Permafrost and fire as regulators of stream chemistry in basins of the Central Siberian Plateau

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Abstract Stream chemistry in permafrost regions is regulated by a variety of drivers that affect hydrologic flowpaths and watershed carbon and nutrient dynamics. Here we examine the extent to which seasonal dynamics of soil active layer thickness and wildfires regulate solute concentration in streams of the continuous permafrost region of the Central Siberian Plateau. Samples were collected from 2006 to 2012 during the frost-free season (May–September) from sixteen watersheds with fire histories ranging from 3 to 120 years. The influence of permafrost was evident through significantly higher dissolved organic carbon (DOC) concentrations in the spring, when only the organic soil horizon was accessible to runoff. As the active layer deepened through the growing season, water was routed deeper through the underlying mineral horizon where DOC underwent adsorption and concentrations decreased. In contrast, mean concentrations of major cations ($Ca^{2+} > Na^+ > Mg^{2+} > K^+$) were significantly higher in the summer, when contact with mineral horizons in the active zone provided a source of cations. Wildfire caused significantly lower concentrations of DOC in more recently burned watersheds, due to removal of a source of DOC through combustion of the organic layer. An opposite trend was observed for dissolved inorganic carbon and major cations in more recently burned watersheds. There was also indication of talik presence in three of the larger watersheds evidenced by Cl^- concentrations that were ten times higher than those of other watersheds. Because climate change affects both fire recurrence intervals as well as rates of permafrost

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degradation, delineating their combined effects on solute concentration allows forecasting of the evolution of biogeochemical cycles in this region in the future.

Introduction

Understanding elemental cycling in the vast forested region of Central Siberia is becoming increasingly important given impending climatic changes and the large land area of this region. Alteration of ecosystem structure and function have already been reported as a result of degrading permafrost (Romanovsky et al. 2010), evidenced by increasing active layer depth and soil temperature (Frey and McClelland 2009), shortened fire return interval (FRI) (Kharuk et al. 2008), and increased river discharge (Peterson et al. 2002; McClelland et al. 2006). While considerable attention has been paid to the fundamental links of C exchange between land and atmosphere in this region (Nakai et al. 2008; Shirokova et al. 2009, 2013), much less is known of the terrestrial-aquatic link of C and other elements, with the exception of a few early studies that examine the link between soil and the aquatic geochemistry of carbon, major and trace elements during baseflow season (Pokrovsky et al. 2005, 2006). Understanding the terrestrial-aquatic link becomes important for establishing accurate contemporary riverine fluxes to the Arctic Ocean so that future changes can be modeled (Holmes et al. 2012). Several studies have begun to describe elemental dynamics in soil as a result of permafrost, fire, and microtopography (Prokushkin et al. 2007; Kawahigashi et al. 2011), yet how these dynamics translate to solute concentrations in streams is poorly understood.

Several studies have established the importance of permafrost in regulating both the source and movement of nutrients through the landscape primarily by constraining the flow of water to upper organic matter rich soils, thereby producing streams with flashy or rapid response hydrology, high DOC concentrations, and low dissolved mineral concentrations (MacLean et al. 1999; Petrone et al. 2006; Bagard et al. 2011). During warmer months, however, as soil thaws and the active layer deepens, water infiltrates underlying mineral soils that are a source of dissolved minerals and a sink for organic matter resulting in lower DOC concentrations and higher dissolved mineral concentrations. The behavior of these elements is expected to change with increasing temperatures and concurrent permafrost degradation; however, the direction of that change is still under investigation as competing hypotheses have emerged. Dissolved organic matter is expected to decrease with permafrost degradation in both Alaska and central Siberia on account of increased adsorption in the newly exposed mineral horizon (Striegl et al. 2005, 2007; Prokushkin et al. 2007), whereas in West Siberia where peatland covers much of the landscape, DOM export is projected to increase by 46 % by the year 2100 (Frey and Smith 2005) due to a release of stored carbon.

The seasonal ebb and flow of solutes in a continuous permafrost zone is further influenced by the presence of fire. Fires can combust the organic layer resulting in increased heat flow to the underlying mineral soil and a deepening of the active layer. In extreme cases, the active layer can increase to a depth that does not completely refreeze the following winter, forming what is known as talik (Yoshikawa et al. 2003). Volatilization of various nutrients can also occur during fires, with effects on soil properties that vary with fire intensity (Verma and Jayakumar 2012). Fire thus has the potential to affect stream chemistry by both removing solute sources and altering the transport of solutes through its effect on water storage and movement (Petrone et al. 2007; Betts and Jones 2009). On an annual scale, the contribution of forest fires to riverine Ca^{2+} fluxes may be as high as 0.5 versus 2.4 t/km^2/year of total river Ca^{2+} flux at N Tunguska River (Pokrovsky et al. 2005). Furthermore, the FRI in Siberian forests is predicted to decrease as a result of vegetation changes due to climate change (Tchebakova et al. 2009) and increased anthropogenic activities, specifically mining and extraction of other natural resources (Stocks et al. 1998; Kharuk et al. 2008).

In this study, we investigated the stream chemistry of sixteen watersheds underlain by continuous permafrost and used the data to assess the impact of permafrost and wildfire on stream solute concentrations. The study site is ideal for this sort of comparative approach in that it provides a natural mosaic of fire-affected watersheds with similar physical characteristics. By comparing stream solute concentrations

Fig. 1 Location of the study sites within Siberia and the specific location of watersheds relative to the Tura research station. N14a not shown
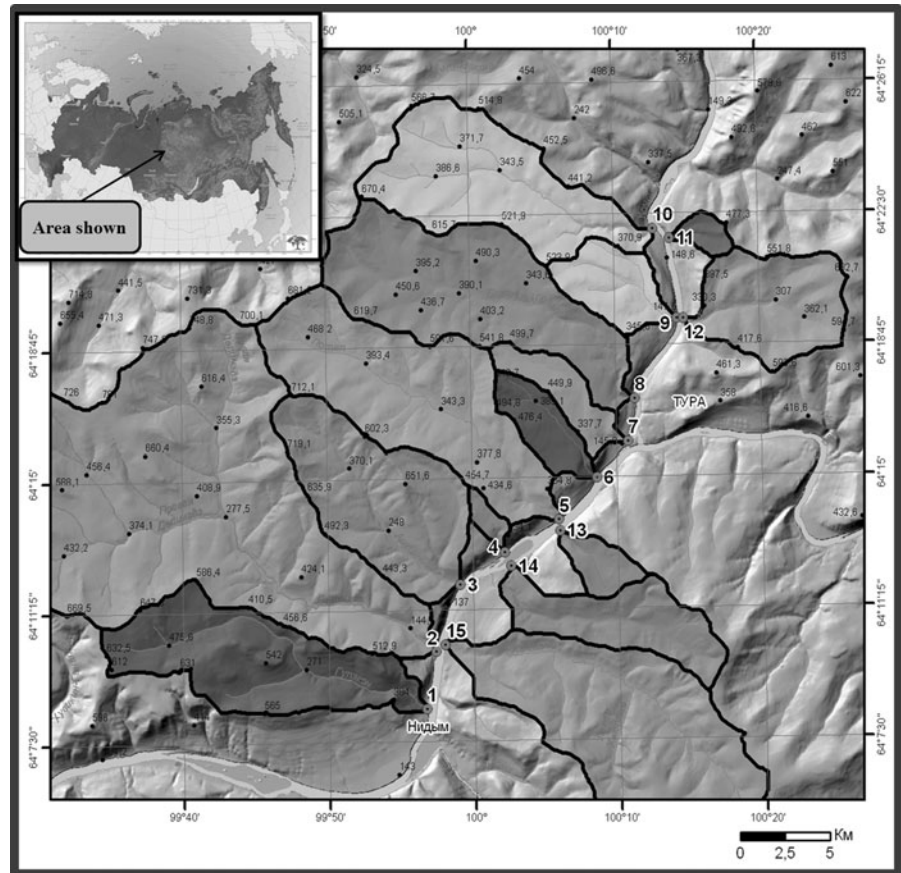
across the range of fire history, we can assess both the immediate effects of fire, as well as the trajectory of recovery post-fire. We hypothesized that permafrost would exert significant seasonal control over measured parameters as depth of the active layer changed from spring to fall and the mineral soil horizon was exposed. With regard to fire, we hypothesized that more recently burned watersheds would exhibit lower DOC concentrations due to combustion of the organic layer and generally higher ion concentrations caused by greater exposure of the mineral horizon due to an increase in active layer depth. Objectives were to (1) quantify stream chemistry of sixteen watersheds during the frost free season over several years, (2) identify the seasonal effect of continuous permafrost on stream solute concentrations via alteration of both solute source and flow path, and (3) characterize the extent to which wildfire influences stream solute concentrations over time. This increase in knowledge of the potential controls on stream solute concentrations is a crucial component for projecting the impact

