbon fixation in the basin of $\sim 4.0 \times 10^{12} \text{ mol C a}^{-1}$. Based on the measured DOC flux of $2.8 \times 10^{10} \text{ mol C a}^{-1}$ (Table 3), this accounts for 0.25% of NPP. Quantifying the annual POC flux is complicated by the very limited dataset available ($n = 29$, with 26 values from the 2013 early freshet period and 3 values during low discharge in 2010 and 2011); however, a first-order estimate of POC flux based on these data using LoadEst is $\sim 1 \times 10^{10} \text{ mol C a}^{-1}$, i.e. $\sim 0.1\%$ of NPP. This is likely an overestimate, as the limited POC training dataset is biased towards the early freshet period, when POC concentrations are relatively high while discharge is not yet at peak values; thus, extrapolating to peak discharge may overestimate high discharge POC concentrations. Furthermore, some portion of POC most likely derives from petrogenic OC, not recently living vegetation, thus a correction could be applied to the calculated POC flux based on POC radiocarbon ages, which would further reduce the flux of POC derived from recent NPP (Galy et al., 2015). In addition, widely varying values of NPP in the Fraser basin are available in the literature. For instance, Liu et al. (2002) report NPP of 189 and $215 \text{ g C m}^{-2} \text{ a}^{-1}$ for the Pacific Maritime and Montane Cordillera ecozones, respectively, within the basin, corresponding to $< 50\%$ of the value of Ludwig et al. (1996) used for our calculations. Though beyond the scope of this study, the issue of basin-scale NPP estimates clearly warrants careful reassessment.

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Accepting these uncertainties, it is clear that DOC dominates the export of terrestrial NPP in the Fraser basin, and annual DOC+POC fluxes transfer 0.25–0.35% of total NPP in the Fraser basin to the coastal ocean. Based on NPP and DOC and POC flux data presented by Ludwig et al. (1996), such a proportion of basin NPP exported as DOC+POC is typical, with most large rivers exporting 0.3–0.5% of NPP (e.g. Columbia: 0.2%; Rhine: 0.3%, Mississippi: 0.3%, St. Lawrence: 0.4%, Mackenzie: 0.5%, Yukon: 0.5%, Congo: 0.5%). The DOC yield of the Fraser River is also not exceptional for its runoff relative to other North American rivers (Spencer et al., 2013). Subtle differences in DOC export efficiency are likely obscured within this broad assessment; however, it is possible that the limited lake and reservoir area in the Fraser basin, which constrains DOC residence time and therefore the opportunity for heterotrophic consumption, may result in relatively efficient DOC export in this basin.

4.3 Early freshet mercury dynamics

Changes in dissolved and total Hg concentrations were examined as a possible consequence of the significant changes in DOC concentration during the early freshet period. Previous studies have identified a strong correlation between DOC concentration and TDHg concentration (e.g. Dittman et al., 2010; Schuster et al., 2011), resulting from the association of Hg with DOM functional groups, particularly reduced sulfur moieties (Gerbig et al., 2011). The TDHg concentrations in the Fraser River during the early freshet period, however, are not clearly correlated with DOC concentration (Fig. 12a). In small headwater tributaries of the Hudson River (Burns et al., 2012b), streams in northern New England (Dittman et al., 2010), and the Yukon River (Schuster et al., 2011), the TDHg concentration observed for a given DOC concentration is generally lower than our observations for the Fraser. In particular, TDHg concentrations on 30 March (10.1 pmol L^{-1}) and 3 April (13.3 pmol L^{-1}) are significantly higher than those predicted based on these previous studies. While the size of this dataset is limited, the concentration changes are sufficiently large to indicate that processes in addition to changes in DOC concentration are likely required to explain the data.

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The DOM optical property data demonstrated that the composition of DOM varies during the early freshet period, thus it is possible that distinct types of DOM bind dissolved Hg more or less strongly (Haitzer et al., 2003). While the relevant compositional characteristics may not be reflected in the optical property data, the lack of correlation between TDHg concentration and DOM optical properties does not support this explanation. To properly investigate this hypothesis, the bulk sulfur content of DOM should be analyzed, or specific sulfur-bearing functional groups quantified via high-resolution mass spectrometry or X-ray spectroscopy.

The concentrations of total Hg in both dissolved and suspended material may provide further insight. The marked increase in THg concentrations over the early freshet period corresponds to an increase in the suspended sediment concentration (Fig. 12b), demonstrating that when suspended sediment concentrations rise above base flow levels, sediments contribute the majority of the THg load.

Regarding the TDHg concentrations, it is possible that at higher SPM concentrations, a greater amount of sedimentary Hg is leached into the dissolved phase. The apparent distribution coefficient (K'_d in units of $L\ kg^{-1}$) of Hg is defined as:

$$K'_d = \text{THg}(\text{SPM})/\text{TDHg} \quad (2)$$

and quantifies the proportion of Hg present in solid vs. dissolved form. The calculated $\log(K'_d)$ values for the six time points sampled during the early freshet vary between 4.5 and 4.9, which are within the range of observations in other rivers (e.g. Hurley et al., 1998; Babiarz et al., 2012; Naik and Hammerschmidt, 2011). Such variation could either be due to disequilibrium between particle-associated and dissolved phases, or to influence of the concentration and/or composition of SPM on the affinity of Hg for the solid phase. Although the Hg concentration of the sediments themselves (SPM THg, Table 1) does not change significantly during this period, the significant decrease in SPM OC content during the early freshet may affect the affinity of Hg for the solid phase, i.e. higher SPM OC content may enhance sorption of dissolved Hg. Our observations, however, do not indicate a correlation between Hg K'_d and SPM %OC.

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sition if throughfall is determined by direct measurement of Hg on plant surfaces, which includes Hg from precipitation. Wet deposition was estimated using precipitation data from the Mercury Deposition Network (<http://nadp.sws.uiuc.edu/mdn>), which includes 6 stations near the Fraser River watershed: the Olympic Peninsula in Washington (WA03; 48.2892° N, -124.6519° E), Seattle, Washington (WA18; 47.6843° N, -122.2588° E), Glacier National Park (MT05; 48.5102° N, -113.9970° E), near Edmonton, Alberta (AB14; 53.3016° N, -114.2016° E), Vancouver, British Columbia (BC06; 49.1000° N, -123.1700° E), and the Strait of Georgia, British Columbia (BC16; 48.7753° N, -123.1281° E). The precipitation Hg concentration records at these sites were weighted by precipitation amount to determine the average concentration at each site, which ranged from 2.8–8.7 ngHg L⁻¹. The mean for all six sites was 4.8 ± 0.3 ngHg L⁻¹. Adopting this value as the Hg concentration of precipitation in the Fraser basin, which receives 742 mm of precipitation annually, results in wet deposition of 3.5 μgHg m² a⁻¹. A recent study by Graydon et al. (2008) in a remote area of northwestern Ontario found throughfall in forested areas to be 2–4× greater than wet deposition, and litterfall of a similar magnitude to throughfall (i.e. a total dry deposition rate 3–7× greater than wet deposition). Assuming similar behavior in the mostly forested Fraser basin, we estimate a total deposition flux of 3.2–6.5 tHg a⁻¹.

