EXPORT OF CARBON, NITROGEN AND MAJOR SOLUTES FROM A BOREAL FOREST WATERSHED: THE INFLUENCE OF FIRE AND PERMAFROST

A

THESIS

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Abstract

Detailed observations of stream, soil, and groundwater chemistry were used to determine the role of fire, permafrost and snowmelt processes on the fluxes of carbon, nitrogen and major solutes from interior Alaskan catchments. We examined an experimentally burned watershed and two reference watersheds that differ in permafrost coverage (high, 53%; medium-burn, 18%; and low, 4%) during the FROSTFIRE prescribed burn in July 1999. The fire elevated stream nitrate concentrations for a short period during the first post-fire storm, but nitrate declined thereafter, suggesting that less severe fires that leave an intact riparian zone may have only a short-term effect on stream chemistry. Nevertheless, we found fundamental differences in hydrochemical differences between watersheds due to the presence of permafrost. Flowpaths in the low-permafrost, likely from the riparian zone, depleted stream nitrate levels while flowpaths in the high permafrost watershed, generated from more distant hillslopes, were a source of nitrate. All watersheds were sources of organic solutes during snowmelt and summer storms. On an annual basis, watersheds were net sources of every individual ion or element (Cl^-, PO_4^{2-}, SO_4^{2-}, DOC, DON, NO_3^-, Na^+, K^+ Mg^{2+}, Ca^{2+}) except NH_4^+, which was a small fraction of the total N concentration in streams. The concentration of NO_3^- was high for an ecosystem with low atmospheric N deposition and compared to non-Alaskan boreal and temperate watersheds, resulting in net N loss. These findings suggest that boreal watersheds in the discontinuous region of interior Alaska may be fundamentally different in their capacity to retain N compared to ecosystems with net N retention.

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CHAPTER ONE

INTRODUCTION

Overview

Watershed science, including biogeochemistry and hydrology, has advanced considerably since its inception the 1960’s. Pioneering studies (e.g., Likens and Bormann 1985) developed the concept of the watershed unit as a framework for studying ecosystem biogeochemical cycling. By measuring meteorological inputs and hydrologic outputs, investigators were able to determine the net retention or export of major nutrients and solutes, and the relative importance of biota, lithology, and hydrology in regulating fluxes. This approach proved useful not only for estimating weathering rates and understanding the cycling of major elements, but also for examining large-scale disturbances such as deforestation (Likens et al. 1970), and detecting regional changes in atmospheric deposition of nitrogen and sulfur (Likens and Bormann 1985). Presently, watershed scientists continue to use the catchment scale, but have recognized the importance of water sources and pathways in altering the chemical composition of runoff to receiving streams (Hill 2000). Water isotope and solute signatures have been used to separate temporal components of flow into pre-event (old water that existed in the catchment prior to the event) and event water (snowpack melt or rain). Most researchers have found that the water generated during storms consists mainly of groundwater that was displaced during the event (Rodhe 1998). Regardless of the source, water flowpaths govern the chemistry of receiving streams. Riparian zones have been identified as crucial ecotones where groundwater discharges during baseflow periods, thereby regulating chemistry between storms. Additionally, because riparian areas often have shallow water tables and saturated soils they can serve as the source area for water and solutes during summer storms or spring snowmelt (Hill 1993).

Stream chemical response to increased flow during snowmelt or storms depends on a number of factors, including the chemistry of new water infiltrating soil, the dissolution or dilution of chemical signatures in source areas, and the mixing of this new storm chemistry with the chemical composition of baseflow. Dissolved organic carbon (DOC) concentration increases with higher flow in nearly all ecosystems because stormflow from surface or riparian soils is elevated in organic matter content (Kaplan and Newbold 2000). Nutrients that are biologically reactive (e.g., NO_3^-, NH_4^+, PO_4^{-3}) may increase or decrease with flow, depending on the season and the activity of plants and microbes along hydrologic flowpaths. On the other hand, weathering products (Ca^{2+}, Mg^{2+}, and Na^+) are often diluted with flow, as storm source areas are often depleted in these ions compared to deep groundwater baseflow. The loss or gain of individual ions on an annual or seasonal basis is the sum of element flux during individual storms and baseflow periods. Therefore, watershed studies need to be considered in the context of climatic, geographical, and biological settings that affect these fluxes (Grimm 2003)

Catchments in interior Alaska are unique in some respects compared to most mid-latitude ecosystems. First, the region was never glaciated during the Pleistocene, and, as a result, mineral soil depth above unconsolidated bedrock can be deep. Second, atmospheric deposition rates of nitrogen and sulfur are low because of little anthropogenic pollution. Lastly, permafrost is discontinuous and found in low lying areas and north-facing slopes that receive less solar radiation than south facing slopes. The presence of permafrost has dramatic consequences for water movement and chemistry; on north-facing slopes and in low-lying valley bottoms permafrost limits hydrologic flow to the organic-rich active layer, whereas on south-facing slopes, water can infiltrate into deeper groundwater flowpaths (Woo 1986). Consequently, streams in watersheds dominated by permafrost tend to have higher DOC and dissolved organic nitrogen (DON) concentrations, but lower dissolved mineral concentrations than watersheds that are mostly permafrost-free (Ray 1988, MacLean et al. 1999).

Currently, there is an urgency to understand the hydrochemistry of high latitude watersheds that are underlain by permafrost that is just below freezing and susceptible to thawing (Osterkamp and Romanovsky 1999). The temperature is increasing at high latitudes due to climate warming, potentially modifying the energy balance of surface soils that insulate permafrost and raising subsoil temperatures? (Serreze et al. 2000). Because water flowpaths that control chemistry are coupled with permafrost distribution, the chemical composition of receiving streams and the retention of carbon and nutrients in the landscape might change if permafrost thaws. An understanding of the current dynamics of permafrost hydrochemistry will provide a baseline to which future landscape conditions can be compared.

Wildfire is a widespread seasonal disturbance in boreal regions, and climate models predict an increase in fire severity and frequency in boreal forests (Flannigan and Van Wagner 1991). The current extent of permafrost coverage is susceptible to wildfire disturbance because intense fire removes the insulating organic layer from the forest floor, thereby accelerating heat flux to soils and increasing the active layer depth. Fire severity plays a particularly important role in interior Alaska. Severe fires can completely burn through the insulating moss layer, causing permafrost to thaw, resulting in improved drainage to the mineral soil below (Hinzman et al. 2003). However, less severe fires may only burn the surface layer, leaving the underlying organic layer intact. Where burning occurs, organic plant biomass is converted into inorganic forms as ash on the forest floor, exposing organic soils to erosion.

Objectives and Chapter Descriptions

The main chapters of this dissertation (chapters 2-4) address a recurring theme in the hydrochemistry of subarctic catchments: How do water flowpaths influence the chemical composition of receiving streams, and the retention of carbon, nitrogen and major solutes at the watershed scale? In chapter two, I integrate landscape factors (permafrost) and large scale disturbance (fire) during summer storm events after a prescribed burn. In chapter three, I address the role of permafrost, flowpaths, and seasonal transitions on annual carbon, nitrogen and major solute budgets. In chapter five, I examine how interannual variations in snowmelt affect the concentration and flux of carbon, nitrogen and major solutes. The aim of this dissertation it to improve our understanding of how ecological and hydrological processes interact to control biogeochemical cycles in boreal forest watersheds. I addressed these questions through detailed observations of stream, soil and groundwater chemistries in three subcatchments of the Caribou Poker Creeks Research Watershed (CPCRW) watershed near Fairbanks, Alaska.

Because watershed biogeochemistry integrates biotic and abiotic processes occurring within the watershed boundary, large-scale experiments are an ideal way to test hypotheses at this scale. In chapter two of my dissertation I present the findings from a prescribed burn, where I examined the role of fire on watershed solute fluxes at CPCRW in interior Alaska as part of a multi-disciplinary fire disturbance project called FROSTFIRE (Hinzman et al. 2003). My objectives were to determine 1) the influence of permafrost on the contribution of storm water to streamflow, 2) the influence of permafrost on the contributing area for flow and 3) the immediate effect of fire on stream chemistry. I hypothesized that the source area and total contribution of “new” water to stream flow during storms would increase with greater permafrost coverage, and that organic soil flow pathways would be more important in controlling stream chemistry in watersheds with greater permafrost coverage. Additionally, I predicted that the fire would increase nitrate concentration in streams in the burn watershed if the source area for the first post-fire storm event included the burned area.

Watershed nutrient retention has been of interest in catchment studies because it enables researchers to interpret how biota (both plants and microbes) assimilate and release nutrients at a large scale. Nitrogen limitation of primary production is a common feature of nearly all ecosystems because nitrogen is not commonly derived from bedrock weathering and must be supplied by nitrogen fixation or atmospheric deposition. As a result, many catchments retain nitrogen (outputs < inputs) and the degree of nitrogen retention may decrease with successional time (Vitousek and Reiners 1975). Because inorganic nitrogen is readily assimilated by nitrogen limited plant-microbe systems, researchers have found that catchments with low rates of nitrogen deposition typically release nitrogen in organic forms (Hedin et al. 1995, Perakis and Hedin 2002). The output of nitrogen from ecosystems is a consequence of biotic processes as well as hydrologic conditions. Despite ecosystem-level nitrogen limitation, catchments may lose nitrogen via hydrologic vectors if nitrogen is unavailable for plant uptake (e.g., DON), or a temporal uncoupling exists between available nitrogen supply and demand.

Whereas alpine and temperate ecosystems have been studied extensively at the watershed scale, fewer studies have been conducted in high-latitude ecosystems. In the third chapter of my dissertation, I examined seasonal changes in stream chemistry and estimated annual budgets of carbon, nitrogen and major solutes in CPCRW. The objectives of this study were to use detailed measurements of stream water chemistry and hydrology from watersheds that differ in permafrost coverage to understand how biological, edaphic, and hydrologic processes interact to control carbon, nitrogen, and other solute losses. I addressed the following questions: 1) how do seasonal changes in flowpath affect relationships between stream chemistry and discharge, 2) what is the relative importance of snowmelt, summer, and the post senescence periods for the export of carbon, nitrogen and solutes, 3) how might a reduction in permafrost coverage affect the net export of carbon, nitrogen, and solutes from boreal watersheds?

Snowmelt is an important hydrochemical event in boreal regions where more than a third of the annual precipitation falls as snow, and snow cover extends for more than half of the year. Despite the long duration of insulative snow cover, cold winter temperatures completely freeze surface soils prior to snowmelt. Frozen soil during snowmelt is unique to subarctic watersheds compared to alpine and temperate ecosystems where unfrozen soils predominate in the spring. In the fourth chapter of my dissertation, I examined the stream hydrochemical response to interannual variations in snowmelt runoff. The purpose of this study was to better understand how the input of snowmelt water affects the concentration and flux of inorganic and organic solutes in a sub-arctic watershed. Specifically, my objectives were to 1) determine the contribution of new water (snowmelt water) and old water (pre-existing water in the catchment) to the snowmelt hydrograph peak using oxygen isotopes and conductivity, 2) identify flowpaths of organic and inorganic solutes to stream flow, and 3) determine the importance of snowmelt to the flux of solutes in the spring season.

References

Flannigan MDF, Van Wagner CE. 1991. Climate change and wildfire in Canada. Can. J. For. Res. 21: 66-72.

Grimm NB, Gergel SE, McDowell WH, Boyer EW, Dent CL, Groffman P, Hart SC, Harvey J, Johnston C, Mayorga E, McClain ME, and Pinay G. 2003. Merging aquatic and terrestrial perspectives of nutrient biogeochemistry. Oecologia. 137: 485-501.

