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# Impact of Wildfire on Stream Nutrient Chemistry and Ecosystem Metabolism in Boreal Forest Catchments of Interior Alaska

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## Abstract

With climatic warming, wildfire occurrence is increasing in the boreal forest of interior Alaska. Loss of catchment vegetation during fire can impact streams directly through altered solute and debris inputs and changed light and temperature regimes. Over longer time scales, fire can accelerate permafrost degradation, altering catchment hydrology and stream nutrient dynamics. In 2004, the 217,000 ha Boundary Fire burned 65% of an established study site in the Caribou-Poker Creeks Research Watershed. We used this opportunity to investigate the impact of wildfire on stream chemistry and metabolism in boreal forest catchments. Wildfire impacts on chemistry were evaluated by examining solute chemistry in four catchments from 2002 to 2007. Ecosystem metabolism was measured over the summer of 2005 in one burned and two unburned catchments. Wildfire led to stream nitrate concentration increasing up to threefold, whereas dissolved organic carbon (DOC) and dissolved organic nitrogen concentrations decreased post-fire. Average stream gross primary production in the burned catchment was double that of the unburned sites (2.4 and 1.2 g O<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>, respectively). Respiration rate was also elevated in the burned stream (6.6 g O<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>) compared with the control streams (1.2 and 4.5 g O<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>). Climatic warming has the potential to impact boreal forest streams through permafrost thaw and increased fire frequency, leading to altered solute inputs and production and respiration rates.

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## Introduction

In the boreal forest, wildfire is a widespread disturbance and fundamental in shaping forest structure, function, and successional processes (Chapin et al., 2006). With climatic warming, the northern boreal forest is predicted to experience earlier onset of the wildfire season combined with a potential increase in the number and size of fires (Kasischke et al., 1995; Stocks et al., 1998). In regions with permafrost, the effects of fire on surface organic layer depth, albedo, and vegetation are likely to initiate a positive feedback on soil temperature, contributing to decreased permafrost extent and increased depth of seasonal thaw (Burn, 1998; Yoshikawa et al., 2003).

Wildfire has the potential to impact boreal forest streams over short time scales via change in catchment vegetation and soil characteristics, and over longer time scales through reduced permafrost extent, altered vegetation successional trajectories, and changes in hydrological pathways. Immediate impacts of fire on stream ecosystems include changes in temperature and light regimes through loss of shading riparian canopy (Gresswell, 1999; Hitt, 2003). Streams are closely coupled to their catchments with allochthonous inputs serving as an important source of organic matter and nutrients. Combustion of terrestrial organic matter may alter delivery of solutes to streams, in particular carbon, nitrogen, phosphorus, and base cations (Bisson et al., 2003; Gresswell, 1999). In addition, loss of riparian vegetation can alter inputs of coarse and fine particulate organic matter and woody debris to streams (Benfield, 1997). A reduced rate of catchment evapotranspiration following wildfire may also lead to changes in

stream discharge and hydrologic flowpaths through watersheds, thereby altering both the magnitude and timing of flows and solute delivery to streams (Earl and Blinn, 2003; Petrone et al., 2007; Williams and Melack, 1997).

Vegetation stand type and permafrost extent are intimately linked and generally maintained through negative feedbacks in boreal forest watersheds. Soils underlying black spruce stands are generally wetter and more acidic than soil underlying deciduous stands (Baldocchi et al., 2000; Ping et al., 2005), which keeps organic soil mineralization low, and promotes maintenance of a thick organic layer and underlying permafrost. When fire in black spruce forest is accompanied by removal of organic soils and disruption of the soil thermal regime, it can lead to establishment of deciduous stands, which is most likely to occur in areas where permafrost is unstable (Chapin et al., 2004). Over successional time scales, change in vegetation type and the loss of underlying permafrost have potential to alter soil nutrient chemistry, soil active layer depth, and catchment hydrologic flowpaths, with associated change in allochthonous inputs to streams.

Alteration of stream physical and chemical properties by fire will likely impact stream ecosystem functioning. Whole stream metabolism is a measure of instream primary production and ecosystem respiration and, as such, is an integrative measure of stream function. The rate of metabolism can have significant ramifications for nutrient uptake in streams, downstream transport of nutrients, and stream food webs (Amon, 2002; Bunn et al., 1999; Hall and Meyer, 1998; Hall and Tank, 2003; Thorp, 2002). Temperature, light, dissolved organic matter, nutrient availability, and discharge are important determinants of production and

TABLE 1

Selected physical characteristics of study catchments at the Caribou-Poker Creeks Research Watershed. Area burned from D. Verbyla (personal communication). Temperature, conductivity, pH, and discharge are summer (June–September) averages ( $\pm$ SE). Riparian canopy is classified as open, closed, or a combination of open and closed (mixed), based on visual assessment.

Watershed	Area (km <sup>2</sup> )	Area Burned (%)	Permafrost (%)	Stream width (m)	Temperature (°C)	Conductivity ( $\mu$ S cm <sup>-1</sup> )	pH	Discharge (L s <sup>-1</sup> )	Riparian canopy	Dominant vegetation
C1	6.7	0	26	N/A	4.9 (1.3)	51.8 (0.3)	7.43 (0.01)	N/A	Open	Coniferous
C2	5.2	0	4	0.65	5.4 (1.1)	76.1 (0.3)	7.64 (0.01)	31 (21)	Open	Deciduous
C4*	10.0	0	19	0.94	5.7 (1.7)	99.1 (0.4)	7.78 (0.01)	75 (64)	Closed	Deciduous
P6	7.0	65	18	0.66	5.6 (1.5)	114.1 (0.7)	7.78 (0.01)	40 (13)	Mixed	Mixed

N/A = data unavailable.

\* 28% of the C4 watershed was burned during a prescription fire in 1999 (FROSTFIRE; Hinzman et al., 2003).

respiration rates in streams (Elser et al., 1990; Elser et al., 2000; Gausch et al., 1995; Uehlinger, 2000). Post-fire alteration of discharge regime, canopy loss, and nutrient enrichment have been shown to alter invertebrate assemblages and stream food webs (Minshall et al., 1997; Spencer et al., 2003; Vieira et al., 2004).

The objectives of this research were twofold. First, we examined the impact of wildfire on stream nutrient and dissolved organic matter (DOM) chemistry over a six-year period. Second, we examined the impacts of wildfire on stream functioning by measuring whole stream metabolism in one stream draining a fire impacted catchment and in two control streams. We hypothesized that wildfire in the surrounding catchment would lead to increased inorganic nutrient input to streams, thereby alleviating any nutrient limitation and resulting in increased rate of GPP. In contrast, we hypothesized that combustion of soil carbon stocks in the surrounding catchment and reduced allochthonous DOM input to streams would result in a lower rate of stream ecosystem respiration.