The total Hg flux of the Fraser River can be estimated based on our observed SPM Hg concentrations during the 2013 early freshet, which showed little variability (mean ± 1 SD: 0.447 ± 0.015 pmol mg⁻¹). Given an average sediment flux in the Fraser River of 17 Mta⁻¹ (Peucker-Ehrenbrink, 2009), we estimate a Fraser River Hg flux of 1.5 t Hg a⁻¹. As this value is 24–47% of total Hg deposition, which represents a watershed delivery efficiency that is typical of temperate watersheds (e.g., Swain et al., 1992), it appears unlikely that there is a significant additional source of Hg to the Fraser River. While natural weathering, legacy mining contamination, and contemporary pollution may contribute some Hg to the Fraser River, these sources do not elevate the Hg load beyond what is deposited by the atmosphere, nor beyond what is typically mobilized from watersheds. If the Fraser River Hg flux is indeed less than the deposition flux

as estimated here, soils and sediments within the basin are accumulating Hg and/or releasing a portion of the deposited Hg back to the atmosphere.

5 Conclusions

This study has demonstrated for the first time the rapid shift in DOC and POC concentration and DOM and POM composition during the rising limb of the spring freshet of the Fraser River, as well as full annual trends in DOC concentration and DOM composition. DOM optical properties demonstrate that during the early spring freshet, as well as during the fall, DOM shifts to a composition consistent with increasing proportions of fresh plant-derived DOM (higher molecular weight, higher aromaticity; e.g. Fellman et al., 2009; Wickland et al., 2007; Fellman et al., 2010), as well as highly aromatic black carbon (Jaffé et al., 2013), relative to microbially-degraded sources of DOM (lower molecular weight, lower aromaticity). These trends demonstrate the hydrologic control of the Fraser River's snowmelt-dominated hydrology and suggests the importance of limited terrestrial water storage to DOM export. The rapid changes in DOM dynamics observed in the Fraser River underscore the utility of optical sensors, which could be deployed across a basin to generate time series of spatially-resolved DOM behavior for process studies and flux estimates.

Concurrent dissolved and particulate Hg samples during the early freshet suggest DOM-Hg dynamics in the Fraser River that are distinct from what has been observed in other rivers, with apparently weaker control of dissolved Hg by DOC concentration. Future work on Hg in the Fraser River should focus on multiple metrics of DOM composition (e.g. molecular and elemental) as well as a dataset covering a wider range of DOC concentrations. In addition, the excess of atmospheric Hg deposition over Hg exported by the Fraser River indicates that any legacy Hg contamination from mining activities in the 19th century or contemporary pollution is not apparent in the Hg load of the Fraser River.

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The characterization of time-varying DOM dynamics in this study adds to the understanding of hydrologic vs. biogeochemical controls on aquatic DOM cycling by revealing seasonal trends in an intermediate-sized temperate, forested river basin. Previous work has focused primarily on small headwater and mountain streams and large tropical and Arctic basins. The distinct climatic and hydrologic conditions of the Fraser basin (notably its snowmelt-dominated hydrology and minimal natural or anthropogenic impoundments) result in a DOC yield similar to that of the large Arctic Yukon River, despite its less extreme hydrograph. The high yield of DOC from the Fraser River relative to the highly impounded nearby Columbia River suggests that the relative lack of lakes and artificial reservoirs in the Fraser basin may be an important factor in transmitting terrestrial DOM to the coastal ocean.

Compared to large rivers globally, the Fraser River exports a typical proportion (0.25–0.35 %) of annual basin net primary productivity as DOC and POC, predominantly as DOC. This proportion is a fundamental metric for quantifying the relative efficiency of terrestrial OC export to the coastal ocean by diverse watersheds. At present, disagreement among published values of basin-scale NPP complicates a global assessment of fluvial NPP export, hence a careful reassessment of these values is critical.

Finally, as a relatively pristine river basin, the Fraser provides an important reference point for natural biogeochemical conditions that no longer exist in most mid- and low-latitude watersheds of comparable size. Anthropogenic impacts from population growth and associated pollution, channel modification, and impoundment have significantly altered flows of carbon, nutrients, and sediment in large and small river basins globally over the past century, and in some areas continue at an accelerating rate. Studies such as this on a largely free-flowing temperate basin have broad implications for the understanding of natural fluvial processes which is not accessible elsewhere. A system such as the Fraser therefore provides a rare window into the impacts of large-scale processes, such as global climatic change, and sustained research on biogeochemical cycling in the Fraser River thus has the potential to demonstrate the response of natural aquatic systems to long-term changes in ecological conditions.

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Table 1. Geochemical data for the 2013 early freshet period. IGSN codes refer to International GeoSample Numbers in the System for Earth Sample Registration (SESAR) database; sample metadata can be accessed at www.geosamples.org. All nutrient ($\text{NO}_2 + \text{NO}_3$, PO_4 , NH_4 , SiO_2) and major element (Ca, Mg, Na, K, Cl, SO_4) concentrations are in $\mu\text{mol L}^{-1}$. TDHg = total dissolved mercury; THg = total mercury (unfiltered water). For sediment %OC, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ data, if calculated uncertainties (1 SD of the mean of triplicate analyses) were less than instrumental uncertainty (0.1 for %OC, 0.3‰ for $\delta^{13}\text{C}$, and 0.4‰ for $\delta^{15}\text{N}$), instrumental uncertainties are shown.