Hedin LO, Armesto JJ, and Johnson AH. 1995. Patterns of nutrient loss from unpolluted old-growth temperate forests: evaluation of biogeochemical theory. Ecology. 76: 493-509.

Hill AR. 1993. Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed. Biogeochemistry. 20:19-44.

Hill AR. 2000. Stream chemistry and Riparian Zones. In: Streams and ground waters, Jones JB and Mulholland PJ (Eds), Academic Press, New York, USA, pp 83-110.

Hinzman LD, Fukuda M, Sandberg DV, Chapin FS III, Dash D· 2003. FROSTFIRE: An experimental approach to predicting the climate feedbacks from the changing boreal fire regime. J. Geophys. Res. 108: 8153.

Kaplan LA, and Newbold JD. 2000. Surface and subsurface dissolved organic carbon. In: Streams and ground waters, Jones JB and Mulholland PJ (Eds), Academic Press, New York, USA, pp 237-258.

Likens GE, Bormann FH, Johnson NM, Fisher DW, Pierce RS. 1970. The effect of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. Ecology Monographs. 40: 23-47.

Likens GE, and Bormann FH. .1995. Biogeochemistry of a forested ecosystem. Springer-Verlag, New York, NY.

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

Osterkamp TE, Romanovsky VE. 1999. Evidence for warming and thawing of discontinuous permafrost in Alaska. *Permafrost and Periglacial Processes*. 10: 17-37.

Perakis SS. 2002. Nutrient limitation, hydrology and watershed nitrogen loss. Hydrological Processes. 16:3507-3511.

Perakis SS, and Hedin LO. 2002. Nitrogen loss from unpolluted South American forests mainly via dissolved organic nitrogen compounds. Nature. 415: 416-419

Ray, SR. 1988. Physical and chemical characteristics of headwater streams at Caribou-Poker creeks research watershed. MS thesis, University of Alaska Fairbanks, Fairbanks, Alaska.

Rodhe A. 1998. Snowmelt-dominated systems. In: C Kendall and JJ McDonnell (Eds) Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam, NL, pp 391-433.

Serreze MC, Walsh JE, Chapin FS, Osterkamp T, Dyurgerov M, Romanovsky V, Oechel WC, Morison J, Zhang T, and Barry RG. 2000. Observational evidence of recent change in the northern high-latitude environment. Climatic Change. 46: 159-207

Sklash MG and Farvolden RN. 1979. The role of groundwater in event runoff. *J. Hydrol*. 43: 45-65.

Vitousek PM, and Reiners WA. 1975. Ecosystem succession and nutrient retention: a hypothesis. Bioscience. 25: 376-381.

CHAPTER TWO

THE INFLUENCE OF FIRE AND PERMAFROST ON SUB-ARCTIC STREAM CHEMISTRY DURING STORMS

Abstract

Permafrost and fire are important regulators of hydrochemistry and landscape structure in the discontinuous permafrost region of interior Alaska. We examined the influence of permafrost and a prescribed burn on concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and other solutes (NO_3^-, Ca^{2+}, K^+, Mg^{2+}, Na^+, K^+) in streams of an experimentally burned watershed and two reference watersheds with varying extents of permafrost in the Caribou Poker Creeks Research Watershed in interior Alaska. The low-permafrost watershed has limited permafrost (3%), the high-permafrost watershed has extensive permafrost (53%), and the burn watershed has intermediate permafrost coverage (18%). The FROSTFIRE prescribed burn, initiated on July 8, 1999, elevated nitrate concentrations for a short period after the first post-fire storm on July 25th, but there was no increase after a second storm in September. During the July storm, nitrate export lagged behind the storm discharge peak, indicating a flushing of soluble nitrate that likely originated from burned soils. Fundamental hydrologic and chemical differences between watersheds were found due to the presence of permafrost by using a three-end member mixing model. Storm flow in the low-permafrost watershed was dominated by precipitation and overland flow from the permafrost-dominated riparian zone, which reduced nitrate at high flow. In contrast, storm water in the high permafrost watershed was dominated by soil flow through the active layer, and nitrate leaching increased concentrations during the storm. Among all watersheds, organic and groundwater flow paths controlled stream chemistry: DOC and DON increased with discharge (organic source) while base cations and SO_4^{2-} (from weathering processes) decreased. Thawing of the active layer increased soil water storage in the high permafrost watershed from July to September and attenuated the hydrologic response and flux of solutes to the stream.

Introduction

In the discontinuous permafrost region of interior Alaska, hydrochemical processes are controlled by the distribution of permafrost. Permafrost occurs predominantly on north-facing slopes and in low-lying valley bottoms and limits hydrologic flow to the organic-rich active layer; whereas, on permafrost-free south-facing slopes, water can infiltrate into deeper groundwater flowpaths (Woo 1986). Consequently, streams in watersheds dominated by permafrost tend to have higher dissolved organic carbon (DOC) and nitrogen (DON), but lower dissolved mineral concentrations, than watersheds that are mostly permafrost-free (Ray 1988, MacLean et al. 1999). Furthermore, in areas of permafrost, the depth of the active layer, that portion of soil above permafrost that freezes and thaws annually, increases throughout the summer, further complicating stream chemistry patterns. Water movement and storage, as well as root and heterotrophic respiration, occur almost exclusively in this seasonally thawed layer. Because of greater water storage capacity, an increase in active layer thickness attenuates the hydrologic response of streams to precipitation inputs. Changes in the depth to permafrost, therefore, affect both hydrologic and biotic processes.

Variation in stream chemistry is most pronounced during storms. Precipitation infiltrates into soils, or moves directly to the stream channel over saturated soils in the riparian zone. Water that composes the hydrograph peak may be "old" water which has been displaced by precipitation, or "new" water from a more direct flowpath to the stream (Sklash and Farvolden 1979). Regardless of source, storm water differs from baseflow because it takes a different path through watersheds and to the stream. Chemical constituents such as dissolved organic carbon may increase in streams due to the dissolution or flushing of compounds in soils that become saturated. Other elements may decline during storms due to the dilution of baseflow chemistry. Nutrients that are biologically reactive may show more complex patterns, depending on the season and the activity of plants and microbes.

Climate models predict an increase in fire severity and frequency in boreal forests (Flannigan and Van Wagner 1991). The current extent of permafrost coverage is susceptible to wildfire disturbance because fire removes the insulating organic layer from the forest floor, thereby accelerating heat flux to soils and increasing the depth of the active layer. Thawing of ice-rich soils can lead to ground slumping (thermokarst) and forest deterioration (Burn 1998, Osterkamp and Romanovsky 1999). Wildfire disturbance has been shown to increase water runoff (Wright 1976, Schindler et al. 1980, Bayley and Schindler 1991), sediment losses (Beaty 1994), and concentrations of major ions and DOC (Bayley and Schindler 1991, Bayley et al. 1992, Chorover et al. 1994, Williams et al. 1997, Williams and Melack 1997). However, due to variations in burn severity, soil fertility, and the spatial extent of burn areas, effects on stream chemistry and hydrology can be limited or undetectable (Richter et al. 1982). Fire severity plays a particularly important role in interior Alaska. Severe fires can completely burn through the insulating moss layer, causing permafrost to thaw, resulting in improved drainage to the mineral soil below (Hinzman et al. 2003). However, less severe fires may only burn the surface layer, leaving the underlying organic layer intact. Where burning occurs, organic plant biomass is converted into inorganic forms as an ash on the forest floor and exposes organic soils to erosion.

In this study, we examined the role of permafrost and fire on watershed solute fluxes. This research was conducted at the Caribou Poker Creeks Research Watershed (CPCRW) in interior Alaska as part of a multi-disciplinary fire disturbance project called FROSTFIRE (Hinzman et al. 2003). We monitored stream chemistry in an experimentally burned watershed with moderate permafrost coverage and two reference watersheds, one with low, and the other with high permafrost coverage during the summer of 1999 before and after the fire Our objectives were to determine 1) the influence of permafrost on the contribution of storm water to streamflow, 2) the influence of permafrost on the contributing area for flow and 3) the immediate effect of fire on stream chemistry. We hypothesized that the source area and total contribution of "new" water to stream flow during storms would increase with greater permafrost coverage and organic soil flow pathways would be more important in controlling stream chemistry in watersheds with greater permafrost coverage. Additionally, we predicted that the fire would increase nitrate concentrations in the burn watershed if the source area for the first post-fire storm event included the burned area. By examining three watersheds with differing amounts of permafrost, we attempt to determine the mechanisms which generate stream flow and chemistry.

Study Site

The CPCRW, part of the Bonanza Creek LTER, is located 50 km northeast of Fairbanks, Alaska and covers 10,620 ha. The climate is continental, with low winter temperatures, high summer temperatures, and an annual mean temperature of -2.5°C. The average annual precipitation for the region ranges from 285 mm at Fairbanks to near 500 mm in upper elevations of CPCRW. Roughly half of the precipitation falls as snow. Snowmelt typically starts in late April and lasts for three to five weeks. During the snow-free period, May and June have the lowest precipitation while July through September have greater rainfall.

The CPCRW boundary includes several sub-basins that differ in permafrost coverage due to aspect (Fig. 2.1). Low sun angles throughout the year result in less energy reaching slopes with northern aspects than slopes with southern aspects. Vegetation is closely related to soil type and permafrost distribution. North-facing slopes are dominated by a black spruce (*Picea mariana*) and feather moss (*Pleurozium schreberi*) community, whereas south slopes are deciduous with a mixture of quaking aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*). Permafrost is also found in riparian zone or valley bottom sites adjacent to the stream due to persistent temperature inversions throughout the winter and poorly drained soils in this zone (Yoshikawa et al. 2002). Maximum depth of thaw on permafrost hillslopes can reach > 1 m while poorly drained sites thaw to only 0.5 m in September prior to re-freezing. Bedrock is unconsolidated Birch Creek schist with surface soils composed of Fairbanks silt loam that have developed in fine loess transported from the Alaska Range.

Three watersheds were examined in this study. The burn watershed has a moderate amount of permafrost (18.8%) and a watershed area of 1040 ha. One reference watershed had high (53.2%) and the other had low permafrost (3.5%) coverage and areas of 520 and 570 ha, respectively (Rieger et al. 1972). From July 8-15, 1999 a prescribed burn was conducted by the Bureau of Land Management and the Alaska Fire Service that moderately to severely burned approximately 28% (320 ha) of the burn watershed (Hinzman et al. 2003). The burn area was limited primarily to the north-facing, black spruce covered slope of the watershed. However, a smaller southeast-facing section was hand-ignited by fire crews within two days of the initial burn. Despite a large burn area much of the riparian zone with saturated soils was unburned.

Methods

Stream discharge was measured continuously from late April through September 1999 in all three streams and periodically throughout the winter when the streambed was ice-free. Stream stage was recorded every hour with a 5psi pressure transducer and a Campbell datalogger (CR10X). The pressure transducer was removed during the fire, reinstalled after the fire, and subsequently recorded every half hour. Periodic discharge measurements were estimated with a Marsh-McBirney electromagnetic current meter to calculate a rating curve and convert stage height to discharge. Precipitation for the July storm was calculated from tipping buckets in the low-permafrost and high-permafrost watersheds. Precipitation in the burn watershed in July and all watersheds in September was calculated from a Remote Automated Weather Station (RAWS; http://fire.ak.blm.gov/) weather station maintained by the Bureau of Land Management, located at Caribou Peak on the boundary of the burn watershed.

