Seasonal hydrology drives rapid shifts in the flux and composition of dissolved and particulate organic carbon and ~~mercury~~major and trace ions in the Fraser River, Canada

Style Definition: Heading 2: Font: Arial, Bold

Style Definition: Heading 3: Font: (Default) Arial, Bold, Not Italic, Indent: Left: 0", Outline numbered + Level: 2 + Numbering Style: 1, 2, 3, … + Start at: 1 + Alignment: Left + Aligned at: 0.25" + Indent at: 0.55"

Britta M. Voss[1,2]*, Bernhard Peucker-Ehrenbrink[1,3], Timothy I. Eglinton[4], Robert G. M. Spencer[5,6], Ekaterina Bulygina[6], Valier Galy[1], Carl H. Lamborg[1,7], Priya M. Ganguli[1], Daniel B. Montluçon[4], Steven Marsh[3], Sharon L. Gillies[3], Jenna Fanslau[3,6,1], Audrey Epp[3,1], and Rosalie Luymes[3,1]

[1] Woods Hole Oceanographic Institution, 360 Woods Hole Road, Woods Hole MA 02543, USA
[2] Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139, USA
[3] University of the Fraser Valley, 33844 King Road, Abbotsford BC V2S 7M7, Canada
[4] Eidgenössische Technische Hochschule, Sonneggstrasse 5, 8092 Zürich, Switzerland
[5] Florida State University, 600 West College Avenue, Tallahassee FL 32306, USA
[6] Woods Hole Research Center, 149 Woods Hole Road, Falmouth MA 02540, USA
[7] University of California Santa Cruz, 1156 High Street, Santa Cruz CA 95064, USA
[*] now at: U.S. Geological Survey, 3215 Marine Street, Suite E-127, Boulder CO 80303, USA
Correspondence to: B. M. Voss (bvoss@whoi.edu)

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~~ions 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 μmol 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~~A smaller dataset of total and dissolved Hg concentrations also ~~varied~~showed variability 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. The snowmelt-dominated hydrology, forested land cover, and minimal reservoir impoundment of the Fraser River may influence the DOC yield of the basin, which is high relative to the nearby Columbia River and of similar magnitude to that of the Yukon River to the north. Anticipated warming and decreased snowfall due to climate changes in the region may cause an overall decrease in DOM flux from the Fraser River to the coastal ocean in coming decades

1 Introduction

Formatted: Font: Not Bold

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 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.

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

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~~settings, 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).~~

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

The residence time of OC derived from fresh litterfall in soils depends on its initial composition and environmental conditions, and varies between less than 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.

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

The ~~time series record of DOC concentration in the~~ Fraser River ~~from Environment~~is a large, mountainous river basin in southwestern Canada. Total basin area is 233,000 km^2 and average annual discharge is 112 km^3 a^{-1} (~~Swain, 2004~~Meybeck and Ragu, 2012). The basin is largely forested and experiences relatively little anthropogenic modification in the form of dams, channelization, or land cover alteration for a basin of its size and latitude. 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. 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, a number of 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 less extreme 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 potential 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 ~~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~~

Field Code Changed

Field Code Changed

~~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.~~
River.

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~~2013~~)~~; Demers et al., 2010). 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 ongoing and 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

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

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~~)~~; Riche et al., 2014)—understanding freshet biogeochemical dynamics under present conditions is critical to detecting future changes and anticipating their consequences.

Field Code Changed

Field Code Changed

Field Code Changed

2 Methods

Formatted: Font: Not Bold

2.1. Discharge and historical data

Formatted: Font: Not Bold, Italic

Continuous discharge and water temperature information (5-minute 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 Figure ~~2~~S1.

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).

Field Code Changed

Field Code Changed

Field Code Changed

2.2. Sample collection and basic water chemistry

Formatted: Font: Not Bold, Italic

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 2013 early freshet (26 March - 22 April), discrete samples for basic water chemistry, SPM concentration, and DOM properties were collected daily, while samples for Hg were collected every 4-5 days. The longer record of DOM properties (2011-2013) constitutes samples collected approximately twice monthly. No field duplicates or blanks were collected for chemical analyses.

Basic water properties were determined with a handheld multiparameter probe (YSI Professional Plus). The probe was equipped with sensors for water temperature (°C), conductivity (µS cm^{-1}), pH, and dissolved oxygen (DO, mg O_2 L^{-1}). DO and pH probes were calibrated according to manufacturer specifications approximately every 5 days.

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. Therefore, all results for "dissolved" constituents represent material that is <0.2 µm. 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.

Field Code Changed

Nutrient samples were collected in pre-cleaned 20 mL polyethylene scintillation vials and stored frozen until analysis. Analyses for dissolved NO_3+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). Instrumental detection was <0.05 µmol L^{-1} for all nutrients.

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. Instrumental precisions and accuracies for cation and anion concentrations were <5% (with the exception of accuracy for Ca, which was 5.3%; Voss et al., 2014).

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 (δ^{18}O) isotope compositions were measured on a Picarro L2120-I cavity ring-down spectrometer. Measured values were calibrated using secondary standards (mean ± 1 s.d.: Mediterranean Sea water, δD 8.12 ± 0.30‰, δ^{18}O 0.95 ± 0.05‰; Jungfrau water, δD -160.28 ± 0.21‰, δ^{18}O -22.50 ± 0.06‰; Zürich water, δD -75.57 ± 0.19‰, δ^{18}O -10.62 ± 0.04‰), which were calibrated against standard reference materials SLAP2, GISP, and VSMOW2 (International Atomic Energy Agency). Precisions for δD and δ^{18}O were 0.3‰ and 0.03‰, respectively; accuracies were 1.0‰ and 0.07‰.

2.3. Turbidity and suspended sediment concentration

Formatted: Line spacing: single

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~~2) 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

Formatted: Font: Not Bold, Italic

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 fluorescence 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 minutes of sample collection. The probe measurement frequency was 30 seconds, 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 (>~500 µmol 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).~~

Field Code Changed

Field Code Changed

Samples for the determination of DOC concentration were collected as 0.2 µm-filtered water (as described above) 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).

Field Code Changed

Field Code Changed

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 MΩ cm^{-1}; Mann et al.,~~

~~2012)~~(MilliQ, 18.2 MΩ cm^{-1}; Mann et al., 2012). Naperian absorption coefficients ($a(\lambda)$) were calculated at integer wavelengths between 200-800 nm from absorbance as follows:

$$a(\lambda) = 2.303 * A(\lambda)/l \qquad (1)$$

where $A(\lambda)$ is the measured absorbance and l is the cell path length in meters (Del Vecchio and Blough, 2002). Absorbance at specific wavelengths can be diagnostic of certain DOM properties (e.g. Spencer et al., 2012). Normalizing DOC concentrations to wavelength-specific absorbance (e.g. SUVA$_{254}$ = absorbance at 254 nm divided by DOC concentration in mg L^{-1}) allows the chromophoric character 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.

~~.~~

For bulk carbon and nitrogen content and stable isotope analysis, suspended sediment samples were weighed in triplicate into combusted silver capsules. Samples were then exposed to concentrated HCl vapor under partial vacuum at 65°C for 3 days to remove carbonate. Organic carbon and nitrogen concentrations (%OC and %N, weight percent of total sediment mass) and stable isotope values (δ^{13}C and δ^{15}N) were measured on an Elemental Analyzer (Carlo Erba 1107) coupled via a Finnigan-MAT Conflo II open split interface to a Delta^{Plus} stable isotope ratio mass spectrometer for measurement of ^{13}C/^{12}C (referenced to Vienna Pee Dee Belemnite) and ^{15}N/^{14}N (referenced to N$_2$ air; IAEA, 1995). Sample %OC, %N, δ^{13}C, and δ^{15}N values were determined from standard reference materials NBS-19 limestone (Coplen et al., 2006), IAEA-N-1 ammonium sulfate (Böhlke et al., 1993), USGS-40 glutamic acid (Qi et al., 2003), and an internal glycine standard. Analytical accuracy and precision of these measurements (1 s.d.) are 0.1 wt~~%~~.% for C and N abundance, 0.3‰ for δ^{13}C, and 0.4‰ for δ^{15}N.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Formatted: Pattern: Clear (White)

Field Code Changed

2.4. Mercury analyses

Formatted: Font: Not Bold, Italic

Water samples for Hg concentrations were collected in pre-cleaned 250 mL glass bottles, that were double-bagged and handled using “clean hands-dirty hands” approaches (Patterson and Settle, 1976), and stored in the dark after collection. Bottles were prepared following procedures outlined in Hammerschmidt et al. (2011); all materials were prepared in ~~a class 100~~an ISO 5 cleanroom. Following established procedures (U.S. EPA, 2002), samples were preserved with BrCl (final concentration of 0.5% w/w) within 30 days of collection, then stored in the dark at 4°C until analysis. Total dissolved Hg (TDHg) concentration represents water samples filtered to 0.2 µm (as described above), while total Hg (THg) concentration represents unfiltered water samples. In 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 $NH_2OH \cdot HCl$ 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 $M\Omega\ cm^{-1}$) blank was analyzed at the beginning of each day of analysis to ensure that background signal was sufficiently low (~0.5 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 standard deviations were <10% of the measured value, or until sample material was exhausted.

Field Code Changed

Field Code Changed

Field Code Changed

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 hour) 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 (3x standard deviation of blank = 0.6 ng), but in two of six samples were not quantifiable (10x standard deviation of blank = 2.0 ng). This limitation does not affect the conclusions drawn from the data~~.

Field Code Changed

3 Results

3.1. Early freshet water ~~quality~~chemistry 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 $m^3 s^{-1}$. 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~~2C).

Nutrient concentrations varied significantly during the early freshet period (NO_3+NO_2: 4-19 µmol L^{-1}, PO_4: 0.2-0.7 µmol L^{-1}; NH_4: 0.4-2.3 µmol L^{-1}; SiO_2: 83-113 µmol L^{-1}; Fig. S2). Nitrate/nitrite and NH_4 concentrations showed slight decreasing trends, continuing the decline from peak winter values that is typical of the seasonal cycle in the Fraser River and other temperate to high-latitude fluvial systems (Cameron, 1996; Voss et al., 2014; Whitfield and Schreier, 1981). Phosphate and dissolved SiO_2 concentrations did not show clear trends. Nutrient concentrations during the early freshet exhibited a substantial portion of the total annual variation. Such large day-to-day variability was not anticipated based on lower frequency (i.e. once to twice monthly) time series sampling presented by Voss et al. (2014).

Concentrations of some major dissolved species (Na, Cl, SO_4) decreased as discharge increased during the early freshet (Fig. S3). Others decreased for the first two weeks, then increased (Mg, K) or remained relatively stable (Ca). Those elements which exhibited a systematic decrease in concentration throughout the early freshet are more significantly influenced by sea salt aerosols in precipitation relative to chemical weathering of rocks than those characterized by more variable behavior. All major species except SiO_2 (which is also a nutrient) showed significant linear correlations ($p<0.01$, 95% confidence interval) with conductivity (a proxy for total dissolved solids).

The stable isotope composition of water (δD, $\delta^{18}O$) showed a steady shift to ~~more depleted~~lighter compositions over the 2013 early freshet (Fig. ~~5~~S4). The change (>15‰ in δD over 27 days) is large and rapid in the context of the total annual variability in this parameter

Formatted: Font: Not Bold

Formatted: Font: Not Bold, Italic

(~40‰ in δD; Voss et al., 2014). Deuterium excess (δD – 8*δ^{18}O; values not shown) decreased during this period from ~8.4 to ~4.7‰.