Date	Parent IGSN	Q_w at Hope ($\text{m}^3 \text{s}^{-1}$)	T ($^{\circ}\text{C}$)	DO (mg L^{-1})	Cond. (μScm^{-1})	pH	Turb. (NTU)	SPM conc. (mg L^{-1})	δD (‰)	$\delta^{18}\text{O}$ (‰)	DOC ($\mu\text{mol L}^{-1}$)	POC ($\mu\text{mol L}^{-1}$)	in situ FDOM (RFUB)	ex situ FDOM (RFUB)
26 Mar 13	GRO000920	980	6.8	12.7	132.0	7.53	3.49 ± 0.16	3.33 ± 0.15	-115.7	-15.35	277	9.2 ± 0.4	693	701
27 Mar 13	GRO000921	981	6.7	12.9	132.5	7.68	3.58 ± 0.17	3.48 ± 0.17	-120.7	-16.13	240	8.1 ± 0.5	628	583
28 Mar 13	GRO000922	984	6.7	12.7	134.2	7.63	3.45 ± 0.16	3.26 ± 0.16	-118.7	-15.87	206		703	722
29 Mar 13	GRO000923	1015	7.2	13.3	135.6	7.66	4.03 ± 0.26	4.24 ± 0.27	-119.8	-15.99	198	10.7 ± 0.7	647	596
30 Mar 13	GRO000178	1042	7.6	11.7	134.4	7.71	4.5 ± 0.6	5.0 ± 0.6	-120.7	-16.05	205	12.6 ± 1.7	605	591
31 Mar 13	GRO000924	1085	7.8	12.3	132.5	7.79			-123.1	-16.38	198		570	593
1 Apr 13	GRO000925	1182	8.4	11.6	130.8	7.80			-122.7	-16.20	205		567	539
2 Apr 13	GRO000926	1294	8.4	12.3	122.2	7.67			-120.7	-16.02	189		555	546
3 Apr 13	GRO000179	1363	8.3	12.3	123.9	7.73	5.7 ± 0.3	7.1 ± 0.4	-120.9	-15.93	199	17.2 ± 1.0	581	572
4 Apr 13	GRO000927	1485	8.2	12.4	122.3	7.71	6.7 ± 0.4	8.6 ± 0.5	-121.8	-16.08	205	19.7 ± 1.4	626	624
5 Apr 13	GRO000928	1774	8.1	12.0	121.3	7.68	8.1 ± 0.3	10.9 ± 0.4	-122.2	-16.04	217	26.4 ± 1.1	696	707
6 Apr 13	GRO000929	1861	8.0	12.2	117.2	7.69	12.6 ± 0.4	18.5 ± 0.6	-122.2	-16.02	234	28.1 ± 1.0	791	825
7 Apr 13	GRO000180	1879	7.2	12.5	109.1	7.67	22.4 ± 1.1	34.9 ± 1.7	-120.1	-15.95	266	41.6 ± 2.1	847	966
8 Apr 13	GRO000930	1936	6.8	12.5	109.2	7.66	39.5 ± 1.4	63.4 ± 2.2	-121.0	-15.78	286	62.8 ± 2.6	844	1142
9 Apr 13	GRO000931	2158	6.8	12.7	118.1	7.70	38.9 ± 1.3	60.8 ± 2.1	-121.6	-16.07	343	58.8 ± 2.2	951	1267
10 Apr 13	GRO000932	2354	7.0	13.0	124.1	7.77	53.0 ± 1.3	85.9 ± 2.1	-123.5	-16.32	415	73.4 ± 1.8	1030	1539
11 Apr 13	GRO000933	2337	6.7	13.2	120.6	7.74	56.6 ± 0.8	91.8 ± 1.4	-125.5	-16.58	413	82.3 ± 1.3	995	1553
12 Apr 13	GRO000181	2435	6.0	13.0	115.5	7.76	43.6 ± 1.1	70.2 ± 1.7	-125.3	-16.42	419	53.6 ± 1.4	1114	1537
13 Apr 13	GRO000934	2511	5.7	12.9	118.1	7.74	38.6 ± 1.1	61.9 ± 1.7	-125.0	-16.21	435	62.7 ± 1.8	1250	1663
14 Apr 13	GRO000935	2579	5.7	13.0	121.7	7.77	30.9 ± 0.7	49.1 ± 1.1	-127.3	-16.64	445	49.0 ± 1.2	1339	1594
15 Apr 13	GRO000936	2479	6.0	13.0	127.4	7.90	81 ± 4	133 ± 6	-128.0	-16.77	458	89 ± 4	929	1710
16 Apr 13	GRO000182	2475	6.6	12.9	124.1	7.81	44.1 ± 0.9	71.0 ± 1.5	-129.1	-16.89	558	62.9 ± 1.4	1303	1776
17 Apr 13 09:00	GRO000937	2385	6.1	13.2	125.8	7.81	39.6 ± 1.1	63.5 ± 1.8	-130.2	-16.98	526	59.3 ± 1.7	1421	1856
17 Apr 13 11:45	GRO000938	2357	6.6	13.3	126.2	7.81	40.6 ± 1.2	65.2 ± 1.9	-131.3	-17.12	522		1396	1836
17 Apr 13 14:30	GRO000939	2349	6.8	13.4	126.3	7.79	40.9 ± 1.7	65.7 ± 2.8	-130.9	-17.13	506			
17 Apr 13 17:45	GRO000940	2355	7.0	13.1	126.3	7.77			-130.3	-16.90	505			
18 Apr 13	GRO000941	2405	6.2	13.2	125.6	7.81	36.5 ± 1.6	58.3 ± 2.5	-131.4	-17.14	497	61 ± 3		
19 Apr 13	GRO000942	2356	6.5	12.9	125.7	7.80	31.2 ± 1.1	49.6 ± 1.7	-129.6	-16.80	493	51.1 ± 2.1		
20 Apr 13	GRO000183	2430	6.8	12.8	124.8	7.74	27.0 ± 1.1	42.5 ± 1.7	-127.8	-16.82	492	52.9 ± 2.4		
21 Apr 13	GRO000943	2906	7.3	12.6	125.4	7.79	27.6 ± 1.9	43.5 ± 2.9	-127.5	-16.87	469	47 ± 3		
22 Apr 13	GRO000945	3078	6.9	12.7	122.5	7.82	25.9 ± 0.4	40.7 ± 0.6	-128.3	-16.74	477			

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Table 1. Continued.