Stream water for chemical analyses was collected with an ISCO autosampler every 4 hours in the high permafrost and low-permafrost watersheds, and every 2 hours in the burn watershed during storms. Samples remained in autosamplers for up to four days between collection. We found that certain chemistry such as pH and NH_4^+ did change during this storage period, but we did not use these stored samples for storm chemistry. Otherwise, sample chemistry did not change appreciably between stored and manually collected samples. Samples were transferred to pre-rinsed 125 ml HDPE bottles in the field and filtered within 12 hours using glass fiber filters (Gelman AE, 0.45 μm nominal pore size). Samples were refrigerated until analysis (<48 hours) or frozen for subsequent analyses. Electrical conductivity was measured in the lab using a hand-held Denver Instruments AP-50 meter. An Alpkem autoanalyzer was used to measure NH_4^+ by the phenol-hypochlorite method (Solorzano 1969), soluble reactive phosphorus (SRP) by the molybdate-antimony method (Murphy and Riley 1962), and NO_3^- by cadmium reduction (Wood et al. 1967). DOC was measured as non-purgeable organic carbon on a Shimadzu TOC 5000. Base cations and anions (Ca^{2+}, K^+, Mg^{2+}, Na^+, and

SO_4^{2-}) were analyzed using induced coupled plasma optical emission spectrometry (Jarrel Ash Inc., IRIS) at the North Research Station of Hokkaido University Forests (NR-HUF), Japan.

We determined water pathways during floods using an end-member mixing analysis (EMMA). Hydrologic studies commonly separate flow of storm discharge peaks into “new” (i.e., precipitation) and “old” (i.e., groundwater) water components using a two end member approach (Hooper and Shoemaker 1986, McDonnell et al. 1991). An important assumption of two end-member separation is that surface soil water components have little storage (Sklash et al. 1976, DeWalle et al. 1988). Because permafrost creates "surface storage" as a perched water table in the dominant organic soil flowpath, we used a three component separation model. DOC and calcium were used as tracers because they showed the largest separation among model components; DOC is high in organic surface soils but low in groundwater and mineral soil while calcium shows the opposite pattern due to weathering in mineral soil and bedrock. In this study, we separated flow into three components: 1) precipitation, 2) organic soil, and 3) groundwater:

$$f_{\mathrm{gw}} + f_{\mathrm{org}} + f_{\mathrm{precip}} = 1 \tag{1}$$

$$[\mathrm{Ca}]_{\mathrm{gw}} f_{\mathrm{gw}} + [\mathrm{Ca}]_{\mathrm{org}} f_{\mathrm{org}} + [\mathrm{Ca}]_{\mathrm{precip}} f_{\mathrm{precip}} = [\mathrm{Ca}]_{\mathrm{stream}} \tag{2}$$

$$\mathrm{DOC}_{\mathrm{gw}} f_{\mathrm{gw}} + \mathrm{DOC}_{\mathrm{org}} f_{\mathrm{org}} + \mathrm{DOC}_{\mathrm{precip}} f_{\mathrm{precip}} = [\mathrm{DOC}]_{\mathrm{stream}} \tag{3}$$

where [Ca] and [DOC] are end-member concentrations, *f* is the fraction of each component contributing to streamwater, and the subscripts precip, org, gw, and stream represent precipitation, organic soil, groundwater, and streamwater, respectively. This equation was solved for each time we collected stream chemistry during a storm and periods between samples were linearly interpolated. The total storm contribution for any given component equals the sum over the storm flow period.

The Ca^{2+} concentration in wet deposition from the on-site National Atmospheric Deposition Site (site AK01; http://nadp.sws.uiuc.edu/) was used for the precipitation signature during both storms. We used the weekly averages (July 20-27 1999 and August 31-September 9) as signatures for each storm. DOC concentrations in precipitation were assumed to equal zero. Ca^{2+} and DOC concentrations in soils were determined by lysimeters installed in the burn watershed. Zero-tension (3 burn and 3 control, n=6) and suction lysimeters (20 burn and 20 control, n=40) were installed along transects extending from the toe slope to the riparian zone in spruce stands in the burn watershed in 1998, prior to the fire event. Hardwood (aspens and birch) stands on the south side of the stream yielded little water in lysimeters and are likely a small component of organic soil flow during the summer period. Zero-tension lysimeters were installed in the Oa horizon, which consisted of a thick layer (>10 cm) of decomposed moss and plant litter. Tension lysimeters made of porous ceramic cups (Soil Moisture Inc. and Prenart Inc.) were installed at the interface between the organic and mineral horizons (between 20cm and 30cm depth). We were unable to measure the immediate effect of the fire in the tension lysimeters because they were frozen in the ground and could not be removed prior to the fire. Consequently, the lysimeters were destroyed during the burn. Those lysimeters that were unburned were sampled after the fire in 1999. Final end member signatures were obtained by taking an average of all lysimeters from 1998 and the unburned lysimeters during 1999. There was no significant difference between years. We did not collect soil water samples in the low and high-permafrost watersheds, but mean concentrations of Ca^{2+} and DOC in spruce stands from MacLean et al (1999) in these watersheds were not significantly different from Ca^{2+} and DOC in the burn watershed. The same groundwater signature was used for all three watersheds by obtaining an average concentration for DOC and Ca^{2+} from seeps, wells and pingo springs from the CPCRW (n=13; White et al. 2002). These average concentrations represent an estimate of the regional groundwater signature at CPCRW.

A sensitivity analysis was performed on EMMA by incorporating sample variability and analytical error in end-member signature estimates. We calculated the standard error of the organic and groundwater end-member concentrations and ran the model using plus and minus the standard error of the mean. Since only one sample was available for the precipitation signature for each storm, we used the analytical error of replicate samples (Gordon 1999). We ran the model by varying end-members individually using the maximum and minimum of the end-member signatures. These model outputs were compared to the original model run using the mean end-member signature.

Linear regressions were performed on chemical concentrations vs. discharge for the July and September storms. Normal probability plots of residuals from regressions were used to test the assumptions of normality. In all cases, stream data conformed to residual normality tests, except for nitrate and sulfate in the burn watershed in July (StatSoft 2000). Transformations did not significantly improve the distribution of nitrate and sulfate regressions so we report raw data for all regressions. Regressions were compared between July and September storms using a t-test on regression slopes (Sokal and Rohlf 1995). Contributing areas were calculated by integrating the discharge from the three stormflow components and dividing by the total precipitation for the storm event (Table 2.2, Eshleman et al. 1993).

Results

Baseflow chemistry prior to the prescribed burn was consistent for each watershed and reflects the stream-specific contribution of groundwater vs. soil flowpaths. The DOC concentration was highest in high permafrost (1341 μM), intermediate in low permafrost (594 μM), and lowest in the burn (357 μM; Table 2.1). Conversely, electrical conductivity, a measure of total dissolved solutes, was highest in the burn (101 μS), intermediate in low permafrost (68 μS), and lowest in high permafrost (50 μS). Ammonium (near 1 μM for all streams) and SRP (<1μM) were consistently low in all streams and were often below detection limits. Nitrate, highest in the burn (45.4 μM), intermediate in low permafrost (40.6 μM), and lowest in high permafrost (21.8 μM), was 20 to 40 fold greater than ammonium and comprised nearly all of the DIN output from the CPCRW watersheds. On annual basis, nitrate concentrations were lowest for all streams during mid-May at the peak of snowmelt. This snowmelt dilution of nitrate was greatest in the high permafrost watershed where nitrate approached zero μM (Fig. 2.3).

Total precipitation amounts were comparable for the July and September storms (22.6 and 22.9 mm, respectively), but maximum precipitation intensity was lower during the July storm (11.4 mm/hr) compared to the September storm (22.4 mm/hr). As a result, storm discharge peaks in the burn and low-permafrost watersheds were lower in July. In contrast, the high permafrost watershed showed the greatest discharge peak in July and declined to less than half of this amount in September (Fig. 2.2). Peak flows for the July storm were four- to five-fold greater in high permafrost (129 L/s) and the burn watershed (107 L/s) than the low-permafrost basin discharge (26 L/s). In September, peak flow remained high in the burn watershed (144.9 L/s) and low in the low-permafrost watershed (43.0 L/s), whereas the high permafrost watershed peak discharge was much lower compared to July (55.1 L/s). The time to peak from precipitation to the storm discharge maximum was shorter overall in September except for the high permafrost watershed flow which took several hours longer to peak than the other watersheds. In July, flow in the burn and high permafrost watersheds peaked similarly, while the low-permafrost peak occurred earlier (Fig. 2.2).

Three EMMA Analysis

The stream concentrations for DOC and Ca^{2+} fell within the bounds of the end-members in the mixing diagram (Figs 2.4 a and b), indicating that the stream water was indeed a mixture of flow from these components. For all streams, the concentrations of

DOC and Ca^{2+} moved closer to the organic soil end-member during storms, indicating that storm flow was largely derived from soils. In particular, the high permafrost watershed received the greatest contribution from organic soils while the low-permafrost watershed had the smallest organic contribution during both events (Fig 2.5). In July, groundwater dominated the hydrograph in the burn watershed; both precipitation and groundwater dominated the hydrograph in low permafrost, and the organic soil component dominated the high permafrost hydrograph. Groundwater continued to dominate the Burn hydrograph in September, and it also composed most of the low- and high-permafrost hydrographs (Fig. 2.5). All watersheds showed a decline in the organic soil component with a concomitant rise in the groundwater component between the July and September storms (Table 2.2).

When EMMA source chemistries were changed by plus or minus a standard error, the sensitivity analysis showed a <10% change in the relative proportions of flow components to storms. The three end-member mixing model was most sensitive to variation in the calcium concentration of groundwater; with the low range of the groundwater calcium concentration the groundwater component increased 6 to 8% with a concomitant 5 to 7% decrease in the precipitation component. The model was also sensitive to the concentration of DOC in the organic soil component. A standard error increase in the soil DOC concentration resulted in a drop in the organic soil component between1 and 3% and an increase in precipitation flow (1-3%). All other tested variations in end-member concentrations produced little change in the model outcome

(<1%). These potential sources of error were small compared to the differences among watersheds.

Hydrograph Separation and Contributing Areas

The groundwater component dominated the hydrograph in all storms except for the low-permafrost and high-permafrost watersheds in July, when the precipitation and organic components were greatest (Fig. 2.5). Comparing the July and September storms, the groundwater component increased with a corresponding decrease in the organic component. Similarly, the precipitation component increased in the burn and high permafrost watersheds, but decreased slightly in the low-permafrost watershed between July and September (Table 2.2).

With the higher precipitation intensity in the September storm, the total storm-contributing area increased for the low-permafrost watershed (8 to 23 ha) and burn watershed (68 to 123 ha). In contrast, the contributing area of the high permafrost watershed declined from 83 to 56 ha due to a smaller contribution from the organic soil component. As a percentage of the watershed area, the total storm contributing area was greatest in the high permafrost watershed in July (14.5%) while the burn watershed (11.8%) was highest in September. The contributing area remained low in the low-permafrost watershed in both July (1.6%) and September (4.4%; Table 2.2).

Stream Water Chemistry and Discharge Relationships

In general, the base cations, sulfate and electrical conductivity, which were most concentrated in groundwater, tended to decline during storm flows. Discharge vs. concentration relationships were statistically significant in 31 of 36 of these cases (Table 2.3). Interestingly, nitrate had both positive and negative relationships with discharge. During the July storm, nitrate was positively correlated with discharge in the burn and high permafrost basins, but negatively correlated with discharge in low permafrost (Figs. 2.6 and 2.7, Table 2.3). In the September storm, nitrate remained positively correlated with discharge in the high permafrost watershed and negatively correlated with discharge in the low permafrost while the burn watershed changed to a negative relationship with discharge. Nitrate showed anticlockwise hysteresis loops in the burn watershed during both storms and in high permafrost in September.