of future change on ecosystem integrity and delivery of solutes to the Arctic Ocean as well as enhancing our ability to accurately model alteration of biogeochemical budgets.

Study area

Our study was conducted in the central portion of the Nizhnyaya Tunguska River (the right tributary of Yenisey River) watershed in the northern region of Central Siberia. The greater region is classified as the Siberian Basaltic Province and is characterized by 248 million year old flood basalts and larch forests. Sixteen watersheds were examined for this study, all of which were located around the town of Tura (Lat: 64°16′43″ and Long: 100°13′55″) (Fig. 1). This region lies in the zone of continuous permafrost and has a cold continental climate with air temperature ranging from −36 to 16 °C and a mean annual air temperature of −9.5 °C. Long-term average annual precipitation is

Table 1 Site name, basin area, and fire history of each watershed

Site name	Basin area (km^2)	Fire history (year of burn)
N1	68.9	1947
N2	224.3	1947
N3	67.6	>100
N4	3.7	>100
N5	91.7	>100
N6	15.4	>100
N7	15.6	>100
N8	89.1	>100
N9	20.8	1993
N10	70.5	1993
N11	4.9	>100
N12	41.0	50 % in 1990
N13	9.6	2009
N14	36.0	20 % in 2009
N14a	9.4	2009
N15	93.5	>100

354 mm/year with 30–40 % as snowfall and the remainder falling during the frost free season between May and September. Streams of this region are flashy with a hydrologic cycle characterized by spring flooding in May and June, summer low flow, summer and fall high flow, and zero flow from October to May as they freeze completely.

Vegetation is typical for Central Siberian deciduous forests (Abaimov 2005) in that the overstory is primarily larch (*L. gmelinii*) and ground cover consists of various species of dwarf shrubs and mosses. The active layer varies in thickness from tens of centimeters on north-facing slopes to over a meter on south-facing slopes and is underlain by permafrost 200–300 m in depth. The landscape is heavily influenced by fire with an average return interval (FRI) of 60 years (Kharuk et al. 2008), and the most recent fires on our study watersheds occurred from 2009 to over a hundred years ago (Table 1).

Field and analytical methods

Repeated stream sampling was used to investigate seasonal and annual means of DOC, DIC, specific UV absorbance (SUVA), and major ions. Samples were collected on a biweekly to monthly basis from twelve

watersheds throughout the frost-free season (May–September) from 2006 to 2012. Sampling from sites 13, 14, 14a, and 15 began in 2012, and therefore the data reflect concentrations from that year only. Measurements of pH and specific conductance (SC) were conducted on unfiltered samples in situ or immediately after return to the laboratory by Anion 7051 (Infraspak-Analit, Russia). In a few hours after collection, all samples were filtered (pre-rinsed 0.22 μm nitrocellulose filters, Millipore) and stored at 4 °C until analysis. DOC concentrations were measured as non-purgeable organic carbon (NPOC) via high temperature combustion using a Shimadzu TOC VSCN analyzer with an uncertainty of 5 % and a detection limit of 0.05 mg C_{org}/L. DIC concentrations were obtained from alkalinity determined following a standard HCl titration procedure using an automatic Schott Titro-Line alpha TA10[plus] titrator with an uncertainty of ± 2 % and a detection limit of 5×10^{-5} M. At the essentially neutral pH values of river water (7.5–8.0), and 1–100 μg/L of dissolved boron (Bagard et al. 2011), the titrated Alkalinity ($[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [B(OH)_4^-]$) represents, within 10 % uncertainty, the total inorganic dissolved carbon. The contribution of weak organic acids to titratable alkalinity was evaluated via (1) titration of filtered river water subjected to UV and H_2O_2 degradation to remove (up to 80–90 %) of dissolved organic matter without modifying the pH of solution and (2) by adding organic-rich, bicarbonate-poor natural water to standard bicarbonate solution and determining its alkalinity. In both cases, the contribution of natural DOM was found to be negligible (within ± 10 % of total titratable alkalinity). The contribution to total titratable alkalinity of Al having the typical concentrations between 10 and 100 μg/L in central Siberian rivers did not exceed 0.2 % of molar DOC concentration (10–20 mg/L, Bagard et al. 2011). Finally, we performed a quantitative comparison between DIC concentration measured by potentiometric titration and by Total Dissolved Carbon Analyzer (Shimadzu VSCN without catalytic combustion step). In a series of 40 samples of Central Siberian rivers and streams we observed a linear 1:1 dependence between the two DIC methods with a correlation coefficient better than 0.95 in a wide range of DOC concentration. The average agreement between potentiometry and total DIC was estimated as ± 10 %. SUVA, a measure of the aromatic carbon content (Weishaar et al. 2003) was measured at 254 nm

Table 2 Stream solute chemistry ($\pm$SE) for each site across all study years (2006–2012)