Date	NO ₂ + NO ₃	PO ₄	NH ₄	SiO ₄	Ca	Mg	Na	K	Cl	SO ₄	SPM %OC	SPM C/N	SPM δ ¹³ C (‰)	SPM δ ¹⁵ N (‰)	TDHg (pmolL ⁻¹)	THg (pmolL ⁻¹)	SPM THg (pmolmg ⁻¹)
26 Mar 13	15.10	0.36	1.46	95	414	161	215	28.3	80.7	100	3.3±0.1	9.7±0.3	-27.7±0.3	1.6±0.7			
27 Mar 13	11.75	0.33	1.86	104	433	167	198	25.0	61.6	105	2.8±0.1	10.5±0.9	-28.1±0.4	1.1±0.4			
28 Mar 13	19.40	0.32	1.85	107	421	165	211	26.8	75.5	103							
29 Mar 13	6.87	0.34	2.29	92	434	172	222	28.0	75.2	104	3.0±0.1	9.61±0.07	-27.1±0.3	2.2±0.4			
30 Mar 13	13.82	0.24	1.48	102	431	164	198	25.6	70.4	104	3.1±0.1	9.0±0.4	-27.3±0.3	2.0±0.5	10.07±0.10	14.5±1.6	0.44
31 Mar 13	11.22	0.23	1.23	101	428	173	211	25.5	60.0	104	4.5±0.1	10.3±0.7	-27.2±0.3	2.0±0.4			
1 Apr 13	9.96	0.22	0.38	97	433	175	210	24.9	56.6	102	4.5±0.2	8.9±0.4	-27.3±0.3	1.4±0.4			
2 Apr 13	6.55	0.23	1.79	88	406	154	187	22.5	54.3	97	3.6±0.1	8.5±0.4	-27.2±0.3	2.0±0.4			
3 Apr 13	9.64	0.29	1.33	90	401	150	170	22.0	51.6	97	2.9±0.1	9.27±0.13	-26.4±0.3	2.1±0.4	13.3±0.8	16.4±1.0	0.46
4 Apr 13	4.24	0.35	0.98	83	390	151	181	22.0	52.1	92	2.8±0.1	9.4±0.9	-27.6±0.6	2.0±0.4			
5 Apr 13	9.64	0.34	1.71	95	396	153	187	23.6	55.4	90	2.9±0.1	9.3±0.2	-26.1±0.3	2.4±0.4			
6 Apr 13	7.44	0.31	1.10	92	385	146	174	23.9	52.2	85	1.8±0.1	9.9±0.8	-27.3±0.4	2.3±0.5			
7 Apr 13	12.23	0.29	0.98	93	317	122	143	20.0	45.6	73	1.4±0.1	10.0±0.6	-26.9±0.3	2.3±0.6	5.9±0.5	41.7±1.6	0.46
8 Apr 13	10.43	0.40	2.12	88	371	140	158	25.1	45.8	71	1.2±0.1	10.5±1.2	-26.9±0.3	2.1±0.6			
9 Apr 13	7.60	0.34	0.82	96	393	150	161	24.4	47.9	75	1.2±0.1	10.7±0.9	-26.8±0.3	2.0±0.4			
10 Apr 13	13.85	0.48	1.15	107	408	158	165	27.1	51.1	77	1.0±0.1	10.3±0.8	-27.0±0.5	2.7±0.4			
11 Apr 13	7.74	0.37	0.87	100	398	159	164	26.5	48.6	78	1.1±0.1	11.0±1.0	-27.1±0.4	1.9±1.0			
12 Apr 13	12.17	0.38	0.92	104	391	148	151	24.9	45.1	74	0.9±0.1	10.9±1.1	-26.9±0.3	1.7±0.7	10.6±1.2	44.3±2.7	0.43
13 Apr 13	11.85	0.45	1.15	103	383	154	155	26.7	49.9	75	1.2±0.1	10.7±0.9	-27.1±0.3	1.8±0.5			
14 Apr 13	7.10	0.28	0.70	94	400	163	158	27.3	46.9	76	1.2±0.1	10.8±1.2	-26.8±0.3	1.9±0.5			
15 Apr 13	11.18	0.38	0.87	108	425	163	156	26.5	45.6	76	0.8±0.1	10.9±0.7	-26.4±0.3	1.9±0.6			
16 Apr 13	11.69	0.38	0.95	107	416	162	154	27.0	58.9	73	1.1±0.1	10.9±1.1	-26.9±0.3	2.3±0.8	11.8±0.3	50.1±1.8	0.43
17 Apr 13 09:00	11.64	0.36	0.79	113	423	172	165	28.4	46.2	73	1.1±0.1	10.7±0.7	-26.7±0.3	2.1±0.6			
17 Apr 13 11:45	10.19	0.36	1.21	111	426	176	168	28.8	65.7	78							
17 Apr 13 14:30	7.77	0.35	0.87	110	426	175	167	28.2	49.1	77							
17 Apr 13 17:45	8.24	0.33	0.88	108	422	172	163	28.5	47.3	75							
18 Apr 13	7.83	0.34	1.24	84	427	171	158	26.8	47.8	78	1.2±0.1	11.1±1.3	-26.8±0.3	2.2±0.8			
19 Apr 13	11.22	0.38	0.91	108	410	165	160	27.8	47.0	73	1.2±0.1	10.8±1.2	-27.5±0.4	2.2±0.4			
20 Apr 13	12.01	0.65	0.88	111	411	169	162	28.3	49.7	77	1.5±0.1	10.9±0.8	-27.6±0.3	1.9±0.4	15.2±1.7	69±13	0.46
21 Apr 13	6.78	0.36	0.64	105	421	170	162	28.1	49.8	74	1.3±0.1	11.1±0.9	-27.7±0.4	2.0±0.6			
22 Apr 13	10.05	0.25	0.79	105	409	164	154	25.9	43.6	72							

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Table 2. Two-year record of DOC concentration and optical properties of the Fraser River main stem at Fort Langley. Sampling in 2012 was not sufficiently high frequency to capture the freshet pulse of DOC. IGSN codes refer to International GeoSample Numbers in the System for Earth Sample Registration (SESAR) database; sample metadata can be accessed at www.geosamples.org.

Date	IGSN	DOC (μmolL^{-1})	a_{254} (m^{-1})	SUVA ₂₅₄ ($\text{LmgC}^{-1}\text{m}^{-1}$)	a_{250}/a_{365}	S_R
21 Apr 2011	GRO000128	532				
3 May 2011	GRO000129	733				
10 May 2011	GRO000130	830				
13 May 2011	GRO000131	671				
25 May 2011	GRO000133	601				
3 Jun 2011	GRO000135	457				
7 Jun 2011	GRO000076	386				
28 Jun 2011	GRO000140	265	19.37	2.64	6.45	0.98
8 Jul 2011	GRO000142	282	20.90	2.68	6.38	0.95
15 Jul 2011	GRO000143	364	28.18	2.80	5.92	0.87
19 Jul 2011	GRO000144	339	28.32	3.02	6.06	0.95
29 Jul 2011	GRO000145	335	26.91	2.90	5.91	0.95
26 Sep 2011	GRO000155	193	12.65	2.37	6.60	1.11
14 Oct 2011	GRO000156	242	17.43	2.61	6.03	1.02
25 Oct 2011	GRO000157	256	16.69	2.36	6.89	0.97
26 Oct 2011	GRO000158	250	16.87	2.44	6.58	1.04
31 Oct 2011	GRO000159	275	17.15	2.25	7.91	0.86
15 Nov 2011	GRO000160	318	18.28	2.08	8.12	0.87
28 Nov 2011	GRO000161	254	19.88	2.83	5.98	0.92
11 Jan 2012	GRO000163	237	22.52	3.43	6.38	0.93
10 Feb 2012	GRO000165	217	20.13	3.35	6.53	1.01
18 May 2012	GRO000168	352	35.67	3.67	5.50	0.92
13 Jun 2012	GRO000220	299	28.89	3.49	5.84	0.89
22 Jun 2012	GRO000207	280	26.92	3.47	5.78	0.88
29 Jun 2012	GRO000169	207	19.26	3.37	6.45	0.94
5 Jul 2012	GRO000170	200	18.28	3.30	6.54	0.96
13 Jul 2012	GRO000171	176	16.33	3.35	6.56	0.98
27 Jul 2012	GRO000222		14.87		6.15	1.10
17 Aug 2012	GRO000239		13.34		7.05	1.11
7 Sep 2012	GRO000172		14.48		6.46	1.17
21 Sep 2012	GRO000221		14.97		6.64	1.11
5 Oct 2012	GRO000223		13.33		6.67	1.11
18 Oct 2012	GRO000173		17.40		5.72	1.00
12 Jan 2013	GRO000218		23.58		5.49	0.85
2 Feb 2013	GRO000174	266	21.02	2.85	5.82	0.92
9 Feb 2013	GRO000175	248	22.55	3.28	5.46	0.89

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Table 2. Continued.

