Terrestrial exports of dissolved and particulate organic carbon affect nearshore ecosystems of the Pacific coastal temperate rainforest

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Abstract

Watersheds of the coastal temperate rainforests of Pacific North America export large amounts of organic carbon (OC) to the coastal ocean. While it has been suggested that terrestrial-derived organic matter could subsidize marine food webs and affect ocean biogeochemistry along the coastal margin, little work has been done to quantify and characterize OC across the freshwater to marine continuum. We conducted monthly and targeted rainfall event surveys of dissolved and particulate organic carbon (DOC and POC) quantity and quality (δ13C, dissolved organic matter characterization) across a freshwater to marine salinity gradient between Calvert and Hecate Islands, British Columbia, Canada. Freshwater DOC concentrations (9.97 ± 0.25 mg L⁻¹) far exceeded those in marine waters (1.24 ± 0.03 mg L⁻¹), while POC concentrations were similar across all sites (0.23 ± 0.01 mg L⁻¹). δ13C-DOC and -POC in freshwaters were constant, but varied seasonally at the marine stations with freshwater and marine processes. Rainfall events facilitated the rapid export of terrestrial DOC and POC to coastal waters, altering water quality and potentially subsidizing microbial productivity across marine surface waters. On an annual basis, primary production in marine waters (21–42 Gg C) exceeded total freshwater OC contributions (1.8–2.2 Gg C); however, freshwater exports were more important during the autumn and winter months, when rainfall was highest and primary production was limited by shorter days and deep turbulent mixing. Our results highlight the importance of storms for connecting the coastal temperate rainforest with surface coastal waters, especially during the summer when connectivity between the freshwater and marine ecosystems is otherwise low.

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Additional Supporting Information may be found in the online version of this article.

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seasonally and spatially with changing terrestrial, freshwater, and marine processes and contributions (Bauer et al. 2013).

Coastal waters around northern North America are characterized by large freshwater inputs from the adjacent landmasses. This transitional zone is now recognized as the Riverine Coastal Domain, a potentially important hotspot between land and sea for the processing of terrestrial materials (Carmack et al. 2015). In the northwestern Atlantic, for example, it is estimated that more than half (59% ± 12%) of all carbon inputs to coastal waters originate from rivers and streams that drain the adjacent landmasses (Najjar et al. 2018). However, despite the diversity of potential terrestrial OC sources (e.g., rainfall, snow, and glacial melt) to nearshore waters of the northeast Pacific (Fellman et al. 2015; Arimitsu et al. 2018), we still know little about carbon dynamics in these marginal waters (Windham-Meyers et al. 2018). Northeast Pacific coastal waters are characterized by high productivity in the spring, summer, and autumn months, supported in part by the seasonal cycle of upwelling/downwelling (Windham-Meyers et al. 2018). This marine seasonality interfaces with large and seasonal freshwater inputs from autumn and winter rainfall (> 2000 mm yr⁻¹; Alaback 1996) across the North Pacific coastal temperate rainforests (NPCTR), and spring and summer snow/glacial melt from the more mountainous regions inland and along the coast (Fellman et al. 2010). This freshwater flux is sufficient to establish a contiguous buoyancy current that moves northward along western North America (Carmack et al. 2015). High OC stocks in soils of the region (McNicol et al. 2019) make the coastal watersheds hotspots of OC exports to nearshore waters (Hood et al. 2006; Fellman et al. 2008, 2009a,b,c; Hatten et al. 2012; Goñi et al. 2013; Oliver et al. 2017). The flux of freshwater and its associated OC may therefore play a potentially significant role in marine ecosystem dynamics in the region.

Given the complexity of OC sources and transformations in coastal waters, understanding the relative importance of each remains challenging. The simultaneous use of bulk DOC and POC concentrations and stable isotopes (δ¹³C) can help to elucidate the key sources and driving processes of OC along the continuum from fresh to marine waters (Murphy et al. 2008; Yu et al. 2010). Fluorescence and absorbance properties of dissolved organic matter (DOM, of which DOC is a major component) can further distinguish between sources and determine the potential for DOM to be taken up, altered, or lost downstream and, by extension, its role in ecosystem functioning (Stedmon and Markager 2005).

We combined field measurements of DOC and POC concentration and quality (δ¹³C and DOM characterization) across a salinity gradient, from small pluvial watersheds (freshwater, 0 salinity units) to nearshore (within ~ 0.5 km of the stream, 10–31 salinity units) waters to marine sites (20–30 salinity units) in the middle of a narrow channel system along the Central Coast of British Columbia, Canada (Fig. 1). The objectives of the study were to: (1) describe the spatial and seasonal variability in DOC and POC quantity and quality along the land-to-ocean aquatic continuum, (2) evaluate the role of rainfall events in establishing and maintaining connectivity between freshwater and marine ecosystems within the NPCTR, and (3) consider the importance of these connections to the biogeochemistry and ecology of nearshore marine systems. We hypothesized that freshwater inputs of OC would always be detectable in the marine environment, and that their influence would be stronger during winter when rainfall events are frequent and primary production is reduced by shorter days and deep turbulent mixing along the coast.

Materials and methods

Site description

The study sites were located within or adjacent to Meay and Kwakshua Channels (hereafter Kwakshua Channel), which separate Calvert and Hecate Islands in the Hakai Luvbalis Conservancy along the Central Coast of British Columbia, Canada (51.66°N, 128.06°W; Fig. 1). Calvert and Hecate Islands are located within the humid NPCTR region, which extends from southeast Alaska to central British Columbia (Fig. 1) and is characterized by cool summers with a rainfall year-round (Alaback 1996). Extensive open-wetlands and short wet-forests composed of mostly short stature western redcedar, yellow-cedar, shore pine, and western hemlock overlie organic-rich soils, including podzols, folic histosols, and deeper hemists (Oliver et al. 2017). Unlike some other coastal systems across the wider NPCTR (e.g., Arimitsu et al. 2018), Kwakshua Channel and the small watersheds that feed it have no glacial and only minimal snow melt inputs that vary by year and watershed.

Climate and seasonality

Between 1981 and 2010, mean annual air temperature and precipitation at nearby Addenbrooke Island (51.61°N, 127.85°W, 21 m above sea level) were 9.2 ± 1.1°C and 3262 mm (> 98% rain), respectively (Environment and Climate Change Canada station 1060080). Local rain gauges within the study area showed strong seasonality of precipitation inputs, with drier conditions May through August (Supporting Information Fig. S1). Over the study period, more than 42% of days had rainfall of at least 5 mm, which was approximately representative of the frequency of rainfall in any given calendar year between 2015 and 2016 (Supporting Information Table S1). More than 15%, 5%, 2%, and 1% of days had more than 25 mm, 50 mm, 75 mm, and 100 mm of rainfall, respectively.

The spring transition in Kwakshua Channel typically occurs between March and May (Thomson et al. 2014) and is marked by a shift toward northwesterly winds that favor upwelling and a phytoplankton bloom. In this region, upwelled waters propagate from Queen Charlotte Sound to Kwakshua Channel each year (Hunt et al. 2018). These waters persist within Kwakshua Channel through the summer until the transition to downwelling-dominant (southeasterly) winds, which occurs between September
and November. Based on these events, we divided the year into four periods, roughly corresponding to the calendar seasons: a (1) period of high freshwater inputs and low marine productivity (winter: December–January–February [DJF]); (2) transition to drier conditions and the spring phytoplankton bloom (spring: March–April–May [MAM]); (3) period of low rainfall and sustained marine primary production (summer: June–July–August [JJA]); and (4) transition back to high rainfall and freshwater inputs (autumn: September–October–November [SON]).

**Survey design**

Stations were established at three locations along the land-to-ocean aquatic continuum (Fig. 1): (1) in freshwater just upstream (< 50 m) of the outlets of seven watersheds (hereafter “freshwater outlets,” salinity = 0, n = 7); (2) at nearshore marine stations adjacent to the freshwater outlets (“marine outlet adjacent,” n = 7, surface salinity = 9.1–31.2, mean distance from outlet = 0.22 ± 0.06 km); and (3) at marine stations in the middle of the primary channels influenced by watershed outputs (“marine midchannel,” n = 6, surface salinity = 20.7–30.5). The seven numbered watersheds were located on Calvert (626, 708, 703, 693) and Hecate (1015, 819, 844) Islands and cumulatively accounted for 62.6% of the catchment area draining into Kwakshua Channel. These watersheds were previously described in detail in Oliver et al. (2017), with key characteristics summarized in Supporting Information Table S2. Briefly, the target watersheds range from 3.2 to 12.8 km² and represent variable topographies (slope range: 21.7–40.3%), and coverage by lakes (0.3–9.1%) and wetlands (23.8–50.2%). Marine outlet adjacent stations were located between 0.10 and 0.57 km of each paired freshwater outlet and ranged in depth from 8 to 78 m (Supporting Information Table S2). The six midchannel stations were distributed across Meay Channel (MEA02), Pruth Bay (Pruth), Kwakshua Channel (KC1, KC7, KC10) and Fitz Hugh Sound (FZH01) and ranged in depth from 8 to 345 m (Supporting Information Table S3). Across all marine stations, only data from surface waters (0–5 m) are presented, representing the region within the water column of greatest freshwater influence. With few exceptions, sites are discussed by type (freshwater outlet, marine outlet adjacent, and marine midchannel), rather than by site name.