Discussion

Our results support the conceptual model hypothesized by MacLean et al. (1999), whereby permafrost restricts water to the active layer, reducing the flux of DIN, DON and DOC to the stream. We expand upon this model by demonstrating that the source area for flow and the mechanism of water movement to the stream play an important role in stream chemistry during periods of high flow. Furthermore, the hydrologic and chemical response is attenuated by an increase in active layer thickness and water storage during the summer months.

Fire Effects

Numerous studies have documented elevated stream solute concentrations following fire (Bayley and Schindler 1991, Bayley et al. 1992, Chorover et al. 1994, Williams et al. 1997, Williams and Melack 1997). . In this study, the hysteresis pattern observed and the shift from a positive to negative nitrate vs. discharge relationship suggests a possible nitrate source in the burn watershed. Compared to the reference watersheds, the burn watershed was the only stream that showed a concentration-discharge relationship with a change in direction; the nitrate concentration-discharge relationship was positive in July but negative in September (Figs 2.6 and 2.7). The anti-clockwise hysteresis of nitrate in the burn watershed in July revealed a lag response of export that can be attributed to a “flushing effect” of nitrate from burned soils whereby readily soluble ions are dissolved by event water (Evans and Davies 1988).

Nitrate dynamics in the burn watershed can be explained by the mixing model analysis and contributing area for each storm. The contributing area (21 ha) for the July storm likely included areas that were burned on either side of the stream. Given the large riparian saturated areas in CPCRW, a likely runoff sequence could begin with flow from the near-stream saturated soils, followed by flow from adjacent hillslope areas as soils become saturated from a perched water table in the active layer (Hooper et al. 1990). Our data are consistent with such a runoff sequence; nitrate initially decreased on the rising limb of the hydrograph due to an influx of nitrate-depleted mixed precipitation and standing water from anoxic riparian soils. Subsequently, nitrate increased as runoff from the burned zones reached the stream.

Permafrost and hydrology

A comparison of the timing and magnitude of hydrographs peaks among the three watersheds suggests that permafrost plays an important role in stream water generation (Figs. 2.2a and b). The quick and short duration response in the low-permafrost watershed likely reflects its small contributing area (5ha in July and 12ha in September), and confinement of flow to saturated riparian soils. Precipitation directly onto saturated areas is consistent with a rapid hydrologic response as water moved to the stream as overland saturated flow or direct channel flow (Hill 1993). This mechanism likely generated the earlier discharge peak observed in the low-permafrost watershed compared to the burn and high permafrost watersheds.

Temporal changes in the active layer affected discharge patterns in the high permafrost watershed. Peak discharge in this watershed was lower in September despite greater precipitation intensity, whereas the low-permafrost and burn watersheds showed faster time to peak and higher discharge in response to this more rapid precipitation. Active layer depths increase steadily throughout the summer months, reaching a maximum in September prior to soil freeze-up (Hinzman et al. in press). Such a change in the active layer depth would increase soil storage and reduce the amount of water that enters the stream from precipitation because soils are slower to become saturated and generate streamflow. Since the hydraulic conductivity of thawed organic soils is high (Woo 1986), the infiltration rate far exceeded the precipitation rate, and less runoff from permafrost dominated hillslopes reached the stream during a late summer storm. In contrast, the contributing areas for the low-permafrost and burn watersheds are less affected by seasonal changes in the active layer. Thawing does occur in these more water-logged soils, but the saturated conditions and standing water prevents rapid infiltration.

In all watersheds, the rise in the groundwater component and decline in the organic component from July to September was consistent with active layer dynamics. As the active layer depth reached the mineral soils, water infiltration increased and greater flow was generated from deeper horizons. From July to September, the contribution of precipitation to stream flow increased in the burn and high permafrost watersheds, but declined slightly in the low-permafrost watershed. We expected an increase in the precipitation component for all streams in response to higher precipitation intensity in September. Valley bottom soils which generated stormflow in the low-permafrost watershed may possibly become more enriched in calcium throughout the summer due to evapotranspiration. Mixing of concentrated valley bottom water with precipitation would diminish calcium dilution during the storm, resulting in a smaller estimation of the precipitation component for the September storm.

Permafrost and Chemistry

Consistent chemical responses among watersheds during storms demonstrate the importance of water flowpaths and weathering processes in regulating stream chemistry. Major cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) always declined with increasing discharge due to dilution of baseflow water, which is enriched in weathering products, by precipitation and water from surface soils. The same surface flowpaths that dilute major cations also enrich organic compounds and metals associated with them. DOC, DON, Al and Fe increased with storm discharge, suggesting that dissolution of organic compounds in the active layer increases with streamflow.

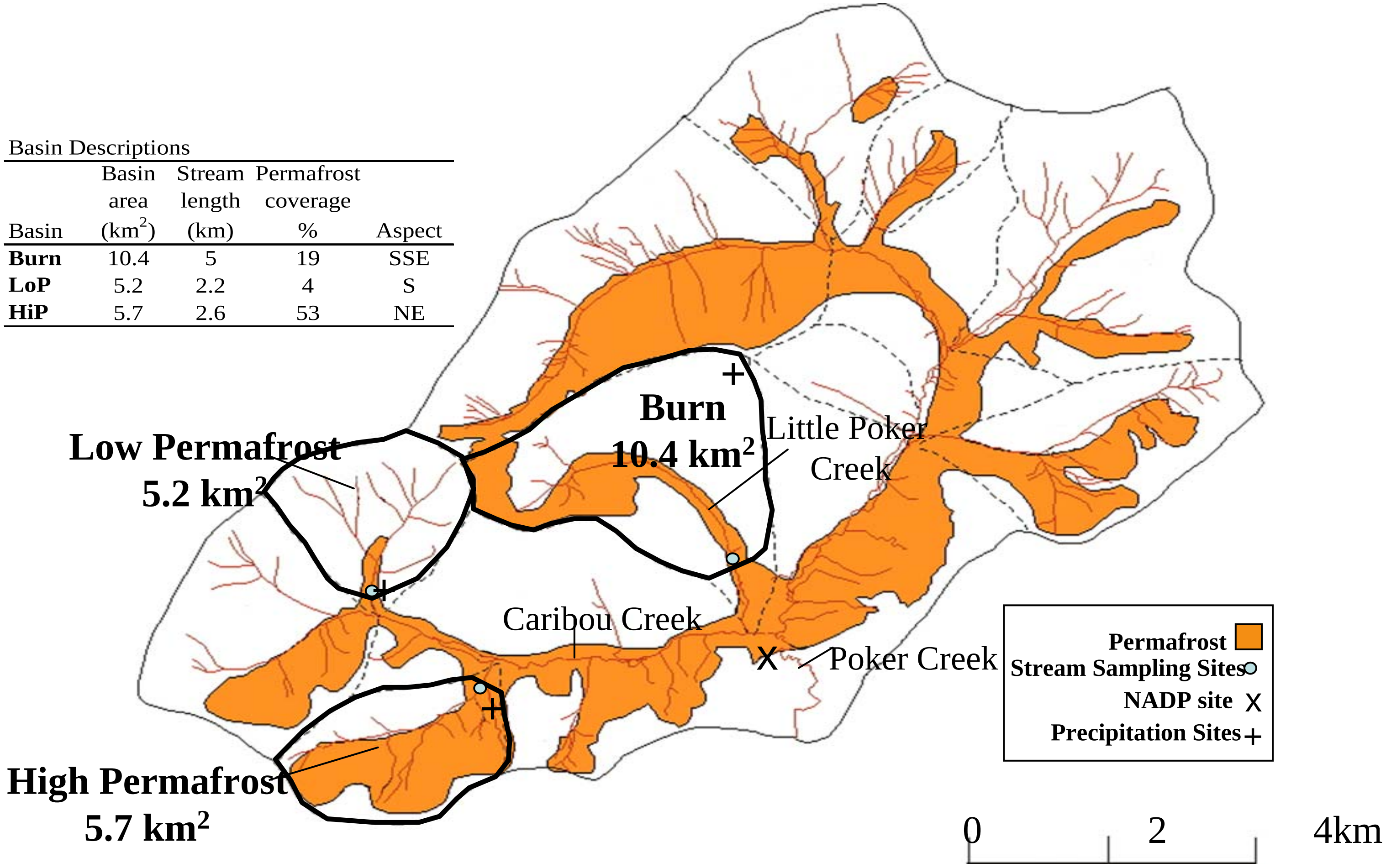
Nitrate differences among watersheds can be attributed to biotic processes and flowpaths governed by permafrost. Nitrate consistently decreased during storms in the low-permafrost watershed, but, simultaneously, increased with flow in the high permafrost watershed. As our mixing model demonstrated, the storm water in the low-permafrost watershed was generated from a small contributing area confined to saturated valley bottom soils. This water was a mixture of low nitrate precipitation and anoxic soil water that dilutes stream nitrate concentrations during peak flows (Hill 1993). In this way, the riparian zone in CPCRW may be acting as a sink for dissolved nitrogen via processes such as denitrification and plant uptake (Peterjohn and Correll 1994). An increase in nitrate with flow in the high permafrost watershed suggests that permafrost-dominated hillslopes are potential sources of nitrate in sub-arctic regions. The contributing area for the high permafrost watershed is much larger than in the low-permafrost watershed, including hillslopes as well as near stream valley bottom zones. Hillslope water moves toward the stream after soils become saturated and generate lateral flow, leaching nitrate as well as organic compounds.

Ecosystem Implications

Since the nitrogen deposition rate is low in low in interior Alaska, biotic processes such as mineralization or nitrogen fixation must be supplying the nitrate flux to streams in the high permafrost watershed during storms. Nitrogen fixation from symbiotic cyanobacterial (*Nostoc* sp) is associated with feather moss (*Pleurozium schreberi*) in boreal forests of Scandinavia (1.5 to 2.0 kg N ha^{-1} yr^{-1}; DeLuca et al. 2002). Feather moss is ubiquitous in permafrost underlain hillslopes at CPCRW and could potentially provide up to five times the rate of atmospheric deposition of nitrogen in CPCRW. Nitrogen fixation by alder (*Alnus crispa and A. tenufolia*) could also be a potential nitrate source, but alder is more common in deciduous stands compared to spruce stands at CPCRW (Troth et al. 1976). At CPCRW, the bulk of stream N output is comprised of nitrate and concentrations are an order of magnitude higher than published concentrations in other boreal (Ford and Naiman 1989, Stottlemyer 1992, Cooke and Prepas 1998) and in arctic ecosystems (Peterson et al. 1992). Given these high concentrations of nitrate in CPCRW streams, it would require a widespread and severe fire disturbance in order to see a significant and long-term change in nitrate chemistry.

Conclusions

While antecedent moisture conditions largely control the soil contribution to flow in temperate, permafrost free watersheds (DeWalle et al. 1988, Hooper et al. 1990), we found that the presence of permafrost and the active layer depth are also important factors generating hillslope runoff. Consequently, organic soils can serve as a source for not only DOC and DON, but also DIN, mainly nitrate. If, in the future, active layer depths become deeper each season due to increasing ambient temperatures and a more frequent and severe fire regime, organic soils could become an even more important source of nitrogen to subarctic streams. Additionally, movement of water from organic to mineral soils will result in a dissolution of weathering ions such as calcium and adsorption of DOC (MacLean et al. 1999). The contributing area for storm flow and the chemistry of these source areas largely affects the chemistry of streams at CPCRW. Storm chemistry in low-permafrost watersheds is influenced mainly by the saturated riparian soils and precipitation while watersheds with greater permafrost coverage are affected by flow from more distant hillslopes underlain by permafrost that reaches the stream following saturation. In interior Alaska, less severe fires which do not affect riparian zones may only have a short-term effect on the water chemistry of receiving streams.