Field Code Changed

Early freshet changes in DOM concentration were monitored in the field by proxy from FDOM probe measurements. 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 (>~500 µmol L^{-1}; Fig. S5A), 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. S5B).

3.2. **Seasonal changes in OC concentration and OM composition**

Formatted: Font: Not Bold, Italic

In both 2011 and 2013, DOC concentrations rose rapidly during the early freshet period from fall/winter levels of ~200 µmol L^{-1} to a peak of 700-900 µmol L^{-1} (Fig. ~~6~~3). 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~~positively correlated with wavelength-specific absorption coefficients (Fig. ~~7~~4).

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.~~ 5). ~~Normalizing DOC concentrations to wavelength-specific absorbance (e.g. SUVA$_{254}$ = absorbance at 254 nm divided by DOC concentration in mg L^{-1}) allows the chromophoric character 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~~5 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~~6). 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 μmol 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 March 26th to a minimum of 4.6 on April 8th, followed by values of ~10 over the following two weeks. The C:N composition of POM also changes, with values before April 6th varying between 8.5 and 9.9 (excepting the values of 10.5 on March 27th and 10.3 on March 31st), and then rising to values between 10-11 for the remainder of the sampling period.~~ The δ^{13}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., in press), or coarser mineral particles with lower capacity for OC loading (Mayer, 1994).~~ The δ^{13}C of POC also varied (-27.7 to -26.1‰); however, no clear trends are apparent.

3.3. Early freshet changes in mercury concentration

Formatted: Font: Not Bold, Italic

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.

6.3. ~~**Early freshet changes in mercury concentration**~~

Formatted: Font: Not Bold, Italic

~~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~~7). In contrast, unfiltered THg concentrations increased significantly in a matter of days during this period, with concentrations before April 7th 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 April 7th to <25% afterwards.

Results of suspended sediment Hg concentrations are presented with consideration of analytical detection limits. Empty combusted nickel boats were analyzed to determine the analytical blank of the sediment Hg analysis: 0.37 ± 0.20 ng Hg (avg. ± 1 SD). The total amount of Hg analyzed in suspended samples ranged from 1.2-4.9 ng. The very low amounts of Hg reported here are above the detection limit (3x standard deviation of blank = 0.6 ng), but in two of six samples were not quantifiable (10x standard deviation of blank = 2.0 ng). This limitation does not, however, affect the conclusions drawn from the data. Concentrations of Hg in SPM were relatively constant, varying between 0.43-0.46 pmol mg^{-1}.

4 Discussion

Formatted: Font: Not Bold

4.1. Rapid geochemical changes in the early freshet

Formatted: Font: Not Bold, Italic

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 δ^{18}O composition, SPM concentration, and OM concentration and composition.

The sudden change in water sources from different portions of the basin is demonstrated by the rapid decrease in δD and δ^{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 δ^{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.

Field Code Changed

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 versus winter precipitation in the Fraser basin (Froehlich et al., 2008~~)~~; Riche et al., 2014). 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.

Field Code Changed

Field Code Changed

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; Michalzik et al., 2001)~~(Michalzik et al., 2003; Michalzik et al., 2001), leading to a pulse of DOM into streams.

Field Code Changed

Field Code Changed

~~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 potential 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)~~.~~. Absent quantitative estimates of

Field Code Changed

headwater fluxes of DOC to the main stem of each of these rivers, these differences in DOC yields suggest that DOC mobilized in the Fraser River is retained more effectively during downstream transport than in the Columbia River, while DOC in the Yukon River is transported roughly as efficiently as in the Fraser. The extensive reservoir impoundment of the Columbia River may be an important factor in the apparently greater loss of terrestrial DOC from this system, while lower terrestrial productivity in the vast arid portions of the Columbia basin likely also generate smaller inputs of soil DOC than in the forested Fraser basin. The more natural hydrologic regime of the Yukon River, and land cover composed largely of forests and wetlands, likely contribute to its similar DOC yield compared to that of the Fraser River.

4.2. Annual cycles of DOM composition and sources

Formatted: Font: Not Bold, Italic

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 SUVA$_{254}$). 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 SUVA$_{254}$), 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) indicates that a secondary peak in DOC concentration (300-500 µmol 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

Field Code Changed

Field Code Changed

Field Code Changed

vegetation to accumulate and DOM export to revert to slower, deeper flow paths~~.~~ (Oswald and Branfireun, 2014). 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~~smaller quantity of DOC mobilized by fall soil flushing ~~is less than~~compared to that of the spring freshet~~, presumably because~~ (evident in the smaller fall pulses of DOC exhibited by the long-term Environment Canada DOC record) is likely due to incomplete recovery of the soil DOC pool ~~has not yet recovered~~ to its pre-freshet size, ~~and~~in addition to the fact that 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 base flow DOM load of the Fraser causes a change in DOM optical properties of a similar magnitude to that seen during the early freshet. It should be noted, however, that optical parameters are not necessarily a linear function of the relative quantity of the functional components responsible for them (Stedmon and Markager, 2003; Yang and Hur, 2014). The spatial extent and magnitude of fall rain events is also highly variable from year-to-year and across different tributary catchments, hence the fall and winter DOM composition changes are likely to be more variable than those during the freshet.

The fact that DOC concentrations peak and begin to fall before discharge reaches its freshet zenith indicates that this hydrologic flushing of DOM is limited by the size of the shallow soil DOM pool, and/or by the differences in snowmelt timing across the basin. Disentangling these effects would require extensive knowledge of seasonal changes in DOM flux and composition from individual tributary basins. If the spring freshet effectively flushes the shallow

Field Code Changed

Field Code Changed

Field Code Changed

soil DOM pool across the basin, this implies a decoupling from the deep soil DOM pool, as negligible shallow DOM is able to persist during high flow conditions, and transfer to deeper soil layers only occurs between late summer and the following spring. ~~If, however, a portion~~A stronger understanding of ~~shallow soil DOM escapes mobilization into streams during~~ the ~~freshet, this material has the opportunity to undergo aging and degradation in deeper soil layers and influence the flux and composition~~nature of ~~DOM during non-freshet conditions. This apparent distinction~~interaction between ~~a deep soil DOM source from a freshet "leak" of shallow soil DOM versus a constant flux of residual degraded shallow soil DOM, could be tested through a~~ shallow and deep soil DOM pools would further inform the results of this study. An investigation of seasonal changes in soil DOM properties (e.g. concentration, optical properties, biolability, ^{14}C age) ~~at different depths. A shift in deep soil DOM properties towards shallow soil DOM composition during spring freshet conditions would suggest that shallow and deep soil DOM pools are indeed coupled~~with depth could build on the results presented here by ~~seasonal~~identifying whether hydrologic flushing imparts a "fresh" DOM signature on deep soil DOM and how long such a signature persists.

The brief rise in S_R at the beginning of the freshet DOC pulse may indicate an initial release of highly soluble and less aromatic, lower molecular weight or non-chromophoric DOM that is quickly overwhelmed by more aromatic, higher molecular weight DOM for the remainder of the pulse as S_R drops (Ward et al., 2012). Such an 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).

Field Code Changed

Field Code Changed

Field Code Changed

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 April 5th – June 7th. 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 m^3 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 900-950 µmol L^{-1}, assuming a base flow DOC concentration of 100-200 µmol 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 ~65 km^3. If this volume is distributed equally across the entire basin (228,776 km^2), it corresponds to a soil depth of ~28 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 m in rapidly-eroding mountainous areas to >3 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.

Field Code Changed

Field Code Changed

Field Code Changed

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

Field Code Changed

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” versus “deep” soil-derived DOC to the total DOC load of the Fraser River (Fig. ~~11~~8). 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_{350} 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, both S_R and a_{250}/a_{365} indicate that, on average, shallow soil-derived DOC constitutes ~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~~8). 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.

Field Code Changed

Field Code Changed

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 g C m^{-2} a^{-1} (however no OC fluxes are reported), corresponding to total terrestrial carbon fixation in the basin of ~4.0×10^{12} mol C a^{-1}. Based on the measured DOC flux of 2.8×10^{10} 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 ~1×10^{10} mol C a^{-1}, i.e. ~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,~~Furthermore, some portion of POC derives from petrogenic OC (Voss, 2014), not

Field Code Changed

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., ~~in press~~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 g C m^{-2} 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.

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~~shortens DOC residence time and therefore limits the opportunity for heterotrophic consumption, may result in relatively efficient DOC export in this basin.

In light of anticipated future changes in regional climate and basin hydrology including a shift towards relatively more rain and less snow, an earlier onset of spring melting producing the freshet, and a rise in annual average air temperature, it is possible that DOM export from the Fraser River may change. Higher temperatures throughout the year may cause higher microbial activity in soils, leading to decreased inputs of soil DOM to streams. A shift towards more rain-dominated precipitation will cause river water temperatures to increase, which may promote increased microbial consumption of DOM in the aquatic realm. The dampening of the onset of the spring freshet may have the most significant impact, by drawing out the flushing of soil DOM over a longer period of time. This will increase the residence time of DOM in the river, providing greater opportunity for consumption of DOM before it reaches the coastal ocean. Thus future changes in climate are likely to decrease the total flux of DOM in the Fraser River.

Formatted: Font color: Black

Field Code Changed

Field Code Changed

Formatted: Font color: Black

Field Code Changed

Formatted: Font color: Black

Field Code Changed

Formatted: Font color: Black

Field Code Changed

Formatted: Font color: Black

Field Code Changed

Formatted: Font color: Black

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. Although sampling for dissolved, total, and sedimentary Hg was not as comprehensive as that for OM and other dissolved species, this contemporaneous dataset allows for an initial assessment of Hg dynamics in an understudied watershed. Previous studies have identified a strong correlation between DOC concentration and TDHg concentration (e.g. Dittman et al., 2010; Schuster et al., 2011~~)~~; Riscassi and Scanlon, 2011; Shanley et al., 2008), including during snowmelt (Shanley et al., 2002; Schuster et al., 2008; Demers et al., 2010), 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~~9A). In small headwater tributaries of the Hudson River (Burns et al., ~~2012b~~2012), 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 March 30th (10.1 pmol L^{-1}) and April 3rd (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.

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~~9B), demonstrating that when suspended sediment concentrations rise above base flow levels, sediments contribute the majority of the THg load.

Formatted: Font: Not Bold, Italic

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Regarding the TDHg concentrations, it is possible that ~~at higher SPM concentrations, a greater amount~~the exchange of ~~sedimentary~~ Hg ~~is leached into the~~ between solid and dissolved ~~phase~~phases changes with changes in SPM concentration. The apparent distribution coefficient (K_d' in units of L kg^{-1}) of Hg is defined as:

$$K_d{}' = THg(SPM)/TDHg \qquad (2)$$

and quantifies the proportion of Hg present in solid versus 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~~. 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,~~However, we do not ~~indicate~~observe a correlation between Hg K_d' and SPM %OC.