## STUDY SITES

Our study was conducted in the Caribou-Poker Creeks Research Watershed (CPCRW; 65.15°N, 147.5°W), located approximately 50 km NE of Fairbanks, Alaska. The CPCRW is a pristine, 104-km<sup>2</sup> catchment reserved for hydrological and ecological research. The climate of CPCRW is continental, with warm summers (mean = 16.4 °C in July), cold winters (mean = -29 °C in January), and low precipitation (411 mm, of which 31% falls as snow). The research site is located in the zone of discontinuous permafrost, with the extent of permafrost underlying sub-catchments of the CPCRW ranging from 3 to 53%. The distribution of permafrost is largely determined by aspect and winter temperature, with permafrost found predominately on north-facing slopes and in valley bottoms (Haugen et al., 1982). Uplands on south-facing slopes are dominated by hardwood forests of Alaskan paper birch (*Betula neoalaskana*) and quaking aspen (*Populus tremuloides*), whereas north-facing slopes generally have black spruce (*Picea mariana*), and feathermosses (*Pleurozium schreberi* and *Hylocomium schreberi*). Several alder species have a patchy distribution in both uplands (*Alnus viridis*) and valley bottoms (*A. incana*). Valley bottoms typically have saturated soil and support growth of mosses (e.g., *Sphagnum* spp., *Hylocomium*) and dwarf shrubs (e.g., *Betula nana*, *Salix* spp., *Vaccinium uliginosum*).

We studied a total of four streams that drained catchments that varied in size from 5.2 to 10.0 km<sup>2</sup> and permafrost extents from 4 to 26% (C1, C2, C4, and P6 catchments; Table 1, Fig. 1). Within the CPCRW, the C4 catchment was partially burned in 1999 by a prescribed fire to assess fire and climate feedbacks in the

boreal forest (FROSTFIRE project; Hinzman et al., 2003). The prescribed fire was of moderate intensity, burned 28% of the catchment area, and was largely restricted to the black spruce-dominated north-facing slopes with the riparian zone left mostly unburned. Stream nitrogen was elevated in C4 during a single post-fire storm flow, after which stream nutrient concentrations were not significantly different from pre-fire levels (Petrone et al., 2007).

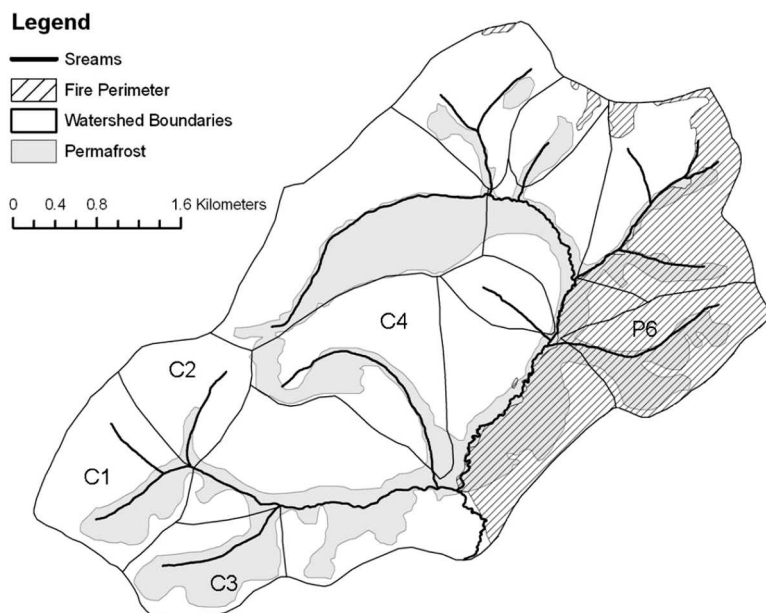
The Boundary Fire burned approximately 217,000 ha of boreal forest in interior Alaska between mid-June and late August 2004. Within the CPCRW, the Boundary Fire burned to the south of Poker Creek and much of the P6 catchment (Fig. 1). The fire was of moderate to severe intensity and burned approximately 65% of the P6 catchment. Burning was primarily in upslope, black spruce-dominated stands. Following the fire, organic soil was largely intact and there was considerable charred litter and dead vegetation remaining. The riparian corridor, which had a width of approximately 40 m, was largely untouched by the fire. Precipitation was unusually low in 2004 and gradually increased from 2005 through 2007 (Fig. 2).

## Methods

The impacts of fire on stream chemistry were assessed by comparing pre- and post-fire stream chemistry in two paired streams (C1 and P6). P6 was the only catchment in the CPCRW with comprehensive pre-fire data that was burned during the wildfire. The C1 stream was selected as the control based on the similarity in catchment size, permafrost extent, dominant vegetation, and similarity in response of stream chemistry with changes in discharge (Table 1). Although the P6 and C4 watersheds had essentially the same extent of permafrost (18 and 19%, respectively), the streams have substantially different responses in streamflow and chemistry during storms. In addition to monitoring stream chemistry, we measured whole-stream metabolism in three streams (C2, C4, and P6) during summer 2005 to evaluate nutrient controls over instream respiration and gross primary production (GPP). All studies were conducted during the ice-free period when streams are free-flowing (typically June to September).

## STREAM CHEMISTRY AND PHYSICAL MEASUREMENTS

Stream stage height was measured continuously every 15 minutes using pressure transducers at Parshall flumes at the C2, C4, and P6 streams. Rating curves were developed for all sites from velocity and stream cross-section measurements. Water chemistry was measured throughout the summers of 2002–2007 in the C1, C2, and C4 streams. The P6 stream was sampled from

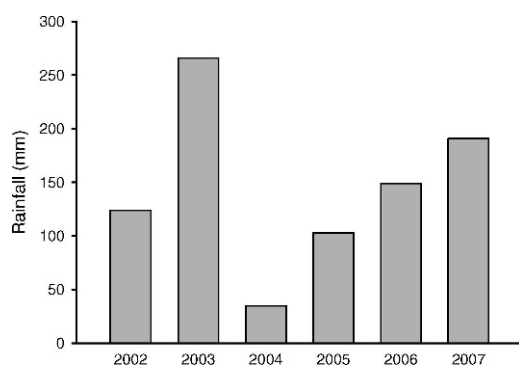


**FIGURE 1.** Map of the Caribou-Poker Creeks Research Watershed showing the sub-catchment boundaries, streams, permafrost distribution, and the extent of the 2004 Boundary Fire. The CPRW is located approximately 50 km NE of Fairbanks, Alaska, at 65.15°N, 147.5°W.

