

Salmon influences on dissolved organic matter in a coastal temperate brown-water stream: An application of fluorescence spectroscopy

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Abstract

We examined how spawning Pacific salmon (genus *Oncorhynchus*) affect streamwater concentrations of inorganic nitrogen and phosphorus and dissolved organic matter in Peterson Creek, a stream in southeast Alaska. When spawning salmon were present, concentrations of ammonium (NH₄-N) increased by more than 100 times over prespawning levels and concentrations of soluble reactive phosphorus increased by more than an order of magnitude. In contrast, concentrations of nitrate (NO₃-N) increased by only two to three times during spawning and were not significantly higher than at an upstream reference site with no salmon. During spawning, concentrations of dissolved organic carbon and dissolved organic nitrogen were significantly higher in the spawning reach compared with the upstream reference site. The influx of salmon-derived dissolved organic matter (DOM) altered the fluorescence index (FI), which has previously been used to distinguish between terrestrial and aquatic sources of DOM, with the FI increasing significantly during the salmon run. Salmon DOM was rich in protein compared with the DOM derived from the terrestrial portion of the watershed. Spawning salmon may be an important source of labile DOM in Peterson Creek.

Southeastern Alaska contains over 4,000 salmon streams (Halupka et al. 2002). These streams serve as conduits through which nutrients derived from marine ecosystems are returned to terrestrial and freshwater aquatic ecosystems. Salmon returning to spawn in their natal streams release nutrients to aquatic ecosystems through several pathways including excretion across gill membranes, leaching from gametes, and leaching from decaying carcasses (Gende et al. 2002). These salmon-derived nutrients (SDN) have previously been shown to increase chlorophyll standing stocks (Johnston et al. 2004; Mitchell and Lamberti 2005) and the density and growth rates of invertebrates and fish in streams (Bilby et al. 1998; Chaloner and Wipfli 2002).

Many previous studies of SDN in aquatic ecosystems have focused on levels of inorganic nutrients (N and P),

because N and P often limit primary productivity in freshwater ecosystems. However, SDN occur predominantly in organic forms (Compton et al. 2006) and salmon carcasses are an important source of organic matter in coastal streams (Bilby et al. 1996; Cederholm et al. 1999). As a result, salmon have the potential to deliver large quantities of dissolved organic matter (DOM) to aquatic ecosystems in spawning streams. DOM affects both the physical and chemical characteristics of aquatic ecosystems and is often the dominant source of carbon and energy for heterotrophic production (Wetzel 1995). Most DOM in freshwater ecosystems is derived from vegetation and soil organic matter in the terrestrial system. This terrestrial DOM is typically dominated by humic and fulvic acids, which are relatively recalcitrant and have a low N content. Because salmon carcasses have a much lower C:N ratio (~4:1; Johnston et al. 2004) than terrestrial vegetation in temperate coniferous forests (>60:1; Prescott et al. 2000), carcasses have the potential to contribute a pulse of relatively nitrogen-rich, labile DOM to streams during the spawning season.

The chemical composition of DOM determines its optical properties; therefore spectroscopic measurements can be used to identify different fractions of DOM in natural waters. Fluorescence spectroscopy has been used in a variety of watershed-scale studies to trace changes in the DOM pool and to fingerprint DOM source or precursor material (Hood et al. 2003; Stedmon et al. 2003; Baker and Spencer 2004). For example, Stedmon et al. (2003) demonstrated that the fluorescence characteristics of DOM derived from forested and agricultural streams were

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dramatically different from the fluorescence characteristics of DOM produced in the downstream estuary. Fluorescence intensity associated with the presence of proteins in the aquatic DOM pool has also been used to distinguish DOM from anthropogenic and natural terrestrial sources (Baker and Spencer 2004).

The purpose of this study was to evaluate the magnitude and timing of the contribution of spawning salmon to streamwater concentrations of DOM (as dissolved organic carbon [DOC] and nitrogen [DON]) and inorganic nutrients in a coastal stream in southeastern Alaska. In addition, we use fluorescence spectroscopy to investigate changes in the chemical composition of the aquatic DOM pool associated with inputs of DOM released from spawning salmon.

Methods

Site description—Sampling was conducted in Peterson Creek, about 50 km north of Juneau, Alaska. The area has a maritime climate with a mean annual temperature of 4.9°C and mean annual precipitation of 1,430 mm, much of which falls in autumn (September–November). Peterson Creek is a brownwater stream located within the glacio-marine terrace subsection of the Tongass National Forest (Nowacki et al. 2001). The lower reaches of the watershed are uplifted marine terraces with some colluvial and alluvial sediments. The underlying bedrock is marine graywacke sandstone and mudstone turbidites (Gehrels 2000). Streamflow in Peterson Creek typically peaks during the autumn rainy season and reaches a minimum during the early spring (March–April). Fifty three percent of the 25 km² watershed area is covered by wetlands, which input large amounts of soil-derived DOC. Annual DOC concentrations range from 4 to 15 mg L⁻¹ C, with concentrations low in spring and peaking during the autumnal discharge maximum. Peterson Creek has low pH typical of many humic streams, with pH values ranging from 4.9 to 5.6.