**Sample collection**

All water samples were collected between 08 January 2014 and 23 November 2016 by staff at the Hakai Institute’s Calvert Island Field Station. Samples for DOM optical characterization were only collected in 2016.

**Freshwater outlets**

Bulk water samples were collected from the freshwater stream outlets at approximately monthly intervals. Samples for DOC, δ¹³C-DOC, and DOM optical characterization were
filtered in the field using a 0.45 μm Millipore® Millex-HP hydrophilic polyethyl sulfate (PES) filter and kept in the dark on ice until analysis. DOC and δ13C-DOC samples were acidified with 200 μL (in 38.8 mL) of 1:1 7.5 mol L⁻¹ H3PO4 immediately upon return to the field station, and kept at 4°C until analysis within 1–2 weeks of collection. No aggregate flocculation was observed in the filtered samples. DOM optical characterization was performed within 24 h of collection. Bulk water samples for POC and δ14C-POC analysis were collected in triplicate-binned bottles and kept cool until processing, described below.

Continuous discharge measurements began across all watersheds on 02 August 2014, except for watershed 708 (22 September 2013). Rating curve construction and discharge estimation methods are described in detail in Oliver et al. (2017) and updated in Korver et al. (2019). All seven watersheds were continuously gauged at 5-min intervals throughout the study period. Daily watershed-specific DOC and POC fluxes were then calculated by relating discharge to measured concentrations over the same period using watershed-specific log-linear models in the R package rLOADEST (Lorenz et al. 2015; R Core Team 2016). Flux estimates were calculated at 15-min intervals between 01 January 2015 and 31 December 2016, producing estimates for two full calendar years (Supporting Information Table S4).

**Marine outlet adjacent and midchannel sampling**

Marine outlet adjacent stations were sampled from a boat within 0–2 h of the freshwater outlet sampling. The six marine midchannel stations were sampled approximately monthly during the winter and every 2 weeks throughout the remainder of the year. At each station, bulk water samples were collected at 0, 1, and 5 m, using Niskin bottles. The collected water was immediately subsampled for POC, chlorophyll a (Chl a), DOC, δ13C-DOC, and DOM optical characterization. The latter three samples were filtered in the field using a 0.45 μm PES syringe filter. Marine DOC and δ13C-DOC samples were acidified with 200 μL (in 38.8 mL) of 6 mol L⁻¹ HCl, and kept cool until analysis. DOM optical characterization was performed within 24 h of collection. A marine sample-specific calibrated YSI was placed into a rinsed jug containing sample water from the Niskin and allowed to equilibrate before temperature and salinity were recorded. Following sample collection, a RBR CTD (conductivity, temperature, depth) was deployed to obtain a water column profile of temperature, conductivity, and pressure, from which salinity was derived. Profile data were fully processed following Halverson et al. (2017) and binned to 1 m depth intervals for the purpose of this analysis.

**Rainfall events**

To understand the influence of rainfall events on the dynamics of the coastal transitional zone within the NPCTR, the freshwater plumes emanating from watersheds 819 and 703 were systematically sampled during rainfall events on 07 August 2015 and 19 September 2015, respectively (Fig. 1). Rainfall was ~ 16 and 50 mm (based on the rainfall gauge at watershed 703, 289 m a.s.l) on each sampling day (Supporting Information Fig. S1). In both cases, sampling days were preceded and followed by days during which rainfall (much, in some cases) exceeded 0.2 mm. Prior to sampling, the extent of the freshwater plume was determined by visually assessing the area for color and turbidity and via direct measurement of conductivity across the plume. Conductivity across the area visibly affected by the plume was compared with the Pruth marine midchannel reference station on the sampling day, located away from the direct influence of the freshwater outlets. As conductivity approached this reference value (typically ~ 45,000 μS cm⁻¹ at the surface), the boundaries of the plume were delineated. A grid of six sampling stations was then established within the plume boundary: one immediately next to the mouth of the river and one at the routine outlet adjacent station, with the remaining four stations distributed across the plume. At each sampling station within the plume, water samples were collected at 0, 1, and 5 m depth with a Niskin bottle. Water samples were transferred to an acid-washed and Milli-Q water-rinsed 1-L polyethylene sample bottle and stored on ice until subsampling and processing, as described above, with one additional variable collected: bacterial cell abundance. For these samples, 1960 μL of sample water was added to tubes prefilled with 40 μL 25% microscopy-grade glutaraldehyde (Sigma-Aldrich, final concentration of 0.5%) and incubated in the dark for approximately 20 min before being frozen at −80°C until analysis. Bacterial cell count samples were additionally collected in the streams draining watershed 819 in July 2015 and watershed 703 in October 2015 as a pseudo-freshwater end-member against which the cell counts across the plumes could be compared. Marine end-members for the August (WS819) and September (WS703) events were the mean of bacterial cell counts at 0 m across KC11, KC12, and KC15 in July 2015, and across KC11 and KC12 in October 2015, respectively. Following subsampling, an YSI reading was taken by placing the YSI directly in the Niskin bottle. A CTD profile of the entire water column was also conducted at each station to quantify temperature and salinity at the time of sampling.

**DOC flocculation experiments**

Experiments to assess the propensity of DOC to flocculate within Kwakshua Channel were conducted in July 2018, based on the approach of Sholkovitz (1976). Freshwater and marine end member samples were collected on 06 July 2018 from the freshwater outlet stream at watershed 819 and at the 50 m depth from Pruth station (salinity = 32), respectively. Unfiltered water from both sources was allowed to equilibrate overnight in a darkened incubator at 13°C. The seawater was then serially diluted in triplicate in cleaned 4-liter polycarbonate containers, with five treatments incubated in parallel representing seawater: freshwater (SW : FW) ratios of 5:0, 4:1,
Sample processing and analytical procedures

All samples were processed and preserved the same day as collection at the Hakai Institute’s laboratory facilities on Calvert Island. DOC and δ13C-DOC were preserved in the field, as described above. All DOC and δ13C-DOC were analyzed at the Ján Veizer Stable Isotope Laboratory at the University of Ottawa (Ottawa, ON, Canada). There, freshwater DOC and δ13C-DOC samples were quantified by the wet oxidation method on a modified OI Analytical (College Station, TX, USA) Aurora model 1030 W TOC analyzer, interfaced with a Thermo Finnigan DeltaPlus XP isotope ratio mass spectrometer (IRMS) (St-Jean 2003). Marine DOC and δ13C-DOC were similarly measured but by high temperature combustion, using a combustion unit interfaced with the total organic carbon (TOC) analyzer and IRMS (Lalonde et al. 2014).

For POC and δ13C-POC samples from marine stations, a known volume of water – up to a maximum of 2 L - was filtered in parallel through each of two pre-combusted 25 mm Whatman glass fiber (GF/F) filters until color was noticeable on the filters. One of the duplicate filters was acidified with 2 mL of 1 M HCl to remove carbonate minerals (particulate inorganic carbon) from the filters. After 30 s, HCl was rinsed off the filter with ~ 5 mL of filtered (0.45 μm PES) seawater. For the freshwater POC samples, only one filter was prepared, without acidification. The freshwater streams were acidic (mean pH ± standard error [SE] = 4.84 ± 0.04, median: 4.77, n = 348), indicating that any inorganic carbon in the samples should occur as (or quickly be transformed to) CO2, and thus precluding the need for filter acidification. Based on this information, we did not acidify the filters, so as to minimize sample manipulation. Each filter was then sealed in a foil packet and stored at ~ 20°C until processing. Filters were dried at 60°C for ~ 24 h, weighed and transported in a travel desiccator to the Hakai Field Station on Quadra Island. There, the whole filters were put into a tinfoil capsule and crimped before being sent and analyzed at the University of California Davis Stable Isotope Facility (Davis, California, USA) using a PDZ Europa ANCA-GSL elemental analyzer coupled to a PDZ Europa 20–20 continuous flow IRMS (Sercos, Cheshire, UK). During analysis, samples were interspersed with several replicates of at least two different laboratory standards calibrated against NIST Standard Reference Materials. A preliminary isotope ratio was measured relative to reference gases analyzed with each sample. These preliminary values were finalized by correcting the values for the entire batch based on the known values of the laboratory standards. The standard deviation was 0.2‰ for 13C. Final delta values were expressed relative to the international standard VPDB (Vienna PeeDee Belemnite).

Bulk Chl a concentrations at the marine outlet adjacent and mid-channel stations were determined by filtering 250 mL of sample water through 47 mm 0.7 μm glass fiber filters (Whatman GF/F). Filters were then placed in individual Falcon tubes and stored in a black bag at ~ 20°C until analysis on site. Concentrations were quantified using a Trilogy Laboratory Fluorometer (Turner Designs, San Jose, California, U.S.A.), following the protocols of Knap et al. (1996).

Preserved samples for microbial (bacterial and archaeal) cell counts were thawed and stained with 1x final concentration SYBR Green I (Invitrogen). Cells were enumerated using the Guava EasyCyte SHT-HPL flow cytometer (Millipore, Darmstadt, Germany), based on previously described methods (Thrash et al. 2017). Samples were diluted between 5- to 10-times with 0.2 μm filtered nuclease-free water to achieve an optimal concentration of 500 cells μL−1 or less when run at a medium flow rate (0.59 μL s−1). Nuclease-free water controls (unstained and stained) and selected unstained samples were also run to gauge instrument and diluent noise and sample autofluorescence, respectively. Instrument gain settings of forward scatter (FSC) = 9.93, side scatter (SSC) = 2.83, GRN-B = 1, YEL-B = 8, RED-B = 8 were used and a green fluorescence (GF) threshold between 9 and 11 was applied, depending on the run, to minimize instrument and background noise. Samples were counted until 3000 events were recorded in a preset count gate encompassing the region on a plot of GF vs. SSC where prokaryotic cells would be. After data acquisition, cells were gated using plots of GF vs. red fluorescence (RF) as well as GF vs. SSC. Given the presence of humic and chromophoric DOM in the samples, GF vs. RF proved the best method for delimiting cell populations and were used to calculate the final abundance of cells in each sample.