Fire history	Site	Na$^+$ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	K$^+$ (µg/L)	Cl$^-$ (mg/L)	SO$_4^{2-}$ (mg/L)
>100	N3	2.40[a] (0.33)	2.06[a] (0.22)	7.08[a] (0.68)	64.70[a] (12.04)	0.11[a] (0.03)	0.47[a] (0.14)
	N4	2.05[a] (0.17)	2.15[a] (0.25)	6.53[a] (0.48)	40.84[ab] (6.61)	0.26[a] (0.12)	0.08[c] (0.01)
	N5	2.18[a] (0.22)	1.83[a] (0.19)	6.52[a] (0.60)	45.77[ab] (7.75)	0.18[a] (0.04)	0.51[a] (0.08)
	N6	2.24[a] (0.30)	2.10[a] (0.20)	7.37[a] (0.60)	46.44[ab] (5.69)	0.10[a] (0.05)	0.40[ab] (0.13)
	N7	2.26[a] (0.32)	2.20[a] (0.31)	7.19[a] (0.84)	66.62[a] (10.39)	0.17[a] (0.12)	0.11[bc] (0.02)
	N8	2.24[a] (0.18)	1.79[a] (0.15)	5.83[a] (0.44)	16.64[b] (3.53)	0.06[a] (0.01)	0.50[a] (0.22)
	N11	2.57[a] (0.08)	2.17[a] (0.07)	6.27[a] (0.25)	73.23[a] (4.54)	0.11[a] (0.02)	0.13[c] (0.01)
	N15	3.48 (0.68)	3.13 (0.06)	5.29 (0.02)	70.65 (23.75)	3.08 (0.6)	0.69 (0.04)
1947	N1	2.12[b] (0.27)	1.88[b] (0.21)	5.84[b] (0.59)	72.89[c] (11.28)	0.21[c] (0.09)	1.60[d] (0.33)
	N2	12.04[c] (2.84)	2.83[b] (0.49)	13.83[b] (2.87)	178.70[d] (29.71)	26.52[b] (7.91)	1.15[e] (0.19)
50 % in 1990	N12	2.40 (0.08)	2.13 (0.06)	6.89 (0.20)	93.29 (6.22)	0.18 (0.02)	0.47 (0.03)
1993	N9	3.47[d] (0.10)	3.01[c] (0.11)	8.61[c] (0.38)	80.88[f] (4.06)	0.10[e] (0.01)	0.37 [g] (0.03)
	N10	7.33[e] (0.48)	3.85[d] (0.33)	16.30[d] (1.45)	132.17[e] (13.61)	26.43[d] (4.62)	0.95[f] (0.06)
20 % in 2009	N14	3.92 (0.59)	4.49 (0.03)	7.14 (0.27)	114.6 (16.40)	0.07 (0.02)	1.56 (0.13)
2009	N13	3.51 (0.04)	3.74 (0.00)	5.69 (0.51)	180.45 (86.95)	0.10 (0.02)	1.46 (0.03)
	N14a	3.62 (0.06)	4.28 (0.29)	7.09 (0.59)	114.85 (51.65)	0.07	1.34

Sites are grouped by fire history and progress from oldest to youngest burn. Letters denote statistical significance between sites within each fire class (Sites N15, N13, N14a were not included in the statistical analysis due to small sample size). There is no SE for site N14a as the mean represents only two values

Note µg/L for K

and normalized to DOC concentration (L/mg/m). Major anion concentrations (Cl$^-$, SO$_4^{2-}$) were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2 % and cation concentrations (Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$) were measured using a Perkin-Elmer 5100 PC atomic absorption spectrometer (AAS) with an uncertainty of 1–2 % (Bagard et al. 2011). Stream water level (cm) and temperature were recorded at site N9 by e+ WATER L 100 (Eijkelkamp, The Netherlands) from first week of June to the end of September (ca. 90 % of flow period length) from 2009 to 2012. Measurements were made every 15 min.

Statistical analysis

Analysis of variance (ANOVA) was used to compare solute means between individual sites and aggregated sites by fire history and also to analyze the effect of site and year on various solutes with a significance threshold of $P < 0.05$. Tukey's HSD was conducted for post hoc comparison of means. Linear regression was used to determine significant relationships between solute concentrations. Variables were tested for normality and log transformed in cases where

kurtosis occurred. All statistics were performed in JMP Pro 10.

Results

Stream chemistry

Streams of this region exhibit a flashy flow regime resulting in chemistry that can be classified as having relatively high DOC concentrations and low inorganic loading. Ion chemistry of streams draining intact and smaller basins (<100 km^2 in area) was dominated by Ca^{2+} > Na$^+$ > Mg^{2+} > K$^+$ among cations and HCO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ among anions (Table 2). Larger watersheds and/or those recently affected by fire (e.g. N2, N15, and N10) had up to tenfold higher mean concentrations of most inorganic constituents including the major cations (Ca^{2+} > Na$^+$ > Mg^{2+} > K$^+$ by mass) and also showed abrupt increases of Cl$^-$ concentrations during the low flow period of 2012 (Fig. 2). Sulfate was highly variable among sites with a range of 0.08 (N4) to 1.60 mg/L and did not correlate with any other parameter.
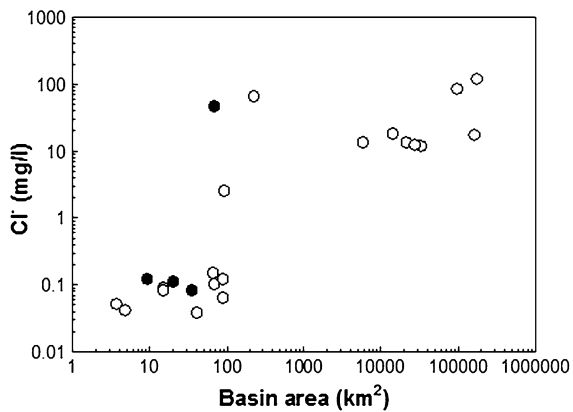
Fig. 2 Chloride concentration in a low flow period (July–August, 2012) in study sites and larger rivers versus watershed size. *Filled circles* are watersheds with recent fire damage (<20 years). The eight largest watersheds are major rivers of the area [Nidym, Kochechum, P. Tunguska, Tembenchi, Yambukan, Vivi, Taimura, and N. Tunguska Rivers (Bagard et al. 2011; Prokushkin et al. 2011)]. Log scale for Cl^- and watershed area

DOC and DIC ($C–HCO_3^-$) concentrations showed opposing trends in all watersheds where watersheds with a higher mean DOC concentration tended to have a lower mean DIC concentration (Fig. 3). SC was generally higher in cases where DOC was lower, although sites N2 and N10 showed exceptionally high conductance (146.2, 143.2 μs/cm respectively). SUVA values followed a similar pattern to DOC concentrations and the two parameters were positively related ($R^2 = 0.41$, $P < 0.0001$).