We sampled two sites in the Peterson Creek watershed (Fig. 1). The upstream site (Upper Peterson) is above a barrier waterfall that blocks spawning salmon, whereas the downstream site (Lower Peterson) receives spawning runs of *Oncorhynchus gorbushcha* (pink salmon), *Oncorhynchus keta* (chum salmon), and *Oncorhynchus kisutch* (coho salmon) in the late summer and autumn (July–September). The maximum wet mass of the Peterson Creek salmon run has been estimated at >200,000 kg (Bethers et al. 1993) and previously measured spawner densities range from 0 to 0.53 fish m⁻² (Mitchell and Lamberti 2005). During this study, salmon were first observed at the site on the 02 August sampling date and the majority of carcasses were washed downstream from the site by 03 September. Salmon returns in southeast Alaska were relatively average in 2004 and the total annual commercial harvest of all salmon in southeast Alaska for 2004 was slightly below the 10-yr average (Alaska Department of Fish and Game 2005). Although Peterson Creek supports large salmon runs, carcass densities during 2004 were not unusually high on the basis of single day counts at the same location within the creek. The average carcass density on Peterson Creek

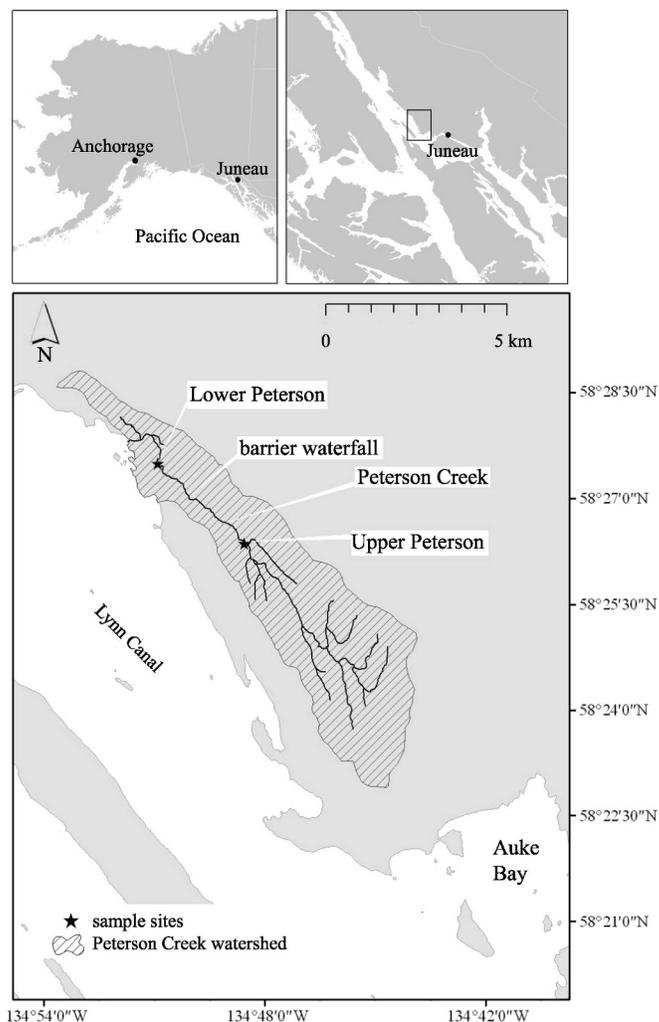


Fig. 1. Map showing the location of Peterson Creek in southeast Alaska. Streamwater samples were collected at sites above (Upper Peterson) and below (Lower Peterson) a barrier waterfall for spawning salmon.

for 2004 was 1.3 kg m⁻² of salmon carcass compared with 3.5 and 1.6 kg m⁻² in 2001 and 2005 respectively (D. Chaloner pers. comm.).

Field and laboratory methods—Water grab samples were collected at the two sites on Peterson Creek during June–October 2004. Samples were collected approximately twice per month until the beginning of the spawning season in late July, when samples were collected two to three times per week at the lower salmon-influenced site. Samples were collected only once per week at the upper site because of logistical constraints and the frequent presence of bears along the trail. At both sites, three replicates were collected for inorganic nutrient and DOM analyses. Water samples were filtered in the field using Whatman GF/F glass fiber filters (0.7 μm) and frozen until analysis, which occurred within 2 weeks after sample collection.