June to September in all years, except 2004 when water samples were collected from July to September (post-Boundary Fire). Stream water samples were collected daily using ISCO autosamplers and an additional grab sample was collected every 1 to 2 weeks. Previous analyses at CPRW have shown that for most solutes, including nitrate and DOC, the concentration measured in autosampler-collected samples (without use of preservatives) stored for two weeks is not significantly different from grab sample concentrations ( $r^2 = 0.95$ ; slope = 0.99; Jones et al., 2005). Samples were collected in acid washed high density polyethylene bottles, stored in a cooler for transport to the lab and filtered within 12 h using glass fiber filters (Gelman A/E). Samples were stored at 4 °C until analysis (usually within 48 h). When samples could not be analyzed immediately, samples were filtered using glass fiber filters (Gelman A/E) and frozen. Several sample dates were missed at each stream due to mechanical failure of the autosamplers.

#### STREAM METABOLISM

In-stream GPP, respiration, and net ecosystem productivity (NEP) were calculated from the diel change in dissolved oxygen



**FIGURE 2.** Summer (June–August) rainfall (mm) at the Caribou-Poker Creeks Research Watershed from 2002 to 2007 (data from the National Atmospheric and Deposition Program station AK01 located in the Caribou-Poker Creeks Research Watershed).

concentration using the single-station, whole-stream technique (Bott, 1996; Odum, 1956). Metabolism was measured over 24 h approximately biweekly in 2005 from June through August in C2 and C4 streams, and approximately biweekly from July through August in the P6 stream. Metabolism was not measured in the P6 stream in June due to equipment failures. Because interior Alaska experiences up to 20 h of daylight during the summer, we calculated daily respiration from the minimum hourly change in dissolved oxygen over the day. On each date, dissolved oxygen was measured every 15 minutes using CS511–L Sensurex dissolved oxygen probes connected to Campbell Scientific CR10X dataloggers (Campbell Scientific). Dissolved oxygen probes were calibrated on each metabolism measurement date using a spectrophotometric dissolved oxygen method (Roland et al., 1999). Triplicate 250-mL water samples were collected in BOD bottles from the thalweg of each stream, and immediately fixed in the field with 2.5 mL  $\text{MnSO}_4$  and 2.5 mL  $\text{KOH-KI}$ . Stream temperature probes were calibrated at the time of metabolism measurements using a high-precision thermometer. To express metabolism on an areal basis, stream widths were measured once at all sites in 2005. All of the study streams have incised stream channels, and, as a consequence, width does not vary appreciably with discharge. Width was measured at 5 m intervals over a 200 m reach and averaged.

Oxygen exchange with the atmosphere was determined using the steady-state injection technique (Hibbs et al., 1998; Mulholland et al., 2001). We conducted eight injections across a range of flows to develop a model relating evasion rate to streamflow. Evasion was quantified in the C2 and C4 streams, which have the lowest and highest streamflows of the streams studied. In the lab prior to injections,  $\text{SF}_6$  was injected into collapsible containers of conservative tracer (dissolved  $\text{Cl}^-$  or  $\text{Br}^-$ ) and allowed to equilibrate for 24 h. The resulting solution was injected into the study stream 300 m upstream from the dissolved oxygen probe using a metering pump (flow rate =  $50 \text{ mL min}^{-1}$ ) until steady-state of the conservative tracer was achieved at the downstream station (approximately 3 h). Prior to each injection, triplicate water and triplicate gas samples (30 mL stream water collected in 60 mL polyethylene syringes) were collected from the thalweg at sampling stations every 50 m downstream from the injection site (300 m total reach length).



Stream discharge ( $Q$ ) at the time of injection was determined using the dilution gauging technique and calculated as

$$Q = C_{inj} / (C_{pl} - C_{bg}) q_{inj} \quad (1)$$

where  $C_{bg}$  is background  $Cl^-$  or  $Br^-$  concentration,  $C_{inj}$  is the concentration of  $Cl^-$  or  $Br^-$  in the injectate,  $C_{pl}$  is stream plateau  $Cl^-$  or  $Br^-$  concentration, and  $q_{inj}$  is the tracer flow rate (Stream Solute Workshop, 1990). Stream velocity ( $v$ ) was calculated as

$$v = d / (t_1 - t_0) \quad (2)$$

where  $d$  is the distance traveled by the conservative solute,  $t_0$  is the injection start time, and  $t_1$  is the time when solute concentration at the downstream station reached half plateau concentration. Stream depth ( $z$ ) was calculated by dividing discharge by velocity and average stream width.

Evasion of  $SF_6$  ( $k(SF_6)$ ) was calculated as

$$k_{(SF_6)} = (1/\tau) \ln(G_1 C_2 / G_2 C_1) \quad (3)$$

where  $\tau$  is the hydrologic travel time between the up- and downstream sampling points,  $G$  is the steady-state tracer gas concentration,  $C$  is the conservative tracer concentration, and the subscripts 1 and 2 are up- and downstream sampling locations, respectively (Generaux and Hemond, 1992).  $SF_6$  evasion was converted to  $O_2$  evasion using the equation

$$k_{O_2(T_S)} = k_{(SF_6)} (Sc_{SF_6} / Sc_{O_2})^n \quad (4)$$

where,  $k_{O_2(T_S)}$  is evasion rate at ambient stream temperature ( $T_S$ ; Elmore and West, 1961),  $Sc_{SF_6}$  and  $Sc_{O_2}$  are the Schmidt numbers for  $SF_6$  and  $O_2$ , respectively (Wanninkhof, 1992), and  $n = 0.7$  (Generaux and Hemond, 1992). Oxygen evasion was standardized to evasion at 20 °C ( $k_{O_2(20^\circ C)}$ ) using the formula

$$k_{O_2(20^\circ C)} = k_{O_2(T_S)} / 1.024^{(T_S - 20)} \quad (5)$$

To develop an evasion model for CPRW streams, we compared evasion against velocity and depth via regression analysis using the general form of the equation by Bennett and Rathburn (1972)

$$k_{O_2(20^\circ C)} = a v^b / z^c \quad (6)$$

where  $a$ ,  $b$ , and  $c$  are constants.

## LABORATORY ANALYSES

Anions ( $NO_3^-$ ,  $SO_4^{2-}$ ) and cations ( $NH_4^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ) were quantified using a Dionex DX-320 Ion Chromatograph. Soluble reactive phosphorus (SRP) was measured using the molybdate blue method using a Beckman DU 640B spectrophotometer (American Public Health Association, 1998). DOC concentration was measured using a Shimadzu 5000 total organic carbon analyzer, which was plumbed to an Antek 7050 nitric oxide chemoluminescent detector to quantify total dissolved nitrogen (TDN). Dissolved organic nitrogen (DON) was calculated as  $TDN - (NH_4^+ + NO_3^-)$ . Dissolved oxygen samples were acidified with 2.5 mL 12N  $H_3PO_4$  and the light absorbance at 430 nm read using a Beckman DU 640B spectrophotometer according to the method described by Roland et al. (1999).  $SF_6$  was measured by allowing syringes to warm to room temperature, adding a 30 mL helium headspace, and equilibrating for 2 h. The headspace was then injected into a Varian CP 3800 gas chromatograph (1 mL) and measured with an electron capture detector.