Date	IGSN	DOC (μmolL^{-1})	a_{254} (m^{-1})	SUVA ₂₅₄ ($\text{L mg C}^{-1} \text{m}^{-1}$)	a_{250}/a_{365}	S_R
16 Mar 2013	GRO000176	242	23.97	3.59	5.21	0.86
23 Mar 2013	GRO000177	209	17.69	3.06	5.88	0.92
27 Mar 2013	GRO000921	240	17.02	2.56	5.98	1.04
28 Mar 2013	GRO000922	206	18.76	3.29	5.80	0.94
29 Mar 2013	GRO000923	198	19.56	3.57	5.62	0.96
30 Mar 2013	GRO000178	205	18.66	3.29	5.73	0.99
31 Mar 2013	GRO000924	198	18.47	3.37	5.72	0.98
1 Apr 2013	GRO000925	205	17.70	3.13	5.98	0.98
2 Apr 2013	GRO000926	189	20.60	3.94	5.34	1.07
3 Apr 2013	GRO000179	199	19.92	3.62	5.58	1.04
4 Apr 2013	GRO000927	205	25.96	4.58	5.49	1.11
5 Apr 2013	GRO000928	217	21.23	3.54	5.51	0.99
6 Apr 2013	GRO000929	234	25.40	3.93	5.38	1.02
7 Apr 2013	GRO000180	266	32.65	4.44	5.30	1.06
8 Apr 2013	GRO000930	286	29.12	3.68	5.48	0.89
9 Apr 2013	GRO000931	343	34.35	3.62	5.52	0.88
10 Apr 2013	GRO000932	415	41.05	3.58	5.64	0.87
11 Apr 2013	GRO000933	413	52.53	4.60	4.94	0.99
12 Apr 2013	GRO000181	419	47.00	4.05	5.18	0.93
13 Apr 2013	GRO000934	435	51.81	4.31	5.08	0.94
14 Apr 2013	GRO000935	445	44.52	3.62	5.42	0.86
15 Apr 2013	GRO000936	458	49.14	3.88	5.28	0.90
16 Apr 2013	GRO000182	558	49.82	3.23	5.48	0.85
17 Apr 2013	GRO000937	526	54.12	3.72	5.36	0.84
17 Apr 2013	GRO000938	522	52.39	3.63	5.44	0.83
17 Apr 2013	GRO000939	506	53.43	3.81	5.39	0.84
17 Apr 2013	GRO000940	505	52.23	3.74	5.41	0.83
18 Apr 2013	GRO000941	497	48.68	3.54	5.51	0.83
19 Apr 2013	GRO000942	493	51.40	3.77	5.40	0.83
20 Apr 2013	GRO000183	492	49.91	3.66	5.27	0.96
21 Apr 2013	GRO000943	469	48.29	3.73	5.30	0.90
22 Apr 2013	GRO000945	477	51.46	3.90	5.31	0.85
01 May 2013	GRO000184		79.94		5.46	0.81
17 May 2013	GRO000946		38.33		5.70	0.84
7 Jun 2013	GRO000949		25.20		5.87	0.91
22 Jun 2013	GRO000947		20.10		5.92	0.95
24 Jul 2013	GRO000948		15.37		6.56	1.10
24 Jul 2013	GRO000948		14.14		6.71	1.05
20 Sep 2013	GRO000950		9.26		7.11	1.07

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Table 3. Discharge-weighted fluxes and concentrations of DOC in the Fraser River. Environment Canada data were accessed online at <http://aquatic.pyr.ec.gc.ca>.

	Environment Canada record at Hope (1998–2013)	This study (2011–2013)
DOC flux (mol C a^{-1})	$2.7 \pm 0.4 \times 10^{10}$	$2.8 \pm 1.0 \times 10^{10}$
DOC yield ($\text{mol C km}^{-2} \text{ a}^{-1}$)	1.2×10^5	1.2×10^5
Discharge-weighted average	277 ± 14	270 ± 71
DOC concentration ($\mu\text{mol L}^{-1}$)		

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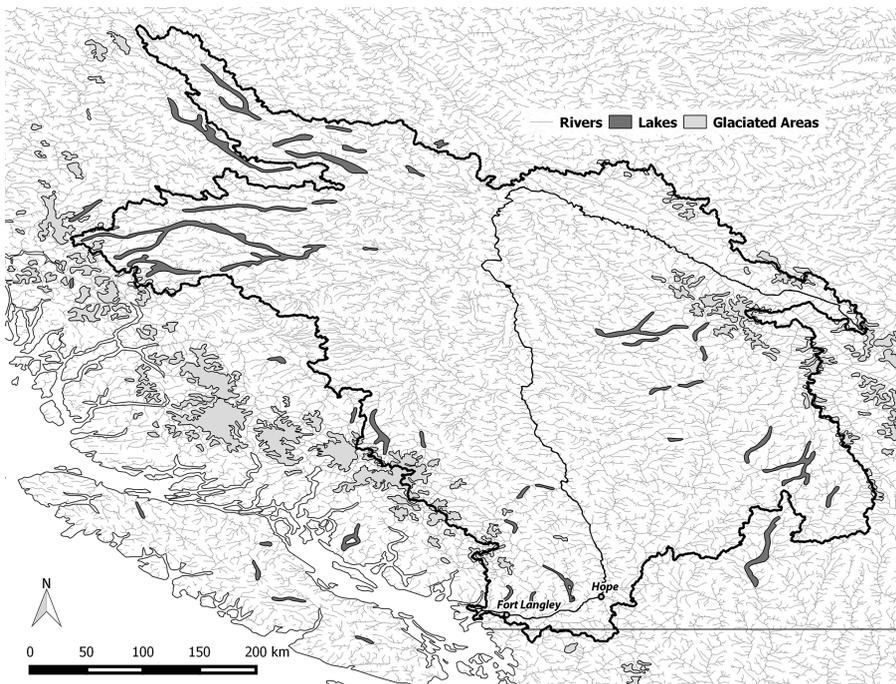


Figure 1. The Fraser River basin, highlighting lakes (natural and man-made; dark grey) and glaciated areas (light grey). Samples were collected at Fort Langley and discharge data (from Environment Canada) are from Hope. River contours and watershed boundaries provided by HydroSHEDS; lake and glacier outlines are derived from the Digital Chart of the World and accessed through Natural Earth Data (<http://www.naturalearthdata.com>).