Concentrations of DOC in streamwater samples were determined by high-temperature catalytic oxidation using a Shimadzu TOC-V organic carbon and total nitrogen

analyzer with detection limits of $0.5 \text{ mg L}^{-1} \text{ C}$ for DOC and $0.1 \text{ mg L}^{-1} \text{ N}$ for total dissolved nitrogen. Nitrate nitrogen ($\text{NO}_3\text{-N}$) was measured on a Dionex ion chromatograph (IC) with a detection limit of $0.01 \text{ mg L}^{-1} \text{ N}$. Ammonium nitrogen ($\text{NH}_4\text{-N}$) was measured with a fluorometric technique following the procedure of Holmes et al. (1999) with a detection limit of $0.01 \text{ mg L}^{-1} \text{ N}$ except for during spawning when ammonium was measured on a Dionex IC. Soluble reactive phosphorus (SRP) was analyzed using the ascorbic acid method (Murphy and Riley 1962) with a 10-cm quartz flow-through cell (lower detection $1.0 \text{ } \mu\text{g L}^{-1} \text{ P}$).

Fluorescence properties were measured on streamwater DOM and DOM from two catchment sources: salmon carcasses and wetland soils. Salmon DOM from six salmon was analyzed after leaching individual fresh pink and chum salmon carcasses from Peterson Creek in deionized water for several hours followed by filtration with Whatman GF/F filters. We did not differentiate between male and female pink and chum salmon because the chemical composition (percentage of lipid and protein, N content, and P content) of salmon tissue from these species is very similar and varies little between males and females (Gende et al. 2004). Wetland soil DOM was collected from a zero-tension lysimeter at 25 cm depth in a peatland within the watershed and analyzed on 12 dates corresponding with sample collection at Upper Peterson. Fluorescence was characterized on a fluoromax-3 (Jobin Yvon Horiba) fluorometer with a xenon lamp. Fluorescence excitation–emission matrices (EEMs) were created by measuring fluorescence intensity across excitation wavelengths ranging from 240 to 450 nm at 5-nm increments and emission wavelengths ranging from 300 to 600 nm at 2-nm increments following the procedures of Cory and McKnight (2005). Filtered samples were allowed to warm to room temperature before optical analysis. Because of high concentrations of DOM, samples were first diluted to avoid inner filter effects. EEMs of MilliQ water, run on the same day and within the same cuvette as the sample, were subtracted from each EEM. Emission and excitation correction files generated by the manufacturer were used to correct instrument bias within the EEMs. Finally, the fluorescence spectra were Raman normalized using the area under the water Raman peak at excitation wavelength 350 nm. The fluorescence index (FI) was calculated as the ratio of the emission intensity at 450 nm to that at 500 nm produced with excitation at 370 nm following the procedures of McKnight et al. (2001). The standard deviation of samples analyzed in triplicate for the FI was typically less than 0.01.

Statistical analyses were done in SPSS (Systat Inc.). All *t*-tests for DOM and nutrient concentrations were for unpaired variances on log-transformed data. The *t*-test for the FI data was for unpaired variances on data that were not log-transformed.

Results

Inorganic nutrient concentrations—Inorganic nutrient concentrations were low before the arrival of spawning salmon in late July at both the upstream and downstream

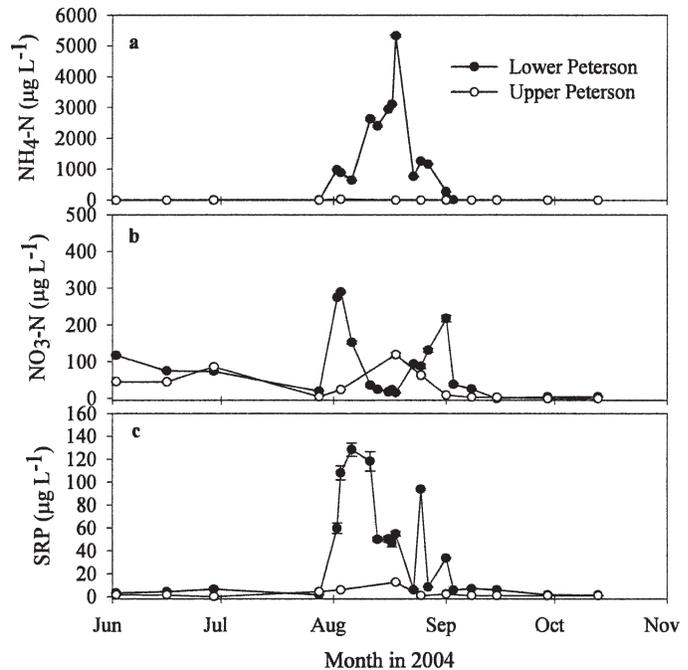


Fig. 2. Mean surface water concentrations (± 1 SE) of (a) $\text{NH}_4\text{-N}$, (b) $\text{NO}_3\text{-N}$, and (c) SRP during the period June–October, 2004. Note the difference in scale between panels.