## DATA ANALYSIS

Differences in stream metabolism among streams were tested using one-way ANOVA ( $\alpha = 0.05$ ). The effects of fire on stream chemistry were tested in two manners. First, we used a two-way ANOVA to test for significant differences in chemistry among streams, and prior and post-fire. The interaction term, in particular, was evaluated to determine if the degree of change in stream chemistry before and after the fire in the burned watershed differed from the other streams. Second, we further evaluated interannual patterns in stream chemistry using a one-way ANOVA with the differences in stream chemistry between the stream draining the burned watershed and a control stream. This second approach was used to maximize our ability to detect interannual changes following the fire. The control was selected based on the greatest similarity in the daily change in stream chemistry between the control and treatment stream, which was the C1 stream. Significant differences among streams ( $p < 0.05$ ) were further evaluated using Tukey's multiple-comparison test.

## Results

### STREAM SOLUTE CHEMISTRY

Stream nitrate concentration varied significantly among CPRW streams (Table 2). Prior to the fire, the mean nitrate concentration in the streams in the lower permafrost watersheds was 0.51 and 0.59 mg N L<sup>-1</sup> (C2 and C4 streams, respectively) compared with 0.24 and 0.28 mg N L<sup>-1</sup> in the streams draining the higher permafrost watersheds (C1 and P6, respectively; Table 2). Stream water DOC concentration, in contrast, exhibited the opposite pattern with greatest concentration in the streams draining the higher permafrost watersheds. Prior to the fire, the mean DOC concentration in streams in the lower permafrost watersheds was 3.3 and 3.4 mg C L<sup>-1</sup> (C2 and C4 streams, respectively) compared with 4.7 and 5.7 mg C L<sup>-1</sup> in streams draining the higher permafrost watersheds (C1 and P6, respectively). While the mean DOC concentration among streams varied nearly twofold, DON concentration prior to the fire only varied from 0.28 to 0.32 mg N L<sup>-1</sup> (Table 2). Coupled to the patterns in DOC, the C:N of dissolved organic matter tended to be greatest in higher permafrost streams with values of 20.8 in P6, 19.0 in C1, 15.1 in C4 and 13.2 in C2 streams. Similar to the pattern in nitrate, sulfate and base cation concentrations tended to be greatest in the streams draining the lower permafrost watersheds for streams in the Caribou Creek sub-watershed (Table 2). In the P6 stream, sulfate and most base cation concentrations were always equal to or greater than in the tributaries of Caribou Creek, suggesting a difference in parent geology (Table 2). SRP concentration was almost always below detection limits (<1 µg L<sup>-1</sup>).

### WILDFIRE IMPACTS ON STREAM CHEMISTRY

Following the wildfire, nitrate, sulfate, and potassium concentrations increased in the impacted stream, whereas DOC and calcium concentrations declined relative to the three undisturbed streams (Tables 2 and 3). Wildfire had a dramatic effect on stream nitrate concentration (Fig. 3, Tables 2 and 3). During 2002–2003, nitrate concentration was on average only 0.08 mg N L<sup>-1</sup> lower in the P6 (burned) stream compared with the C1 (control) stream. Nitrate concentration post-fire in 2004 did not significantly change in the P6 stream compared with the control, although 2004 was a dry summer with little rainfall (Fig. 2) and low streamflow. In subsequent summers following the

TABLE 2

Mean summer (June–September) stream solute concentrations ( $\pm$ SE) prior and post fire for the four study streams. Superscript letters indicate significantly different concentrations of solute.

Parameter	Stream							
	C1		C2		C4		P6	
	Pre-fire	Post-fire	Pre-fire	Post-fire	Pre-fire	Post-fire	Pre-fire	Post-fire
Nitrate (mg N L <sup>-1</sup> )	0.24 (0.01) <sup>a</sup>	0.34 (0.01) <sup>c</sup>	0.51 (0.01) <sup>d</sup>	0.67 (0.01) <sup>e</sup>	0.59 (0.01) <sup>e</sup>	0.73 (0.01) <sup>h</sup>	0.28 (0.01) <sup>b</sup>	0.64 (0.01) <sup>f</sup>
DON (mg N L <sup>-1</sup> )	0.28 (0.01) <sup>a,b,c</sup>	0.34 (0.01) <sup>d</sup>	0.32 (0.01) <sup>b,c,d</sup>	0.27 (0.01) <sup>a</sup>	0.30 (0.01) <sup>a,b,c,d</sup>	0.28 (0.01) <sup>a,b</sup>	0.32 (0.02) <sup>a,b,c,d</sup>	0.33 (0.01) <sup>c,d</sup>
DOC (mg C L <sup>-1</sup> )	4.7 (0.2) <sup>b</sup>	5.0 (0.1) <sup>b</sup>	3.3 (0.1) <sup>a</sup>	3.3 (0.1) <sup>a</sup>	3.4 (0.2) <sup>a</sup>	3.3 (0.1) <sup>a</sup>	5.7 (0.2) <sup>c</sup>	5.1 (0.1) <sup>c</sup>
Sulfate (mg L <sup>-1</sup> )	3.0 (0.1) <sup>a</sup>	3.3 (0.1) <sup>a</sup>	5.7 (0.1) <sup>b</sup>	6.7 (0.1) <sup>c</sup>	6.3 (0.1) <sup>c</sup>	7.8 (0.1) <sup>c</sup>	13.4 (0.2) <sup>e</sup>	15.5 (0.1) <sup>f</sup>
Sodium (mg L <sup>-1</sup> )	0.99 (0.02) <sup>a</sup>	0.97 (0.02) <sup>a</sup>	1.11 (0.02) <sup>b</sup>	1.02 (0.02) <sup>a</sup>	1.29 (0.02) <sup>c,d</sup>	1.24 (0.02) <sup>c,d</sup>	1.29 (0.03) <sup>c,d</sup>	1.35 (0.02) <sup>d</sup>
Magnesium (mg L <sup>-1</sup> )	1.45 (0.02) <sup>a</sup>	1.57 (0.02) <sup>b</sup>	3.00 (0.02) <sup>d</sup>	3.16 (0.02) <sup>e</sup>	2.78 (0.02) <sup>c</sup>	2.96 (0.02) <sup>d</sup>	2.75 (0.04) <sup>c</sup>	2.99 (0.02) <sup>d</sup>
Potassium (mg L <sup>-1</sup> )	0.30 (0.01) <sup>a</sup>	0.38 (0.01) <sup>b</sup>	0.38 (0.01) <sup>b</sup>	0.41 (0.01) <sup>b</sup>	0.55 (0.01) <sup>c</sup>	0.62 (0.01) <sup>d</sup>	0.39 (0.01) <sup>b</sup>	0.57 (0.01) <sup>c</sup>
Calcium (mg L <sup>-1</sup> )	8.6 (0.1) <sup>b</sup>	7.2 (0.1) <sup>a</sup>	12.3 (0.1) <sup>d</sup>	10.0 (0.1) <sup>c</sup>	18.9 (0.1) <sup>e</sup>	14.8 (0.1) <sup>e</sup>	21.8 (0.2) <sup>h</sup>	17.3 (0.1) <sup>f</sup>

fire (2005–2007), nitrate concentration in the P6 stream increased substantially compared with the pre-fire difference between burned and control streams (mean difference 0.30 mg N L<sup>-1</sup>; Table 3, Fig. 3). Post-fire, nitrate concentration in the P6 stream was on average over twofold greater with 0.65 mg N L<sup>-1</sup> compared with 0.28 mg N L<sup>-1</sup> in years 2002–2004 (Table 3, Fig. 3).