Field Code Changed

Field Code Changed

Field Code Changed

~~Given the general dependence of Hg distribution on associations with OC (Aiken et al., 2011), the concentration of POC, regardless of SPM OC content, is likely the most relevant factor in the observed K_d' behavior. This influence may result in stronger adsorption of dissolved Hg onto particles at higher POC concentration, causing a shallower slope in the TDHg-DOC relationship than if POC concentration were constant. POC-enhanced Hg sorption would be expected to cause a decrease in TDHg, yet the slope of the TDHg-DOC relationship in the Fraser is steeper than that observed in other rivers. Furthermore, there is no apparent correlation between POC concentration and K_d' in our Fraser River samples.~~ Thus it appears that other processes (such as changes in the chemical composition of DOM or POM) or synergistic effects are responsible for the trends observed in dissolved and particulate Hg during the Fraser River early freshet period. The most practical first step towards better understanding of Hg dynamics in this system is to generate a larger dataset of TDHg concentrations.

Mercury-assisted gold mining in British Columbia, which involved the mobilization of ~58 x 10^6 m^3 of sediment in the central Fraser basin (Nelson and Church, 2012), has been

Field Code Changed

proposed as the source of elevated Hg concentrations found in delta and lake sediments across the basin (Hales, 2000; Gallagher et al., 2003~~)~~; Johannessen et al., 2005). Although the majority of the Hg contamination was most likely removed from the basin within decades due to its preferential association with rapidly mobilized fine-grained (OC-rich) sediments, the ongoing transport of mining-mobilized sediment through the basin ~~(Nelson and Church, 2012)~~(Nelson and Church, 2012) creates the potential for continued contamination.

Field Code Changed

Field Code Changed

Field Code Changed

In order to assess whether the Hg load of the Fraser River is elevated from possible legacy gold mining contamination or other pollution, we have estimated the expected Hg deposition flux assuming Hg is entirely derived from deposition of atmospheric aerosols and plant material. Soluble Hg^{2+} in precipitation constitutes wet deposition, while Hg derived from vegetation can be characterized as a combination of throughfall (adsorbed Hg on the surfaces of plant tissues) and litterfall (Hg within plant tissues; Graydon et al., 2008). Total deposition is the sum of wet and dry deposition. Dry deposition can be expressed as the sum of throughfall and litterfall, less open wet deposition 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, -124.6519), Seattle, Washington (WA18; 47.6843, -122.2588), Glacier National Park (MT05; 48.5102, -113.9970), near Edmonton, Alberta (AB14; 53.3016, -114.2016), Vancouver, British Columbia (BC06; 49.1000, -123.1700), and the Strait of Georgia, British Columbia (BC16; 48.7753, -123.1281). 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 ng Hg L^{-1}. The mean for all six sites was 4.8 ± 0.3 ng Hg 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 µg Hg m^{2} a^{-1}. A recent study by Graydon et al. (2008) in a remote area of northwestern Ontario found throughfall in forested areas to be 2-4x greater than wet deposition, and litterfall of a similar magnitude to throughfall (i.e. a total dry deposition rate 3-7x greater than wet deposition). Assuming similar behavior in the mostly forested Fraser basin, we estimate a total deposition flux of 3.2-6.5 t Hg a^{-1}.

Field Code Changed

Field Code Changed

The total Hg flux of the Fraser River can be roughly estimated based on our observed SPM Hg concentrations during the 2013 early freshet, which showed little variability (mean ± 1 s.d.: 0.447 ± 0.015 pmol mg^{-1}). Given an average sediment flux in the Fraser River of 17 Mt a^{-1} (Peucker-Ehrenbrink, 2009), we estimate a Fraser River Hg flux of 1.5 t Hg a^{-1}. ~~As~~ This is necessarily a first-order estimate, as SPM concentration and THg are not perfectly correlated in our dataset, indicating that other factors play an important role in Hg export. However, this value is 24-47% of total Hg deposition, which represents a watershed delivery efficiency that is ~~typical of~~similar to or somewhat higher than other temperate watersheds (~~e.g., Swain~~Brigham et al., ~~1992~~2009~~)~~; Swain et al., 1992)~~, it appears unlikely that~~. It is therefore difficult to determine from these data whether there is a significant ~~additional~~ source of Hg beyond atmospheric deposition to the Fraser River. ~~While~~ As the potential additional sources of Hg to the Fraser River, including 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,~~it appears that soils and sediments within the basin are accumulating Hg and/or releasing a portion of the deposited Hg back to the atmosphere.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

5 Conclusions

Formatted: Font: Not Bold

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~~OM dynamics in a snowmelt-dominated ~~hydrology~~river basin 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.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

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~~ and hydrologic conditions.

The characterization of time-varying DOM dynamics in this study adds to the understanding of hydrologic versus 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.

Acknowledgements

Formatted: Font: Not Bold

This work was partially supported by a WHOI Ocean Ventures Fund award to BMV and NSF grants EAR-1226818 to BPE, OCE-0851015 to TIE, BPE, and VG, and OCE-0851101 to RGMS, and support to BPE from Jane and James Orr. Sediment EAIRMS analysis was performed by Carl Johnson at WHOI. Thanks to Michael Bothner and Michael Casso (USGS Woods Hole) for providing analytical support and use of the DMA-80 for sediment Hg measurements, to Scot Birdwhistell for assistance with ICPMS measurements, and to students and colleagues at the University of the Fraser Valley for sample collection. Two anonymous reviewers offered helpful comments that improved the final form of the manuscript.

References

Formatted: Font: Not Bold

Length of Growing Season in British Columbia: http://www.agr.gc.ca/eng/science-and-innovation/agricultural-practices/climate/future-outlook/climate-change-scenarios/length-of-growing-season-in-british-columbia, access: 16 November 2014, 2014.

~~Aiken, G. R., Hsu-Kim, H., and Ryan, J. N.: Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids, Environ. Sci. Technol., 45, 3196-3201, 10.1021/es103992s, 2011.~~

Amos, H. M., Jacob, D. J., Kocman, D., Horowitz, H. M., Zhang, Y., Dutkiewicz, S., Horvat, M., Corbitt, E. S., Krabbenhoft, D. P., and Sunderland, E. M.: Global biogeochemical implications of mercury discharges from rivers and sediment burial, Environ. Sci. Technol., 48, 9514-9522, 10.1021/es502134t, 2014.

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., Aalto, R. E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9, 53-60, 10.1890/100014, 2011.

Babiarz, C., Hoffmann, S., Wieben, A., Hurley, J., Andren, A., Shafer, M., and Armstrong, D.: Watershed and discharge influences on the phase distribution and tributary loading of total mercury and methylmercury into Lake Superior, Environ. Pollut., 161, 299-310, 10.1016/j.envpol.2011.09.026, 2012.

Bagard, M.-L., Chabaux, F., Pokrovsky, O. S., Viers, J., Prokushkin, A. S., Stille, P., Rihs, S., Schmitt, A.-D., and Dupré, B.: Seasonal variability of element fluxes in two Central Siberian rivers draining high latitude permafrost dominated areas, Geochim. Cosmochim. Acta, 75, 3335-3357, 10.1016/j.gca.2011.03.024, 2011.

Battin, T. J.: Dissolved organic matter and its optical properties in a blackwater tributary of the upper Orinoco river, Venezuela, Org. Geochem., 28, 561-569, 1998.

Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik, L. J.: The boundless carbon cycle, Nat. Geosci., 2, 598-600, 10.1038/ngeo618, 2009.

Bianchi, T. S., Garcia-Tigreros, F., Yvon-Lewis, S. A., Shields, M., Mills, H. J., Butman, D., Osburn, C., Raymond, P., Shank, G. C., DiMarco, S. F., Walker, N., Reese, B. K., Mullins-Perry, R., Quigg, A., Aiken, G. R., and Grossman, E. L.: Enhanced transfer of terrestrially derived carbon to the atmosphere in a flooding event, Geophys. Res. Lett., 40, 116-122, 10.1029/2012gl054145, 2013.

Böhlke, J. K., Gwinn, C. J., and Coplen, T. B.: New reference materials for nitrogen-isotope-ratio measurements, Geostand. Newsl., 17, 159-164, 1993.

Brigham, M. E., Wentz, D. A., Aiken, G. R., and Krabbenhoft, D. P.: Mercury cycling in stream ecosystems. 1. Water column chemistry and transport, Environ. Sci. Technol., 43, 2720-2725, 2009.

Burns, D. A., Riva-Murray, K., Bradley, P. M., Aiken, G. R., and Brigham, M. E.: Landscape controls on total and methyl Hg in the upper Hudson River basin, New York, USA, J. Geophys. Res., 117, 10.1029/2011jg001812, 2012.

Burns, D. A., Aiken, G. R., Bradley, P. M., Journey, C. A., and Schelker, J.: Specific ultra-violet absorbance as an indicator of mercury sources in an Adirondack River basin, Biogeochemistry, 113, 451-466, 10.1007/s10533-012-9773-5, ~~2012a~~2013.

~~Burns, D. A., Riva-Murray, K., Bradley, P. M., Aiken, G. R., and Brigham, M. E.: Landscape controls on total and methyl Hg in the upper Hudson River basin, New York, USA, J. Geophys. Res., 117, 10.1029/2011jg001812, 2012b.~~

Cai, W.-J.: Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration?, Annu. Rev. Mar. Sci., 3, 123-145, 10.1146/annurev-marine-120709-142723, 2011.

Cameron, E. M.: Hydrogeochemistry of the Fraser River, British Columbia: seasonal variation in major and minor components, J. Hydrol., 182, 209-225, 1996.

Cohen Commission~~:~~. The Cohen Commission of Inquiry into the Decline of Sockeye Salmon in the Fraser River, Chapter 2: Recommendations, vol. 3, 64~~,~~ pp., 2012.

Cole, J. J., and Caraco, N. F.: Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism, Mar. Freshwat. Res., 52, 101-110, 2001.

Coplen, T. B., Brand, W. A., Gehre, M., Gröning, M., Meijer, H. A. J., Toman, B., and Verkouteren, R. M.: New guidelines for δ^{13}C measurements, Anal. Chem., 78, 2439-2441, 10.1021/ac052027c, 2006.

Del Vecchio, R., and Blough, N. V.: Photobleaching of chromophoric dissolved organic matter in natural waters: kinetics and modeling, Mar. Chem., 78, 231-253, 2002.

Demers, J. D., Driscoll, C. T., and Shanley, J. B.: Mercury mobilization and episodic stream acidification during snowmelt: Role of hydrologic flow paths, source areas, and supply of dissolved organic carbon, Water Resour. Res., 46, W01511, 10.1029/2008WR007021, 2010.

Déry, S. J., Hernández-Henríquez, M. A., Owens, P. N., Parkes, M. W., and Petticrew, E. L.: A century of hydrological variability and trends in the Fraser River Basin, Environ. Res. Lett., 7, 10.1088/1748-9326/7/2/024019, 2012.

Dittman, J. A., Shanley, J. B., Driscoll, C. T., Aiken, G. R., Chalmers, A. T., Towse, J. E., and Selvendiran, P.: Mercury dynamics in relation to dissolved organic carbon concentration and quality during high flow events in three northeastern U.S. streams, Water Resour. Res., 46, W07522, 10.1029/2009wr008351, 2010.

Dornblaser, M. M., and Striegl, R. G.: Nutrient (N, P) loads and yields at multiple scales and subbasin types in the Yukon River basin, Alaska, J. Geophys. Res., 112, G04S57, 10.1029/2006jg000366, 2007.