DOM characterization

In 2016, DOM samples from freshwater and marine environments were characterized by absorbance and fluorescence spectroscopy, using an Aqualog spectrofluorometer (Horiba Scientific, Edison, New Jersey, U.S.A.) at the Hakai Institute’s Calvert Island field station, as described in Oliver et al. (2017). Absorbance and fluorescence were run simultaneously in a 1 cm acid-cleaned cuvette on an Aqualog spectrophotometer (Horiba Instruments, New Jersey, U.S.A.) equipped with a CCD detector. Excitation and absorbance wavelengths were scanned from low to high energy (red to UV) to reduce effects of photobleaching during analysis. Excitation and absorbance scans were performed with 0.5–10 s integration times at wavelengths of 230–600 nm. Emission spectra were collected at 1.64 nm intervals at wavelengths of 250–600 nm. Procedures for spectral correction included baseline correction, removal of inner filter effects, Raman water peak area correction, and removal of Rayleigh scatter (Murphy et al. 2013). Samples with absorbance values greater than 0.2 at 254 nm were...
diluted and reanalyzed, and spectral correction performed using the appropriate dilution factor correction (Ohno 2002).

Interpretations of DOM composition based on optical characterization alone can be challenging without accompanying detailed chemical characterization. We recognize these limitations, and consider interpretations of optical characteristics within the context of previous studies linking chemical characterization of DOM to optical parameters. The freshness index, the ratio between the emission intensity at 380 nm and the maximum emission intensity between 420 and 435 nm at 310 nm excitation (Hansen et al. 2016), was calculated for each excitation-emission matrix (EEM) to quantify the relative contribution of recent vs. latent sources (McKnight et al. 2001; Xenopoulos et al. 2003). The spectral slope ratio ($S_{275-295}/S_{350-400}$) has been shown to negatively correlate with molecular weight and to generally increase with increased exposure to solar radiation (Helms et al. 2008; Spencer et al. 2009; Hansen et al. 2016). We conducted parallel factor analysis (PARAFAC) using the dEEEM toolbox in Matlab (MathWorks, Massachusetts, U.S.A.) to separate the complex DOM pool into discrete components (Stedmon and Markager 2005; Murphy et al. 2013). A total of five components were identified across all compartments and validated using core consistency and split-half analysis (Stedmon and Bro 2008; Murphy et al. 2013).

Statistical analyses

All statistical analyses were completed in R (R Core Development Team 2016), using packages nlme (Pinheiro et al. 2017), lme4 (Bates et al. 2015), MASS (Venables and Ripley 2002), lsmeans (Lenth 2016), and vegan (Oksanen et al. 2018). SEs are reported throughout, unless otherwise stated.

Mixed effect ANOVA models were used to assess the differences in DOC and POC quantity (concentration) and quality ($\delta^{13}$C) between site types and seasons. Site type (freshwater outlet, marine outlet adjacent, marine midchannel) and season were coded as fixed effects, while station ID was coded as a random effect. Tukey multiple comparisons were assessed on all pairwise combinations of seasons and site types, with statistical significance defined based on a Bonferroni-corrected alpha ($\alpha$) level of 0.0008 ($\alpha = 0.05/66$ comparisons).

Physical and chemical drivers of PARAFAC component intensity and percent representation were determined on all samples using redundancy analysis (RDA). The full explanatory matrix included day of year, season, salinity, water temperature, wind speed, and wind direction at the time of sampling measured at Pruth station, DOC concentration ([DOC]), $\delta^{13}$C-DOC, and total fluorescence ($F_{\text{max}}$). Variance inflation factors (VIFs) for many explanatory variables within the full models were greater than 10, indicating high collinearity (Borcard et al. 2011). Forward step-selection was used to select the most parsimonious model. In all cases, VIFs for the terms in the reduced models were less than 10, and the explanatory power of the resulting model was not diminished by the variable reduction (adjusted $R^2$ for full and reduced models $= 0.298$ and 0.295, respectively).

Estimation of freshwater and marine contributions to coastal carbon pools

To estimate freshwater carbon inputs to Kwakshua Channel, we took the combined DOC and POC fluxes (i.e., TOC) from six of the seven watersheds (all except watershed 1015, which drains into waters just north of the entrance to Meay Channel), representing 43.6 km$^2$ or 62.6% of the drainage area of the Channel system, and upscaled this quantity to the entire drainage area of the Meay-Kwakshua Channel system (69.6 km$^2$). This value represents the lower bound estimate of C export to the channel. The 26.0 km$^2$ of land drained by ungauged streams that flow into Kwakshua Channel are predominately low elevation watersheds with high wetland cover and should thus yield higher amounts of TOC than the larger gauged watersheds (Oliver et al. 2017). We therefore applied the high TOC yield estimates (33.0 Mg C km$^{-2}$ yr$^{-1}$ in Supporting Information Table S5) from watershed 844 to the ungauged area to obtain a putative upper bound on C export from the watersheds.

To estimate primary production within the Kwakshua Channel system, we applied areal primary production rates measured at Rivers Inlet (51.43°N, 127.36°W; Shiller 2012) and Saanich Inlet Sta. 509 (48.70°N, 123.50°W; Timothy and Soon 2001) to the combined area of Pruth Bay, Meay, and Kwakshua channels (38.5 km$^2$). Although it rests at a similar latitude to the Kwakshua sites, Rivers Inlet receives considerable glacial inputs during the summer, which can have an important effect on stratification and nutrient availability in nearshore waters (Hodal 2010; Shiller 2012). The more southerly Saanich Inlet bears many similarities to Kwakshua Channel; it contains semi-sheltered waters without the influence of glacial inflows, but typically has higher primary production than the Central Coast (BC3 in Jackson et al. 2015). Together, these estimates provide a range of primary productivity across the region. Upwelling of deep waters could also contribute carbon to Kwakshua surface waters (Hill and Wheeler 2002); however, this specific process has not been estimated here.

Results

DOC and POC concentrations and fluxes at the land–ocean interface

Freshwater outlets

Mean monthly rainfall ranged between 51.5 ± 0.3 mm (May) and 464 ± 2.1 mm (December) and was strongly positively correlated with discharge from the seven watersheds (Pearson product-moment correlation, $r = 0.975$, t = 13.8, $p < 0.05$; Fig. 2A). Freshwater exports were highest in the winter and autumn months, when rainfall typically exceeded 300 mm month$^{-1}$, and lowest May through June, when
Fig. 2. Seasonality of DOC and POC in freshwater and marine (averaged measurements from 0, 1, and 5 m) compartments along the land to ocean aquatic continuum between 08 January 2014 and 31 December 2016. Monthly means ± SE presented across the calendar year for (A) rainfall and mean discharge from watershed 703, (B) cumulative DOC and POC fluxes from the seven focal watersheds, and mean (C) DOC concentrations, (D) $\delta^{13}$C-DOC signatures, (E) POC concentrations, (F) $\delta^{13}$C-POC signatures, and (G) chlorophyll $a$ concentrations across all compartments of the continuum.
rainfall was often less than 100 mm month\(^{-1}\). Both freshwater DOC and POC fluxes to the nearshore environment mirrored these seasonal discharge dynamics (Fig. 2B). DOC fluxes greatly exceeded POC fluxes, by more than 20-fold in some months.

Mean monthly DOC concentrations across all freshwater outlets ranged between 8.42 ± 0.59 (February) and 14.14 ± 0.87 mg L\(^{-1}\) (September) (Fig. 2C; full data range = 2.84–20.72 mg L\(^{-1}\), see Supporting Information Fig. S2), the highest concentrations along the continuum. These mean concentrations were more or less constant from winter through the summer, while autumn concentrations were significantly higher than in any other season (mixed effects ANOVA; \(p < 0.0001\), Supporting Information Fig. S2). \(\delta^{13}\)C-DOC signatures (annual mean = −26.56 ± 0.03‰, full range = −27.66 to −23.40‰, Supporting Information Fig. S2) were variable, but indicated that the DOC was predominately terrestrial throughout the year (Fig. 2D).

Mean monthly POC concentrations in the freshwater outlets ranged between 0.13 ± 0.02 (January) and 0.47 ± 0.05 mg L\(^{-1}\) (August; Fig. 2E). POC concentrations were consistently between one and two orders of magnitude lower than DOC (full range = 0.02 and 1.86 mg L\(^{-1}\), Supporting Information Fig. S2). Concentrations in the winter and spring were up to threefold lower than those in summer and fall, potentially due to seasonally lower terrigenous primary production and litter production in these forested watersheds. \(\delta^{13}\)C-POC showed little seasonal variability (annual mean = −26.56 ± 0.03‰, full range = −29.05 to −25.50‰ in Supporting Information Fig. S2), indicating a consistent, predominately terrigenous source of POC to the streams throughout the year (Fig. 2F).