DOC and DON exhibited the opposite pattern to nitrate with the concentration declining post-fire. Prior to the fire the DON concentration in the P6 stream was on average 0.05 mg N L<sup>-1</sup> greater than in the control stream (2002 and 2003; Table 3, Fig. 4). Post-fire, DON concentration in the burned stream declined compared with the control to the point that DON concentration in the control stream exceeded the burned stream in 2005 (Table 3, Fig. 4). Similar to the pattern in DON, DOC concentration declined in the burned stream post-fire, although the response was delayed until the wetter years of 2006 and 2007. From 2002 to 2005, the DOC concentration in P6 stream was on average 1.2 mg C L<sup>-1</sup> greater than in the control stream (Table 3, Fig. 5). In 2006 and 2007, however, the DOC concentration in the P6

stream significantly declined relative to the control stream to the point at which the burned stream had on average 0.5 mg C L<sup>-1</sup> less than the unburned stream (Table 3). Coupled to the change in DOC and DON concentrations, the C:N of DOM significantly declined in the burned stream compared with the reference. Prior to the fire, the C:N of the DOM in the P6 stream averaged 22.9 (2002 and 2003), but tended to decline post-fire (2004, 2006, 2007).

#### ECOSYSTEM METABOLISM

Gas evasion rate was quantified across streamflows ranging from 19 to 60 L s<sup>-1</sup> and velocities from 0.13 to 0.24 m s<sup>-1</sup>. Using our field-based measurements of gas evasion and streamflow with a generalized form of the Bennett and Rathburn (1972) model, the equation that best described oxygen evasion was ( $R^2 = 0.72$ )

$$k_{O_2(20^\circ C)} = 0.0008v^{-0.6031}/z^{1.7813} \quad (7)$$

Across injections, the gain in streamflow across a 200 m injection reach averaged 2.6% (0.013% m<sup>-1</sup>).

TABLE 3

Mean summer (June–September) stream solute concentrations and the mean difference in concentrations between streams ( $\pm$ SE) for the C1 (control) and P6 (burned) sub-catchments of the Caribou-Poker Creeks Research Watershed from 2002 to 2007. For differences in solute concentrations, superscript letters indicate years with significantly different differences between the C1 and P6 streams.

Parameter	Watershed	Year					
		2002	2003	2004	2005	2006	2007
Nitrate (mg N L <sup>-1</sup> )	C1	0.385 (0.101)	0.220 (0.005)	0.237 (0.003)	0.315 (0.009)	0.376 (0.006)	0.331 (0.015)
	P6	0.283 (0.008)	0.272 (0.010)	0.293 (0.007)	0.587 (0.013)	0.695 (0.012)	0.606 (0.020)
	Difference	-0.175 (0.164) <sup>a</sup>	0.021 (0.012) <sup>a</sup>	0.061 (0.008) <sup>a</sup>	0.259 (0.018) <sup>b</sup>	0.341 (0.017) <sup>b</sup>	0.292 (0.024) <sup>b</sup>
DON (mg N L <sup>-1</sup> )	C1	0.268 (0.009)	0.308 (0.007)	0.268 (0.013)	0.214 (0.017)	0.36 (0.039)	0.426 (0.030)
	P6	0.307 (0.011)	0.346 (0.012)	0.303 (0.009)	0.178 (0.013)	0.342 (0.012)	0.448 (0.025)
	Difference	0.056 (0.008) <sup>a</sup>	0.050 (0.012) <sup>a</sup>	0.081 (0.010) <sup>b</sup>	-0.080 (0.027) <sup>c</sup>	0.010 (0.034) <sup>a</sup>	-0.003 (0.017) <sup>a</sup>
DOC (mg C L <sup>-1</sup> )	C1	4.62 (0.31)	5.68 (0.23)	3.54 (0.15)	4.68 (0.26)	3.54 (0.16)	7.2 (0.60)
	P6	6.18 (0.27)	6.64 (0.34)	3.84 (0.06)	5.66 (0.17)	3.61 (0.16)	6.32 (0.28)
	Difference	1.61 (0.25) <sup>a</sup>	1.65 (0.26) <sup>a</sup>	0.74 (0.06) <sup>a</sup>	0.88 (0.17) <sup>a</sup>	0.16 (0.13) <sup>b</sup>	-0.93 (0.44) <sup>b</sup>
DOC:DON	C1	19.2 (1.0)	21.4 (0.6)	15.9 (0.4)	29.3 (1.1)	12.8 (0.4)	20.2 (1.0)
	P6	23.4 (0.6)	22.4 (0.8)	15.1 (0.4)	39.5 (1.6)	12.7 (0.5)	18.7 (0.9)
	Difference	3.2 (0.7) <sup>a</sup>	2.3 (0.7) <sup>a</sup>	-1.1 (0.4) <sup>b</sup>	16.9 (2.1) <sup>c</sup>	-0.6 (0.6) <sup>b</sup>	-0.6 (0.9) <sup>b</sup>