Dornblaser, M. M., and Striegl, R. G.: Suspended sediment and carbonate transport in the Yukon River Basin, Alaska: Fluxes and potential future responses to climate change, Water Resour. Res., 45, W06411, 10.1029/2008wr007546, 2009.

Downing, B. D., Pellerin, B. A., Bergamaschi, B. A., Saraceno, J. F., and Kraus, T. E. C.: Seeing the light: The effects of particles, dissolved materials, and temperature on in situ measurements of DOM fluorescence in rivers and streams, Limnol. Oceanogr. Methods, 10, 767-775, 10.4319/lom.2012.10.767, 2012.

Easthouse, K. B., Mulder, J., Christophersen, N., and Siep, H. M.: Dissolved organic carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, southern Norway, Water Resour. Res., 28, 1585-1596, 1992.

Fellman, J. B., Hood, E., Edwards, R. T., and D'Amore, D. V.: Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds, J. Geophys. Res., 114, G01021, 10.1029/2008jg000790, 2009.

Fellman, J. B., Spencer, R. G. M., Hernes, P. J., Edwards, R. T., D'Amore, D. V., and Hood, E.: The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems, Mar. Chem., 121, 112-122, 10.1016/j.marchem.2010.03.009, 2010.

Fleck, J. A., Gill, G., Bergamaschi, B. A., Kraus, T. E. C., Downing, B. D., and Alpers, C. N.: Concurrent photolytic degradation of aqueous methylmercury and dissolved organic matter, Sci. Total Environ., 484, 263-275, 10.1016/j.scitotenv.2013.03.107, 2014.

Froehlich, K., Kralik, M., Papesch, W., Rank, D., Scheifinger, H., and Stichler, W.: Deuterium excess in precipitation of Alpine regions – moisture recycling, Isot. Environ. Health Stud., 44, 61-70, 10.1080/10256010801887208, 2008.

Gallagher, L., Macdonald, R. W., and Paton, D. W.: The historical record of metals in sediments from six lakes in the Fraser River Basin, British Columbia, Water, Air, Soil Pollut., 152, 257-278, 2003.

Galy, V., Peucker-Ehrenbrink, B., and Eglinton, T.: Global carbon export from the terrestrial biosphere controlled by erosion, Nature, ~~in press~~521, 204-207, 10.1038/nature14400, 2015.

Gangloff, S., Stille, P., Pierret, M.-C., Weber, T., and Chabaux, F.: Characterization and evolution of dissolved organic matter in acidic forest soil and its impact on the mobility of major and trace elements (case of the Strengbach watershed), Geochim. Cosmochim. Acta, 130, 21-41, 10.1016/j.gca.2013.12.033, 2014.

Gerbig, C. A., Ryan, J. N., and Aiken, G. R.: The effects of dissolved organic matter on mercury biogeochemistry, in: Environmental Chemistry and Toxicology of Mercury, edited by: Liu, G., Cai, Y., and O'Driscoll, N., John Wiley & Sons, Inc., Hoboken, NJ, 259-292, 2011.

Graydon, J. A., St. Louis, V. L., Hintelmann, H., Lindberg, S. E., Sandilands, K. A., Rudd, J. W. M., Kelly, C. A., Hall, B. D., and Mowat, L. D.: Long-term wet and dry deposition of total and methyl mercury in the remote boreal ecoregion of Canada, Environ. Sci. Technol., 42, 8345-8351, 10.1021/es801056j, 2008.

Haitzer, M., Aiken, G. R., and Ryan, J. N.: Binding of mercury(II) to dissolved organic matter: The role of the mercury-to-DOM concentration ratio, Environ. Sci. Technol., 36, 3564-3570, 10.1021/es025699i, 2002.

Haitzer, M., Aiken, G. R., and Ryan, J. N.: Binding of mercury(II) to aquatic humic substances: Influence of pH and source of humic substances, Environ. Sci. Technol., 37, 2436-2441, 10.1021/es026291o, 2003.

Hales, W. J.: Impact of human activity on deltaic sedimentation, marshes of the Fraser River delta, British Columbia, PhD Thesis, Geography, University of British Columbia, Vancouver, BC, 187 pp., 2000.

Hammerschmidt, C. R., Bowman, K. L., Tabatchnick, M. D., and Lamborg, C. H.: Storage bottle material and cleaning for determination of total mercury in seawater, Limnol. Oceanogr. Methods, 9, 426-431, 10.4319/lom.2011.9.426, 2011.

Holmes, R. M., McClelland, J. W., Raymond, P. A., Frazer, B. B., Peterson, B. J., and Stieglitz, M.: Lability of DOC transported by Alaskan rivers to the Arctic Ocean, Geophys. Res. Lett., 35, L03402, 10.1029/2007gl032837, 2008.

Holmes, R. M., McClelland, J. W., Peterson, B. J., Tank, S. E., Bulygina, E., Eglinton, T. I., Gordeev, V. V., Gurtovaya, T. Y., Raymond, P. A., Repeta, D. J., Staples, R., Striegl, R. G., Zhulidov, A. V., and Zimov, S. A.: Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas, Estuaries Coasts, 35, 369-382, 10.1007/s12237-011-9386-6, 2012.

Hope, D., Billett, M. F., and Cresser, M. S.: A review of the export of carbon in river water: Fluxes and processes, Environ. Pollut., 84, 301-324, 1994.

Hurley, J. P., Cowell, S. E., Shafer, M. M., and Hughes, P. E.: Partitioning and transport of total and methyl mercury in the lower Fox River, Wisconsin, Environ. Sci. Technol., 32, 1424-1432, 1998.

IAEA: Reference and intercomparison materials for stable isotopes of light elements, IAEA-TECDOC-825, Vienna, 1995, 159 pp.,

Jaffé, R., Ding, Y., Niggemann, J., Vähätalo, A. V., Stubbins, A., Spencer, R. G. M., Campbell, J., and Dittmar, T.: Global charcoal mobilization from soils via dissolution and riverine transport to the oceans, Science, 340, 345-347, 10.1126/science.1231476, 2013.

Johannessen, S. C., MacDonald, R. W., and Eek, K. M.: Historical trends in mercury sedimentation and mixing in the strait of Georgia, Canada, Environ. Sci. Technol., 39, 4361-4368, 10.1021/es040535i, 2005.

Keil, R., Salemme, K., Forrest, B., Neibauer, J., and Logsdon, M.: Differential presence of anthropogenic compounds dissolved in the marine waters of Puget Sound, WA and Barkley Sound, BC, Mar. Pollut. Bull., 62, 2404-2411, 10.1016/j.marpolbul.2011.08.029, 2011.

Kelly, B. C., Ikonomou, M. G., Higgs, D. A., Oakes, J., and Dubetz, C.: Mercury and other trace elements in farmed and wild salmon from British Columbia, Canada, Environ. Toxicol. Chem., 27, 1361-1370, 10.1897/07-527~~.s1~~, 2008.

Laraque, A., Castellanos, B., Steiger, J., Lòpez, J. L., Pandi, A., Rodriguez, M., Rosales, J., Adèle, G., Perez, J., and Lagane, C.: A comparison of the suspended and dissolved matter dynamics of two large inter-tropical rivers draining into the Atlantic Ocean: the Congo and the Orinoco, Hydrol. Processes, 27, 2153-2170, 10.1002/hyp.9776, 2013.

Liu, J., Chen, J. M., Cihlar, J., and Chen, W.: Net primary productivity mapped for Canada at 1-km resolution, Global Ecol. Biogeogr., 11, 115-129, 10.1046/j.1466-822X.2002.00278.x, 2002.

Lloret, E., Dessert, C., Pastor, L., Lajeunesse, E., Crispi, O., Gaillardet, J., and Benedetti, M. F.: Dynamic of particulate and dissolved organic carbon in small volcanic mountainous tropical watersheds, Chem. Geol., 351, 229-244, 10.1016/j.chemgeo.2013.05.023, 2013.

Ludwig, W., Probst, J.-L., and Kempe, S.: Predicting the oceanic input of organic carbon by continental erosion, Global Biogeochem. Cycles, 10, 23-41, 1996.

MacDonald, D., Sinclair, J., Crawford, M., Prencipe, H., and Meneghetti, M~~.:~~. The Cohen Commission of Inquiry into the Decline of Sockeye Salmon in the Fraser River, Technical

Report 2: Potential effects of contaminants on Fraser River sockeye salmon, Nanaimo, BC, 603~~,~~ pp., 2011.

Mann, P. J., Davydova, A., Zimov, N., Spencer, R. G. M., Davydov, S., Bulygina, E., Zimov, S., and Holmes, R. M.: Controls on the composition and lability of dissolved organic matter in Siberia's Kolyma River basin, J. Geophys. Res., 117, G01028, 10.1029/2011jg001798, 2012.

~~Mayer, L. M.: Relationships between mineral surfaces and organic carbon concentrations in soils and sediments, Chem. Geol., 114, 347-363, 1994.~~

Michalzik, B., Kalbitz, K., Park, J.-H., Solinger, S., and Matzner, E.: Fluxes and concentrations of dissolved organic carbon and nitrogen: A synthesis for temperate forests, Biogeochemistry, 52, 173-205, 2001.

Michalzik, B., Tipping, E., Mulder, J., Lancho, J. F. G., Matzner, E., Bryant, C. L., Clarke, N., Lofts, S., and Esteban, M. A. V.: Modelling the production and transport of dissolved organic carbon in forest soils, Biogeochemistry, 66, 241-264, 2003.

Mills, R. T. E., Tipping, E., Bryant, C. L., and Emmett, B. A.: Long-term organic carbon turnover rates in natural and semi-natural topsoils, Biogeochemistry, 118, 257-272, 10.1007/s10533-013-9928-z, 2014.

Morrison, J., Quick, M. C., and Foreman, M. G. G.: Climate change in the Fraser River watershed: flow and temperature projections, J. Hydrol., 263, 230-244, 2002.

Naik, A. P., and Hammerschmidt, C. R.: Mercury and trace metal partitioning and fluxes in suburban Southwest Ohio watersheds, Water Res., 45, 5151-5160, 10.1016/j.watres.2011.07.023, 2011.

Nelson, A. D., and Church, M.: Placer mining along the Fraser River, British Columbia: The geomorphic impact, Geol. Soc. Am. Bull., 124, 1212-1228, 10.1130/b30575.1, 2012.

O'Donnell, J. A., Aiken, G. R., Kane, E. S., and Jones, J. B.: Source water controls on the character and origin of dissolved organic matter in streams of the Yukon River basin, Alaska, J. Geophys. Res., 115, G03025, 10.1029/2009jg001153, 2010.

Oswald, C. J., and Branfireun, B. A.: Antecedent moisture conditions control mercury and dissolved organic carbon concentration dynamics in a boreal headwater catchment, Water Resour. Res., 50, 6610-6627, 10.1002/2013WR014736, 2014.

Patterson, C. C., and Settle, D. M.: The reduction of orders of magnitude errors in lead analyses of biological material and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collection, handling and analysis, in:

Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis, edited by: LaFleur, P. D., U.S. National Bureau of Standards Special Publication 422, Washington, D.C., 321-351, 1976.