**Marine outlet adjacent and midchannel stations**

DOC and POC concentrations, and \(\delta^{13}\)C-DOC and \(\delta^{13}\)C-POC were indistinguishable between the marine outlet adjacent and midchannel stations (ANOVAs, \(p = 0.29–0.37\)). Mean DOC concentrations at the marine outlet adjacent and midchannel stations were 1.29 ± 0.04 mg L\(^{-1}\) (0.67–12.17 mg L\(^{-1}\)) and 1.15 ± 0.04 mg L\(^{-1}\) (0.47–7.27 mg L\(^{-1}\)), respectively (Supporting Information Fig. S2).

Mean monthly outlet adjacent DOC concentrations ranged between 0.87 ± 0.03 (July) and 1.63 ± 0.23 mg L\(^{-1}\) (September; Fig. 2C). Integrated upper water column (0–5 m) DOC concentrations decreased between spring and summer before increasing again in the autumn (Fig. 2C), largely due to changes directly at the surface (0 m, Fig. 3). DOC concentrations were only significantly different between summer (1.10 ± 0.03 mg L\(^{-1}\)) and winter (1.55 ± 0.15 mg L\(^{-1}\); \(p < 0.0001\)). Meanwhile, monthly mean midchannel DOC concentrations ranged between 0.86 ± 0.06 (October) and 2.83 ± 1.49 mg L\(^{-1}\) (August; Fig. 2C). On average, concentrations were highest during the winter (1.31 ± 0.05 mg L\(^{-1}\)) and summer (1.23 ± 0.15 mg L\(^{-1}\)), and lowest during the autumn (0.93 ± 0.05 mg L\(^{-1}\)) (Supporting Information Table S6). \(\delta^{13}\)C-DOC across all marine stations shifted seasonally, between −24.57 ± 0.26‰ (outlet adjacent) or −24.41 ± 0.30‰ (midchannel) in winter, indicating more terrestrial material, and −22.25 ± 0.06‰ (outlet adjacent) or −22.24 ± 0.14‰ (midchannel) through the summer, suggesting a greater contribution from marine autochthonous production (Barber et al. 2017) (Figs. 2D, 3).

Chl \(a\) concentrations at the marine outlet adjacent and midchannel stations exhibited distinct seasonality, ranging from a mean of 0.36 μg L\(^{-1}\) in January to monthly means between 2.12 and 7.00 μg L\(^{-1}\) from March through June (Fig. 2G). On average, Chl \(a\) concentrations were slightly higher at the marine midchannel stations except during the spring (Supporting Information Table S6; Fig. 3). There were two peaks in Chl \(a\) concentrations throughout the year: the first (and largest) peak occurred in April–May and the second in August–September, a bimodal phenology characteristic of the region (region BC4 in Jackson et al. 2015). Chl \(a\) concentrations did not vary significantly between 0 and 5 m depth (Fig. 3, \(p < 0.05\)).

Mean monthly POC concentrations ranged between 0.08 ± 0.01 mg L\(^{-1}\) (December) and 0.81 ± 0.05 mg L\(^{-1}\) (March) at the outlet adjacent sites, and between 0.19 ± 0.03 mg L\(^{-1}\) (January) and 0.43 ± 0.05 mg L\(^{-1}\) (June) at the midchannel sites (Fig. 2E). Like for \(\delta^{13}\)C-DOC, we observed a seasonal shift in \(\delta^{13}\)C-POC from values reflective of a greater terrestrial contribution through the autumn transition and winter (−24.7 ± 0.1%o) to those suggesting more in situ production in the spring and summer (−21.0 ± 0.1%o; Figs. 2F, 3). Both \(\delta^{13}\)C-DOC and \(\delta^{13}\)C-POC in the marine samples were positively correlated with Chl \(a\) concentration (\(r = 0.294\) and \(r = 0.536\), respectively; Supporting Information Fig. S3); however, these bulk relationships—especially for \(\delta^{13}\)C-DOC—were highly variable.

**DOM characterization**

The freshness index was typically less than 1.0, indicating that the majority of DOM found across all stations throughout the year was, by definition, more recently produced and less humic-like DOM (Parlanti et al. 2000; Wilson and Xenopoulos 2009) (Supporting Information Fig. S4A). On average, the spectral slope ratio (\(S_{SR}\)) of DOM at the marine stations indicated a more marine-like signal (\(S_{SR} > 1.0\), 1.05 ± 0.04) and a greater prevalence of low-molecular weight compounds during the spring and summer months when primary production in coastal waters was highest, but a more terrestrial-like signal (higher molecular weight compounds, 0.93 ± 0.05) during the autumn and winter months as freshwater inputs to the channel increased (Supporting Information Fig. S4B). When averaged across all watersheds, the \(S_{SR}\) of all freshwater samples was more or less constant throughout the year (0.79 ± 0.00), but individual values ranged between 0.23 and 1.15.

Five fluorescent components (C1–C5) were identified across both freshwater and marine sites of the continuum using
Fig. 3. Seasonal depth profiles (0, 1, and 5 m) of the outlet adjacent and midchannel marine stations in relation to freshwater inputs. Means ± SE of DOC concentrations, δ\(^{13}\)C-DOC signatures, POC concentrations, and δ\(^{13}\)C-POC signatures are shown across all stations. Winter, 01 December to 28/29 February; spring, 01 March to 31 May; summer, 01 June to 31 August; autumn, 01 September to 30 November.
PARAFAC, including four humic-like components (C1–C4) and one protein-like component (C5) (Supporting Information Fig. S5, Table S7). Based on similarity scores greater than 0.98, all components were matched to PARAFAC models previously reported in the OpenFluor database (Murphy et al. 2014). On average, fluorescence of the freshwater DOM was higher than for the marine stations, and increased through the year, driven largely by increases in the fluorescence of C1–C3 (Supporting Information Fig. S6). Maximum fluorescence for freshwater and marine DOM was observed in October and February, respectively. C1 was the most common component across all pools and represented more than 40% of total composition of the fluorescing pool of DOM (Supporting Information Table S7). The contributions of C1, C3, and C4 oscillated, but were more or less constant throughout the year (Supporting Information Fig. S7). While the contribution of C2 to the marine DOM pool was the same as for the freshwater pool through April, the C2 contribution to the marine DOM pool decreased in May, distinguishing the fresh and marine stations through the summer and autumn. Although absolute C5 fluorescence was lower across the marine stations than in the freshwater samples through the year (except November, Supporting Information Fig. S6), C5 contributed more to total marine DOM fluorescence through the autumn and winter months, accounting for up to 23.5% ± 0.03% of total fluorescence (Supporting Information Fig. S7).

The RDA models of drivers of DOM composition across the land-to-ocean continuum using component maximum fluorescence intensity (F_max) or percent fluorescence (%F_max) as the response variable were virtually identical (Supporting Information Table S8). Thus, only the F_max model is discussed and presented here. Results for the %F_max model are presented in the Supporting Information Fig. S8. Overall, 29.5% of DOM composition was explained by the model (F = 12.7, p < 0.001). Three axes were statistically significant (p < 0.05), representing 18.8%, 10.4%, and 3.1% of variation, respectively. RDA1 represented the distribution of sites based on salinity and fluorescence and was dominated by DOC concentration, total F_max, and salinity, where freshwaters had higher DOC concentrations and fluorescence than the marine sites (Fig. 4). Along RDA1, C1 and C2 represented the freshwater and marine sites, respectively. RDA2 and RDA3 represented seasonal variability in the system, with RDA2 separating the winter and spring samples (Fig. 4), and RDA3 the spring and summer samples (Supporting Information Table S8). In both cases, these separations were most noticeable in the marine samples.

Mixing dynamics during rainfall events

Surface salinity at the outlet adjacent marine stations was substantially lower during the two rainfall events than the monthly mean (Fig. 5), suggesting the widespread influence of rainfall-heightened freshwater exports to the Kwakshua Channel system. Based on concentration, DOC mixed quasi-conservatively across the freshwater plumes (Fig. 5A). δ13C-DOC values across the plume were comparable to the mean monthly freshwater reference value in August (Fig. 5B). In September, this was also true for δ13C-DOC at lower salinities (< 15), but above a salinity of 15, δ13C-DOC became heavier, approaching the monthly reference values for the marine stations. POC concentrations across the plume were higher than the monthly mean concentrations in both freshwater and marine water (Fig. 5C). δ13C-POC was comparable to the freshwater reference values across the plume during both rainfall events (Fig. 5D). Microbial cell counts across the plumes were higher than in samples collected as seasonal reference concentrations in either freshwater or marine water (Fig. 5E).