Seasonal and inter-annual variation of stream chemistry and permafrost

There was significant inter-seasonal variation in solute concentrations in all streams during the frost-free season which followed the increase in active layer thickness (ALT) (Fig. 4; Table 3). In particular, DOC and SUVA were significantly higher in the spring at
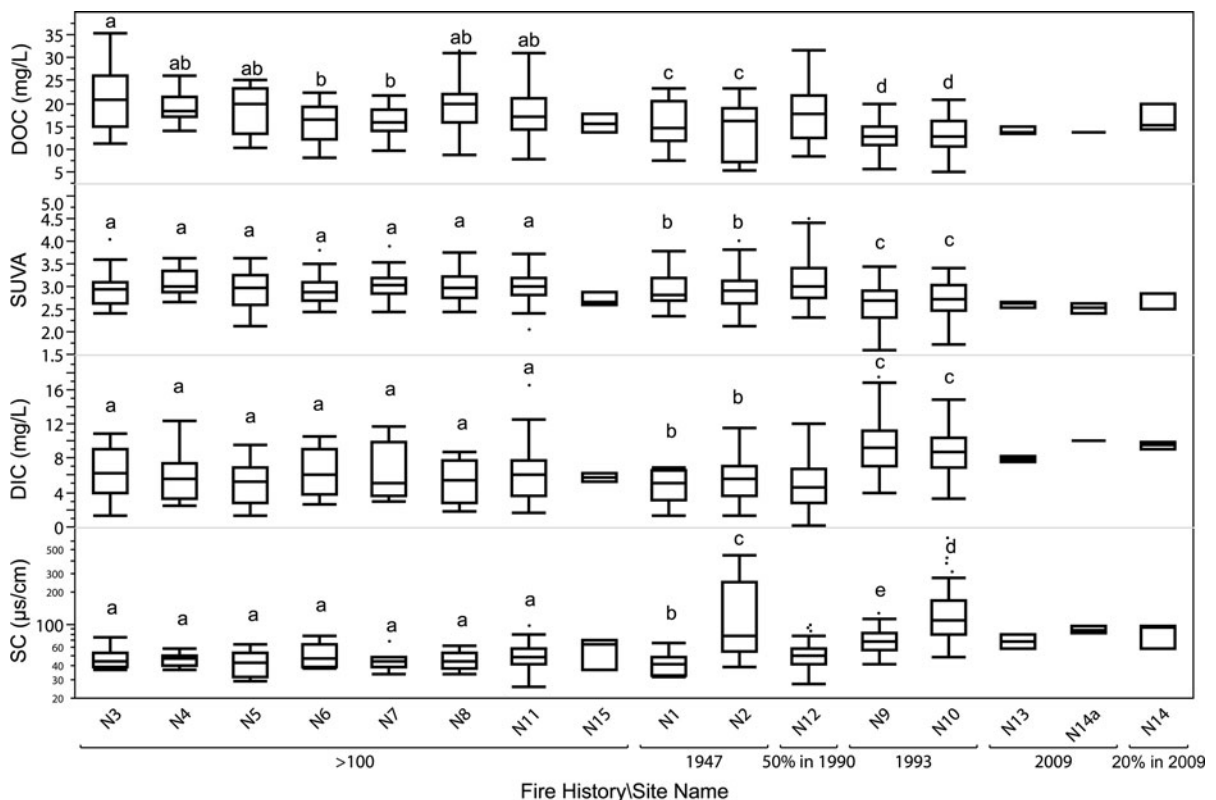
Fig. 3 Summary statistics for DOC, SUVA, DIC, and SC by each site for all study years (2006–2012). Sites are grouped by fire history and progress from oldest to youngest burn. *Letters* denote statistical significance between sites within each fire class (Sites N15, N13, N14a were not included in the statistical analysis due to small sample size). Log scale for SC
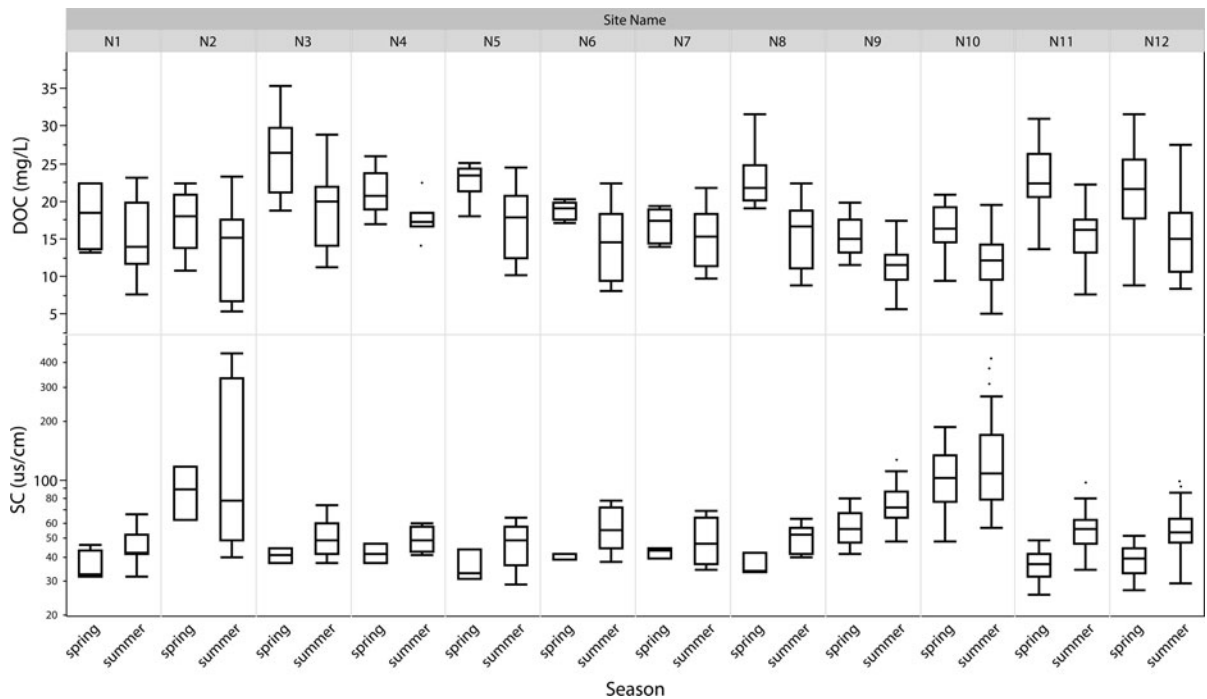
Fig. 4 Summary statistics for DOC and SC by season for selected streams. Note log scale for SC

minimum thaw depth and then gradually declined throughout the summer season as ALT deepened. In contrast, DIC, major cations, and sulfate were significantly higher in the summer than in the spring reflecting deeper hydrological flowpaths. In the dormant season (September–October), stream DOC and SUVA generally tended to increase and inorganic solutes decreased as stream runoff rose due to lower evapotranspiration.

Stream chemistry also showed large inter-annual variation driven by precipitation patterns during the frost-free season. Stream runoff (water level) for watershed N9 was on average much lower in 2009 than 2010 (Fig. 5), coinciding with precipitation during the frost-free season (Table 4). Both years saw a great deal of variation in water level driven by precipitation events, with levels ranging from 0 to 55 cm in 2009 and 30 to >100 cm in 2010. In 2010, the stream hydrograph was much more dynamic than in 2009, with a typical spring snowmelt, summer low flow with episodic storm events, and elevated fall flow. In contrast, during 2009, water level steadily declined throughout the summer and didn't peak again until early September. DOC and major cation concentrations showed contrasting responses to water

levels, with higher DOC concentrations (14.9 vs. 9.86 mg/L) and a lower sum of cations (15.3 vs. 21.9 mg/L) during the wetter year of 2010.

Stream chemistry and fire

Variability in stream solute concentrations could primarily be explained by fire history as there was little significant variability within fire class for most solutes. For DOC, DIC, and SUVA, sites with similar fire histories did not significantly vary from one another with the exception of DOC for sites N3 and N6 in the >100 year category. There was more variation for SC within fire histories due to the higher ion concentrations of N2 and N10, both of which were significantly higher than other sites with similar fire histories. This same trend applied to all other ions with the exception of SO_4^{2-}. Sulfate was significantly higher ($P < 0.01$) in site N1 than site N2 for the 1947 fire history. For the >100 fire history sites, SO_4^{2-} and K^+ were the only two ions to significantly vary among sites.

When those solutes that did not significantly vary within similar fire histories were aggregated by fire history, watersheds that burned over 100 years ago

Table 3 Mean seasonal solute concentration (±SE) for all sites across all study years (2006–2012)