Pereira, R., Isabella Bovolo, C., Spencer, R. G. M., Hernes, P. J., Tipping, E., Vieth-Hillebrand, A., Pedentchouk, N., Chappell, N. A., Parkin, G., and Wagner, T.: Mobilization of optically invisible dissolved organic matter in response to rainstorm events in a tropical forest headwater river, Geophys. Res. Lett., 41, 1202-1208, 10.1002/2013gl058658, 2014.

Peucker-Ehrenbrink, B.: Land2Sea database of river drainage basin sizes, annual water discharges, and suspended sediment fluxes, Geochem. Geophys. Geosyst., 10, Q06014, 10.1029/2008gc002356, 2009.

Peuravuori, J., and Pihlaja, K.: Molecular size distribution and spectroscopic properties of aquatic humic substances, Anal. Chim. Acta, 337, 133-149, 1997.

Qi, H., Coplen, T. B., Geilmann, H., Brand, W. A., and Böhlke, J. K.: Two new organic reference materials for $\delta^{13}C$ and $\delta^{15}N$ measurements and a new value for the $\delta^{13}C$ of NBS 22 oil, Rapid Commun. Mass Spectrom., 17, 2483-2487, 10.1002/rcm.1219, 2003.

Raymond, P. A., McClelland, J. W., Holmes, R. M., Zhulidov, A. V., Mull, K., Peterson, B. J., Striegl, R. G., Aiken, G. R., and Gurtovaya, T. Y.: Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers, Global Biogeochem. Cycles, 21, GB4011, 10.1029/2007gb002934, 2007.

Raymond, P. A., and Saiers, J. E.: Event controlled DOC export from forested watersheds, Biogeochemistry, 100, 197-209, 10.1007/s10533-010-9416-7, 2010.

Riche, O., Johannessen, S. C., and Macdonald, R. W.: Why timing matters in a coastal sea: Trends, variability and tipping points in the Strait of Georgia, Canada, J. Mar. Syst., 131, 36-53, 10.1016/j.jmarsys.2013.11.003, 2014.

Riscassi, A. L., and Scanlon, T. M.: Controls on stream water dissolved mercury in three mid-Appalachian forested headwater catchments, Water Resour. Res., 47, W12512, 10.1029/2011WR010977, 2011.

Rochelle-Newall, E. J., and Fisher, T. R.: Production of chromophoric dissolved organic matter fluorescence in marine and estuarine environments: an investigation into the role of phytoplankton, Mar. Chem., 77, 7-21, 2002.

Sandford, R. C., Hawkins, J. M. B., Bol, R., and Worsfold, P. J.: Export of dissolved organic carbon and nitrate from grassland in winter using high temporal resolution, in situ UV sensing, Sci. Total Environ., 456-457, 384-391, 10.1016/j.scitotenv.2013.02.078, 2013.

Saraceno, J. F., Pellerin, B. A., Downing, B. D., Boss, E., Bachand, P. A. M., and Bergamaschi, B. A.: High-frequency in situ optical measurements during a storm event: Assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes, J. Geophys. Res., 114, G00F09, 10.1029/2009jg000989, 2009.

Schuster, P. F., Shanley, J. B., Marvin-Dipasquale, M., Reddy, M. M., Aiken, G. R., Roth, D. A., Taylor, H. E., Krabbenhoft, D. P., and DeWild, J. F.: Mercury and organic carbon dynamics during runoff episodes from a Northeastern USA watershed, Water, Air, Soil Pollut., 187, 89-108, 10.1007/s11270-007-9500-3, 2008.

Schuster, P. F., Striegl, R. G., Aiken, G. R., Krabbenhoft, D. P., Dewild, J. F., Butler, K., Kamark, B., and Dornblaser, M.: Mercury export from the Yukon River Basin and potential response to a changing climate, Environ. Sci. Technol., 45, 9262-9267, 10.1021/es202068b, 2011.

Shanley, J. B., Schuster, P. F., Reddy, M. M., Roth, D. A., Taylor, H. E., and Aiken, G. R.: Mercury on the move during snowmelt in Vermont, Eos, 83, 45-48, 10.1029/2002EO000031, 2002.

Shanley, J. B., Alisa Mast, M., Campbell, D. H., Aiken, G. R., Krabbenhoft, D. P., Hunt, R. J., Walker, J. F., Schuster, P. F., Chalmers, A., Aulenbach, B. T., Peters, N. E., Marvin-DiPasquale, M., Clow, D. W., and Shafer, M. M.: Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach, Environ. Pollut., 154, 143-154, 10.1016/j.envpol.2007.12.031, 2008.

Shrestha, R. R., Schnorbus, M. A., Werner, A. T., and Berland, A. J.: Modelling spatial and temporal variability of hydrologic impacts of climate change in the Fraser River basin, British Columbia, Canada, Hydrol. Processes, 26, 1840-1860, 10.1002/hyp.9283, 2012.

Spencer, R. G. M., Hernes, P. J., Ruf, R., Baker, A., Dyda, R. Y., Stubbins, A., and Six, J.: Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo, J. Geophys. Res., 115, G03013, 10.1029/2009jg001180, 2010.

Spencer, R. G. M., Butler, K. D., and Aiken, G. R.: Dissolved organic carbon and chromophoric dissolved organic matter properties of rivers in the USA, J. Geophys. Res., 117, G03001, 10.1029/2011jg001928, 2012.

Spencer, R. G. M., Aiken, G. R., Dornblaser, M. M., Butler, K. D., Holmes, R. M., Fiske, G., Mann, P. J., and Stubbins, A.: Chromophoric dissolved organic matter export from U.S. rivers, Geophys. Res. Lett., 40, 1575-1579, 10.1002/grl.50357, 2013.

Stedmon, C. A., and Markager, S.: Behaviour of the optical properties of coloured dissolved organic matter under conservative mixing, Estuar. Coast. Shelf Sci., 57, 973-979, 10.1016/s0272-7714(03)00003-9, 2003.

Stepanauskas, R., Moran, M. A., Bergamaschi, B. A., and Hollibaugh, J. T.: Sources, bioavailability, and photoreactivity of dissolved organic carbon in the Sacramento–San Joaquin River Delta, Biogeochemistry, 74, 131-149, 10.1007/s10533-004-3361-2, 2005.

Striegl, R. G., Aiken, G. R., Dornblaser, M. M., Raymond, P. A., and Wickland, K. P.: A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn, Geophys. Res. Lett., 32, L21413, 10.1029/2005gl024413, 2005.

Sun, L., Perdue, E. M., Meyer, J. L., and Weis, J.: Use of elemental composition to predict bioavailability of dissolved organic matter in a Georgia river, Limnol. Oceanogr., 42, 714-721, 1997.

Swain, E. B., Engstrom, D. R., Brigham, M. E., Henning, T. A., and Brezonik, P. L.: Increasing rates of atmospheric mercury deposition in midcontinental North America, Science, 257, 784-787, 10.1126/science.257.5071.784, 1992.

Swain, L. G~~.:~~., Water quality assessment of the Fraser River at Hope (1979 – 2004), B.C. Ministry of Environment and Environment Canada, 74~~,~~ pp., 2004.

Townsend-Small, A., McClelland, J. W., Max Holmes, R., and Peterson, B. J.: Seasonal and hydrologic drivers of dissolved organic matter and nutrients in the upper Kuparuk River, Alaskan Arctic, Biogeochemistry, 103, 109-124, 10.1007/s10533-010-9451-4, 2011.

U.S. EPA~~:~~. Method 1631, Revision E: Mercury in water by oxidation, purge, and trap, and cold vapor atomic fluorescence spectrometry, U.S. EPA Office of Science and Technology, Washington, D.C., 38~~,~~ pp., 2002.

U.S. EPA~~:~~. Method 7473, Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry, Revision 0, U.S. EPA Office of Science and Technology, Washington, D.C., 17~~,~~ pp., 2007.

Vold, T~~.:~~., Soils in the Cariboo River Valley, B.C., with selected engineering interpretations, B.C. Ministry of Environment, Victoria, B.C., 23~~,~~ pp., 1979.

Voss, B. M.: Spatial and temporal dynamics of biogeochemical processes in the Fraser River, Canada: A coupled organic-inorganic perspective, PhD Thesis, Marine Chemistry & Geochemistry, MIT/WHOI, Woods Hole, USA, 276 pp., 2014.

Voss, B. M., Peucker-Ehrenbrink, B., Eglinton, T. I., Fiske, G., Wang, Z. A., Hoering, K. A., Montluçon, D. B., LeCroy, C., Pal, S., Marsh, S., Gillies, S. L., Janmaat, A., Bennett, M., Downey, B., Fanslau, J., Fraser, H., Macklam-Harron, G., Martinec, M., and Wiebe, B.: Tracing river chemistry in space and time: Dissolved inorganic constituents of the Fraser River, Canada, Geochim. Cosmochim. Acta, 124, 283-308, 10.1016/j.gca.2013.09.006, 2014.

Walling, D. E., and Foster, I. D. L.: Variations in the natural chemical concentration of river water during flood flows, and the lag effect: Some further comments, J. Hydrol., 26, 237-244, 1975.

Ward, N. D., Richey, J. E., and Keil, R. G.: Temporal variation in river nutrient and dissolved lignin phenol concentrations and the impact of storm events on nutrient loading to Hood Canal, Washington, USA, Biogeochemistry, 111, 629-645, 10.1007/s10533-012-9700-9, 2012.

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and Mopper, K.: Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, Environ. Sci. Technol., 37, 4702-4708, 10.1021/es030360x, 2003.

Whitfield, P. H., and Schreier, H.: Hysteresis in relationships between discharge and water chemistry in the Fraser River basin, British Columbia, Limnol. Oceanogr., 26, 1179-1182, 1981.

Wickland, K. P., Neff, J. C., and Aiken, G. R.: Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability, Ecosystems, 10, 1323-1340, 10.1007/s10021-007-9101-4, 2007.

Wickland, K. P., Aiken, G. R., Butler, K., Dornblaser, M. M., Spencer, R. G. M., and Striegl, R. G.: Biodegradability of dissolved organic carbon in the Yukon River and its tributaries: Seasonality and importance of inorganic nitrogen, Global Biogeochem. Cycles, 26, GB0E03, 10.1029/2012gb004342, 2012.

Writer, J. H., Leenheer, J. A., Barber, L. B., Amy, G. L., and Chapra, S. C.: Sewage contamination in the upper Mississippi River as measured by the fecal sterol, coprostanol, Water Res., 29, 1427-1436, 1995.

Yang, L., and Hur, J.: Critical evaluation of spectroscopic indices for organic matter source tracing via end member mixing analysis based on two contrasting sources, Water Res., 59, 80-89, 10.1016/j.watres.2014.04.018, 2014.

Zhao, Y., Krzic, M., Bulmer, C. E., and Schmidt, M. G.: Maximum bulk density of British Columbia forest soils from the Proctor Test: Relationships with selected physical and chemical properties, Soil Sci. Soc. Am. J., 72, 442, 10.2136/sssaj2007.0075, 2008.

Zheng, W., Liang, L., and Gu, B.: Mercury reduction and oxidation by reduced natural organic matter in anoxic environments, Environ. Sci. Technol., 46, 292-299, 10.1021/es203402p, 2012.