Controlled mixing experiments

Based on our observation of elevated POC concentrations across the freshwater plumes, we conducted a series of controlled incubations, combining fresh and marine waters in defined ratios, to investigate the possibility of DOC flocculation as a DOC sink (and POC source) with coastal mixing in Kwakshua Channel. Over the salinity gradient established during these experiments, DOC concentrations were lower than predicted by conservative mixing (Fig. 6A) and POC concentrations were slightly higher (Fig. 6B). At salinities greater than 15 ppt, corresponding to the 3 : 2 and 4 : 1 SW : FW treatments, δ13C-POC was more terrestrial than predicted by conservative mixing of the two end-members (Fig. 6C).
Fig. 5. Rainfall event surveys of (A) DOC concentration, (B) 13C-DOC, (C) POC concentration, (D) 13C-POC, and (E) microbial prokaryote cell counts at 0 m across the freshwater plume during rainfall events on 07 August 2015 (watershed 819) and 19 September 2015 (watershed 703). Stations \((n = 6)\) across the plume are shown in relation to monthly mean ± SE values for the freshwater and outlet adjacent (marine) sites and across all marine midchannel stations and samplings for the months of August (for the 07 August 2015 event) and September (19 September 2015 event). Rainfall event samplings conducted at the routine marine adjacent outlet stations are circled.
Estimated contribution of terrestrial OC to surface waters

By scaling areal estimates of primary production rates from nearby Rivers Inlet (Shiller 2012) and Saanich Inlet Sta. S-09 (Timothy and Soon 2001) to the combined areas of Pruth Bay, Meay and Kwakshua Channels (38.5 km²), we estimated that primary production contributed between 21.2 and 42.4 Gg C (based on Rivers Inlet) or 22.1 Gg C (based on Saanich Inlet) to Kwakshua Channel each year. In comparison, the combined DOC-POC freshwater inputs scaled to the drainage area of the Kwakshua Channel system were only between 1.8 and 2.2 Gg C yr⁻¹, or 9- to 24-times lower than in situ marine primary production. This relationship was seasonally nuanced, with freshwaters making up the majority of carbon inputs to the channel during the winter season, but less than 1% at the height of summer (based on monthly estimates from Timothy and Soon 2001; Supporting Information Fig. S9).

Discussion

The coastal temperate rainforests of Pacific North America export large amounts of OC to the coastal ocean that are expected to play an important role in marine ecosystem dynamics. However, to date, little work has been done to quantify and characterize OC across the freshwater to marine continuum, particularly for pluvial watersheds. In this study, we used a combination of routine monthly and rainfall event-based sampling to characterize the flux of terrestrial OC to the nearshore environment. Below we discuss the origins, processing, and fate of OC at the land–ocean interface, and the potential implications of terrestrial OC subsidies for nearshore marine ecosystems.

Origins of DOC and POC at the land–ocean interface

Calvert and Hecate Islands

The δ¹³C-DOC signatures within the freshwater outlets suggest that DOC there was likely a combination of leaching of litterfall from C₃ plants (weighted global average of −28.5‰; Kohn 2010) and humic substances produced within the organic-rich soils (Tipping et al. 2005). The mean δ¹³C-DOC (−26.65 ± 0.03‰) within the freshwater outlets was heavier than the global average for C₃ plants, suggesting a particularly important contribution from humic acids (−26.8 to −13.8‰; Stuermer et al. 1978). Wetter forests and wetlands cover up to 62% of the total Calvert and Hecate Island landscape (Thompson et al. 2016), and leaching of the extensive soil carbon stocks (McNicol et al. 2019) during rainy periods is likely to be an important contributor to DOC in the streams. In the marine waters, the δ¹³C-DOC signatures shifted seasonally, from lighter, more terrestrial values in December and January (Fig. 2D), when terrestrial inputs are highest, to heavier, more distinctly marine signatures in the spring and summer, when terrestrial inputs are reduced and primary production increases due to greater incident light, water temperatures, and thermal stratification.

Previous work has indicated that the temporal variability in freshwater DOM composition exported from these catchments was largely driven by precipitation and temperature, which (in addition to watershed properties) control the residence time of terrestrial material and degradation prior to export (Oliver et al. 2017). Due to the high amounts of rainfall across the region and the small size of these coastal watersheds,
DOM export from the watersheds is often rapid, although the drier season and the presence of lakes may increase the capacity for within-catchment degradation (Oliver et al. 2017). While seasonal variability in freshwater exports is observed in some optical indicators of DOM composition (e.g., $S_0$; see Oliver et al. 2017 for a discussion of watershed-specific $S_0$ and DOM composition), the change that we observe may be relatively small in comparison to watersheds from other Pacific coastal regions that experience a wider range of seasonally pronounced DOM sources and controls on processing (i.e., glacial and snow melt; Fellman et al. 2010), and the difference between freshwater and marine water (Supporting Information Fig. S4).

Optical properties of DOM derived from EEMs and PARAFAC analysis can offer additional insights into the sources and susceptibility of DOM to downstream processing across different environments (Murphy et al. 2013). C1, the most common component across both freshwater and marine pools (Supporting Information Table S7), has been previously reported to be a degradation product of terrestrial organic matter (Shutova et al. 2014). However, C1 shares spectral characteristics with oceanic humic-like DOM produced at depth that can be found in high concentrations in surface waters of upwelling regions (Jørgensen et al. 2011), likely explaining its ubiquity across both freshwater and marine systems. The fact that C1 clustered with the spring and summer marine sites (i.e., when upwelling conditions were strongest), but was equally common across the freshwater sites, supports the possibility of both terrestrial and oceanic origins of this component. Notably, C2, C3, and C4 were all previously reported in a survey of Swedish lakes (Kothawala et al. 2014). There, these humic-like components were observed along a gradient from darkly colored, highly aromatic DOM strongly associated with iron (Fe) and aluminum (Al) and susceptible to flocculation (C3), to less aromatic, less colored DOM with weaker association to Fe and Al and greater persistence in the water column (C4). C2 exhibited intermediate properties to C3 and C4. Humic-like C2 is noteworthy in our study because it was the only component to display a strongly seasonal separation between the freshwater and marine samples during the late spring (Supporting Information Fig. S7). At this time, the contribution of C2 to the marine DOM pool is diminished, compensated for by an increase in C1, perhaps from upwelled waters. Finally, tryptophan-like C5 was first described in surface waters of the Southern Ocean (Stedmon et al. 2011) and was more prevalent in our marine samples (Supporting Information Table S7), but has since been shown to be ubiquitous across different water types (Yu et al. 2015). Interestingly, the C5 contribution to the marine DOM pool actually increased during the autumn and winter. Tryptophan-like DOM components have been associated with enhanced bacterioplankton growth (Fellman et al. 2010), which may be stimulated by increasing terrestrial DOM inputs at that time of year. However, lignin and tannins may exhibit fluorescence similar to protein-like compounds (Maie et al. 2007; Hernes et al. 2009), potentially confounding these results in regions with high terrestrial inputs like the NPCTR. Together, the concentration, optical and stable isotope data suggest that while the quality of freshwater inputs to marine waters remain more or less constant through the year, the character of surface waters in the marine environment oscillates seasonally between being more terrestrial in winter and autumn and more marine through the spring–summer.

**Variability across the NPCTR**

Although there exists a paucity of data spanning the land–ocean interface across the northeast Pacific (Windham-Meyers et al. 2018), DOC—and more broadly DOM—has long been of interest in freshwater systems across the NPCTR. The freshwater DOC concentrations on Calvert and Hecate Islands (2.8–20.7 mg L$\textsuperscript{−1}$) were typically higher than those measured in June in some wetland-rich watersheds of SE Alaska (1.3–4.0 mg L$\textsuperscript{−1}$ in Peterson Creek, St. James, and Montana Rivers; Fellman et al. 2010) and Oregon (1–7 mg L$\textsuperscript{−1}$; Hood et al. 2006), but similar to others in SE Alaska sampled during stormflows (1.4–18.7 mg L$\textsuperscript{−1}$, Fellman et al. 2009b). Fewer estimates of $\delta^{13}$C-DOM exist, but those from the Calvert and Hecate watersheds were comparable to wetland-rich watersheds in SE Alaska ($−27.1 \text{ to } −25.3\%$; Fellman et al. 2010). DOM across the region typically contains a large fraction of humic compounds, especially during high flow events (Hood et al. 2006; Fellman et al. 2009a,b).

The POC concentrations in the streams of Calvert and Hecate Islands (0.02 and 1.86 mg L$\textsuperscript{−1}$) were at the low end of or lower than the range of concentrations previously observed in Oregon and Northern California (0.2–35.3 mg L$\textsuperscript{−1}$ in Goñi et al. 2013; or 0.15–25 mg L$\textsuperscript{−1}$ in Hatten et al. 2012). Watershed-specific characteristics, such as an increased incidence of landslides and a supply of petrogenic carbon from sedimentary rock, may lead to enhanced concentrations of POC in Oregon and California (Goñi et al. 2013). By contrast, the Calvert watersheds drain igneous intrusive bedrock and show little evidence of recent landsliding.

Though coastal, rain-dominated and wetland-rich watersheds like those found on Calvert and Hecate Islands are a common feature of the NPCTR, the region also contains numerous watersheds characterized by high elevation terrain covered by alpine tundra and glaciers. These glacierized watersheds can export water transporting more labile, microbially derived DOM to coastal waters than their nonglacierized counterparts (Fellman et al. 2010), with potentially important implications for downstream ecosystems. Extending surveys of both DOC and POC at the land–ocean interface across the region to capture the wide variety of coastal watersheds types will thus be necessary to fully understand the role of freshwater exports on carbon cycling in coastal waters across the northeast Pacific.
Fate of terrestrial OC in nearshore surface waters

The apparent conservative mixing of DOC in estuaries has been reported across many systems, but in reality, DOC within these dynamic waters is subject to numerous small, concurrent changes in its sources and sinks (Cifuentes and Eldridge 1998; Abril et al. 2002; Gao et al. 2019). In contrast, the concentrations of POC across the plumes were much higher than the monthly mean concentrations in both fresh and marine waters. This observation is likely due to a combination of: (1) higher POC concentrations exported by streams during storms (e.g., Goni et al. 2013), and (2) the conversion of terrestrial DOC to POC (i.e., flocculation) in the marine environment (Sholkovitz 1976; Sholkovitz et al. 1978). Our experimental results indicate that at least a portion of the DOC exported from the streams may flocculate in coastal waters, producing POC of apparent terrestrial origin, though how important this process is relative to the flushing of terrestrial POC remains unconstrained. In addition to the greater transport of terrestrial materials by the streams during high rainfall events, freshwater inputs to the coastal zone may also occur via overland flow outside of the channelized streams. These diffuse inputs would entrain litter and other POC that has accumulated on the forest floors that may contribute to sustained increases in POC during rainfall events. How long or far this terrestrial POC remains in suspension beyond the plume is unknown.