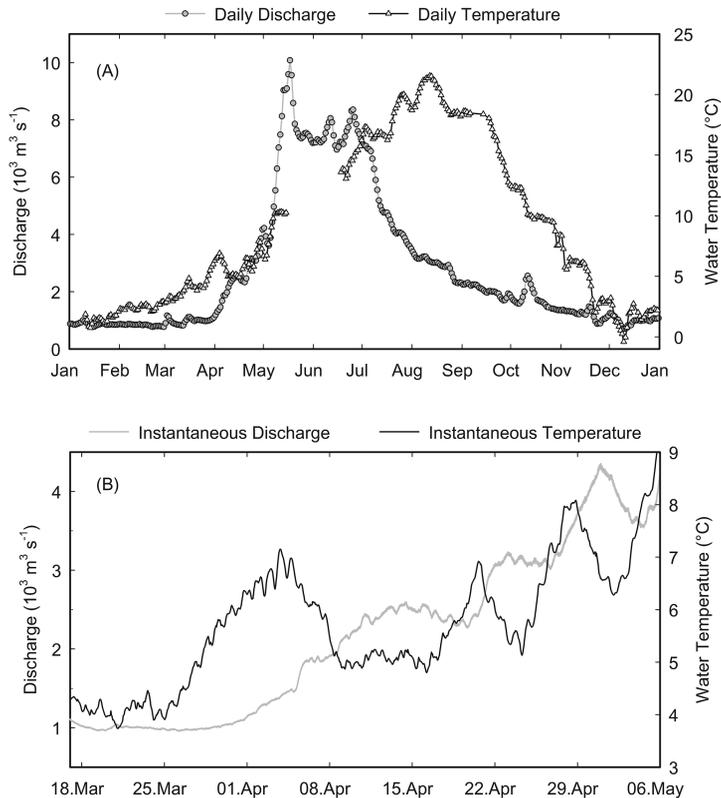


Figure 2. Water discharge and temperature during the study year 2013 from Environment Canada real-time records of the Fraser River at Hope. “Instantaneous” discharge is derived from gauge height measurements at 5-minute frequency; “instantaneous” water temperature measurements are hourly. **(a)** Full year, showing the relationship between seasonal warming and water discharge; **(b)** inset of the early freshet period, when daily fluctuations in water temperature create diurnal discharge pulses.

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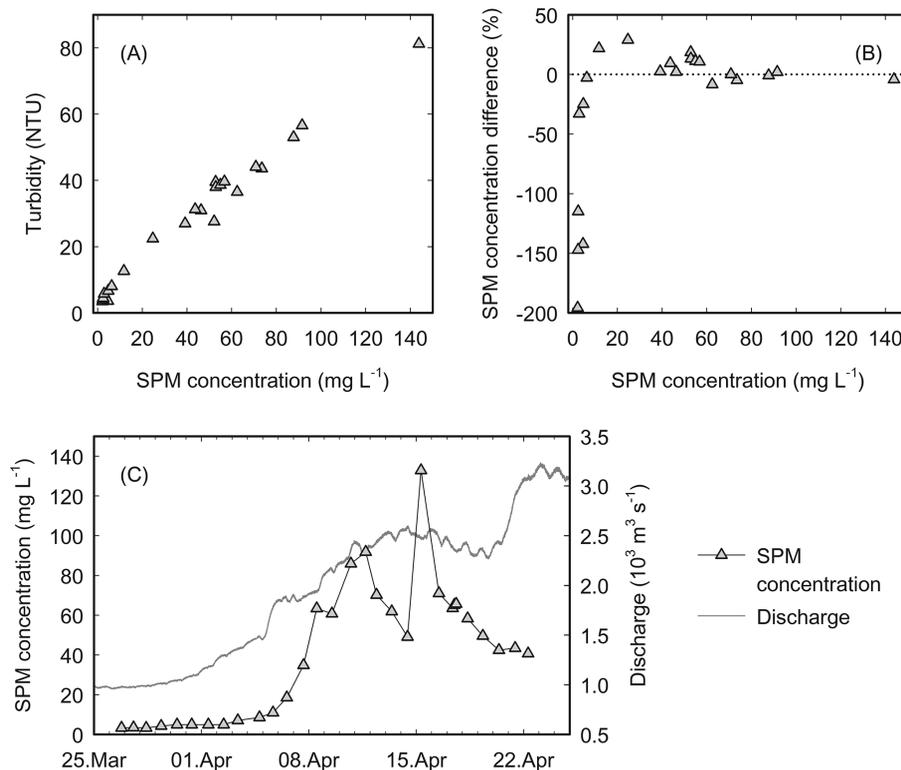


Figure 3. (a) Measured SPM concentration correlated strongly with turbidity (measured with a nephelometer). (b) The difference between the two measurements was most pronounced at very low sediment concentrations. Turbidity values were considered more reliable as sample processing for measured SPM concentration values likely biases results due to loss of material. (c) Suspended sediment concentrations increased rapidly during the early freshet period.

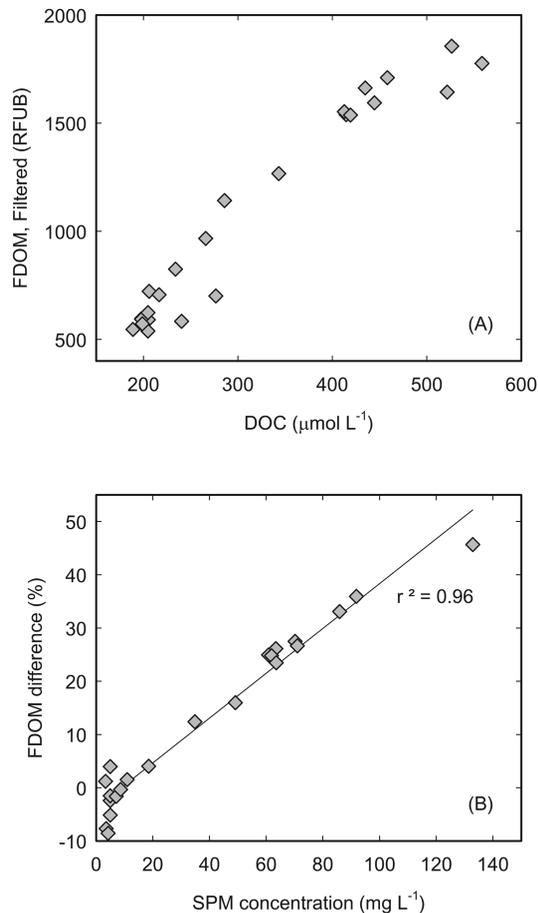


Figure 4. (a) Filtered fluorescent dissolved organic matter (FDOM) was positively correlated with DOC concentration. (b) The difference between ex situ (filtered) and in situ FDOM values was strongly dependent on SPM concentration.