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 (NO_2+NO_3, PO_4, NH_4, SiO_2) and major element (Ca, Mg, Na, K, Cl, SO_4) concentrations are in µmol L^{-1}.~~ TDHg = total dissolved mercury; THg = total mercury (unfiltered water). For sediment %OC, δ^{13}C, and δ^{15}N data, if calculated uncertainties (1 s.d. of the mean of triplicate analyses) were less than instrumental uncertainty (0.1 for %OC, 0.3‰ for δ^{13}C, and 0.4‰ for δ^{15}N), instrumental uncertainties are shown.

Date	Parent IGSN	Q_w at Hope	T	DO	Cond.	pH	Turb.	SPM conc.	δD	$\delta^{18}O$	DOC	POC	*in situ* FDOM	*ex situ* FDOM	NO_2+ NO_3	PO_4	NH_4	SiO_4	Ca	Mg	Na	K	Cl	SO_4	SPM %OC	SPM C/N	SPM $\delta^{13}C$	SPM $\delta^{15}N$	TDHg	THg	SPM THg
		($m^3 s^{-1}$)	(°C)	(mg L^{-1})	(μS cm^{-1})		(NTU)	(mg L^{-1})	(‰)	(‰)	(μmol L^{-1})	(μmol L^{-1})	(RFUB)	(RFUB)	←				(μmol L^{-1})					→			(‰)	(‰)	(pmol L^{-1})	(pmol L^{-1})	(pmol mg^{-1})
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	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	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	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	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	19.40	0.32	1.85	107	421	165	211	26.8	75.5	103							
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	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	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	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	GRO000924	1085	7.8	12.3	132.5	7.79			-123.1	-16.38	198		570	593	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			
01.Apr.13	GRO000925	1182	8.4	11.6	130.8	7.80			-122.7	-16.20	205		567	539	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			
02.Apr.13	GRO000926	1294	8.4	12.3	122.2	7.67			-120.7	-16.02	189		555	546	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			
03.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	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
04.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	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			
05.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	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			
06.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	7.44	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			
07.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	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
08.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	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			
09.Apr.13	GRO000931	2158	6.8	12.7	118.1	7.70	38.0±1.3	60.8±2.1	-121.6	-16.07	343	58.8±2.2	951	1267	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	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	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	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	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	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	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	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	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	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	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	GRO000936	2479	6.0	13.0	127.4	7.90	81±4	133±6	-128.0	-16.77	458	89±4	929	1710	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	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	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	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	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	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	10.19	0.36	1.21	111	426	176	168	28.8	65.7	78							
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				7.77	0.35	0.87	110	426	175	167	28.2	49.1	77							
17.Apr.13 17:45	GRO000940	2355	7.0	13.1	126.3	7.77			-130.3	-16.90	505				8.24	0.33	0.88	108	422	172	163	28.5	47.3	75							
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			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	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			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	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			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	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			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	GRO000945	3078	6.9	12.7	122.5	7.82	25.9±0.4	40.7±0.6	-128.3	-16.74	477				10.05	0.25	0.79	105	409	164	154	25.9	43.6	72							

Formatted: Left, Indent: Left: 0.16"

Formatted: Indent: Left: 0.09", Right: -0.13", Space After: 10 pt, Don't add space between paragraphs of the same style

Formatted: Centered, Right: -0.2"

Formatted: Centered, Right: -0.14"

Formatted Table

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 at 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 (μmol L^{-1})	a_{254} (m^{-1})	SUVA$_{254}$ (L mgC^{-1} m^{-1})	a_{250}:a_{365}	S_R
21.Apr.2011	GRO000128	532				
03.May.2011	GRO000129	733				
10.May.2011	GRO000130	830				
13.May.2011	GRO000131	671				
25.May.2011	GRO000133	601				
03.Jun.2011	GRO000135	457				
07.Jun.2011	GRO000076	386				
28.Jun.2011	GRO000140	265	19.37	2.64	6.45	0.98
08.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
05.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
07.Sep.2012	GRO000172		14.48		6.46	1.17
21.Sep.2012	GRO000221		14.97		6.64	1.11
05.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
02.Feb.2013	GRO000174	266	21.02	2.85	5.82	0.92
09.Feb.2013	GRO000175	248	22.55	3.28	5.46	0.89
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
01.Apr.2013	GRO000925	205	17.70	3.13	5.98	0.98
02.Apr.2013	GRO000926	189	20.60	3.94	5.34	1.07
03.Apr.2013	GRO000179	199	19.92	3.62	5.58	1.04
04.Apr.2013	GRO000927	205	25.96	4.58	5.49	1.11
05.Apr.2013	GRO000928	217	21.23	3.54	5.51	0.99
06.Apr.2013	GRO000929	234	25.40	3.93	5.38	1.02
07.Apr.2013	GRO000180	266	32.65	4.44	5.30	1.06
08.Apr.2013	GRO000930	286	29.12	3.68	5.48	0.89
09.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
07.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

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. Sampling for both Environment Canada and this study was performed at approximately twice monthly frequency, with the exception of our 2013 freshet sampling, for which sampling was daily.

	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 (mol C km^{-2} a^{-1})	1.2×10^{5}	1.2×10^{5}
Discharge-weighted average DOC concentration (µmol L^{-1})	277 ± 14	270 ± 71

Formatted: Indent: Left: 0", Add space between paragraphs of the same style, Position: Vertical: 2.93", Relative to: Page

Formatted Table

Formatted: Position: Vertical: 2.93", Relative to: Page

Formatted: Position: Vertical: 2.93", Relative to: Page

Formatted: Position: Vertical: 2.93", Relative to: Page

Table 4. Estimates of soil DOC sources calculated using LoadEst (Runkel et al., 2004). Uncertainties represent 1 s.d. of the average for the three years of the record (2011 – 2013). Shallow and deep soil DOC fractions indicate the fraction of the total DOC load estimated to derive from shallow and deep soil DOC pools, respectively. Calculations were made based on shallow and deep soil DOM end-members defined by observed maximum and minimum S_R and a_{250}/a_{365} values.

	S_R	a_{250}/a_{365}
shallow soil end-member	0.81	4.94
deep soil end-member	1.17	8.12
shallow soil DOC fraction	0.611 ± 0.018	0.638 ± 0.014
deep soil DOC fraction	0.459 ± 0.036	0.364 ± 0.015

Field Code Changed

Formatted: Position: Vertical: 3.19", Relative to: Page

Formatted Table

Formatted: Position: Vertical: 3.19", Relative to: Page

Formatted: Position: Vertical: 3.19", Relative to: Page

Formatted: Position: Vertical: 3.19", Relative to: Page

Formatted: Position: Vertical: 3.19", Relative to: Page

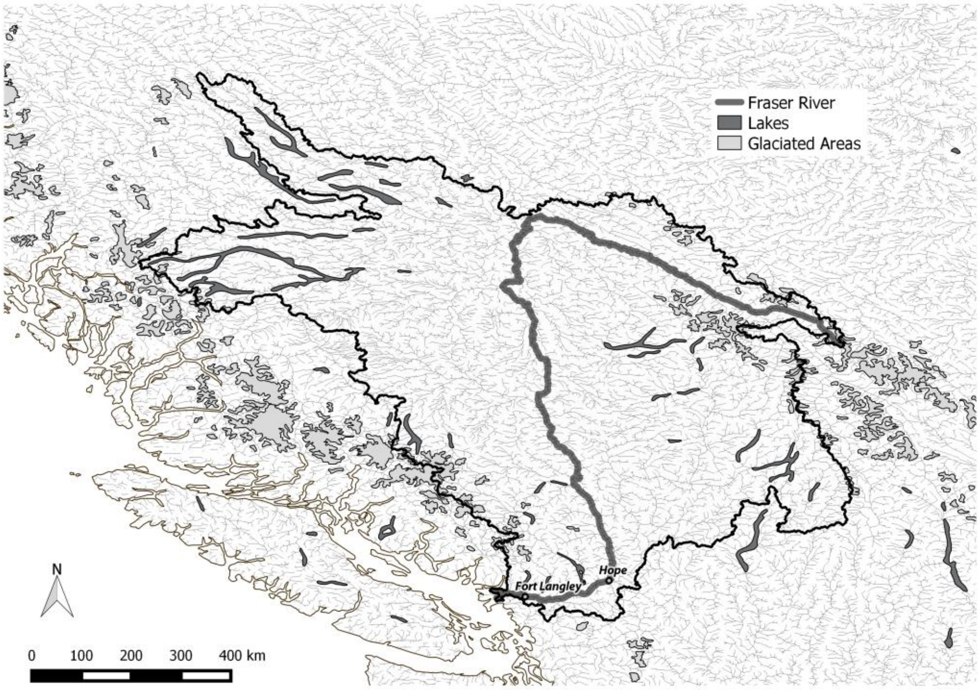

Figure 1. The Fraser River basin, highlighting lakes (natural and man-made; dark grey) and glaciated areas (light grey). Samples were collected at Fort Langley and discharge data (from Environment Canada) are from Hope. River contours and watershed boundaries provided by HydroSHEDS; lake and glacier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

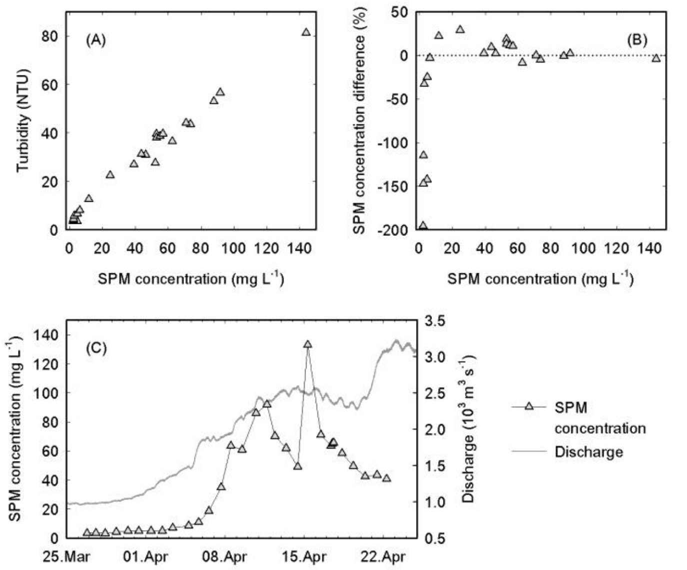

Figure 2. (A) Measured suspended particulate matter (SPM) concentration determined from the mass of sediment recovered from filtered water correlated strongly with turbidity measured with a nephelometer. (B) SPM concentration difference was calculated as the difference between the SPM concentration determined from the mass of sediment recovered from filtered water and that estimated from the linear correlation in panel A. (C) Suspended sediment concentrations increased rapidly during the early freshet period.