Basin Descriptions

Basin	Basin area (km^2)	Stream length (km)	Permafrost coverage %	Aspect
Burn	10.4	5	19	SSE
LoP	5.2	2.2	4	S
HiP	5.7	2.6	53	NE

Fig. 2.1 Permafrost distribution and site descriptions at the Caribou-Poker Creeks Research Watershed (CPCRW)

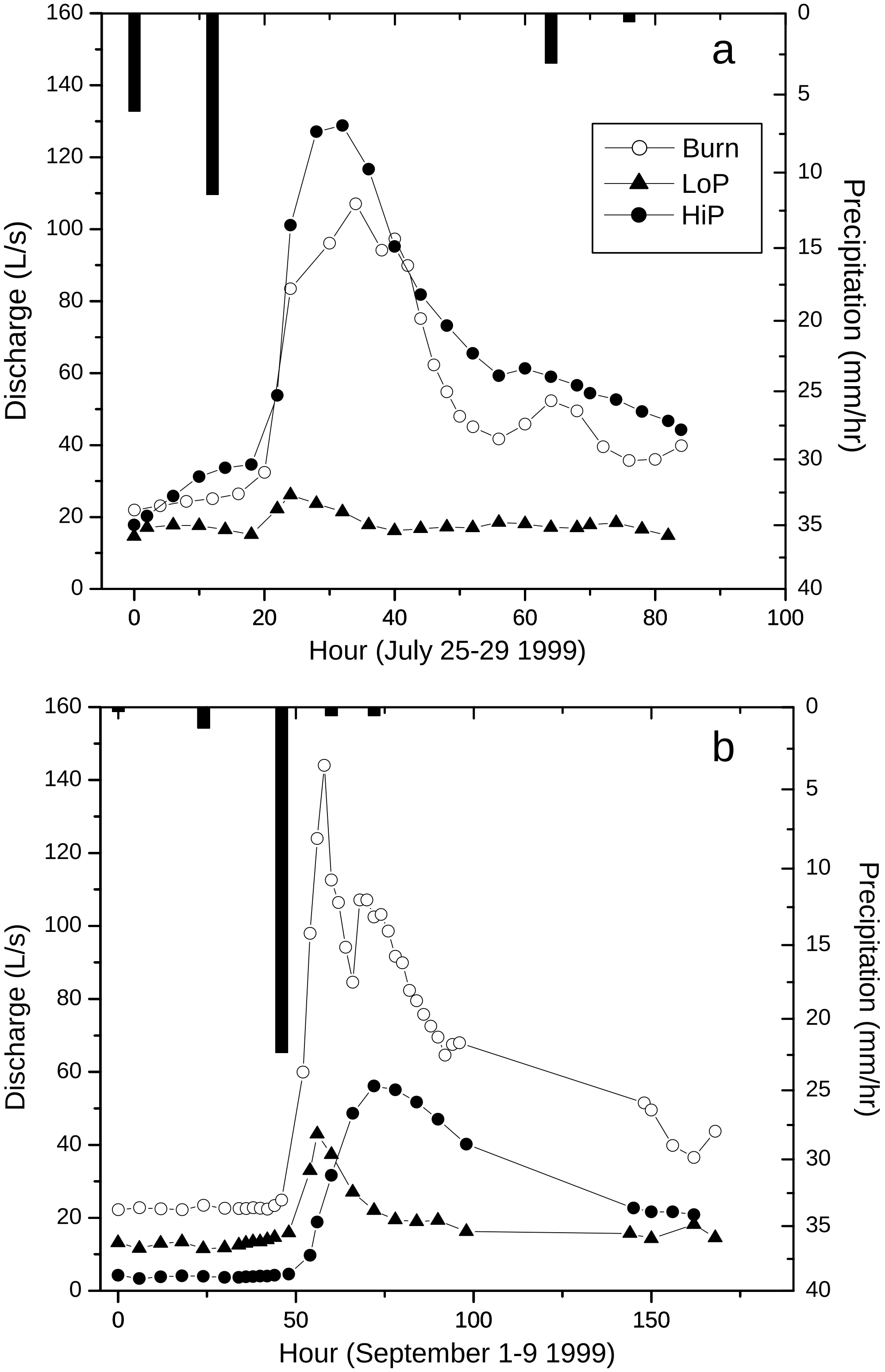


Fig 2.2 Precipitation and discharge for the Burn, LoP and HiP basins

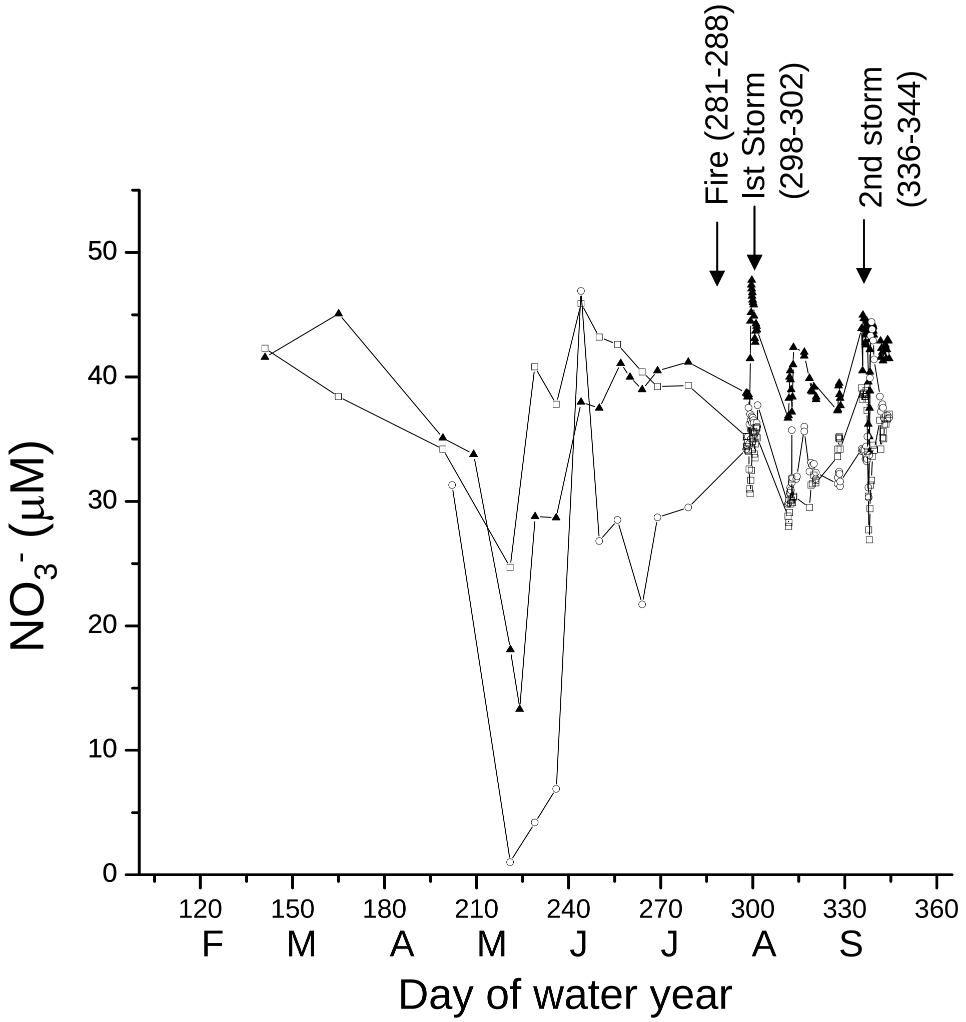


Fig 2.3 Annual pattern of nitrate concentration for the three watersheds. Burn (closed triangles), LoP (open squares) and HiP (open circles).

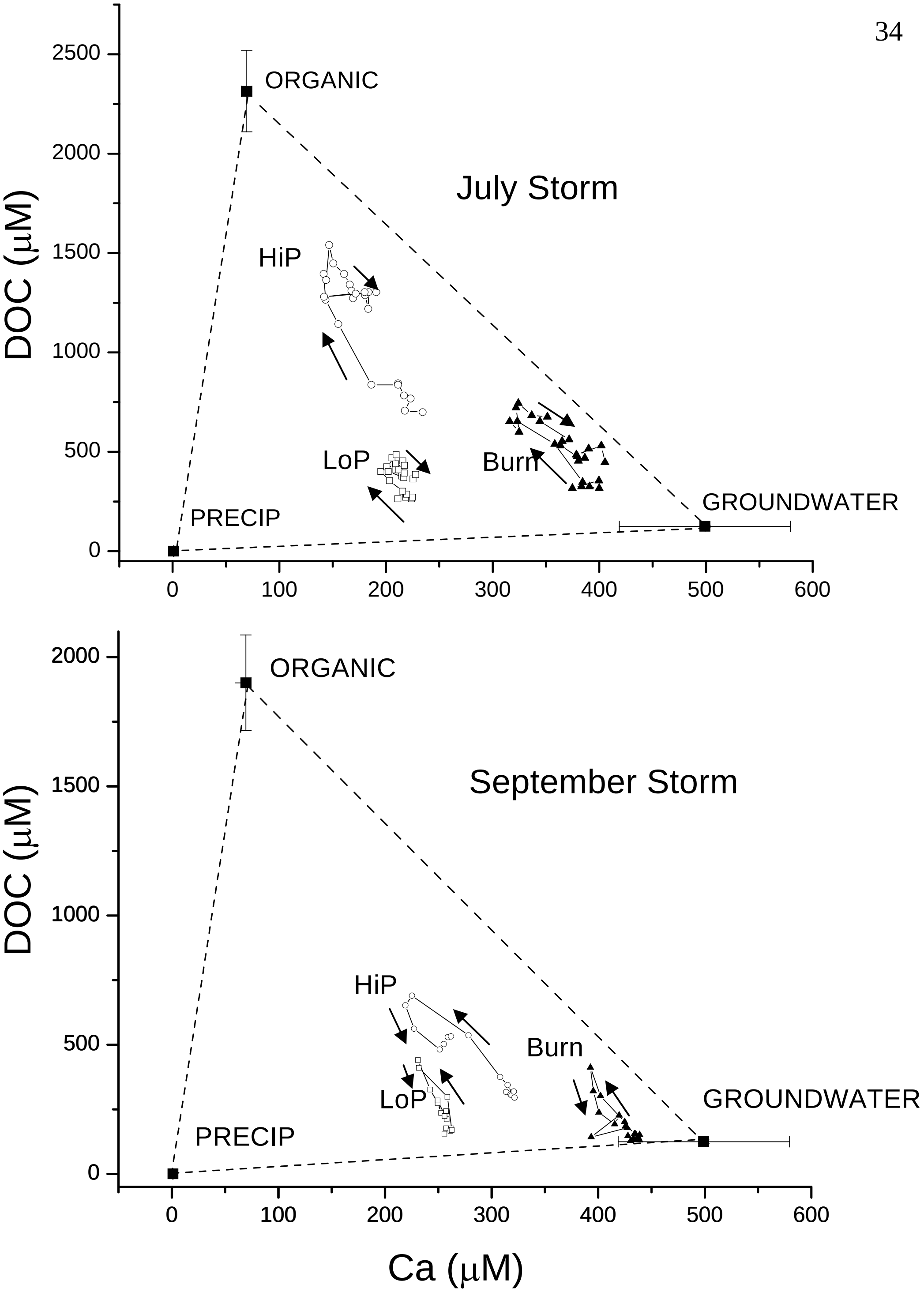


Fig 2.4. Mixing diagram using DOC and calcium as end-members with the Burn (closed triangles), LoP (open squares) HiP (open circles) stream concentrations during the July (top panel) and September (bottom panel) storms. The closed squares of the mixing triangle represent the end-member concentrations and error bars (±SE).