Both terrestrial DOC and POC may serve important functions within nearshore marine ecosystems. Terrestrial DOC and POC may be incorporated into the pelagic food web by microbes (Meinhard et al. 2002; Grossart et al. 2007), directly consumed by heterotrophic and mixotrophic protists and zooplankton (in the case of POC), or remineralized and lost to the atmosphere as CO₂. Although bacterial productivity experiments were not conducted here, microbial communities at the freshwater–marine interface can respond quite rapidly to changing inputs, as evidenced by the high cell counts (relative to the seasonal reference value) across the plumes (Fig. SE), with both DOC and POC capable of stimulating microbial production (Wainright 1987; Tranvik and Sieburth 1989; Crump et al. 1998; Wikner and Andersson 2012). In the Delaware Estuary, for example, mean community growth rates are 0.2 ± 0.3 d⁻¹ (Lankiewicz et al. 2016), but when grown in dilution (Yokokawa et al. 2004) or batch cultures (Lankiewicz et al. 2016), dominant marine bacterial taxa grew at rates reaching 6 d⁻¹ during exponential growth. This highlights the potential for marine bacteria to respond in a matter of hours when resources are available. The copiotrophic bacterial taxa that typically exhibit these high growth rates (Kirchman 2016; Lankiewicz et al. 2016) require higher concentrations of DOM and nutrients for growth. These taxa are also capable of utilizing pulses of high-molecular weight DOM from terrestrial sources (Fellman et al. 2010). In contrast, oligotrophic bacteria that maintain lower and more constant growth rates would be less likely to respond to episodic inputs of terrestrial DOM. Increasing terrestrial DOM inputs from river runoff could also catalyze a shift from primary production by phytoplankton toward heterotrophic production by bacterioplankton, as was observed in the Baltic Sea over a 13-yr period (Wikner and Andersson 2012). Our results suggest that similar trophic shifts may be possible over much shorter time scales, in response to episodic increases in freshwater discharge caused by intense rainfall events.

We also note that the drier summer season events sampled here were more isolated and generally smaller than rainfall events during the wet season, when precipitation more frequently exceeds 25 mm d⁻¹ (Supporting Information Fig. S1). The nearshore consequences of heightened winter terrestrial DOC and POC exports, however, remain to be seen. Although winter rainfall events could result in more dramatic and persistent trophic shifts than in the summer, cooler temperatures may slow the response of microbes in surface waters at that time, and/or favor the development of more stable communities adapted to colder temperatures and higher freshwater inputs. The winter ecology of these dynamic nearshore surface waters should be an important focus of future research.

Importance of terrestrial inputs to carbon dynamics in nearshore surface waters

From mid-spring through summer, the freshwater signal within the marine environment is muted by reduced freshwater discharge and increased marine primary production. While the effects of rainfall events on coastal waters during the drier summer season are likely short-lived, they act to recall the connection between watersheds and coastal waters during an otherwise low connectivity period. This is in contrast to the wet season, when more frequent rainfall events and lower marine autochthonous production make the terrestrial signal a defining feature of nearshore surface waters. Based on the high microbial cell counts observed across the freshwater plumes, rainfall events may also catalyze both short-term (event-based) and seasonal shifts in the fundamental function of nearshore pelagic food webs, depending on the time of year.

Other potentially important sources of OC along the coast are salt marshes and tidal wetlands (Windham-Meyers et al. 2018), which are prevalent across the NPCTR, especially in the more northerly parts of the region (McCowan et al. 2017). In more arid regions, salt marshes can be the dominant source of DOM to coastal waters (Clark et al. 2008). On the Atlantic coast, salt marshes and tidal wetlands contribute disproportionately to the carbon budgets of coastal waters, relative to their area (Najjar et al. 2018). Although not a dominant feature within Kwaššua Channel, these systems will be essential to consider when thinking about the wider northeast Pacific region. Concerted sampling efforts to quantify DOC and POC concentrations (and fluxes), as well as stable isotopes and other qualitative molecular compositional tools, are necessary to resolve the complexity of carbon cycling across the remarkable diversity of coastal environments.
Connectivity between land and sea in an era of rapid change

By 2080, annual precipitation across the Central Coast of British Columbia is projected to increase by 9%, relative to the 1961–1990 baseline (global climate model ensemble median based on A2 emissions scenarios; Pacific Climate Impacts Consortium 2019). This change is largely predicted to occur as a result of increases in the frequency and intensity of extreme autumnal (mid-August to December) rainfall events (Radić et al. 2015), with concomitant, albeit less certain, reductions in summertime rainfall (Pacific Climate Impacts Consortium 2019). These extreme events may facilitate the efficient flushing of vast quantities of terrestrially derived organic matter to the coastal zones, allowing it to bypass processing within freshwater ecosystems (Bianchi et al. 2013). This has important implications for the future of land–ocean connectivity.

Although marine primary production greatly exceeded allochthonous terrestrial carbon contributions on an annual basis, a fact which is unlikely to change in this region, increasing rainfall and thus freshwater DOC and POC exports during the autumn and winter could significantly increase terrestrial carbon contributions to the nearshore waters of the NPCTR region. Even during the drier summer season, however, storms increase the connectivity between terrestrial and coastal ecosystems, altering the quality of OC and potentially enhancing microbial production in receiving surface coastal waters. The predicted climatic changes across the region could therefore amplify the already dramatic seasonal transition between the marine (spring–summer) and terrestrially dominated (winter–autumn) coastal surface waters, affect the availability of key nutrients (Billen and Garnier 2007), and stimulate heterotrophic microbial production (Wikner and Andersson 2012), with consequences for the carbon balance in coastal waters.

Conclusions

Using a data set collected over more than two full years, and spanning the land-to-ocean aquatic continuum along the Central Coast of British Columbia, we showed that the composition of nearshore marine DOC and POC pools vary seasonally, oscillating between freshwater and marine influences, with consequences for the carbon balance and trophic dynamics in coastal surface waters. This seasonal fluctuation was mimicked over much shorter time scales by the ebb and flow of rainfall events, which define the coastal temperate rainforest, and were essential in establishing and maintaining a connection between land and sea throughout the year. Particularly in summer, when rainfall occurred less frequently, these events may have instigated a critical change in surface waters, increasing the availability of terrestrially derived OC, which in turn, may have subsidized marine bacteria, an important trophic shift during a season otherwise characterized by elevated marine primary production. These results highlight the value and importance of year-round sampling in more remote locations to provide a comprehensive understanding of the biogeochemistry and ecology of dynamic coastal environments.

Data availability statement

All hydrological, and carbon chemistry data associated with the routine monthly and targeted rainfall events are publicly available in Korver et al. (2019) and Oliver et al. (2020), respectively, through the Metadata Portal at https://hecate.hakai.org.

References

Abril, G., M. Nogueira, H. Etcheber, G. Cabeçadas, E. Lemaire, and M. J. Brogueira. 2002. Behaviour of organic carbon in nine contrasting European estuaries. Estuar. Coast. Shelf Sci. 54: 241–262. doi:10.1016/ecs.2001.0844

Alaback, P. B. 1996. Biodiversity patterns in relation to climate: The coastal temperate rainforests of North America, p. 105–133. In R. G. Lawford, E. Fuentes, and P. B. Alaback [eds.], High-latitude rainforests and associated ecosystems of the west coast of the Americas: Climate, hydrology, ecology, and conservation. Springer.

Arimitsu, M. L., K. A. Hobson, D. A. N. Webber, J. F. Piatt, E. W. Hood, and J. B. Fellman. 2018. Behaviour biogeochemical subsidies from glacier runoff into Alaska’s coastal marine food webs. Glob. Chang. Biol. 24: 387–398. doi:10.1111/gcb.13875

Asmala, E., D. G. Bowers, R. Autio, H. Kaartokallio, and D. N. Thomas. 2014. Qualitative changes of riverine dissolved organic matter at low salinities due to flocculation. J. Geophys. Res. Biogeosci. 119: 1919–1933. doi:10.1002/2014JG002722

Barber, A., M. Sirois, G. Chaillou, and Y. Gélinas. 2017. Stable isotope analysis of dissolved organic carbon in Canada’s eastern coastal waters. Limnol. Oceanogr. 62: S71–S84. doi: 10.1002/ino.10666

Bates, D., M. Maechler, B. Bolker, and S. Walker. 2015. Fitting linear mixed-effects models using lme4. J. Stat. Softw. 67: 1–48. doi:10.18637/jss.v067.i01

Bauer, J. E., W.-J. Cai, P. A. Raymond, T. S. Bianchi, C. S. Hopkinson, and P. A. G. Regnier. 2013. The changing carbon cycle of the coastal ocean. Nature 504: 61–70. doi:10.1038/nature12857

Bianchi, T. S., and others. 2019. Enhanced transfer of terrestrially derived carbon to the atmosphere in a flooding event. Geophys. Res. Lett. 40: 116–122. doi:10.1029/2012GL054145

Billen, G., and J. Garnier. 2007. River basin nutrient delivery to the coastal sea: Assessing its potential to sustain new production of non-siliceous algae. Mar. Chem. 106: 148–160. doi:10.1016/j.marchem.2006.12.017

Borcard, D., F. Gillet, and P. Legendre. 2011. Numerical ecology with R. Springer.