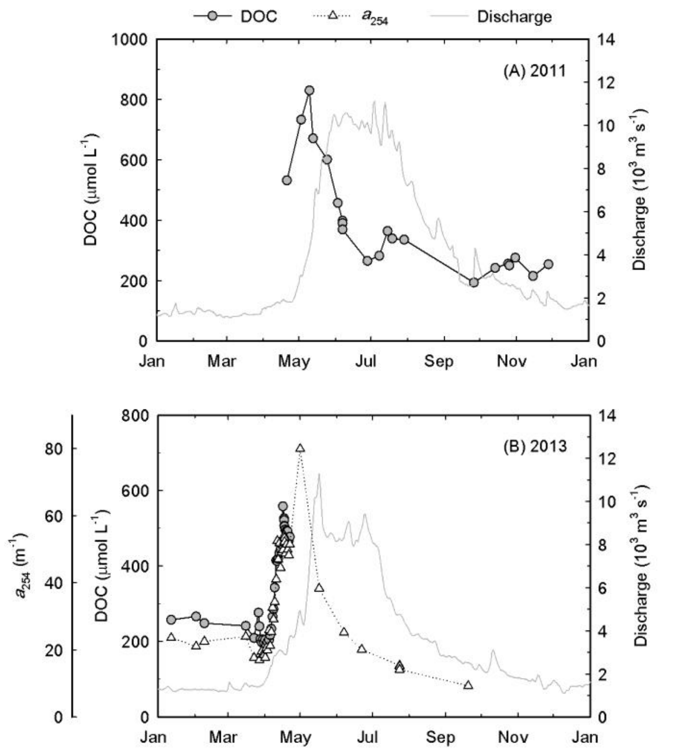

Figure 3. Concentrations of dissolved organic carbon (DOC) peak during the early stages of the spring freshet and decrease over the course of the summer.

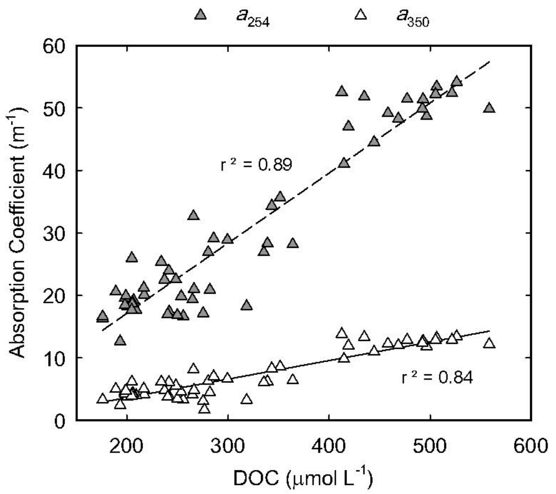

Figure 4. DOC concentration is strongly correlated with absorption coefficients (shown here at 254 and 350 nm).

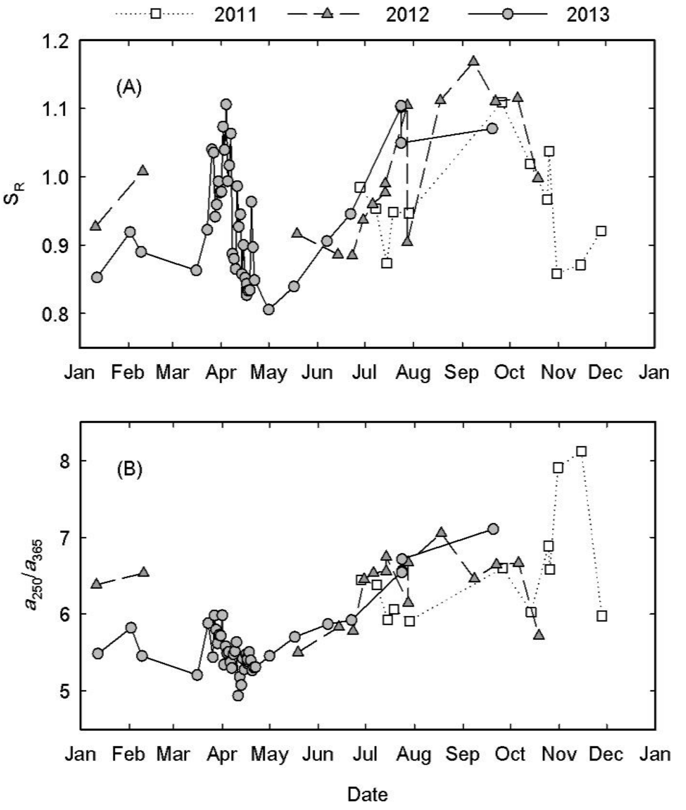

Figure 5. (A) Spectral slope ratio (S_R) and (B) absorbance ratio (a_{250}/a_{365}) show rapid changes in DOM composition during the early freshet DOC pulse. A more gradual return to pre-freshet composition follows throughout the summer. A second cycle occurs in late winter.

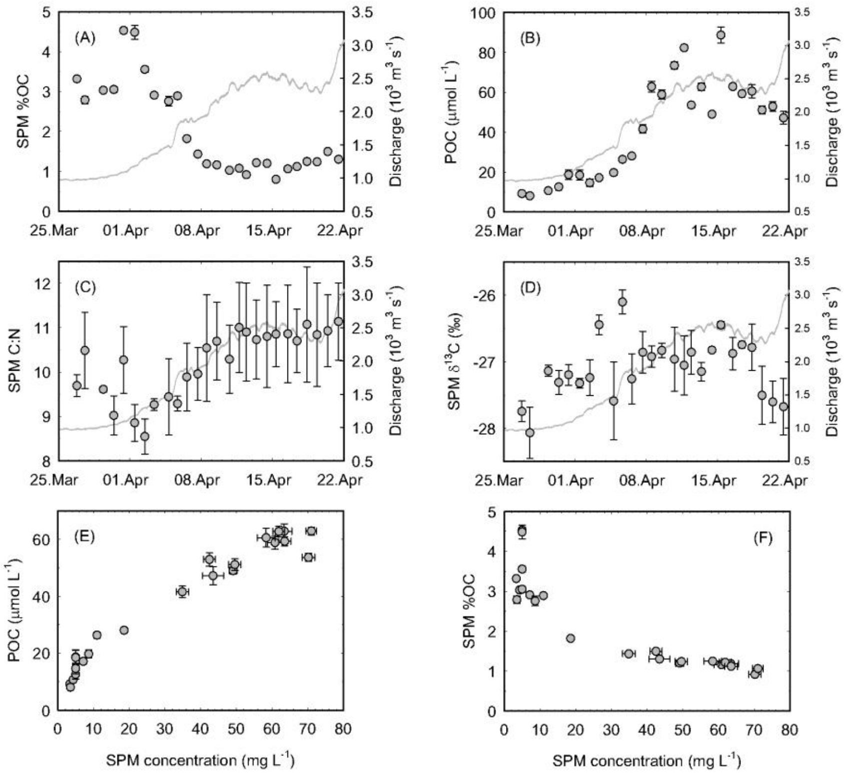

Figure 6. The abundance and composition of POC shifted during the early freshet period towards (A) relatively lower %OC, (B) higher POC concentration, and (C) higher C:N. (D) No distinct temporal trend is evident in δ^{13}C. (E) POC concentration and (F) SPM OC content are tightly coupled with SPM concentration. Error bars represent 1 s.d. of triplicate measurements. Discharge is shown as gray lines in (A)-(D).

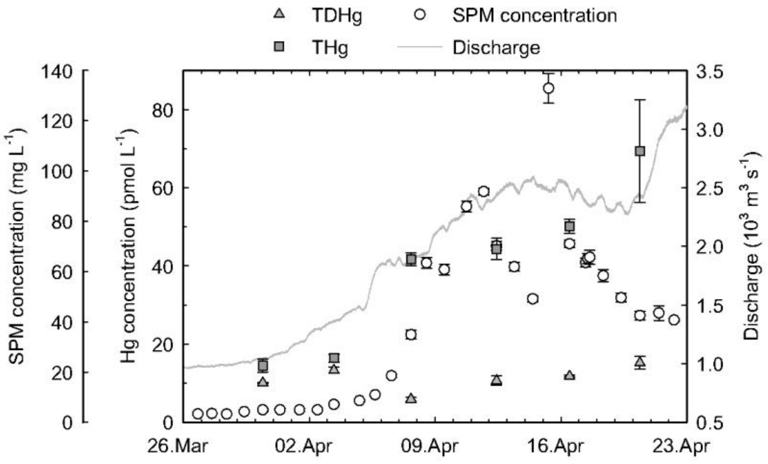

Figure 7. Total mercury concentrations in filtered (TDHg) and unfiltered (THg) water samples during the 2013 early freshet period. Error bars represent 1 s.d. of repeated measurements.

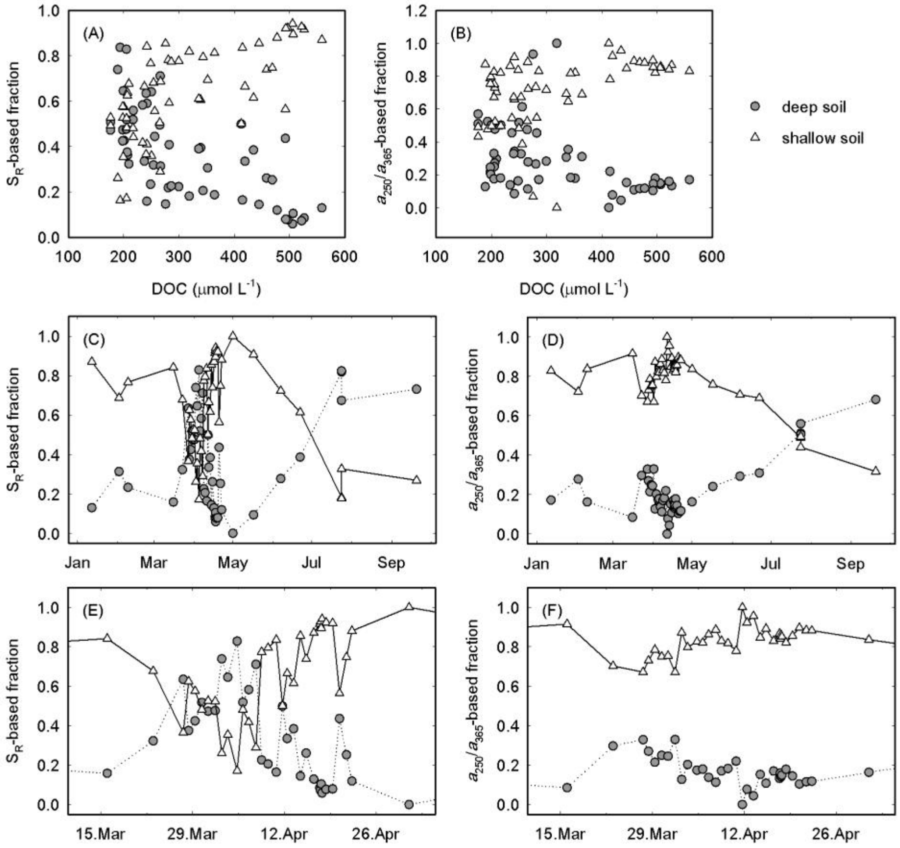

Figure 8. The contributions of deep and shallow soil DOC to total Fraser DOC were estimated based on the observed maximum and minimum values of DOC optical properties (spectral slope ratio, S_R, and absorbance ratio, a_{250}/a_{365}). These fractions are related to the DOC concentration (A and B), and change throughout the year (C and D, shown here for 2013; E and F detail the 2013 early freshet period).