Site	Season	SUVA	DIC (mg/L)	Na$^+$ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	K$^+$ (µg/L)	Cl$^-$ (mg/L)	SO$_4^{2-}$ (mg/L)
N1	Spring-snowmelt	3.56 (0.16)	1.71 (0.46)	1.24 (0.43)	1.32 (0.50)	4.90 (1.86)	46.65 (9.64)	–	–
	Summer-fall	2.87 (0.09)	5.27 (0.38)	2.39 (0.32)	1.96 (0.23)	6.70 (0.51)	86.02 (17.29)	0.22 (0.10)	1.75 (0.33)
N2	Spring-snowmelt	3.67 (0.15)	2.13 (0.54)	2.94 (0.70)	1.30 (0.20)	5.95 (0.78)	50.71 (8.65)	3.51 (1.39)	0.45 (0.13)
	Summer-fall	2.72 (0.10)	6.38 (0.54)	15.32 (4.31)	3.21 (0.66)	18.55 (5.00)	254.81 (38.94)	35.37 (9.95)	1.42 (0.21)
N3	Spring-snowmelt	3.36 (0.21)	4.43 (1.66)	1.47 (0.28)	1.50 (0.31)	5.75 (1.09)	44.41 (6.83)	0.04 (0.01)	0.14 (0.04)
	Summer-fall	2.80 (0.07)	6.64 (0.81)	2.73 (0.40)	2.32 (0.29)	8.17 (0.79)	78.66 (19.08)	0.14 (0.05)	0.63 (0.17)
N4	Spring-snowmelt	3.37 (0.08)	3.61 (0.67)	1.89 (0.20)	1.87 (0.19)	6.03 (0.37)	36.81 (6.61)	0.13 (0.04)	0.06 (0.02)
	Summer-fall	2.87 (0.05)	7.62 (1.20)	2.37 (0.29)	2.71 (0.55)	7.52 (1.16)	48.92 (16.03)	0.39 (0.22)	0.10 (0.02)
N5	Spring-snowmelt	3.43 (0.08)	2.16 (0.43)	1.62 (0.28)	1.36 (0.23)	5.40 (0.69)	39.71 (14.82)	0.25 (0.07)	0.20 (0.05)
	Summer-fall	2.74 (0.09)	5.92 (0.59)	2.61 (0.27)	2.17 (0.23)	7.72 (0.83)	52.43 (10.00)	0.16 (0.05)	0.64 (0.09)
N6	Spring-snowmelt	3.25 (0.12)	3.36 (0.43)	1.45 (0.19)	1.61 (0.20)	6.52 (0.48)	38.91 (9.57)	–	–
	Summer-fall	2.88 (0.10)	7.02 (0.73)	2.61 (0.35)	2.42 (0.28)	8.41 (0.99)	52.79 (8.00)	0.12 (0.06)	0.49 (0.16)
N7	Spring-snowmelt	3.42 (0.15)	3.46 (0.27)	2.00 (0.41)	1.76 (0.19)	6.01 (0.36)	55.30 (10.16)	–	–
	Summer-fall	2.91 (0.08)	7.55 (1.06)	2.65 (0.51)	2.87 (0.60)	8.96 (1.80)	83.6 (19.78)	0.05 (0.02)	0.12 (0.04)
N8	Spring- snowmelt	3.29 (0.10)	2.53 (0.25)	1.56 (0.12)	1.25 (0.13)	4.42 (0.40)	12.95 (5.51)	–	–
	Summer-fall	2.82 (0.07)	6.60 (0.53)	2.91 (0.16)	2.30 (0.15)	7.36 (0.51)	18.43 (4.69)	0.07 (0.02)	0.74 (0.31)
N9	Spring- snowmelt	2.90 (0.07)	6.51 (0.38)	2.68 (0.11)	2.29 (0.09)	6.41 (0.34)	66.53 (4.30)	0.08 (0.01)	0.27 (0.04)
	Summer-fall	2.47 (0.06)	11.08 (0.43)	3.88 (0.10)	3.37 (0.13)	9.78 (0.49)	88.18 (5.48)	0.12 (0.01)	0.43 (0.04)
N10	Spring-snowmelt	3.08 (0.08)	5.64 (0.36)	5.46 (0.53)	2.69 (0.38)	11.92 (1.14)	101.80 (14.79)	26.19 (10.21)	0.64 (0.09)
	Summer-fall	2.59 (0.06)	9.53 (0.26)	7.98 (0.61)	4.26 (0.41)	17.91 (1.90)	142.82 (17.49)	26.51 (5.22)	1.04 (0.07)
N11	Spring-snowmelt	3.28 (0.04)	3.27 (0.19)	2.00 (0.11)	1.72 (0.54)	4.96 (0.28)	58.82 (3.76)	0.06 (0.01)	0.08 (0.01)
	Summer-fall	2.88 (0.03)	7.29 (0.33)	2.85 (0.08)	2.39 (0.09)	6.89 (0.31)	79.81 (6.21)	0.13 (0.02)	0.15 (0.01)
N12	Spring-snowmelt	3.54 (0.08)	2.72 (0.18)	1.52 (0.08)	1.47 (0.06)	5.4 (0.21)	97.90 (11.78)	0.19 (0.03)	0.26 (0.01)
	Summer-fall	2.88 (0.04)	6.99 (0.28)	2.94 (0.07)	2.52 (0.06)	8.12 (0.23)	90.07 (6.66)	0.18 (0.02)	0.60 (0.05)

Note µg/L for K
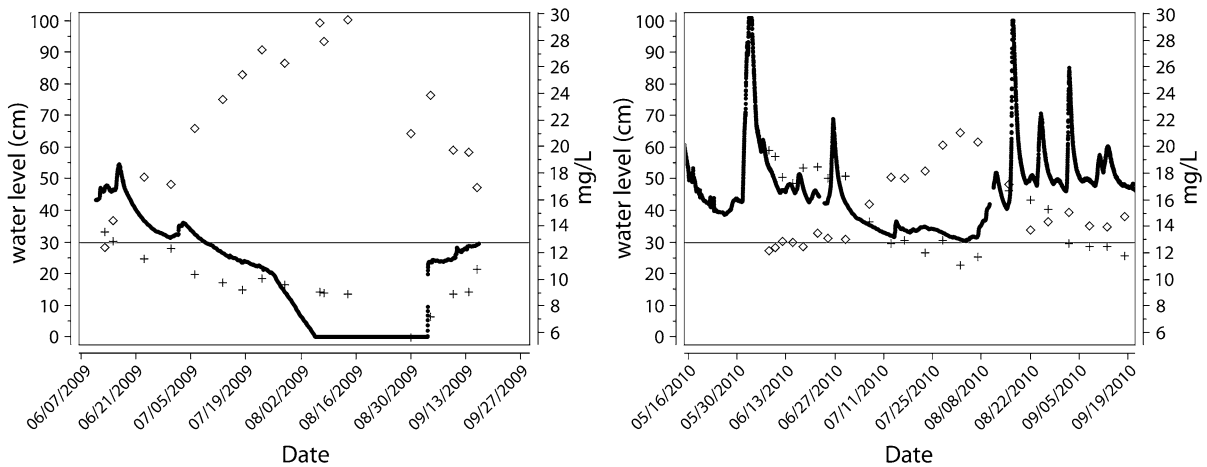
Fig. 5 Seasonal patterns in water level (*filled circle*), DOC concentration (+), and sum of major cations (Na^+, Mg^{2+}, Ca^{2+}, K^+) (*open diamond*) in 2009 (dry year) and 2010 (wet year) for site N9. *Straight line* indicates stagnant water level (no flow)

Table 4 Climatic data of the region for the entire study period

| Year	Precipitation (mm) (June–August)	Mean air temperature (°C) (June–August)
2006	67	15.4
2007	225	13.9
2008	225	13.8
2009	86	14.5
2010	179	13.4
2011	254	14.8
2012	83	15.1

had a significantly higher mean DOC concentration (17.99 mg/L) and DOC aromaticity (SUVA = 3.00) than watersheds that burned in 1993 (13.08 mg/L, 2.66) ($P < 0.0001$) and significantly lower mean DIC concentration (5.95 compared to 9.04 mg/L) and SC (50.1 compared to 102.8 us/cm) ($P < 0.0001$) (Fig. 6). The partial burn of basin N12 in 1990 did not appear to affect stream solute concentration as this stream chemistry was consistently statistically similar to streams in watersheds burned over 100 years ago with the exception of DIC in which N12 was significantly lower ($P < 0.0001$). Sites burned in 1947 (N1, N2) were statistically similar to sites burned over 100 years ago with respect to DOC, DIC, and SUVA. Ion concentrations were consistently higher in 1993 and 1947 watersheds than watersheds burnt >100 years ago (Table 5) due to the exceptionally high values in site N2 and N10; however, when sites N2 and N10 were excluded from the analysis, there

continued to be significant variation in ions (SC, Na^+, Mg^{2+}, and Ca^{2+}) by fire history with the remaining 1993 burn site (N9) having higher values while the remaining 1947 burn site (N1) had values similar to >100 years watersheds. Due to the small sample size of the 2009 watersheds ($n = 4$), statistical comparisons were not possible but solute concentrations were similar to 1993 watersheds with the exception of Cl^- (Fig. 6). Outliers for DOC and SUVA observed in Fig. 6 all occurred in the spring season of 2010 where outliers for DIC and SC were primarily a product of site N2 in the 1947 fire class and N10 in the 1993 fire class during 2009.