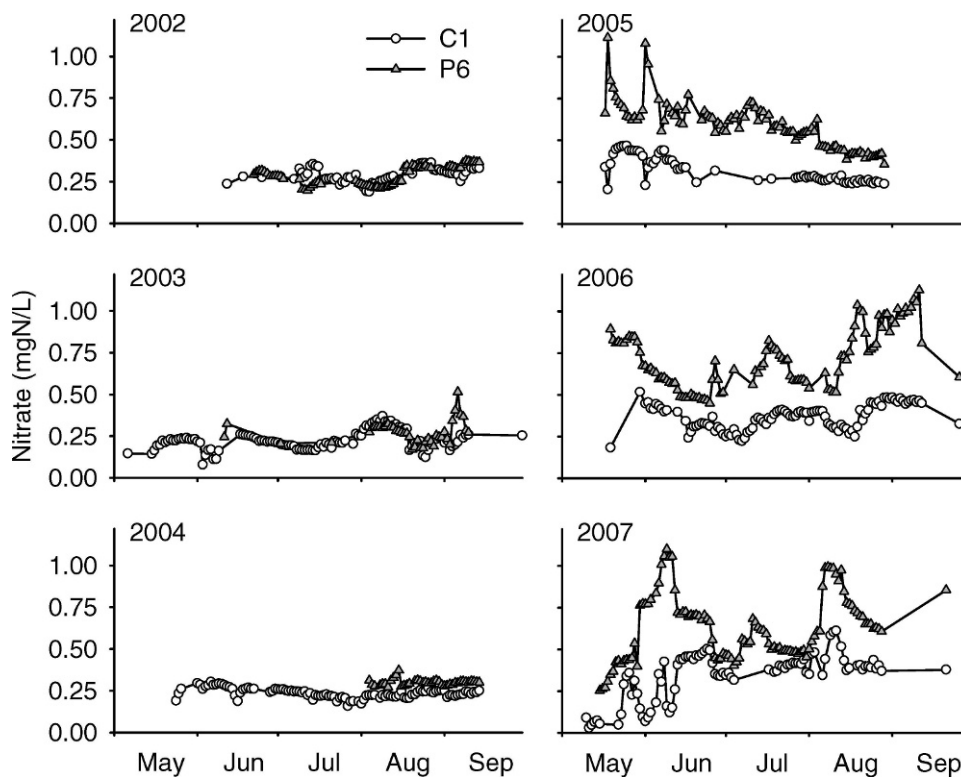


FIGURE 3. Pre- and post-fire nitrate concentration in burned (P6) and control (C1) catchments of Caribou-Poker Creeks Research Watershed for 2002–2007. The Boundary Fire burned through P6 in July 2004.

GPP and respiration were greatest in the burn-impacted P6 stream compared with the control C2 and C4 streams ( $p < 0.05$ ; Fig. 6). GPP in the burned stream was double that of the unburned streams with a summer mean of  $2.4 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$  compared with an average rate of  $1.2 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$  (Fig. 6). Similarly, respiration rate was higher in the P6 stream with a summer average of  $6.6 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , whereas average respiration rate in the unburned C2 and C4 streams was 1.2 and

$4.5 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , respectively (Fig. 6). GPP and respiration were not statistically correlated with stream temperature. However, GPP may be related to canopy cover. With a closed riparian canopy, the C4 stream had the lowest GPP (average  $0.9 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) whereas C2, with an open canopy, had a higher average GPP of  $1.5 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ . P6, however, had a mixed canopy cover that was undamaged by the wildfire and substantially higher production than either C2 or C4 (Figure 6).

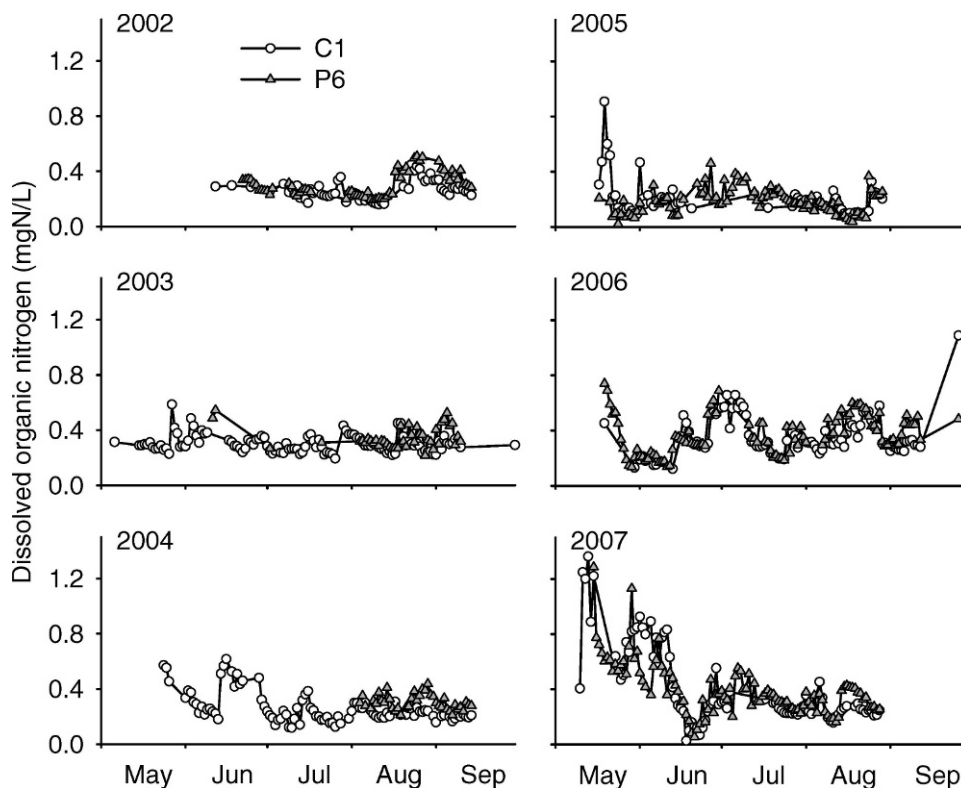


FIGURE 4. Pre- and post-fire dissolved organic nitrogen concentration in burned (P6) and control (C1) catchments of Caribou-Poker Creeks Research Watershed for 2002–2007. The Boundary Fire burned through CPCRW in July 2004.

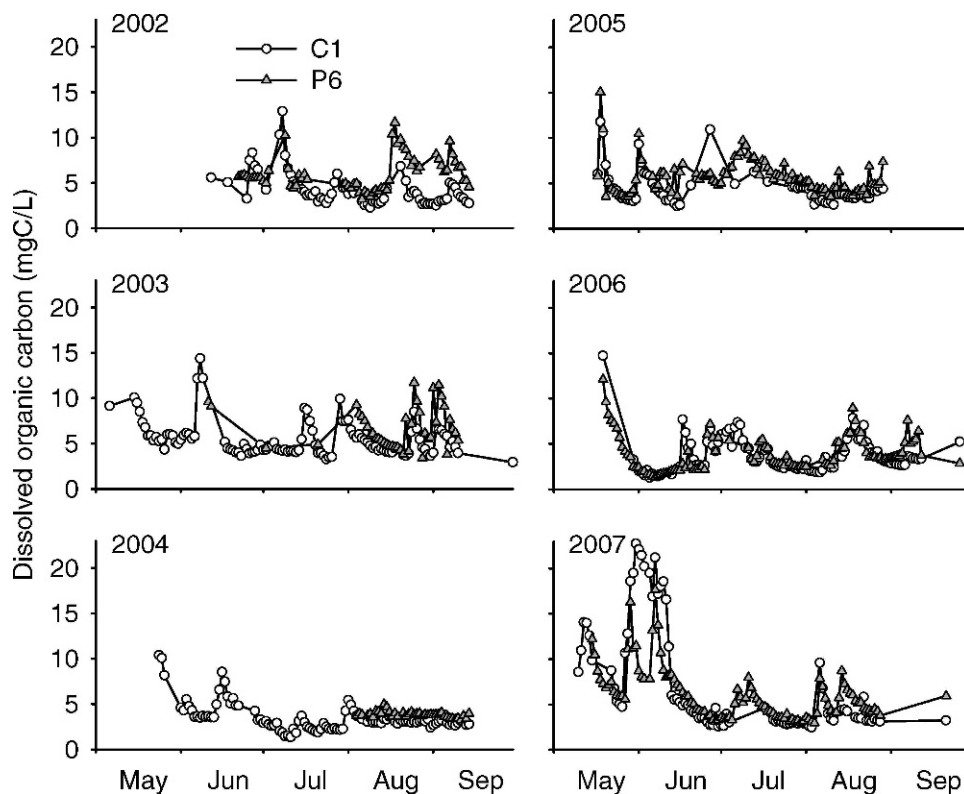


FIGURE 5. Pre- and post-fire dissolved organic carbon concentration in burned (P6) and control (C1) catchments of Caribou-Poker Creeks Research Watershed for 2002–2007. The Boundary Fire burned through CPRW in July 2004.