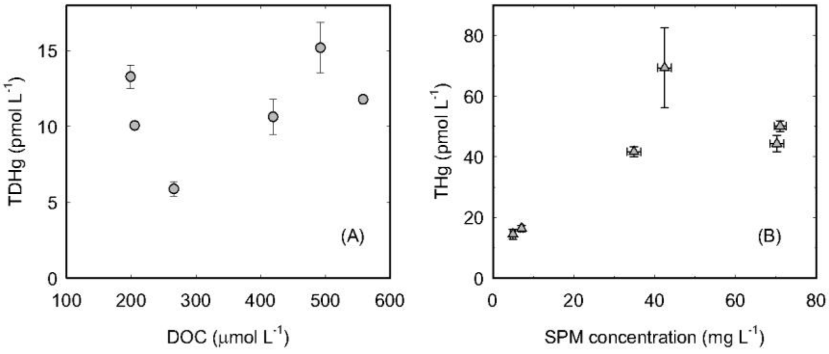

Figure 9. (A) Total dissolved mercury and DOC concentration across the early freshet in 2013 were weakly correlated ($r^2 = 0.15$). (B) Total Hg concentration (unfiltered) is positively correlated with SPM concentration ($r^2 = 0.51$).

Supplemental Material

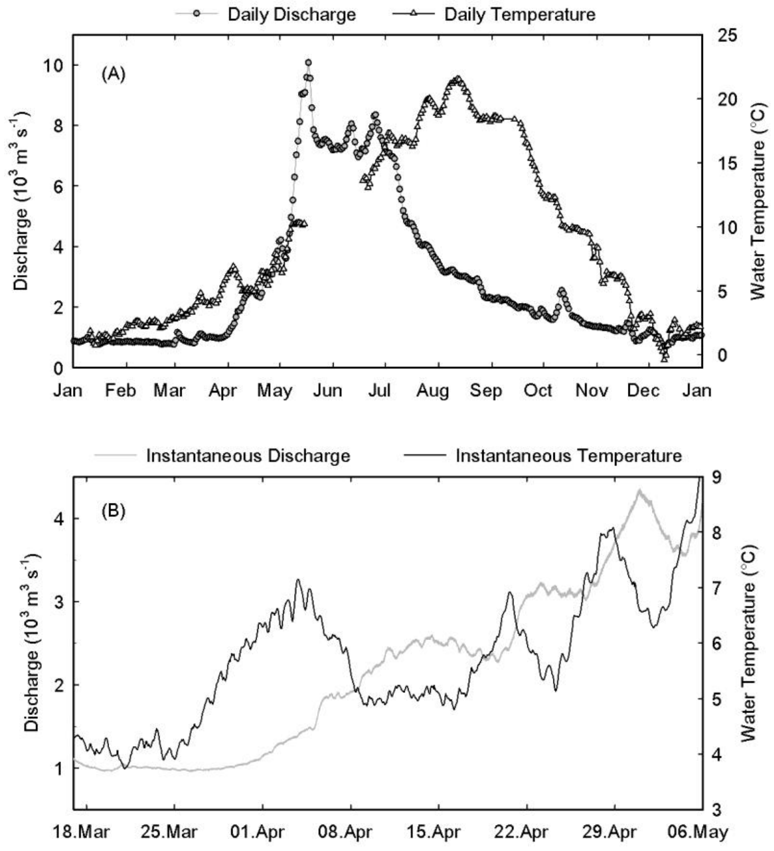

Figure S1. Water discharge and temperature during the study year 2013 from Environment Canada real-time records of the Fraser River at Hope. “Instantaneous” discharge is derived from gauge height measurements at 5-minute frequency; “instantaneous” water temperature measurements are hourly. (A) Full year, showing the relationship between seasonal warming and water discharge; (B) Inset of the early freshet period, when daily fluctuations in air temperature are transmitted to the observed water temperature, and create daily pulses of snowmelt, seen in diurnal peaks in discharge ~~pulses~~.

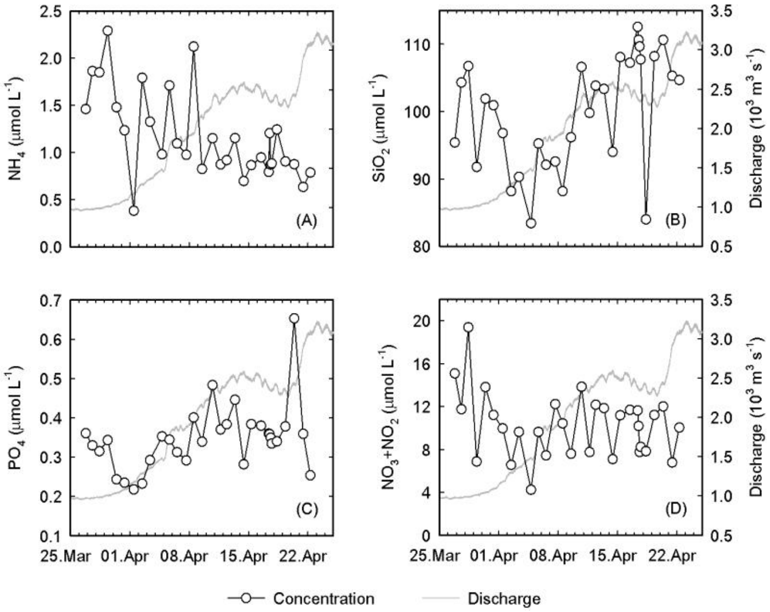

Figure S2. Early freshet 2013 trends in dissolved nutrient concentrations.

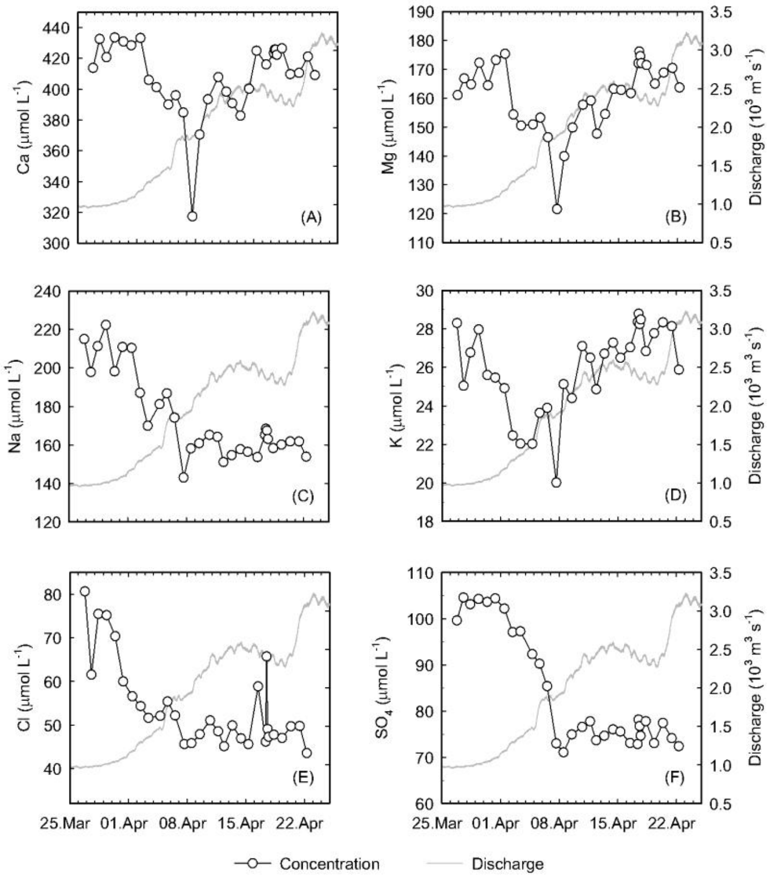

Figure S3. Early freshet 2013 trends in dissolved major element concentrations.

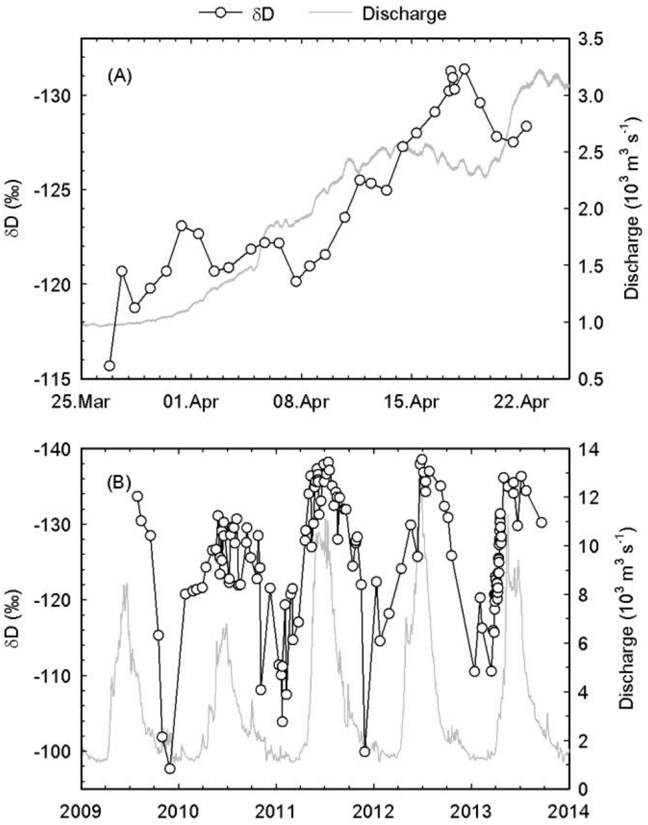

Figure S4. (A) During the early freshet period of 2013, the stable isotope composition of Fraser River water becomes lighter as discharge increases. (B) In the context of the 4-year record of δD in the Fraser River (total variability ~40 ‰), the changes observed during the 1-month period of the early freshet (~16 ‰) are significant.

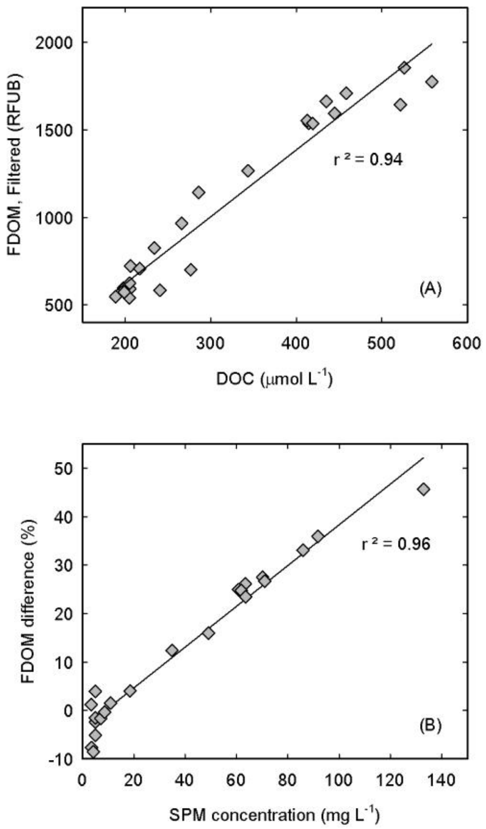

Figure S5. (A) Filtered fluorescent dissolved organic matter (FDOM) was positively correlated with DOC concentration. (B) The difference between filtered *ex situ* (filtered) and *in situ* FDOM values was strongly dependent on SPM concentration.

~~Figure 12. (A) The relationship between total dissolved mercury and DOC concentration is not as strong as has been observed in other systems (Dittman et al., 2010; Schuster et al., 2011; Burns et al., 2012b). (B) Total Hg concentration (unfiltered) is positively correlated with SPM concentration.~~

Formatted: Add space between paragraphs of the same style, Line spacing: Multiple 1.15 li