Discussion

Permafrost effect

Watersheds of central Siberia followed the conceptual permafrost model developed by MacLean et al. (1999), where the presence of permafrost constrains the flow of water to upper organic rich soils, resulting in flashy seasonal streams with high DOC concentrations and low dissolved mineral concentrations. As the active layer deepens throughout the frost-free season, the relative proportion of DOC and inorganic loading contribution to stream chemistry changes as the mineral soil horizon becomes part of the active zone. The mineral soil horizon not only reduces DOC concentration through abiotic adsorption (McDowell and Likens 1988), but also becomes a source of
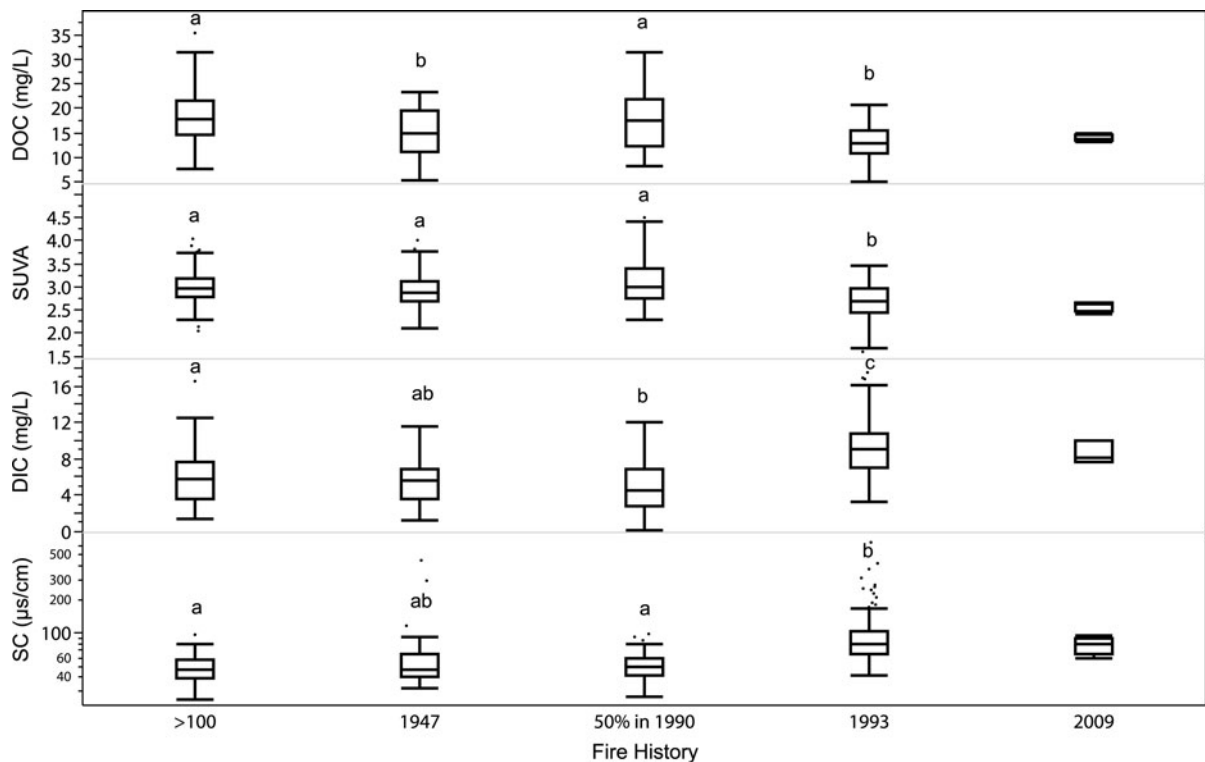
Fig. 6 Summary statistics for DOC, SUVA, DIC, and SC by fire history. *Letters* denote statistical significance by fire history (2009 fire history was not included in the statistical analysis due to small sample size). Log scale for SC

Table 5 Mean solute concentration (±SE) for cations in streams differentiated by fire history

Fire History (year of burn)	Na$^+$ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	K$^+$ (µg/L)
>100	2.44[c] (0.06)	2.10[b] (0.05)	6.41[b] (0.17)	59.06[c] (3.10)
1947	8.63[a] (2.04)	2.50[b] (0.33)	11.16[a] (2.02)	142.32[a] (21.66)
50 % in 1990	2.42[c] (0.08)	2.15[b] (0.06)	6.83[b] (0.20)	92.32[b] (5.97)
1993	5.40[b] (0.27)	3.43[a] (0.16)	12.14[a] (0.75)	105.25[b] (6.83)
20 % in 2009	3.92 (0.60)	4.50 (0.03)	7.14 (0.28)	114.6 (16.40)
2009	3.57 (0.05)	4.01 (0.20)	6.39 (0.51)	147.65 (45.42)

Letters denote statistical significance by fire history (20 % in 2009 and 2009 fire histories were not included in the statistical analysis due to small sample size)

Note µg/L for K

dissolved minerals. Results indicate that our initial hypothesis that permafrost would exert significant control over measured parameters due to a changing active depth layer was supported. There are several lines of evidence in our data supporting our initial hypothesis and the MacLean model, the most apparent being that spring DOC concentrations were consistently higher than summer concentrations across all sites (Fig. 4) and all study years regardless of climatic

conditions, fire history or watershed size. Permafrost dominated systems have been widely documented as being much more effective at transporting DOC through the landscape when flow paths are primarily restricted to the organic soil horizon (Carey 2003), particularly during the spring. Petrone et al. (2006) reported that the snowmelt period in a high permafrost watershed in Alaska generated 25 % of stream flow and more than half of the annual DOC flux where

Prokushkin et al. (2011) reported snowmelt runoff as 55–71 % of annual water flux and a DOC flux of 64–82 % of annual flux for larger rivers in the Central Siberian Plateau.

An opposite trend was observed for inorganic constituents and SC in which values were almost always higher in the summer (Fig. 4; Table 3) due to an additional source of solutes through exposure of the mineral horizon by the seasonal permafrost thaw coupled with less water flowing through the landscape during the summer low flow hydrologic period. Seasonal differences in DIC and other inorganic ions followed the SC trend and were higher in the summer than the spring, which we attribute to longer and deeper flow paths that develop as the active layer increases throughout the summer. Increased retention time in the soil leads to higher rates of both CO_2 production via enhanced soil respiration (Striegl et al. 2007) and bedrock weathering via increased rock-water interactions in deeper soil horizons (Bagard et al. 2011). In addition to a changing seasonal source, these solutes are also affected by the amount of water flowing through the landscape and thus, become diluted during higher flows and more concentrated during summer low flows. The contrasting trend in inorganic ions and DOC has proven to be a robust characteristic of permafrost dominated watersheds indicating that the permafrost feature exerts a significant amount of control on stream chemistry across different bedrocks and vegetation types.