Similarly, GPP and respiration were unrelated to stream nitrate or DOC concentrations.

## Discussion

### CPCRW STREAM CHEMISTRY

In this study, stream solute concentrations varied widely among sub-catchments and tended to vary in response to extent of permafrost (MacLean et al., 1999), although other factors such as permafrost distribution, catchment size, mineral geology, and vegetation composition also undoubtedly affect solute chemistry. Permafrost serves as a barrier to the infiltration of precipitation into deep soil horizons and is therefore an important regulator of stream solute concentrations in the region of discontinuous permafrost (Carey, 2003; Jones et al., 2005; MacLean et al., 1999; Petrone et al., 2006). In catchments underlain by extensive

permafrost, hydrological flowpaths are restricted to the upper organic soil horizon, with streams receiving greater DOM inputs. In contrast, in low permafrost catchments precipitation can infiltrate through organic horizons to the deeper mineral soils, producing streams characterized by reduced DOM inputs and greater nutrient concentrations (Jones et al., 2005; MacLean et al., 1999; Petrone et al., 2006). High DOC concentration in surface soil has been attributed to DOC leaching from leaf litter and high biological activity, whereas reduction of DOC as flow passes through mineral soil is thought due to abiotic sorption of DOC to soil particles (McDowell and Likens, 1988). In CPRW, sulfate, sodium, and calcium concentrations are considerably higher in groundwater than in shallow soil, suggesting recently thawed permafrost soil, mineral soil, and weathering as the primary sources of these solutes to streamflow (Petrone et al., 2006).

### WILDFIRE AND SOLUTE DYNAMICS

Comparison of pre- and post-fire control (C1) and burned (P6) stream chemistry revealed that wildfire resulted in significant change in stream solute concentrations in the burned catchment. A significant decline in stream DOC concentration in P6 was observed two years following the wildfire. While soil organic matter was likely altered immediately post fire, the effect on stream chemistry was not realized until the wetter year of 2006 (2004 and 2005 had particularly low summer precipitation; Fig. 2). Stream DOC concentration is linked to rainfall and flushing of organic matter from soil organic horizons in CPRW streams (Petrone et al., 2006). The flush of DOC in the C1 catchment in 2007 highlights this relationship, when DOC that had likely accumulated in soil during the dry period was delivered to the stream. The lack of a corresponding flush of DOC in P6 reinforces the interpretation that soil carbon stocks had declined in this catchment post-fire. The delayed decline in stream DOC concentration we observed may be a natural response to fire,

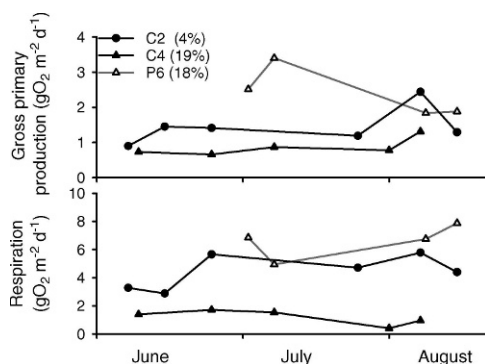


FIGURE 6. Summer 2005 rates of (a) gross primary production and (b) ecosystem respiration for three sub-catchments of the Caribou-Poker Creeks Research Watershed and the Boston Creek catchment. Permafrost extent in parentheses.



but is more likely a product of low summer precipitation during and in the year following the fire.

The reduction in DOC concentration observed in 2006 and 2007 may be caused by several processes, including combustion of soil carbon stocks, transformation of soil carbon to more recalcitrant and less soluble carbon compounds, or decreased microbial mineralization of organic carbon due to a post-fire reduction in microbial biomass (Certini, 2005). A reduction in allochthonous inputs of coarse and fine particulate organic matter were likely not contributing to the observed reduction in DOC as riparian vegetation remained intact along the length of the P6 stream. Following the prescribed burning of the C4 catchment in 1999 (FROSTFIRE; Hinzman et al., 2003), both soil water DOC and water extractable organic carbon from the organic horizon of burned slopes declined (Shibata et al., 2003). Ping et al. (2005) proposed that in boreal forest soils, fire leads to oxidative combustion of immobile and labile soil organic matter, which is lost to the atmosphere through and conversion to CO species. The results from research following the FROSTFIRE, coupled with the importance of the organic horizon in DOC delivery to streams in the CPRW, suggests the observed reduction in stream DOC concentration in the P6 catchment was due to combustion and conversion of soil organic carbon stocks in surface soils.

Elevated stream nitrogen concentration, as observed in this study, is a common response to fire (Bayley and Schindler, 1991; Hauer and Spencer, 1998; Minshall et al., 1997; Williams and Melack, 1997). Increased soil ammonium concentration, commonly observed following fire, is potentially due to increased microbial or thermal decomposition of vegetation and soil organic matter (Chorover et al., 1994; Wan et al., 2001). Any increase in available ammonium has the potential to be rapidly nitrified and, in turn, increase soil nitrate availability (Certini, 2005; Wan et al., 2001). Despite evidence that soil nitrification is not stimulated in black spruce stands of CPRW following fire (Lyle, 2006; Smith et al., 2000), stream nitrate concentration increased in this study, suggesting there may have been decreased microbial competition with vegetation for ammonium and increased nitrification. Alternatively, the pattern of increased nitrate concentration may be due to increased soil active depth, with two possible mechanisms leading to nitrate concentration increases. First, increased thaw depth initiated by wildfire (latent heat transfer and lower surface albedo) may have improved soil drainage and increased aeration, thus reducing nitrate removal via denitrification. Second, increased active layer depth and improved drainage may have increased percolation of precipitation to deep mineral soils, similar to the high nitrate levels in streams draining low permafrost watersheds.