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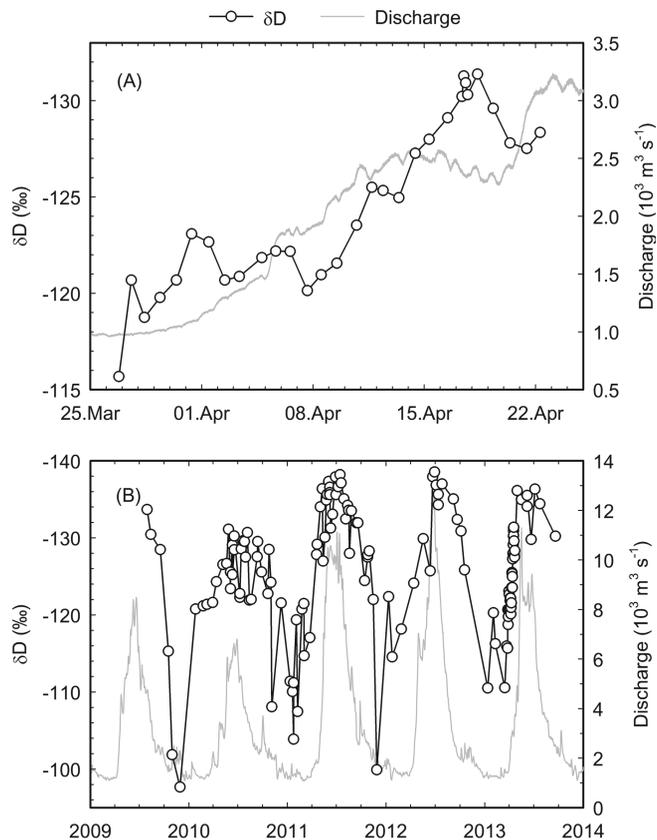


Figure 5. (a) During the early freshet period of 2013, the stable isotope composition of Fraser River water becomes lighter as discharge increases due to a shift from precipitation and ground-water sources towards snowmelt-dominated runoff sources. (b) In the context of the 4-year record of δD in the Fraser River (total variability $\sim 40\text{‰}$), the change observed during the 1-month period of the early freshet ($\sim 16\text{‰}$) is very rapid.

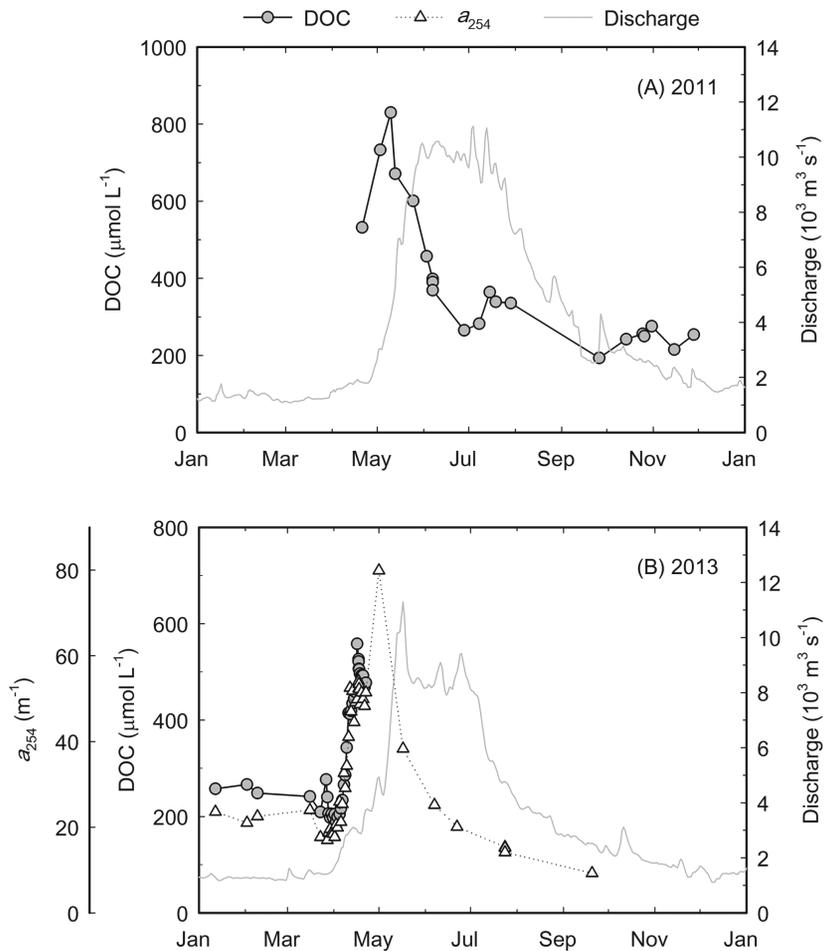


Figure 6. Concentrations of dissolved organic carbon (DOC) peak during the early stages of the spring freshet and decrease over the course of the summer.

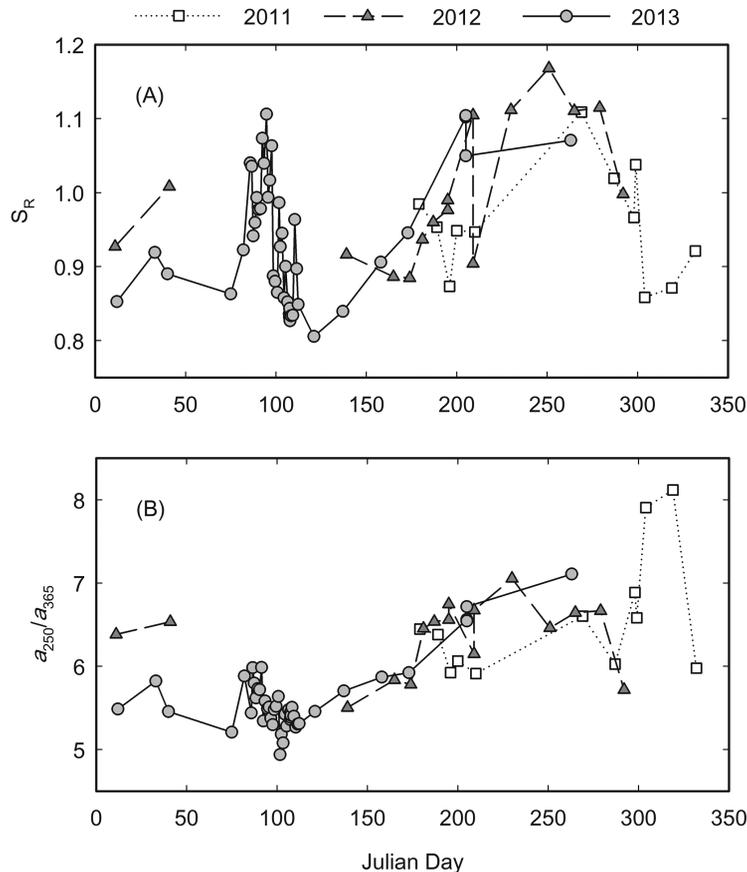


Figure 8. Spectral slope ratio (a) and absorbance ratio (b) show rapid changes in DOM composition during the early freshet DOC pulse, around Julian Day 100. A more gradual return to pre-freshet composition follows throughout the summer. A second cycle occurs in late winter, likely associated with soil flushing during fall rain events.