There was also a marked seasonal shift in DOC quality evidenced by the higher spring SUVA values observed across all sites. Higher SUVA values are indicative of a greater proportion of aromatic compounds in the DOC pool. This could be a product of the flushing event that occurs with spring snowmelt where lignin-rich terrestrial compounds are transferred to the stream through relatively shallow flow paths versus the autochthonous inputs during the summer. A similar finding was documented by Prokushkin et al. (2011) in larger rivers of this area. How this aromaticity translates to bioavailability cannot be determined without conducting incubation experiments as the relationship between these two parameters is still under debate. Other studies have documented spring DOC in the Arctic to be much more labile than summer DOC (Holmes et al. 2008) due to the prevalence of shallow flow paths and also that the

DOC tends to be younger in age during the spring and less processed (Raymond et al. 2007).

Stream chemistry is tightly coupled to flow path through the landscape, particularly in a permafrost dominated system where flow is constrained by depth of the active layer. Evidence of this is seen through the remarkably different response of cations and DOC to high and low flow (Fig. 5). The frost free season of 2009 was exceptionally dry [82 mm rainfall in total for June–August or <50 % of long-term mean (1929–2012)] resulting in flow paths primarily through the mineral horizon which led to higher cation loads and probable abiotic adsorption of DOC. In contrast, the frost free season of 2010 saw 179 mm of rainfall resulting in overall lower cation concentrations and higher DOC loading. As the soil became saturated, a mixing of flow paths through both the mineral horizon and organic horizon occurred, causing changes in the relative proportion of DOC and cation contribution to overall stream chemistry. Fluctuations in solutes with water level as shown in Fig. 5 are indicative of DOC operating very much in concert with flow, whereas cations become diluted as more water moves through the landscape and the mineral horizon is no longer the dominant flow path.

Wildfire effect

Our extensive dataset provides a clear indication that fire in the larch dominated region of central Siberia exerts significant control over many aspects of stream chemistry and more specifically, confirms our initial hypothesis that more recently burned watersheds exhibit lower DOC concentrations due to carbon combustion and higher ion concentrations caused by greater exposure of the mineral horizon (Fig. 6). Furthermore, the influence of fire extends beyond immediate effects and was still being observed almost 20 years after a burn. Of course, the extent and severity of a fire are important in determining how dramatically a site may be affected, as was seen with site N12 that was burned >50 % and showed no visible difference from sites burned >100 years ago. It is possible that because the riparian zone in this watershed remained intact, stream chemistry was not as heavily affected highlighting the importance of riparian ecosystems in regulating stream chemistry. Nonetheless, our space for time approach in examining the influence of fire in a continuous permafrost

system provides valuable insight into drivers of stream chemistry.

Variation in solute response to fire can be explained by examining the different sources and flow paths of solutes through the landscape and understanding how each was affected. The reduction in DOC concentration in more recently burned watersheds was most likely a result of combustion of the organic horizon. The organic horizon in permafrost systems exerts significant control over DOC concentration because water is much more likely to be routed through that flow path due to infiltration restriction by permafrost. By removing much of that C stock in terrestrial ecosystems, the C source of hydrological export is dramatically reduced. This finding was further confirmed by Kawahigashi et al. (2011), who found that organic horizon thickness was much greater in control plots versus burn plots in these same watersheds. The losses of organic layer C due to fire were 0.5–2.5 kg/cm^2, and varied depending on cryogenic topography (mounds vs. troughs) and fire severity. Moreover, the water soluble fraction of organic carbon in remnant material decreased 2–3 times compared to intact organic layers, and approached the latter values ~ 50 years after a fire (Kawahigashi et al. 2011).

It is evident that increased permafrost thaw occurred due to a fire, affecting the dynamics of active layer depth and water movement through the landscape. A deeper active layer increases the amount of water storage capacity of soils and changes the flow path of water from the organic to the mineral horizon (MacLean et al. 1999). Fire also affected the quality of DOC evidenced by the lower SUVA values in more recently burned sites due to removal of mobile terrestrial aromatic C in the upper organic soil horizon.

Fire effect on major ions was not as clear-cut as what we observed for dissolved organic carbon. Major cations (Na^+, Mg^{2+} and Ca^{2+}) followed the expected result in that concentrations were higher in more recently burned watersheds whereas SO_4^{2-} and Cl^- did not show consistent variation among streams and years. Consistently higher DIC concentrations in streams draining recently burned basins indicated increased soil respiration in the soils under warmer soil temperatures. The underlying mechanism resulting in higher cation concentrations in streams draining recently burned watersheds is likely dual: dissolution of ashed organic material and/or temperature-related enhanced OM mineralization and weathering rates.

Moreover, fire causes an increase in active layer depth resulting in greater exposure of the mineral horizon. This can lead to soil temperature increases and enhanced rock-water interactions, both of which result in a larger release of cations.

Although fire can increase ion concentrations in streams, it is apparent that the larger streams (N2, N10, and N15) are exhibiting ionic concentrations higher than those that can be explained by a fire through the changes in active layer depth (Fig. 2). This is indicative of an additional source of solutes that is not affected either directly or indirectly by wildfire. The especially high Cl^- concentrations in these watersheds suggest a stream connection to underlying evaporitic deposits that exist beneath the basalt bedrock (Zharkoy 1984). This occurrence in rivers draining Central Siberian Plateau marks the degradation of permafrost and has been formally documented as a "through talik" formation, described as an area of ground that remains unfrozen throughout the year. Taliks are formed when soil/ground thawing is so great that the active layer increases to a depth that does not freeze during winter and can therefore act as an additional source of solutes to the stream (Yoshikawa et al. 2003). For our study area, Cl^- appears to be a strong indicator of permafrost degradation as it reflects talik formation and connection of a stream to underlying evaporitic deposits. While evidence of permafrost degradation is most apparent in the larger rivers of the region (Fig. 2), we expect increasing concentrations of Cl^- in the smaller streams as permafrost degrades due to decreased FRI and warming temperatures. Furthermore, of the smaller study basins, the two with the highest Cl^- concentrations were both subject to fire in the last 60 years and Cl^- concentrations remain elevated, possibly indicating that permafrost recovery is not occurring. In contrast to Cl^-, other solutes do show evidence of recovery from fire. Those watersheds burned over 60 years ago (N1 and N2) exhibit stream DOC concentrations similar to that of the intact basins. In addition, N1 also showed concentrations of DIC and major cations that were similar to intact basins, indicating a recovery of soil structures and permafrost depth. Kawahigashi et al. (2011) also reported recovery of solute concentrations and composition of the organic horizon within a half century of a fire using a space for time approach in these same watersheds. In those smaller watersheds where talik formation does not occur, stream chemistry can be

expected to return to pre-fire conditions within $\sim$60 years.

Conclusion

As our initial hypothesis stated and similar to other studies in sub-arctic regions (MacLean et al. 1999; Petrone et al. 2006), the influence of permafrost results in strong seasonal patterns in stream solute concentration with high organic matter loading in the spring and high cation loading in the summer as permafrost thaws and the active layer deepens. Furthermore, our second hypothesis regarding the effect of wildfire on stream chemistry was also confirmed in that in larch dominated basins of the Central Siberian Plateau, active layer depth as affected by periodic wildfires exerts significant control over stream chemistry. Wildfire was shown to increase active layer depth leading to higher concentrations of cations from a more exposed mineral horizon and it also depleted a primary source of carbon through combustion of the organic layer leading to generally lower DOC concentrations. From our data it also appears that the influence of fire on stream chemistry begins to recede after approximately 60 years as the system returns to pre-fire conditions. Interactions among FRI, degrading permafrost, and conditions leading to the formation of taliks appear to be important drivers of the response of streams in continuous permafrost watersheds of Central Siberia to climate change. The space for time approach we have used to characterize the response of these small watersheds to fire provides a useful chemical baseline that will allow us to more accurately forecast anticipated changes.