Carmack, E., P. Winsor, and W. Williams. 2015. The contiguous panarctic riverine coastal domain: A unifying concept. Prog. Oceanogr. 139: 13–23. doi:10.1016/j.pocean.2015.07.014
Cauwet, G. 2002. Chapter 12 - DOM in the coastal zone, p. 579–609. In D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter. Academic Press.

Cifuentes, L. A., and P. M. Eldridge. 1998. A mass- and isootope-balance model of DOC mixing in estuaries. Limnol. Oceanogr. 43: 1872–1882. doi:10.4319/lo.1998.43.8.1872

Clark, C. D., L. P. Litz, and S. B. Grant. 2008. Saltmarshes as a source of chromospheric dissolved organic matter (CDOM) to Southern California coastal waters. Limnol. Oceanogr. 53: 1923–1933. doi:10.4319/lo.2008.53.5.1923

Crump, B. C., J. A. Baross, and C. A. Simonstad. 1998. Dominance of particle-attached bacteria in the Columbia River Estuary, USA. Aquat. Microb. Ecol. 14: 7–18. doi:10.3354/ame014007

Dai, M., Z. Yin, F. Meng, Q. Liu, and W.-J. Cai. 2012. Spatial distribution of riverine DOC inputs to the ocean: An updated global synthesis. Curr. Opin. Environ. Sustain. 4: 170–178. doi:10.1016/j.cosust.2012.03.003

Fellman, J. B., D. V. D’Amore, E. Hood, and R. D. Boone. 2008. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. Biogeochemistry 88: 169–184. doi:10.1007/s10533-008-9203-x

Fellman, J. B., E. Hood, D. V. D’Amore, R. T. Edwards, and D. White. 2009a. Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. Biogeochemistry 95: 277–293. doi:10.1007/s10533-009-9336-6

Fellman, J. B., E. Hood, R. T. Edwards, and D. V. D’Amore. 2009b. Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. J. Geophys. Res. Biogeoosci. 114: G01021. doi:10.1029/2008JG000790

Fellman, J. B., E. Hood, R. T. Edwards, and J. B. Jones. 2009c. Uptake of allochthonous dissolved organic matter from soil and salmon in coastal temperate rainforest streams. Ecosystems 12: 747–759. doi:10.1007/s10021-009-9254-4

Goñi, M. A., J. A. Hatten, R. A. Wheatcroft, and J. C. Borgeld. 2013. Particulate organic matter export by two contrasting small mountainous rivers from the Pacific Northwest, U.S.A. J. Geophys. Res. Biogeoosci. 118: 112–134. doi:10.1002/jgrg.20024

Grossart, H.-P., K. W. Tang, T. Kjørboe, and H. Ploug. 2007. Comparison of cell-specific activity between free-living and attached bacteria using isolates and natural assemblages. FEMS Microbiol. Lett. 266: 194–200. doi:10.1111/j.1574-6968.2006.00520.x

Halverson, M., and others. 2017. Guidelines for processing RBR CTD profiles. Can. Tech. Rep. Hydrogr. Ocean Sci. 314. p. iv + 38.

Hansen, A. M., T. E. C. Kraus, B. A. Pellerin, J. A. Fleck, B. D. Downing, and B. A. Bergamaschi. 2016. Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation. Limnol. Oceanogr. 61: 1015–1032. doi:10.1002/lno.10270

Harding, J. M. S., and J. D. Reynolds. 2014. From earth and ocean: Investigating the importance of cross-ecosystem resource linkages to a mobile estuarine consumer. Ecosphere 5: 54. doi:10.1890/ES14-00029.1

Hatten, J. A., M. A. Goñi, and R. A. Wheatcroft. 2012. Chemical characteristics of particulate organic matter from a small, mountainous river system in the Oregon Coast Range, USA. Biogeochemistry 107: 43–66. doi:10.1007/s10533-010-9529-z

Helms, J. R., A. Stubbins, J. D. Ritchie, E. C. Minor, D. J. Kieber, and K. Mopper. 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnol. Oceanogr. 53: 955–969. doi:10.4319/lo.2008.53.3.0955

Hernes, P. J., B. A. Bergamaschi, R. S. Eckard, and R. G. M. Spencer. 2009. Fluorescence-based proxies for lignin in freshwater dissolved organic matter. J. Geophys. Res. Biogeoosci. 114: G00F03. doi:10.1029/2009JG000938

Hill, J. K., and P. A. Wheeler. 2002. Organic carbon and nitrogen in the northern California current system: Comparison of offshore, river plume, and coastal upwelled waters. Prog. Oceanogr. 53: 369–387. doi:10.1016/S0079-6611(02)00307-X

Hitchcock, J. N., S. M. Mitrovic, W. L. Hadwen, D. L. Roelke, I. O. Growns, and A.-M. Rohlfs. 2016. Terrestrial dissolved organic carbon subsidizes estuarine zooplankton: An in situ mesocosm study. Limnol. Oceanogr. 61: 254–267. doi:10.1002/lno.10207

Hodal, M. 2010. Net physical transports, residence times, and new production for rivers inlet, British Columbia. M.Sc. thesis. Univ. of British Columbia.

Hood, E., M. N. Gooseff, and S. L. Johnson. 2006. Changes in the character of stream water dissolved organic carbon export.
during flushing in three small watersheds, Oregon. J. Geophys. Res. Biogeosci. 111: G01007. doi:10.1029/2005JG000082

Hunt, B. P. V., J. M. Jackson, J. Del Bel Belluz, and J. Barrette. 2018. Hakai oceanography program: British Columbia central coast time series (2012–2017), p. 33–37. In P. C. Chandler, S. A. King, and J. Boldt [eds.], State of the physical, biological and selected fishery resources of Pacific Canadian marine ecosystems in 2017, Fisheries and Oceans Canada.

Jackson, J. M., R. E. Thomson, L. N. Brown, P. G. Willis, and G. A. Borstad. 2015. Satellite chlorophyll off the British Columbia Coast, 1997–2010. J. Geophys. Res. Oceans 120: 4709–4728. doi:10.1002/2014JC010496

Jørgensen, L., C. A. Stedmon, T. Kragh, S. Markager, M. Middelboe, and M. Søndergaard. 2011. Global trends in the fluorescence characteristics and distribution of marine dissolved organic matter. Mar. Chem. 126: 139–148. doi:10.1016/j.marchem.2011.05.002

Kirchman, D. L. 2016. Growth rates of microbes in the oceans. Ann. Rev. Mar. Sci. 8: 285–309. doi:10.1146/annurev-marine-122414-033938

Knap, A. A., A. Michaels, H. Close, H. Ducklow, and A. Dickson. 1996. Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements, p. 170, UNESCO. Reprint of the IOC manuals and guides no. 29.

Kohn, M. J. 2010. Carbon isotope compositions of terrestrial C3 plants as indicators of (paleo)ecology and (paleo)climate. Proc. Natl. Acad. Sci. USA 107: 19691–19695. doi:10.1073/pnas.1004933107

Korver, M. C., W. C. Floyd, and R. Brunsting. 2019. Observed stream flow from seven small coastal watersheds in British Columbia, Canada, version 3. Hakai Institute.

Kothawala, D. N., C. A. Stedmon, R. A. Müller, G. A. Weyhenmeyer, S. J. Köhler, and L. J. Tranvik. 2014. Controls of dissolved organic matter quality: Evidence from a large-scale boreal lake survey. Glob. Chang. Biol. 20: 1101–1114. doi:10.1111/gcb.12488

Lalonde, K., P. Middlestead, and Y. Gélinas. 2014. Automation of $^{13}C$/$^{12}C$ ratio measurement for freshwater and seawater DOC using high temperature combustion. Limnol. Oceanogr.: Methods 12: 816–829. doi:10.4319/lom.2014.12.816

Lankiewicz, T. S., M. T. Cottrell, and D. L. Kirchman. 2016. Growth rates and rRNA content of four marine bacteria in pure cultures and in the Delaware estuary. ISME J. 10: 823–832. doi:10.1038/ismej.2015.156

Lenth, R. V. 2016. Least-squares means: The R package lsmeans. J. Stat. Softw. 69: 1–33. doi:10.18637/jss.v069.i01

Lorenz, D., R. Runkel, and L. De Cicco. 2015. Roadnet: River load estimation. U.S. Geological Survey.