Comparing the results of our study with a previous study conducted in CPRW on fire impacts on stream chemistry (Hinzman et al., 2003), stream nitrate in the former study increased for a short period during a single post-fire storm, but was not elevated at any other time (Petrone et al., 2007). The difference in the response of stream chemistry between the fires is likely due to extent of catchment burned and the fire intensity. The 2004 wildfire in P6 burned 65% of the catchment, compared with 28% of C4 burned during FROSTFIRE. In addition, although the riparian zone was not burned in the P6 catchment, the fire burned closer to the stream channel than during the FROSTFIRE burn. The type of vegetation and soil burned may also play an important role in nutrient export to streams. In a study of soil chemistry following wildfire in interior Alaska, soil solution nitrogen was slightly elevated in black spruce forests, in contrast to soil in aspen, birch, and white spruce stands where soil nitrogen concentrations declined following fire (Dyrness et al., 1989). The

1999 and 2004 fires both burned black spruce predominately, indicating that the difference in catchment area burned and proximity to the stream are the likely causes of the sustained elevation of stream nitrate at P6.

Stream phosphorus concentration has been shown to either dramatically increase (Earl and Blinn, 2003; Prepas et al., 2003), albeit for a brief period, or be unchanged by fire (Minshall et al., 1997; Stephens et al., 2004). Prior to the 2004 wildfire, SRP concentration in the C1 and P6 streams was below detection limit ( $<1 \mu\text{g P L}^{-1}$ ), and we observed no detectable post-fire increase in stream SRP concentration in P6. Other studies in the boreal forest, however, have reported a change in stream phosphorus concentration after fire. In a study in the boreal forest of Canada, total dissolved phosphorus was unchanged after fire, but particulate phosphorus increased significantly during periods of high discharge (Prepas et al., 2003). In northwest Montana, stream phosphorus concentration was over fivefold higher in burned than control streams, and this difference was sustained for a period of several years (Hauer and Spencer, 1998). The observed increase in nitrate, sulfate, and cations in P6 may have been accompanied by increased total phosphorus concentration, but given our monitoring program we were unable to detect a change.

#### *METABOLISM, WILDFIRE, AND PERMAFROST*

Stream respiration and productivity have been shown to be influenced by various environmental factors, including light (Acuña et al., 2004; Mulholland et al., 2001; Young and Huryn, 1996), temperature (Lamberti and Steinman, 1997; Sinsabaugh, 1997), nutrient concentrations, organic matter supply (Acuña et al., 2004; Kreutzweiser and Capell, 2003), discharge (Lamberti and Steinman, 1997; Uehlinger, 2000; Young and Huryn, 1996), and catchment disturbance (Houser et al., 2005). In this study, both GPP and respiration were higher in the stream draining the burned than unburned catchments, suggesting that fire did indeed have some indirect impact on ecosystem metabolism.

GPP and respiration were not correlated with temperature, although average daily stream temperature varied little over CPRW sub-catchments in the summer of 2005. Average daily temperature ranged from 4.8 to 7.9 °C across metabolism measurement dates in all streams, and is unlikely the cause of differences in metabolism at these times. Given the high nitrate concentration in streams of CPRW, GPP is not likely nitrogen limited. Moreover, nitrate concentrations were higher in the C2 and C4 streams than the P6 stream, but GPP rates were lower. The relationship between canopy cover and production was inconclusive, with the highest production occurring in the stream with a mixed riparian cover. Additionally, although algal standing stocks were not measured, we did not observe any obvious difference in substrate biomass among streams. Rather, production may be controlled by phosphorus availability. Given the very low concentration of SRP in CPRW streams, limitation of production by this nutrient is highly likely, as was found in another study in interior Alaska (Slavik et al., 2004). Considering the low ambient concentration of SRP in CPRW streams, even a minor SRP increase may have been sufficient to stimulate GPP in streams draining burned catchments.

Stream respiration rates in CPRW were greatest in the stream impacted by fire, perhaps due to increased input of labile DOC (Findlay et al., 2003; Kreutzweiser and Capell, 2003) or extent of the hyporheic and transient storage zones (Fellows et al., 2001; Mulholland et al., 2001). Carbon bioavailability has been found to be both positively (Striegl et al., 2005) and negatively

(Kawahigashi et al., 2004) correlated with permafrost extent. In CPRW streams, significant differences in stream DOC concentration with catchment stand type suggest differences in carbon lability among streams. Moreover, White et al. (2008) found that biologically labile DOC increased with discharge in CPRW streams, when flow bypasses mineral soils. We observed a significant decrease in C:N ratio of DOM following wildfire in P6, which may be contributing to the higher respiration rate observed in this stream. Similarly, the variability in catchment permafrost extent and soil saturation among CPRW sub-catchments may result in differences in size of the hyporheic zone and transient storage among streams.

#### WARMING, WILDFIRE, PERMAFROST, AND ECOSYSTEM METABOLISM

Our ability to draw conclusions from this study regarding drivers on ecosystem metabolism in boreal forest streams is limited by the lack of treatment replication. Due to the unexpected nature of the 2004 Boundary Fire and confounding effect of permafrost coverage on stream chemistry, we were constrained by availability of pre-existing study sites. Despite this, we have established that wildfire leads to sustained change in stream solute chemistry. The role of stream nutrient concentrations and environmental parameters in driving ecosystem metabolism remains unclear and warrants further investigation, particularly during this period of rapid change in the region of discontinuous permafrost.

Understanding wildfire impacts on stream metabolism and nutrient chemistry in boreal forest streams needs to be viewed in light of discontinuous permafrost extent and vegetation feedbacks and their effect on catchment hydrology. Wildfire impacts on stream chemistry may be exacerbated by climatic warming and permafrost degradation. Over the last century, climatic warming has resulted in a 2.1% reduction in permafrost extent at CPRW, and over one-third of the catchment now has either unstable or actively thawing permafrost (Hinzman et al., 2006). In the boreal forest, wildfire most often burns through the highly flammable black spruce stands (Kasischke et al., 2006). Permafrost typically underlies black spruce stands, and with fire dramatically altering the thermal balance of soils, permafrost is likely to become unstable and/or begin to degrade (Hinzman et al., 2006; Ping et al., 2005). After fire, black spruce may reestablish, leading to stabilization of permafrost, or, alternatively, black spruce forests may be replaced with deciduous stands (Chapin et al., 2004) under which further degradation of the underlying permafrost is likely. Fire effects on permafrost extent could be substantial under a changing climate, and where permafrost is already near the point of thawing, wildfire may accelerate the rate of degradation.

From this and previous research, it is clear that climatic change and increased wildfire occurrence may impact stream chemistry and function in the region of discontinuous permafrost via two pathways. Short- to medium-term changes to stream solute concentrations after fire may alter nutrient limitation and increase rates of whole-stream metabolism. Over longer time scales, reduction in the extent of underlying permafrost within watersheds from wildfire and/or warming will lead to change in watershed hydrologic flowpaths and nutrient inputs into streams, and again may alter ecosystem functioning.

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