References

Abaimov AP (2005) Features and main trends of dynamics of forests and woodlands in permafrost zone of Siberia. Sib Ecol J 4:663–675

Bagard ML, Chabaux F, Pokrovsky OS, Viers J, Prokushkin AS, Stille P, Rihs S, Schmitt SD, Dupre B (2011) Seasonal variability of element fluxes in two Central Siberian rivers draining high latitude permafrost dominated areas. Geochim Cosmochim Acta 75:3335–3357

Betts EF, Jones JB (2009) Impact of wildfire on stream nutrient chemistry and ecosystem metabolism in boreal forest catchments of Interior Alaska. Arct Antarct Alp Res 41:407–417

Carey SK (2003) Dissolved organic carbon fluxes in a discontinuous permafrost subarctic alpine catchment. Permafr Periglac Process 14:161–171

Frey KE, McClelland JW (2009) Impacts of permafrost degradation on arctic river biogeochemistry. Hydrol Process 23:169–182

Frey KE, Smith LC (2005) Amplified carbon release from vast West Siberian peatlands by 2100. Geophys Res Lett 32:L09401

Holmes RM, McClelland JW, Raymond PA, Frazer BB, Peterson BJ, Stieglitz M (2008) Lability of DOC transported by Alaskan rivers to the Arctic Ocean. Geophys Res Lett 35:L03402. doi:10.1029/2007GL032837

Holmes RM, McClelland JW, Peterson BJ, Tank SE, Bulygina E, Eglinton TI, Gordeev VV, Gurtovaya TY, Raymond PA, Repeta DJ, Staples R, Striegl RG, Zhulidov AV, Zimov SA (2012) Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas. Estuar Coasts 35:369–382

Kawahigashi M, Prokushkin A, Sumida H (2011) Effect of fire on solute release from organic horizons under larch forest in Central Siberian permafrost terrain. Geoderma 166:171–180

Kharuk VI, Ranson KJ, Dvinskaya ML (2008) Wildfires dynamic in the larch dominance zone. Geophys Res Lett 35:L01402. doi:10.1029/2007GL032291

MacLean R, Oswood MW, Irons JG III, McDowell WH (1999) The effect of permafrost on stream biogeochemistry: a case study of two streams in the Alaskan (USA) taiga. Biogeochemistry 47:239–267

McClelland JW, Dery SJ, Peterson BJ, Holmes RM, Wood EF (2006) A pan-Arctic evaluation of changes in river discharge during the latter half of the 20th century. Geophys Res Lett 33:L06715. doi:10.1029/2006GL025753

McDowell WH, Likens GE (1988) Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecol Monogr 58:177–195

Nakai Y, Matsuura Y, Kajimoto T, Abaimov AP, Yamamoto S, Zyryanova OA (2008) Eddy covariance CO_2 flux above a Gmelin larch forest on continuous permafrost in Central Siberia during a growing season. Theor Appl Climatol 93:133–147

Peterson BJ, Holmes RM, McClelland JW, Vorosmarty CJ, Lammers RB, Shiklomanov AI, Shiklomanov RB, Rahmstorf S (2002) Increasing river discharge to the Arctic Ocean. Science 298:2171–2173

Petrone KC, Jones JB, Hinzman LD, Boone RD (2006) Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost. J Geophys Res 111:G02020. doi:10.1029/2005JG000055

Petrone KC, Hinzman LD, Shibata H, Jones JB, Boone RD (2007) The influence of fire and permafrost on sub-arctic stream chemistry during storms. Hydrol Process. doi:10.1002/hyp.6247

Pokrovsky OS, Schott J, Kudryavtzev DI, Dupré B (2005) Basalts weathering in Central Siberia under permafrost conditions. Geochim Cosmochim Acta 69:5659–5680

Pokrovsky OS, Schott J, Dupre B (2006) Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basaltic terrain in Central Siberia. Geochim Cosmochim Acta 70:3239–3260

Prokushkin AS, Gleixner G, McDowell WH, Ruehlow S, Schulze ED (2007) Source and substrate-specific export of dissolved organic matter from permafrost-dominated forested watershed in central Siberia. Glob Biogeochem Cycles 21:GB4003. doi:10.1029/2007GB002938

Prokushkin AS, Pokrovsky OS, Shirokova LS, Korets MA, Viers J, Prokushkin SG, Amon RMW, Guggenberger G, McDowell WH (2011) Sources and the flux pattern of dissolved carbon in rivers of the Yenisey basin draining the Central Siberian Plateau. Environ Res Lett 6:045212. doi:10.1088/1748-9326/6/4/045212

Raymond PA, McClelland JW, Holmes RM, Zhulidov AV, Mull K, Peterson BJ, Striegl RG, Aiken GR, Gurtovaya TY (2007) Flux and age of dissolved organic carbon exported to the Arctic Ocean: a carbon isotopic study of the five largest arctic rivers. Glob Biogeochem Cycles 21:GB4011. doi: 10.1029/2007GB002934

Romanovsky VE, Smith SL, Christiansen HH (2010) Thermal state of permafrost in Russia. Permafr Periglac Process 21:136–155

Shirokova L, Pokrovsky O, Kirpotin S, Dupre B (2009) Heterotrophic bacterio-plankton in thawed lakes of the northern part of Western Siberia controls the CO_2 flux to the atmosphere. Int J Environ Stud 66:433–445

Shirokova LS, Pokrovsky OS, Kirpotin SN, Desmukh C, Pokrovsky BG, Audry S, Viers J (2013) Biogeochemistry of organic carbon, CO_2, CH_4, and trace elements in thermokarst water bodies in discontinuous permafrost zones of Western Siberia. Biogeochemistry 113:573–593. doi:10.1007/s10533-012-9790-4

Stocks BJ, Fosberg MA, Lynham TJ, Mearns L, Wotton BM, Yang Q, Jim JZ, Lawrence K, Hartley GR, Mason JA, McKenney DW (1998) Climate change and forest fire potential in Russian and Canadian boreal forests. Clim Change 38:1–13

Striegl RG, Aiken GR, Dornblaser MM, Raymond PA, Wickland KP (2005) A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. Geophys Res Lett 32:L21413

Striegl RG, Dornblaser MM, Aiken GR, Wickland KP, Raymond PA (2007) Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001–2005. Water Resour Res 43:W02411. doi:10.1029/2006WR005201

Tchebakova NM, Parfenova E, Soja AJ (2009) The effects of climate, permafrost and fire on vegetation change in Siberia in a changing climate. Environ Res Lett 4:045013. doi:10.1088/1478-9326/4/4/045013

Verma S, Jayakumar S (2012) Impact of forest fire on physical, chemical, and biological properties of soil: a review. IA-EES 2:168–176

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4702–4708

Yoshikawa K, Bolton WR, Romanovsky VE, Fukuda M, Hinzman LD (2003) Impacts of wildfire on the permafrost in the boreal forests of Interior Alaska. J Geophys Res 108:8148. doi:10.1029/2001JD000438

Zharkoy MA (1984) Paleozoic salt bearing formations of the world. Springer, Berlin