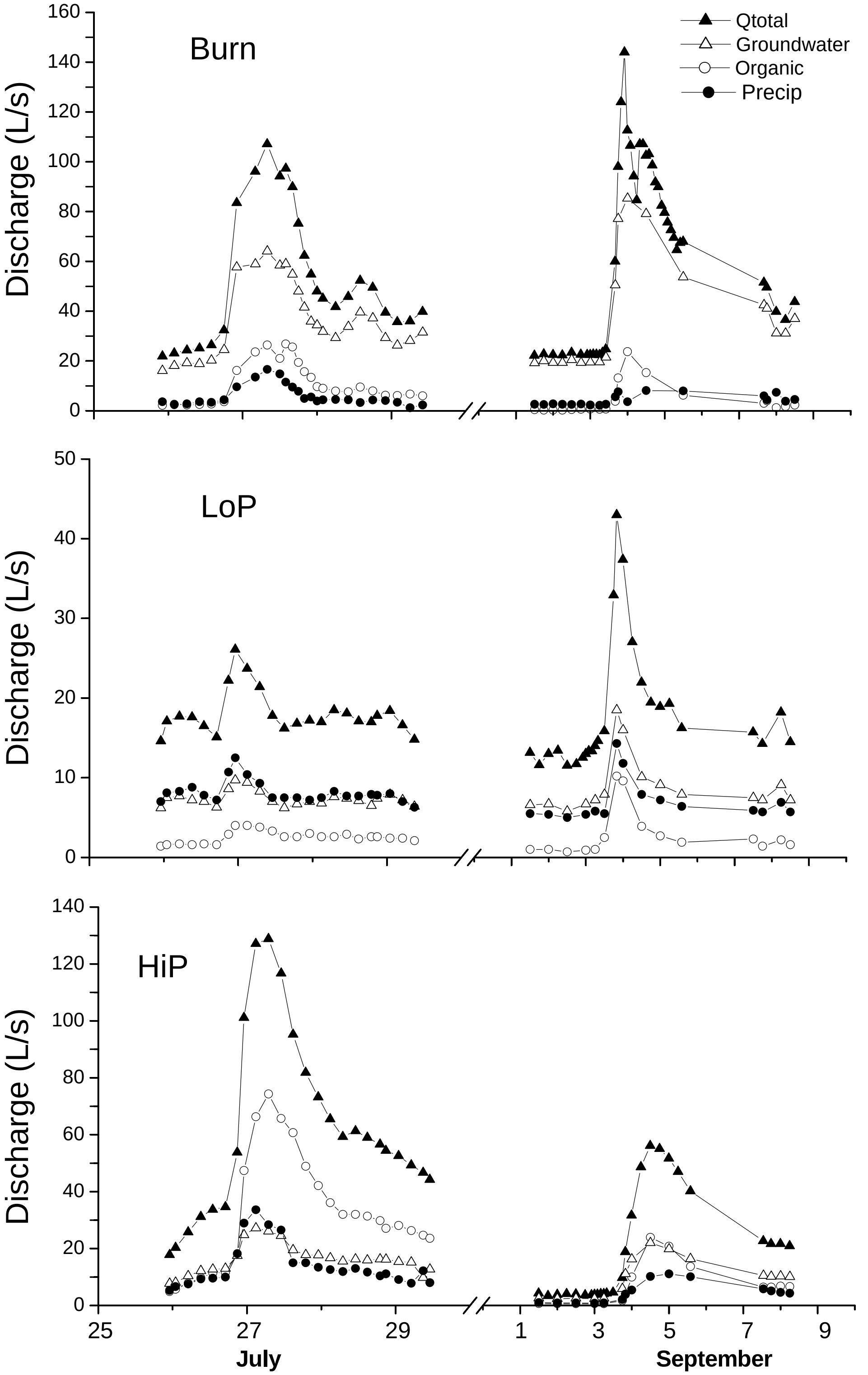


Fig. 2.5. Contribution of the PRECIP (precipitation), ORG (organic), and GW (groundwater) components to the total discharge for the Burn, LoP (low-permafrost) and HiP (high-permafrost) basins during the July and September storm events.

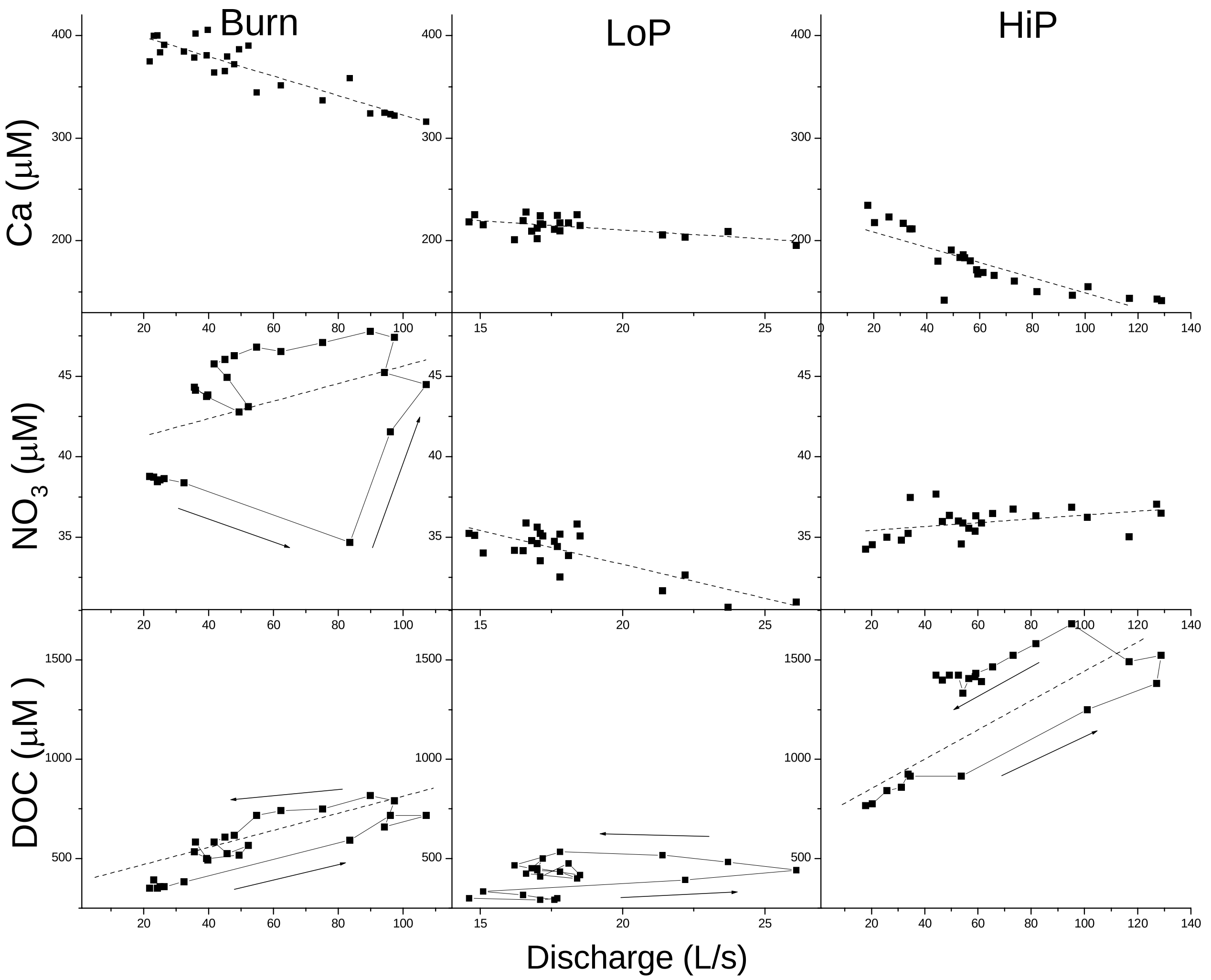


Fig 2.6. Concentration vs. discharge plots of selected chemistry for the Burn, LoP (low-permafrost) and HiP (high-permafrost) basins during the July storm event. Those relationships that are significant are shown with a linear regression line. Hysteresis patterns are shown by connecting points throughout the storm and arrows show the direction of the time series.

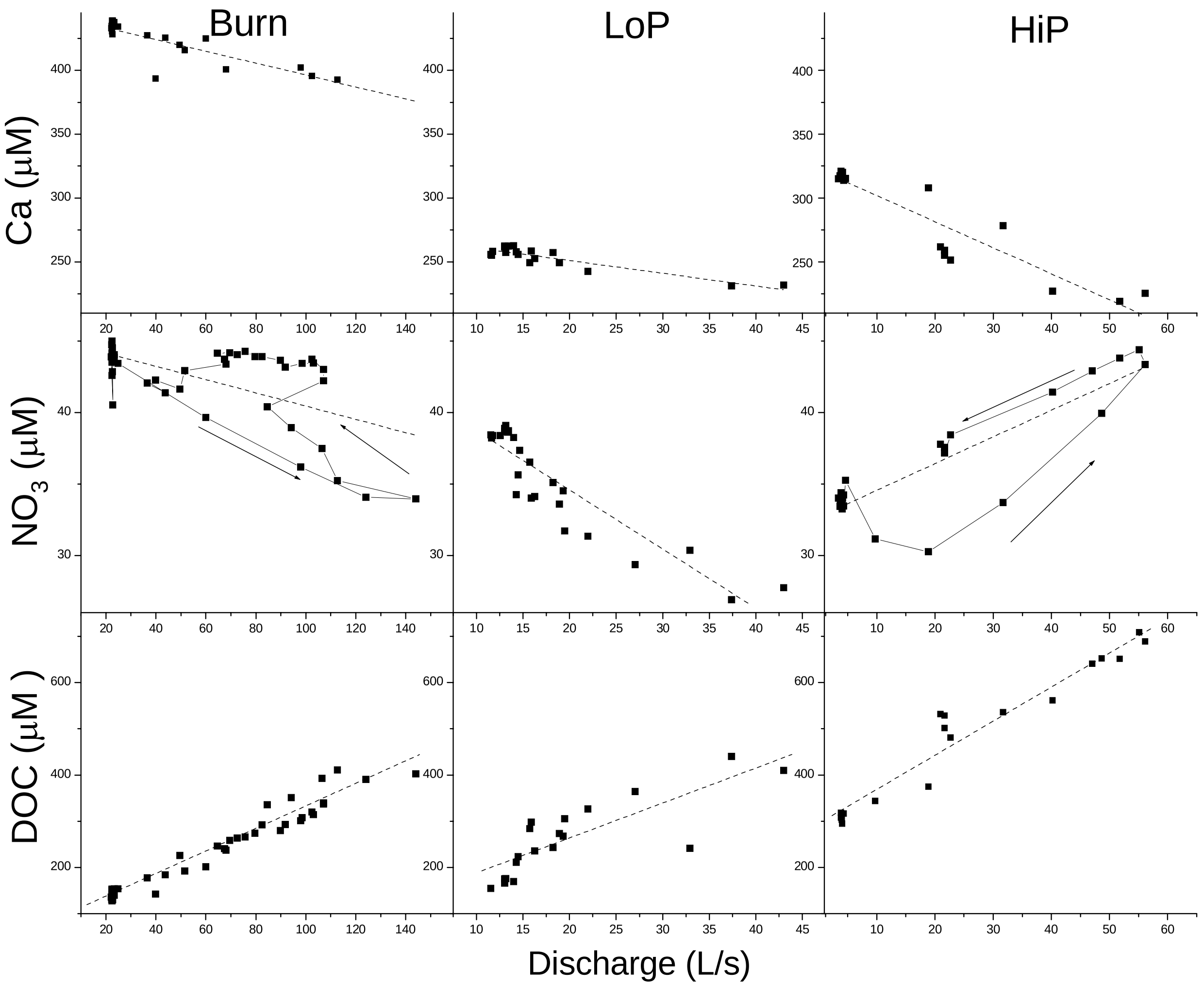


Fig. 2.7. Concentration vs. discharge plots of selected chemistry for the Burn, LoP (low-permafrost) and HiP (high-permafrost) basins during the July storm event. Those relationships that are significant are shown with a linear regression line. Hysteresis patterns are shown by connecting points throughout the storm and arrows show the direction of the time series.