sites. Concentrations of $\text{NO}_3\text{-N}$ were typically less than $100 \text{ } \mu\text{g L}^{-1}$, whereas concentrations of $\text{NH}_4\text{-N}$ and SRP were consistently less than $20 \text{ } \mu\text{g L}^{-1}$ at both sites (Fig. 2). After spawning salmon arrived at the beginning of August, concentrations of inorganic N and P increased dramatically at the Lower Peterson site. Concentrations of $\text{NH}_4\text{-N}$ increased by more than 100 times and concentrations of SRP increased by more than an order of magnitude compared with prespawning levels at the lower site. Both $\text{NH}_4\text{-N}$ and SRP remained elevated throughout the salmon spawning period. In contrast, concentrations of $\text{NO}_3\text{-N}$ increased by only two to three times and showed two distinct peaks near the beginning and end of the salmon spawning period. At the Upper Peterson site, concentrations of inorganic N and P remained largely unchanged during the salmon spawning period. After most salmon carcasses were flushed from the watershed in early September, inorganic N and P concentrations at both sites decreased to prespawning levels.

For the entire spawning period, concentrations of ammonium (*t*-test; $p = 0.002$) and SRP ($p < 0.001$) were significantly higher at Lower Peterson compared with Upper Peterson (Fig. 3). In contrast, there was not a significant difference in concentrations of nitrate ($p = 0.2$) between the two sites (Fig. 3).

DOM concentrations and characterization—Streamwater concentrations of DON increased from less than $0.1 \text{ mg L}^{-1} \text{ N}$ in June to $0.4 \text{ mg L}^{-1} \text{ N}$ in October (Fig. 4a). During the same period, concentrations of DOC increased from less than $2 \text{ mg L}^{-1} \text{ C}$ to greater than $10 \text{ mg L}^{-1} \text{ C}$ (Fig. 4b). Outside of the spawning period, concentrations of DON and DOC were similar at Upper and Lower

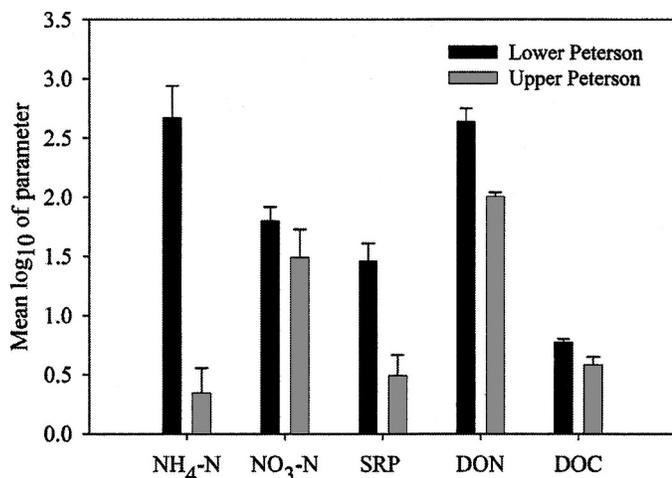


Fig. 3. Mean log₁₀ concentrations (± 1 SE) of NH₄-N, NO₃-N, SRP, DON, and DOC during salmon spawning above (Upper Peterson) and below (Lower Peterson) the barrier waterfall. All concentrations are in micrograms per liter except DOC, which is in milligrams per liter.

Peterson. During spawning, DON concentrations were more than 1 mg N L⁻¹ higher and DOC concentrations were more than 5 mg C L⁻¹ higher at the salmon-influenced Lower Peterson site. For the entire spawning period, concentrations of DON (*t*-test, $p < 0.01$) and DOC (*t*-test, $p < 0.05$) were significantly higher at Lower Peterson compared with Upper Peterson (Fig. 3).

Outside of the salmon spawning period, the FI of DOM at both sites was close to the average FI value of DOM leached from wetland soils within the catchment (1.27) during the study (Fig. 4c). When spawning salmon were present, the FI increased by more than 0.1 toward the average FI value for salmon DOM (1.77) at the Lower Peterson site, while the FI at the Upper Peterson site remained close to the average value of wetland soil DOM (1.27). During the whole spawning period, the FI of DOM at Lower Peterson ($n = 14$, mean = 1.38) was significantly higher than the FI of DOM at Upper Peterson ($n = 6$, mean = 1.32, *t*-test, $p < 0.001$).