Maie, N., N. M. Scully, O. Pisani, and R. Jaffé. 2007. Composition of a protein-like fluorophore of dissolved organic matter in coastal wetland and estuarine ecosystems. Water Res. 41: 563–570. doi:10.1016/j.watres.2006.11.006

McCowen, C. J., and others. 2017. A global map of saltmarshes. Biodivers. Data J. 5: e11764. doi:10.3897/BDJ.5.e11764

McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46: 38–48. doi:10.4319/lo.2001.46.1.0038

Niccoli, G., and others. 2019. Large, climate-sensitive soil carbon stocks mapped with pedology-informed machine learning in the North Pacific coastal temperate rainforest. Environ. Res. Lett. 14: 014004. doi:10.1088/1748-9326/aaed52

Meinhard, S., H.-P. Grossart, B. Schweitzer, and H. Ploug. 2002. Microbial ecology of organic aggregates in aquatic ecosystems. Aquat. Microb. Ecol. 28: 175–211. doi:10.3354/ame028175

Murphy, K. R., C. A. Stedmon, T. D. Waite, and G. M. Ruiz. 2008. Distinguishing between terrestrial and autochthonous organic matter sources in marine environments using fluorescence spectroscopy. Mar. Chem. 108: 40–58. doi:10.1016/j.marchem.2007.10.003

Murphy, K. R., C. A. Stedmon, D. Graeber, and R. Bro. 2013. Fluorescence spectroscopy and multi-way techniques. Anal. Methods 5: 6557–6566. doi:10.1039/C3AY4116E0

Murphy, K. R., C. A. Stedmon, P. Wenig, and R. Bro. 2014. OpenFluor– an online spectral library of auto-fluorescence by organic compounds in the environment. Anal. Methods 6: 658–661. doi:10.1039/C3AY41935E

Najjar, R. G., and others. 2018. Carbon budget of tidal wetlands, estuaries, and shelf waters of eastern North America. Global Biogeochem. Cycles 32: 389–416. doi:10.1002/2017GB005790

Ohno, T. 2002. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. Environ. Sci. Technol. 36: 742–746. doi:10.1021/es0155276

Oksanen, J., and others. 2018. Package ‘vegan’, ordination methods, diversity analysis and other functions for community and vegetation ecologists.

Olver, A. A., and others. 2017. A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia. Biogeosciences 14: 3743–3762. doi:10.5194/bg-14-3743-2017

Olver, A. A., and others. 2020. Dissolved and particulate organic carbon chemistry for freshwater and marine stations from 2014 through 2016 on Calvert and Hecate Islands, British Columbia, Canada, version 1.0. Hakai Institute.

Pacific Climate Impacts Consortium. 2019. Summary of climate change for central coast in the 2080s. Univ. of Victoria.

Parlanti, E., K. Worz, L. Geoffroy, and M. Lamotte. 2000. Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. Org. Geochem. 31: 1765–1781. doi:10.1016/S0146-6380(00)00124-8

Pinheiro, J., D. Bates, S. DebRoy, D. Sarkar, and R. C. Team. 2017. nlme: Linear and nonlinear mixed effects models. Available from https://cran.r-project.org/web/packages/nlme/index.html

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St. Pierre et al. Land–ocean interface carbon dynamics

R Development Core Team. 2016. R: A language and environment for statistical computing. R Foundation for Statistical Computing.

Radic, V., A. J. Cannon, B. Menounos, and N. Gi. 2015. Future changes in autumn atmospheric river events in British Columbia, Canada, as projected by CMIPS global climate models. J. Geophys. Res. Atmos. 120: 9279–9302. doi:10.1002/2015JD023279

Shiller, V. J. 2012. Spring and summer phytoplankton community dynamics and comparison of FRRF- and 13C-derived measurements of primary productivity in rivers inlet, British Columbia. M.Sc. thesis. Univ. of British Columbia.

Sholkovitz, E. R. 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochim. Cosmochim. Acta 40: 831–845. doi:10.1016/0016-7037(76)90035-1

Sholkovitz, E. R., E. A. Boyle, and N. B. Price. 1978. The removal of dissolved humic acids and iron during estuarine mixing. Earth Planet. Sci. Lett. 40: 130–136. doi:10.1016/0012-821X(78)90082-1

Shutova, Y., A. Baker, J. Bridgeman, and R. K. Henderson. 2014. Spectroscopic characterisation of dissolved organic matter changes in drinking water treatment: From PARAFAC analysis to online monitoring wavelengths. Water Res. 54: 159–169. doi:10.1016/j.watres.2014.01.053

Spencer, R. G. M., and others. 2009. Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. J. Geophys. Res. Biogeosci. 114: G03010. doi:10.1029/2009JG000968

Stedmon, C. A., and S. Markager. 2005. Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis. Limnol. Oceanogr. 50: 686–697. doi:10.4319/lo.2005.50.2.0686

Stedmon, C. A., and R. Bro. 2008. Characterizing dissolved organic matter fluorescence with parallel factor analysis: A tutorial. Limnol. Oceanogr.: Methods 6: 572–579. doi:10.4319/lom.2008.6.572

Stedmon, C. A., D. N. Thomas, S. Papadimitriou, M. A. Granskog, and G. S. Dieckmann. 2011. Using fluorescence to characterize dissolved organic matter in Antarctic Sea ice brines. J. Geophys. Res. Biogeosci. 116: G03027. doi:10.1029/2011JG001716

St-Jean, G. 2003. Automated quantitative and isotopic (13C) analysis of dissolved inorganic carbon and dissolved organic carbon in continuous-flow using a total organic carbon analyser. Rapid Commun. Mass Spectrom. 17: 419–428. doi:10.1002/rcm.926

Stuermer, D. H., K. E. Peters, and I. R. Kaplan. 1978. Source indicators of humic substances and proto-kerogen. Stable isotope ratios, elemental compositions and electron spin resonance spectra. Geochim. Cosmochim. Acta 42: 989–997. doi:10.1016/0016-7037(78)90288-0

Thompson, S. D., T. A. Nelson, I. Giesbrecht, G. Frazer, and S. C. Saunders. 2016. Data-driven regionalization of forested and non-forested ecosystems in coastal British Columbia with LiDAR and RapidEye imagery. Appl. Geogr. 69: 35–50. doi:10.1016/j.apgeog.2016.02.002

Thomson, R. E., M. Heesemann, E. E. Davis, and R. A. S. Hourston. 2014. Continental microseismic intensity delineates oceanic upwelling timing along the west coast of North America. Geophys. Res. Lett. 41: 6872–6880. doi:10.1002/2014GL061241

Thrash, J. C., J. L. Weckhorst, and D. M. Pitre. 2017. Cultivating fastidious microbes, p. 57–78. In T. J. McGinity, K. N. Timmis, and B. Nogales [eds.], Hydrocarbon and lipid microbiology protocols: Isolation and cultivation. Springer.

Timothy, D. A., and M. Y. S. Soon. 2001. Primary production and deep-water oxygen content of two British Columbian fjords. Mar. Chem. 73: 37–51. doi:10.1016/S0304-4203(00)00071-2

Tipping, E., M. Fröberg, D. Berggren, J. Mulder, and B. Bergkvist. 2005. DOC leaching from a coniferous forest floor: Modeling a manipulation experiment. J. Plant Nutr. Soil Sci. 168: 316–324. doi:10.1111/j.1365-2486.2004.21645

Tranvik, L. J., and J. M. Sieburth. 1989. Effects of flocculated humic matter on free and attached pelagic microorganisms. Limnol. Oceanogr. 34: 688–699. doi:10.4319/lo.1989.34.4.0688

Venables, W. N., and B. D. Ripley. 2002. Modern applied statistics with S, 4th ed. Springer.

Wainright, S. C. 1987. Stimulation of heterotrophic microplankton production by resuspended marine sediments. Science 238: 1710–1712. doi:10.1126/science.238.4834.1710

Winkler, J., and A. Andersson. 2012. Increased freshwater discharge shifts the trophic balance in the coastal zone of the northern Baltic Sea. Glob. Chang. Biol. 18: 2509–2519. doi:10.1111/j.1365-2486.2012.02718.x

Wilson, H. F., and M. A. Xenopoulos. 2009. Effects of agricultural land use on the composition of fluvial dissolved organic matter. Nat. Geosci. 2: 37–41. doi:10.1038/ngeo391

Windham-Meyers, L., and others. 2018. Chapter 15: Tidal wetlands and estuaries, p. 596 43. In N. G. Cavallero and others. [eds.], Second state of the carbon cycle report (SOCCR2): A sustained assessment report. U.S. Global Change Research Program.

Xenopoulos, M. A., and others. 2003. Regional comparisons of watershed determinants of dissolved organic carbon in temperate lakes from the Upper Great Lakes region and selected regions globally. Limnol. Oceanogr. 48: 2321–2334. doi:10.4319/lo.2003.48.6.2321

Yokokawa, T., T. Nagata, M. T. Cottrell, and D. L. Kirchman. 2004. Growth rate of the major phylogenetic bacterial groups in the Delaware estuary. Limnol. Oceanogr. 49: 1620–1629. doi:10.4319/lo.2004.49.5.1620

Yu, F., and others. 2010. Bulk organic C and C/N as indicators for sediment sources in the Pearl River delta and estuary, southern China. Estuar. Coast. Shelf Sci. 87: 618–630. doi:10.1016/j.ecss.2010.02.018

Yu, H., and others. 2015. Impact of dataset diversity on accuracy and sensitivity of parallel factor analysis model of...
dissolved organic matter fluorescence excitation-emission matrix. Sci. Rep. 5: 10207. doi:10.1038/srep10207

Acknowledgments
We thank field and support staff from the Hakai Institute for data collection and management. In particular, Bryn Fedje coordinated much of the field sampling, Isabelle Desmarais ran the flocculation experiments, Ray Brunsting supported the collection and management of rainfall and discharge data, Justin Del Bel Belluz managed the chlorophyll data, and Keith Holmes produced Fig. 1. We gratefully acknowledge that this work took place on the traditional territories of the Heiltsuk and Wuikinuxv First Nations. This work was funded by the Tula Foundation, Hakai Institute, and Campus Alberta Innovates Program (CAIP).

Conflict of Interest
None declared.

Submitted 06 August 2019
Revised 04 March 2020
Accepted 17 May 2020

Associate editor: Peter Hernes