Table 2.1. Pre-fire chemistry of surface stream water in the Burn, LoP and HiP watersheds during baseflow conditions, June 1999.

	Watershed					
	Burn		LoP		HiP	
	Mean	(SE)	Mean	(SE)	Mean	(SE)
Conductivity (μS/cm)	100.6	0.4	67.7	0.1	49.6	0.8
Nitrate (μM)	45.4	0.3	40.6	0.1	21.8	0.1
Ammonium (μM)	1.1	0.2	1.3	0.3	0.9	0.2
Phosphate (μM)	0.5	0.0	0.4	0.0	0.3	0.0
DOC (μM)	356.6	8.1	593.9	11.1	1341.0	10.6

Table 2.2 Hydrograph separation results from the three end-member mixing model for the Burn, high permafrost, and low permafrost watersheds for the July and September 1999 storm events. Total new water is the sum of soil and precipitation components. Contributing area is equal to the discharge component volume/precipitation volume.

	Total Storm Discharge	Total Precip-itation	Max Precip-itation	Groundwater Discharge		Organic Discharge		Precipitation Discharge		Total Storm Water Contributing Area	Total Storm Water Contributing Area/Watershed Area
site	m^3	mm	mm/hr	m^3	% of total	m^3	% of total	m^3	% of total	ha	%
<u>July</u>											
Burn	15331	22.6	11.4	10635	69.4	3446	22.5	1250	8.2	68	6.5
Low Permafrost	1867	22.6	11.4	749	40.1	317	17.0	801	42.9	8	1.6
High Permafrost	18649	22.6	11.4	4828	25.9	10740	57.6	3081	16.5	83	14.5
<u>September</u>											
Burn	28169	22.9	22.4	22452	79.7	2549	9.0	3168	11.2	123	11.8
Low Permafrost	5232	22.9	22.4	2529	48.3	610	11.7	2093	40.0	23	4.4
High Permafrost	12808	22.9	22.4	6461	50.4	2977	23.2	3370	26.3	56	9.8

Table 2.3. Regression coefficients for stream chemical concentrations versus discharge for the July and September 1999 storm events. The regression equation is [y] = M Q + b where [y] is concentration, M is the slope and b is the intercept. SE is the standard error of the slope and intercept. Values in parentheses are negative. Concentrations are uM unless reported otherwise. A significant T statistic indicates a difference between slopes for the two storm events.

	July								**September**							**Event**	
Species	Site	n	Slope	±SE	Intercept	±SE	R2	*P*	n	Slope	±SE	Intercept	±SE	R2	*P*	T stat	*P*
NO_3^-	Burn	25	0.05	0.03	40.18	1.56	0.12	<0.05	40	(0.05)	0.01	45.09	0.78	0.31	<0.001	2.75	<0.01
	LoP	23	(0.42)	0.07	41.75	1.31	0.61	<0.001	25	(0.41)	0.04	42.70	0.79	0.81	<0.001	(0.10)	-
	HiP	24	0.01	0.01	35.19	0.40	0.12	<0.05	25	0.19	0.02	32.68	0.55	0.76	<0.001	(6.65)	<0.001
SO_4^{2-}	Burn	24	(0.10)	0.02	72.61	1.30	0.45	<0.001	ns	-	-	-	-	-	-	-	-
	LoP	22	(1.01)	0.18	83.12	3.25	0.59	<0.001	17	(0.46)	0.05	77.24	0.96	0.84	<0.001	(2.44)	<0.01
	HiP	23	(0.28)	0.08	60.25	5.42	0.34	<0.01	17	(0.81)	0.10	95.28	2.52	0.78	<0.001	2.94	<0.01
Conductivity	Burn	24	(0.20)	0.02	113.88	1.31	0.77	<0.001	40	(0.15)	0.01	117.84	0.39	0.95	<0.001	(1.81)	-
(µS/cm-2)	LoP	23	(0.48)	0.14	87.96	2.50	0.34	<0.01	25	(0.32)	0.04	88.75	0.86	0.68	<0.001	(0.88)	-
	HiP	24	(0.24)	0.03	65.07	2.02	0.74	<0.001	25	(0.50)	0.03	88.51	0.93	0.89	<0.001	4.21	<0.001
Ca	Burn	25	(0.95)	0.10	417.60	5.90	0.79	<0.001	18	(0.46)	0.07	442.72	3.84	0.70	<0.001	(2.88)	<0.01
	LoP	23	(1.77)	0.56	245.85	10.29	0.29	<0.01	17	(1.00)	0.11	271.06	2.21	0.82	<0.001	(1.14)	-
	HiP	24	(0.77)	0.10	225.82	6.90	0.72	<0.001	17	(2.04)	0.21	322.39	5.08	0.85	<0.001	4.17	<0.001
Mg	Burn	25	(0.25)	0.03	118.78	1.62	0.78	<0.001	18	(0.12)	0.01	133.58	0.75	0.80	<0.001	(3.17)	<0.01
	LoP	23	(0.82)	0.23	122.50	4.23	0.34	<0.01	17	(0.54)	0.06	142.12	1.23	0.81	<0.001	(0.96)	
	HiP	24	(0.17)	0.02	56.70	1.50	0.73	<0.001	17	(0.43)	0.04	80.35	0.93	0.89	<0.001	4.41	<0.001

Table 2.3. continued

	July								**September**							**Event**	
Species	Site	n	Slope	±SE	Intercept	±SE	R2	*P*	n	Slope	±SE	Intercept	±SE	R2	*P*	T stat	*P*
K	Burn	25	(0.04)	0.00	19.62	0.29	0.69	<0.001	18	ns	-	-	-	-	-	-	-
	LoP	23	(0.11)	0.03	13.31	0.54	0.35	<0.01	17	ns	-	-	-	-	-	-	-
	HiP	24	(0.03)	0.00	10.34	0.22	0.76	<0.001	17	(0.05)	0.00	10.07	0.12	0.84	<0.001	2.38	<0.05
Na	Burn	25	(0.15)	0.02	54.49	1.46	0.61	<0.001	18	(0.09)	0.01	50.57	0.48	0.84	<0.001	(1.93)	-
	LoP	23	ns	-	-	-	-	-	17	ns	-	-	-	-	-	-	-
	HiP	24	(0.06)	0.02	38.96	1.21	0.36	<0.001	17	(0.16)	0.01	41.98	0.31	0.90	<0.001	3.08	<0.01
DON	Burn	24	0.19	0.04	46.62	2.49	0.46	<0.001	36	ns	-	-	-	-	-	-	-
	LoP	21	ns	-	-	-	-	-	15	ns	-	-	-	-	-	-	-
	HiP	23	0.14	0.03	51.08	2.13	0.47	<0.001	18	1.69	0.16	22.82	3.91	0.87	<0.001	(8.12)	<0.001
DOC	Burn	25	4.64	0.62	318.33	36.97	0.70	<0.001	40	2.42	0.09	85.06	6.66	0.95	<0.001	3.12	<0.01
	LoP	23	ns	-	-	-	-	-	18	7.58	1.29	110.29	28.08	0.65	<0.001	-	-
	HiP	24	6.09	1.41	894.17	98.20	0.43	<0.001	17	7.40	0.47	294.53	15.04	0.94	<0.001	(0.69)	-
Al	Burn	25	ns	-	-	-	-	-	18	ns	-	-	-	-	-	-	-
	LoP	23	ns	-	-	-	-	-	17	ns	-	-	-	-	-	-	-
	HiP	24	0.02	0.00	0.56	0.26	0.41	<0.05	17	0.01	0.00	0.70	0.04	0.51	<0.01	1.51	-
Fe	Burn	25	0.01	0.00	0.09	0.04	0.80	<0.001	11	0.00	0.00	(0.12)	0.03	0.90	<0.001	1.49	-
	LoP	23	0.02	0.00	(0.06)	0.09	0.34	<0.01	16	0.01	0.00	(0.14)	0.03	0.82	<0.001	0.48	-
	HiP	24	0.02	0.00	0.48	0.11	0.84	<0.001	17	0.02	0.00	0.03	0.02	0.94	<0.001	0.97	-

REFERENCES

Bayley SE, and Schindler DW. 1991. The role of fire in determining water chemistry in northern coniferous forests. In Ecosystem Experiments. Scope #45, Mooney HA, Medina E, Schindler DW, Schulze ED, Walker BH (eds). John Wiley and Sons Ltd, New York; 145-165.

Bayley SE, Schindler DW, Beaty KG, Parker BR, and Stainton MP. 1992. Effects of multiple fires on nutrient yields from stream draining boreal forest and fen watersheds: nitrogen and phosphorus. Can. J. Fish Aquat. Sci. 49: 584-596.

Beaty KG. 1994. Sediment transport in a small stream following two successive forest fires. Can. J. Fish. Aquat. Sci. 51: 2723-2733.

Burn CR. 1998. The response (1958-1997) of permafrost and near-surface ground temperatures to forest fire, Takhini River valley, southern Yukon Territory. Can. J. Earth Sci. 35: 184-199.

Chorover J, Vitousek PM, Everson DA, Esperanza AM, and Turner D. 1994. Solution chemistry profiles of mixed-conifer forests before and after fire. Biogeochemistry 26: 115-144.

Cooke SE, and Prepas EE. 1998. Stream phosphorus and nitrogen exports from agricultural and forested watersheds on the Boreal Plain. Can. J. Fish Aquat. Sci. 55: 2292-2299.

DeLuca TH, Zackrisson O, Nilsson M-C, and Sellstedt A. 2002. Quantifying nitrogen-fixation in feather moss carpets of boreal forests. Nature. 419: 917-920.

DeWalle DR, Swistock BR, and Sharpe WE. 1988. Three-component tracer model for stormflow on a small Appalachian forested catchment J. of Hydrol. 104: 301-310.

Eshleman KN, Pollard JS, and O'Brien AK. 1993. Determination of contributing areas for saturation overland flow from chemical hydrograph separations. Water. Resour. Res. 29: 3577-3587.

Evans C, and Davies TD. 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episodic hydrochemistry. Water Resour. Res. 34: 129-137.

Flannigan MDF, and Van Wagner CE. 1991. Climate change and wildfire in Canada. Can. J. For. Res. 21: 66-72.

Ford TE, and Naiman RJ. 1989. Groundwater - surface water relationships in boreal forest watersheds: Dissolved organic carbon and inorganic nutrient dynamics. Can. J. Fish. Aquat. Sci. 46: 41-49

Gordon, JD. 1999. External quality-assurance results for the National Atmospheric Deposition Program/National Trends Network, 1995/1996. USGS Water Resources Investigations Report 99-4072, Denver, CO

Haugen, RK, Slaughter, CW, Howe, KE, and Dingman SL. 1982. Hydrology and Climatology of the Caribou-Poker Creeks Research Watershed, Alaska. CRREL Report 82-26, 35p.