The fluorescence EEMs for the individual catchment sources of DOC showed pronounced differences. Salmon DOM showed a sharp primary emission peak at an excitation of 275 nm and an emission of 306 nm (Fig. 5). In contrast, the peatland soil DOM had a broader peak at an excitation of < 240 nm and an emission of 450 nm (Fig. 5). The fluorescence EEMs for streamwater DOM at the Lower Peterson site suggest that there was a change in both the source and composition of streamwater DOM during the salmon spawning period. Before the spawning period, EEMs at both the upstream and downstream sites showed a primary peak at an excitation of < 240 nm and an emission of 450–454 nm, similar to the EEM for wetland soil DOM (Fig. 6). During the spawning period, the EEM for DOM at the Lower Peterson site with spawners contained an additional peak at an excitation of 275 nm and an emission of 308 nm. In October, after the end of the

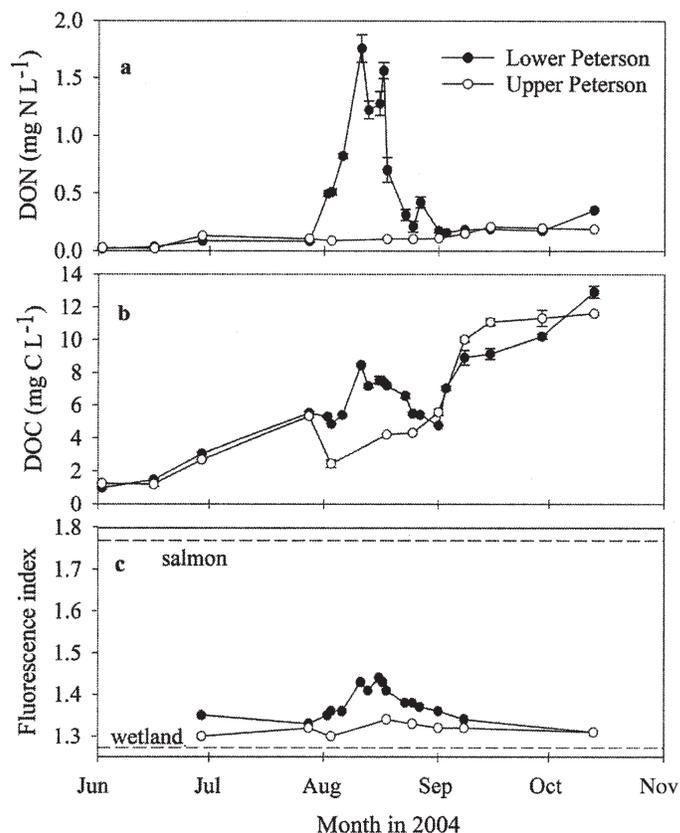


Fig. 4. Mean surface water concentrations (± 1 SE) of (a) DON, (b) DOC, and (c) the fluorescence index of DOC. The average fluorescence index values for DOM from 6 salmon (average = 1.77, SE = 0.02) and DOM from 12 wetland samples (average = 1.27, SE = 0.03) are shown in panel c as dashed lines.

spawning season, EEMs for DOM at both sites were similar to the prespawning period, showing a primary peak at an excitation of < 240 nm and an emission of 450–454 nm.

Discussion

Inorganic nutrients—The maximum concentrations of ammonium (2,000–5,000 $\mu\text{g L}^{-1}$ NH₄-N) and SRP (50–120 $\mu\text{g L}^{-1}$ P) recorded during the spawning season were substantially larger than previously reported increases in streamwater nutrient concentrations during spawning. In studies in Peterson Creek (Chaloner et al. 2004; Mitchell and Lamberti 2005) and in other streams in Alaska, Canada, and the Great Lakes (Sugai and Burrell 1984; Schuldt and Hershey 1995; Minakawa and Gara 1999; Johnston et al. 2004; R. T. Edwards unpubl. data), streamwater concentrations of NH₄-N associated with salmon spawning did not exceed 300 $\mu\text{g L}^{-1}$ and concentrations of SRP did not exceed 40 $\mu\text{g L}^{-1}$. This large discrepancy could be due in part to the fact that the sampling frequency during spawning in all of these studies was relatively coarse (e.g., monthly to bimonthly) and may have failed to capture the peak in streamwater nutrient concentrations. In addition, concentrations of N and P in