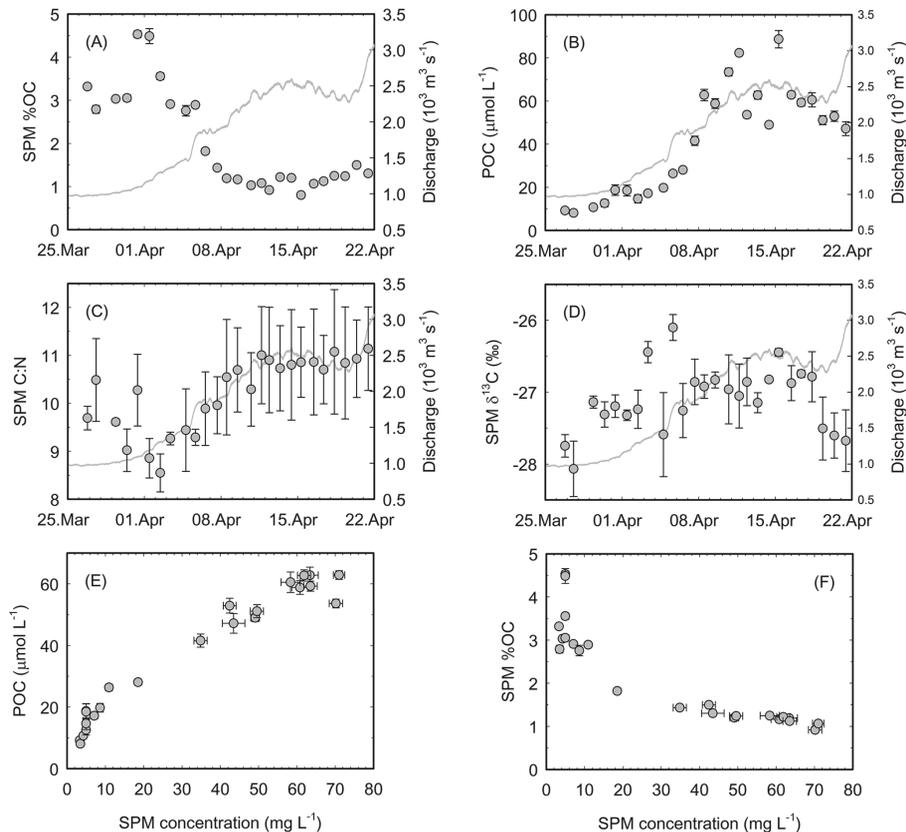


Figure 9. The abundance and composition of POC shifted during the early freshet period towards (a) relatively lower %OC, (b) higher POC concentration (due to increased sediment concentration), and (c) higher C : N. (d) No distinct temporal trend is evident in $\delta^{13}\text{C}$. (e) POC concentration and (f) SPM OC content are nonlinearly coupled with SPM concentration. Error bars represent 1 SD of triplicate measurements. Discharge is shown as gray lines in (a–d).

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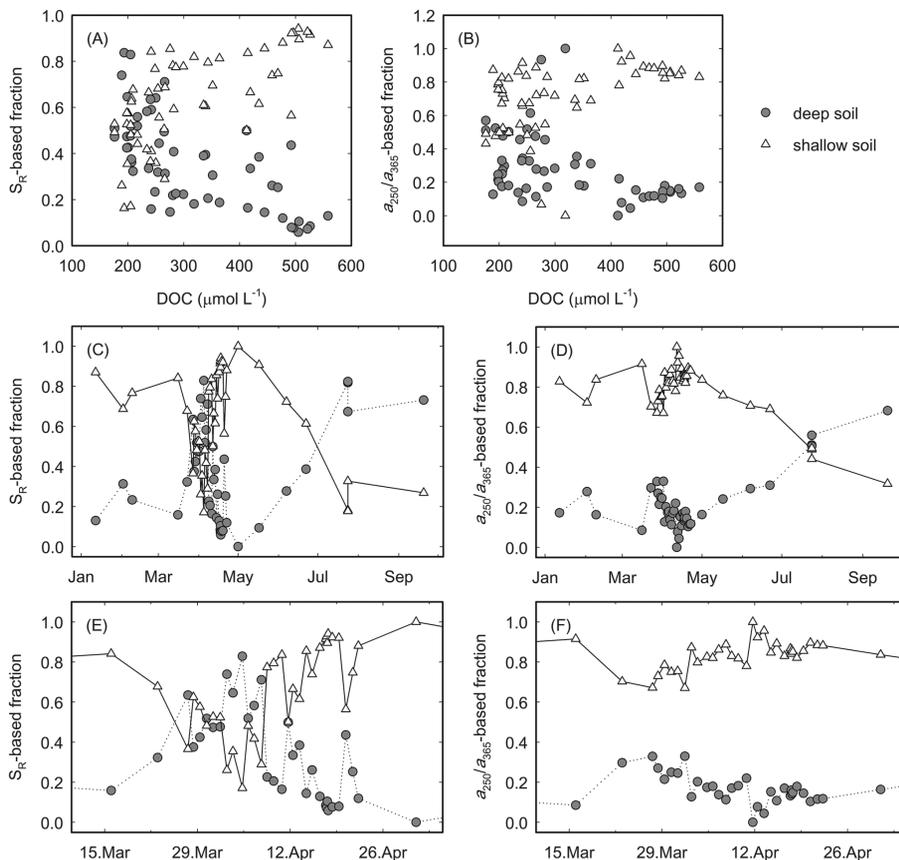


Figure 11. The contributions of deep and shallow soil DOC to total Fraser DOC were estimated based on the observed maximum and minimum values of DOM optical properties (spectral slope ratio, S_R , and absorbance ratio, a_{250}/a_{365}). These fractions are related to the DOC concentration (**a** and **b**), and change throughout the year (**c** and **d**, shown here for 2013; **e** and **f** detail the 2013 early freshet period).

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