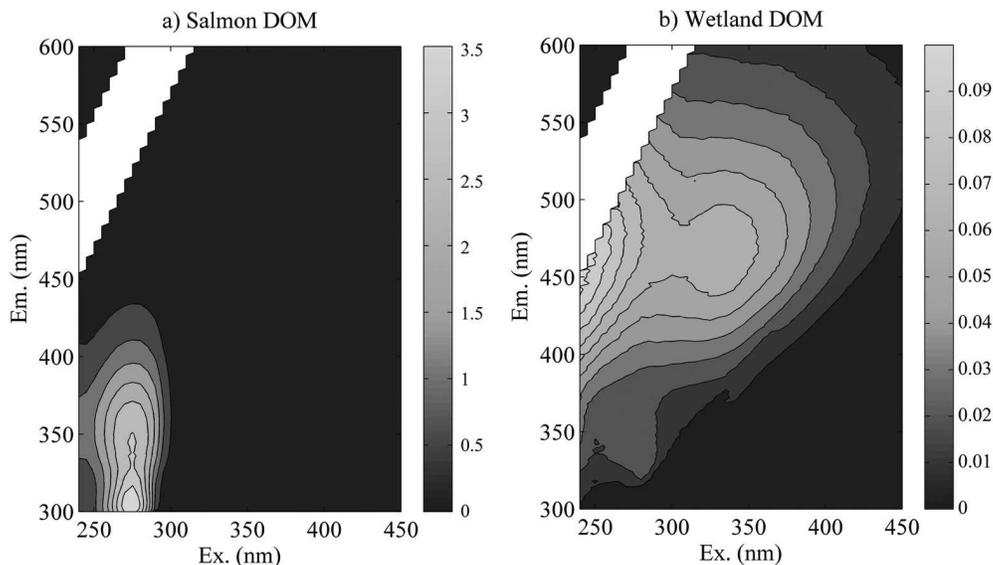


Fig. 5. Fluorescence EEMs for DOM derived from two individual catchment sources: (a) salmon carcasses and (b) wetland soils. Excitation (Ex.) wavelengths range from 250 to 450 nm and emission (Em.) wavelengths range from 300 to 600 nm. Fluorescence intensities are in Raman units.

our study were likely elevated because of drought conditions during the summer of 2004. During the main portion of the spawning period in August, mean discharge in Montana Creek, a 36 km² catchment that borders Peterson Creek to the south, was only 30% of the 20-yr average for that month. Low streamflow can increase salmon-derived nutrient concentrations by two mechanisms: (1) decreased dilution of nutrients leached from fish, and (2) higher retention and longer residence time for carcasses, which are typically flushed out to the estuary during periods of high flow. Because salmon runs in southeastern Alaska and carcass densities in Peterson Creek were not unusually high

in the summer of 2004, the greatly elevated concentrations of N and P that we documented suggest that hydrologic conditions can have a dramatic influence on streamwater nutrient concentrations associated with spawning salmon. In addition, low flow conditions during spawning and associated high streamwater nutrient concentrations may become more common if the climate in southeast Alaska continues its present warming trend. Mean annual temperature in Juneau has increased by more than 1.5°C since 1943 (Motyka et al. 2002) and climate warming has been shown to increase winter streamflows and decrease summer streamflows in this region (Neal et al. 2002).

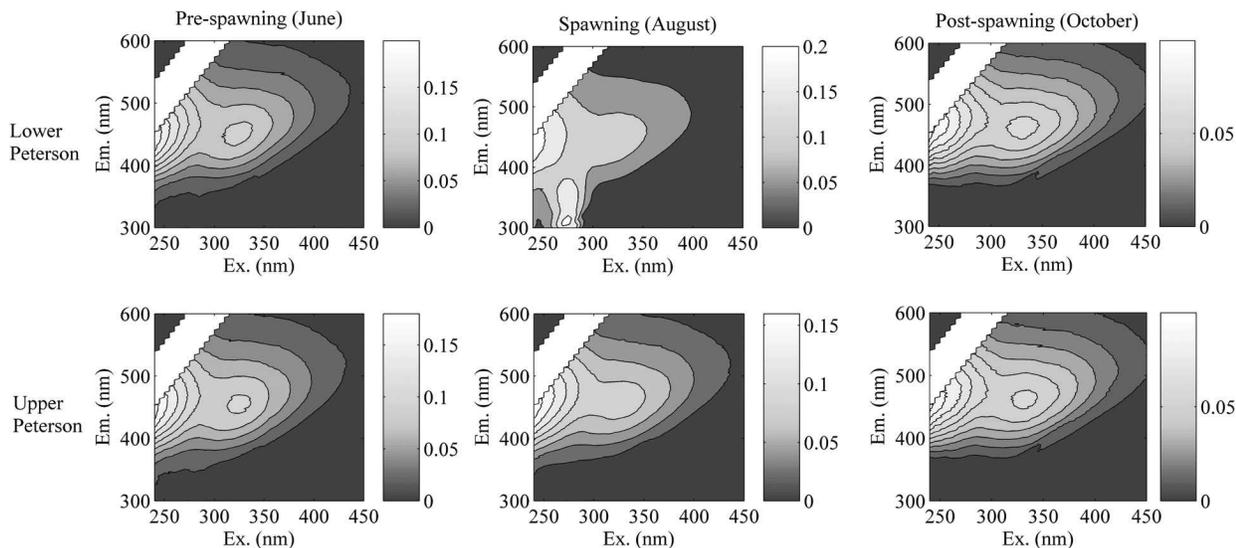


Fig. 6. Fluorescence EEMs for DOM before, during, and after the salmon spawning period at the Upper and Lower Peterson sites. Fluorescence intensities are in Raman units. Excitation (Ex.) wavelengths range from 250 to 450 nm and emission (Em.) wavelengths range from 300 to 600 nm. Fluorescence intensities are in Raman units.

In contrast to $\text{NH}_4\text{-N}$ and SRP, concentrations of $\text{NO}_3\text{-N}$ were not significantly higher at the downstream salmon-influenced site compared with the upstream site on Peterson Creek. These findings agree with the results of Chaloner et al. (2004) and Mitchell and Lamberti (2005), who found that the presence of spawning salmon did not significantly influence concentrations of $\text{NO}_3\text{-N}$ in six southeast Alaska streams. There were, however, two pronounced increases in concentrations of $\text{NO}_3\text{-N}$ at Lower Peterson on either end of the spawning period, suggesting that a small percentage of the streamwater $\text{NH}_4\text{-N}$ was being nitrified. Unlike $\text{NH}_4\text{-N}$ and SRP, concentrations of $\text{NO}_3\text{-N}$ did not remain elevated throughout the spawning season. The sharp decrease in $\text{NO}_3\text{-N}$ concentrations during the middle of August was likely a result of rapid denitrification. Pinay et al. (2003) found that riparian soils in sockeye salmon spawning streams in the Wood River Lakes Region of southwestern Alaska had significantly higher denitrification potential than those in nonsalmon-bearing streams. Denitrification potential was limited by both C and N, which are both supplied by spawning or decaying salmon. Thus it is likely that the drop in nitrate concentrations that we observed during peak spawning was caused when labile C and N from decaying carcasses increased denitrification.

The extent to which streamwater inorganic nutrients leached from salmon are exported downstream of spawning grounds and to estuarine systems largely depends on nutrient retention within the stream. In headwater streams, $\text{NH}_4\text{-N}$ and SRP are removed from the water column predominantly by photosynthetic and heterotrophic organisms and sorption to sediments. Although we did not measure uptake during this study, we did observe a dramatic increase in heterotrophic fungal abundance at and immediately downstream of the spawning grounds at Lower Peterson. During spawning, we documented the occurrence of 2–4-cm thick mats of the water mold *Saprolegnia* spp. that covered almost the entire stream bottom. In the presence of these mats, streamwater dissolved oxygen concentrations fell to less than $2 \text{ mg L}^{-1} \text{ O}_2$, confirming that heterotrophic utilization of salmon-derived carbon was occurring. These findings suggest that in Peterson Creek heterotrophic microbial productivity was an important sink for inorganic nutrients from spawning salmon.

DOM—Concentrations of DOC and DON at both sites were close in magnitude when spawning salmon were not present at the downstream site. DOC and DON concentrations generally increased across the study period at both sites; however, there was a sharp drop in the concentration of DOM at Upper Peterson in early August. This decrease in DOM occurred at the end of a 2-month dry period (June and July) after the end of snowmelt in which precipitation was 65% of normal at the Juneau airport 22 km south of the site. The lowering of the water table in the Peterson Creek watershed during this period likely decreased the hydrological connectivity between wetlands and surface waters. Moreover, the sharp increase in DOC concentrations evident at both sites in early September corresponded

with 8.1 cm of precipitation during a 12-d period, which increased the elevation of the water table in the Peterson Creek riparian zone by 25 cm (E. Hood unpubl. data). Flushing of DOC from wetlands to streams during storms is a commonly observed phenomenon in the wetland-dominated watersheds like Peterson Creek (R. T. Edwards unpubl. data).

During spawning in August, differences in DOM concentrations between our upstream and downstream sites suggest that spawning salmon contributed to an increase of more than 5 mg C L^{-1} as DOC and 1 mg N L^{-1} as DON in streamwater at the Lower Peterson site. As with inorganic nutrients, concentrations of salmon-derived DOM recorded in this study were likely magnified by the low summer discharge in 2004. Reports of the influence of spawning salmon on DON concentrations are rare. However, our finding that DOC concentrations were significantly higher in the spawning reach of Peterson Creek compared with the upstream reach differs from previous studies that have shown no significant increase in DOC associated with spawning salmon (Sugai and Burrell 1984; Chaloner et al. 2004; Mitchell and Lamberti 2005). A study on spawning Chinook salmon in a Lake Ontario stream did find that concentrations of DOC were significantly correlated with salmon carcass density (Sarica et al. 2004). Our results similarly suggest that spawning salmon can contribute substantially to DOM loads in small coastal streams.

The detection of DOM from salmon depends in part on background concentrations of DOM within a watershed. Because Peterson Creek is a brown-water stream that has high ($4\text{--}12 \text{ mg L}^{-1} \text{ C}$) background concentrations of DOC during late summer and early fall, the proportional increase in DOC concentrations associated with spawning salmon was lower than it would have been in a clearwater stream. Abundant wetland soils are the primary source for DOC in Peterson Creek and hydrologic connectivity between these organic soils and the stream is the dominant control on streamwater concentrations of DOC (R. T. Edwards unpubl. data). The high C:N ratio of streamwater DOM outside of the spawning season, which varied from 41 to 67, reflects this wetland source. During the spawning season, DOC:DON ratios decreased to less than 10, reflecting DOM inputs from nitrogen-rich salmon tissue. The C:N ratio of aquatic DOM can be a good indicator of lability, with increasing lability at low C:N and C:P ratios (Sun et al. 1997; Lennon and Pfaff 2005).

The decrease in the C:N ratio of streamwater DOM associated with the presence of spawners indicates that organic material leached from salmon may be an important source of labile DOM within the larger DOM pool in Peterson Creek. Sobczak et al. (2002) have previously shown that the introduction of bioavailable DOC to streamwater enhances nitrate uptake via microbial assimilation. Thus, the introduction of labile DOM from salmon that we documented also has implications for the microbially mediated control of the downstream flux of N in salmon streams. In addition, the biological uptake of labile salmon C is likely the primary pathway by which DOM is converted to particulate organic matter (POM) in Peterson

Creek because brown-water streams typically have low concentrations of divalent cations that mediate the conversion of DOM to POM by physical complexation.

Fluorescence properties of salmon DOM—A change of 0.1 or greater has previously been identified as being indicative of a change in DOM source material (McKnight et al. 2001). The fact that the FI of streamwater DOM increased by greater than 0.1 during spawning suggests that DOM from salmon alters the chemical properties of the DOM pool in streamwater during spawning. The elevated value for the FI of salmon DOM is consistent with previous studies showing that fluorescence properties of DOM are related to lignaceous aromatic compounds in precursor materials such that DOM derived from autochthonous aquatic material lacking lignin has a relatively high FI value (~1.8), whereas DOM derived from allochthonous terrestrial material with lignin has a lower FI value (~1.3; McKnight et al. 2001). The FI has been shown to be effective in tracking changes in the proportion of aquatic (algal) versus terrestrial DOM in streamwater (Hood et al. 2003). Our results suggest that the FI may be a similarly effective tool for identifying the presence of DOM leached from salmon in the bulk streamwater DOM pool. An increase in the FI has also been correlated with a decrease in the aromatic carbon content of aquatic DOM (Cory and McKnight 2005). This suggests that inputs of DOM from salmon decrease the overall aromaticity of the streamwater DOM pool. Decreases in the aromatic carbon content of aquatic DOM have been shown to be strongly correlated with lower C:N ratios (McKnight et al. 1994; Hood et al. 2005). This finding is consistent with our observation that the FI of DOM increased and the C:N ratio of DOM decreased during the spawning season.

Fluorescence measurements from a wide range of environments have identified a variety of fluorescent “fractions” that are associated with different DOM precursor materials. For example, Stedman and Markager (2005) identified a humic fluorophore group that is abundant in streams draining forested watersheds and wetlands. The peak for this humic fluorophore group (excitation <250 nm, emission 448 nm) is nearly identical to the primary peak observed in peatland leachate and in streamwater samples collected in Peterson Creek outside of the salmon spawning season. This suggests that in the absence of salmon, the aquatic DOM pool in Peterson Creek is dominated by humic material leached from wetlands within the catchment. Because Peterson Creek watershed has a high proportion of wetlands (53%), this finding is also consistent with previous studies showing that wetland soils contribute more per unit area to aquatic DOM loads in undisturbed watersheds (e.g., Gorham et al. 1998).

Fluorescence spectroscopy has also previously been used to identify sewage effluent in English rivers and estuaries largely because of the high protein-like fluorescence associated with the DOM discharged from sewage treatment works (Baker and Spencer 2004). The unique protein-like fluorescence peak (excitation 275 nm, emission 306–308 nm) present in DOM at Lower Peterson during the

spawning period has been linked to the protein tyrosine (Stedman and Markager 2005). Our findings suggest that salmon carcasses contribute identifiable protein-rich DOM to the aquatic DOM load in Peterson Creek during spawning. Moreover, this salmon-derived DOM can be easily fingerprinted using fluorescence spectroscopy because it is chemically different from the terrestrially derived DOM that forms the bulk of the aquatic DOM load in coastal streams.

Fluorescence spectroscopy may also provide quantitative information about the presence of salmon-derived DOM. Yamashita and Tanoue (2003) report that protein-like fluorescence intensities for tyrosine and tryptophan were correlated to concentrations of total hydrolyzable amino acids in marine waters. Thus, measures of protein-like fluorescence intensity may be useful to estimate concentrations of salmon-derived amino acids and to provide information about the dynamics of this labile DOM fraction in coastal streams. Furthermore, it is likely that longitudinal stream and estuary sampling downstream of spawning grounds would provide insight into the uptake or processing length for labile salmon-derived DOM.

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