Hill AR. 1993. Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed. Biogeochemistry. 20:19-44.

Hinzman LD, Fukuda M, Sandberg DV, and Chapin FS III, Dash D. 2003. FROSTFIRE: An experimental approach to predicting the climate feedbacks from the changing boreal fire regime. J. Geophys. Res. 108: 8153.

Hinzman LD, Bolton BW, Jones JB and Petrone KC. Hydrological Processes in Alaska’s Boreal Forest. In BNZ LTER synthesis chapter: Alaska’s Changing Boreal Forest, Oswood MW and Chapin FS (eds), in press.

Hooper RP, and Shoemaker CA. 1986. A comparison of chemical and isotopic hydrograph separation. Water Resour. Res. 22: 1444-1454.

Hooper RP, Christophersen N, and Peters NE. 1990. Modeling streamwater chemistry as a mixture of soilwater end-members – an application to the Panola Mountain catchment, Georgia, U.S.A. J. Hydrol. 116: 321-343.

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

Murphy J, and Riley JP. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36.

Osterkamp TE, and Romanovsky VE. 1999. Evidence for warming and thawing of discontinuous permafrost in Alaska. Permafrost and Periglacial Processes. 10: 17-37.

Peterjohn WT, and Correll DL. 1994. Nutrient dynamics in an agricultural watershed: Obervations on the role of a riparian forest. Ecology. 65: 1466-1475.

Peterson BJ, Corliss T, Kriet K, and Hobbie JE. 1992. Nitrogen and phosphorus concentrations and for the upper Kuparak River on the North Slope of Alaska in 1980. Hydrobiologia. 240: 61-69.

Ray, SR. 1988. Physical and chemical characteristics of headwater streams at Caribou-Poker creeks research watershed. MS thesis, University of Alaska Fairbanks, Fairbanks, Alaska.

Rieger S, Furbush CE, Schoephorster DB, Summerfield H, and Geiger LC Jr. 1972. Soils of the Caribou-Poker creeks research watershed, Interior Alaska. CRREL Technical Report 236, US Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.A.

Richter DD, Ralston CW, and Harms WR. 1982. Prescribed fire: effects on water quality and forest nutrient cycling. Science. 215: 661-663.

Schindler DW, Newbury RW, Beaty KG, Prokopowich J, Ruszczynski T, and Dalton JA. 1980. Effects of windstorm and forest fire on chemical losses from forested watersheds and on the quality of receiving streams. Can. J. Fish. Aquat. Sci. 37: 328-334.

Sklash MG, Farvolden RN, and Fritz P. 1976. A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. Can. J. Earth Sci. 13: 271-283.

Sklash MG and Farvolden RN. 1979. The role of groundwater in event runoff. J. Hydrol. 43: 45-65.

Sokal RR and Rohlf FJ. 1994. Biometry: The Principles and Practice of Statistics in Biological Research, W H Freeman & Co, San Francisco, U.S.A.

Solorzano L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceanogr. 14: 799-801.

StatSoft I. 2000. STATISTICA for Windows. 2300 East 14th Street, Tulsa, OK 74104, StatSoft, Inc.

Stottlemyer, R. 1992. Nitrogen mineralization and streamwater chemistry, Rock Creek watershed, Denali National Park, Alaska, U.S.A. Arctic and Alpine Research. 24: 291-303.

Troth JL, Deneke FJ, and Brown LM. 1976. Upland aspen/birch and black spruce stands and their litter and soil properties in interior Alaska. For. Sci. 22: 33-44.

White D, Yoshikawa K, and Garland DS 2002. Use of dissolved organic matter to support hydrologic investigations in a permafrost-dominated watershed. Cold Regions Science and Technology. 35: 27-33.

Williams MR, Brown AD, and Melack JM. 1997. Geochemical and hydrologic controls on the composition of surface water in a high-elevation basin, Sierra Nevada, California. Limnol Oceanogr. 38: 775-797 .

Williams MR, and Melack JM. 1997. Effects of prescribed burning and drought on the solute chemistry of mixed-conifer forest streams of the Sierra Nevada, California. Biogeochemistry. 39: 225-253.

Woo MK. 1986. Permafrost hydrology in North America. Atmos. Ocean 24: 201-234.

Wood ED, Armstrong FAJ, Richards FA. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. J. Mar. Biol. Assoc. UK 47: 23-31.

Wright RF. 1976. The impact of forest fire on the nutrient influxes to small lakes in northeastern Minnesota. Ecology 57: 649-663.

Yoshikawa K, Hinzman LD, and Gogineni P. 2002. Ground temperature and permafrost mapping using an equivalent latitude/elevation model. Journal of Glaciology and Geocryology 24: 526-531.

CHAPTER THREE

SEASONAL EXPORT OF CARBON, NITROGEN AND MAJOR SOLUTES FROM ALASKAN CATCHMENTS WITH DISCONTINUOUS PERMAFROST

Abstract

Frequent measurements of stream chemistry during snowmelt and summer storms were used in three watersheds that differ in permafrost coverage (high, 53%; medium, 18%; and low, 4%) to determine the role of water flowpaths on the fluxes of carbon, nitrogen and major solutes from Alaskan catchments. The slope of the relationship between NO_3^- and SO_4^- in streams lessened from winter to summer in the high permafrost watershed but not in the other watersheds, indicating a change from groundwater to surface flow where permafrost is present. Concentrations of dissolved organic carbon (DOC) decreased in the low and medium permafrost watersheds throughout the summer as flow shifted to deeper soils, but the active layer (the seasonally thawed layer of soil above the permafrost) in the high permafrost watershed remained a source for DOC and NO_3^- during late summer storms. Permafrost constrained water flow to the active layer, resulting in higher DOC but lower dissolved mineral fluxes (Ca^{2+} Mg^{2+} K^+ Na^+) in the high permafrost watershed than in the watersheds with less permafrost coverage. However, the decline in dissolved mineral fluxes was not linearly related to permafrost coverage across watersheds. The flux of weathering ions may also be explained by flowpath length and total water runoff, since the medium permafrost watershed, which is slightly larger, yielded the greatest loss of all major elements (Ca^{2+} Mg^{2+} K^{+} Na^{+} SO_4^{2-} NO_3^{-} NH_4^{+} Cl^{-}) except DOC. Despite differences among watersheds in permafrost coverage, hydrologic flowpaths, area, and total runoff, all watersheds were net sources of every individual ion or element (Cl^{-}, PO_4^{2-}, SO_4^{2-}, DOC, DON, NO_3^{-}, Na^{+}, K^{+} Mg^{2+}, Ca^{2+}) except NH_4^{+}, which was a small fraction of the total N concentration in streams. Overall, the concentration of NO_3^{-} was high for an ecosystem with low atmospheric N deposition and compared to non-Alaskan boreal and temperate watersheds, resulting in net N loss. These findings suggest that boreal watersheds in the discontinuous region of interior Alaska may be fundamentally different in their capacity to retain N compared to ecosystems with net N retention.

Key Words: Active layer, boreal, DOC, flowpath, nitrate, nitrogen, solutes, snow melt, watershed, permafrost.

Introduction

Understanding the role of boreal forests in global element cycling is becoming increasingly important as temperature increases at higher latitudes in response to a changing climate (Serreze et al. 2000). Much attention has focused on elemental fluxes from land to the atmosphere in boreal ecosystems, but we know less about the flux of C, N and other major solutes from watersheds in stream flow. A warmer climate could affect numerous factors that control hydrologic elemental fluxes such as the timing and contribution of snow pack meltwater, soil water storage during summer, or large-scale alterations in subsurface flowpaths through watersheds with permafrost degradation.

In interior Alaska, permafrost controls hydrochemistry throughout the year by constraining flow to the organic-rich active layer, the portion of soil that thaws and re-freezes annually (Woo 1986). A decline in permafrost may improve soil conditions for decomposition and increase the turnover and pool sizes of carbon and nitrogen that could potentially be flushed from soils to streams. However, the same conditions that improve decomposition are likely to thaw more of the active layer, increase water storage, and lengthen water flowpaths from soils to streams. Longer flowpaths may decrease elemental flux to streams through adsorption and uptake by plants and microbes. Conversely, certain elements may increase in concentration along flowpaths due to leaching from soils or weathering of bedrock

Previous studies in interior Alaska have shown that a permafrost-dominated watershed had higher fluxes of DOC but lower fluxes of dissolved solutes such as Ca^{2+}, Mg^{2+}, and Na^{+} than an adjacent watershed with little permafrost (Ray 1988, MacLean et al. 1999). This difference in solute fluxes was hypothesized to be due to shallow flow through the organic-rich active layer in the high permafrost watershed, whereas in the low permafrost watershed, water infiltrates into deeper mineral layers where DOC adsorption and weathering occur. While these observations are a valuable starting point for understanding permafrost effects on watershed biogeochemistry, we lack understanding about how the release of snow pack meltwater or seasonal changes in the active layer may affect elemental fluxes.

The objectives of this study were to use detailed measurements of stream water chemistry and hydrology from watersheds that differ in permafrost coverage to understand how biological, edaphic, and hydrologic processes interact to control C, N, and other solute losses. The greatest variations in stream chemistry occur during periods of high flow, such as snowmelt or summer rain storms. In subarctic watersheds, the snowmelt period is important because more than a third of the precipitation occurs as snow and the snow cover period extends for up to seven months of the year. The depth of the snowpack and the timing of melt are likely to change under a warmer climate. Furthermore, the response of stream chemistry in the subarctic may change throughout the summer as the depth of the active layer increases. The signature of stream chemistry provides a useful tool to examine flowpaths in boreal watersheds as surface flow through organic soils increases the concentration of DOC, whereas groundwater flowpaths may enrich concentrations of major solutes such as Mg^{2+}, Ca^{2+}, and Na^{+}. In this study, we addressed the following questions: 1) How do seasonal changes in flowpath affect relationships between stream chemistry and discharge, 2) What is the relative importance of snowmelt, summer, and the post senescence periods for the export of carbon, nitrogen and solutes, 3) How might a reduction in permafrost coverage affect the net export of C, N and solutes from boreal watersheds?

Study Site

The Caribou Poker Creeks Research Watershed (CPCRW) is part of the Bonanza Creek Long Term Ecological Research (LTER) site and is located 50 km northeast of

Fairbanks, Alaska. The climate is continental with exceptionally low winter temperatures, high summer temperatures, and a mean annual temperature of -2.5°C. The average annual precipitation for the region ranges from 285 mm for Fairbanks to near 500 mm in upper elevations of CPCRW. Roughly one-third of the precipitation falls as snow, snow cover extends from mid-October to late April, and snow melt lasts for three to five weeks. During the snow-free period, May and June have the lowest precipitation while July through September have greater rainfall.

The CPCRW boundary includes several sub-basins that differ in permafrost coverage due to aspect. Low sun angle throughout the year results in less energy reaching slopes with northern aspects than slopes with southern aspects. Vegetation is closely related to soil type and permafrost distribution. North-facing slopes are dominated by a black spruce (*Picea mariana*) and feather moss (*Pleurozium schreberi* and others) community, whereas south slopes are deciduous with a mixture of quaking aspen (*Populus tremuloides*) and paper birch (*Betula neoalaskana*). Permafrost is also found in riparian zone or valley bottom sites adjacent to the stream due to persistent temperature inversions throughout the winter and poorly drained soil in this zone (Yoshikawa et al. 2002). Maximum thaw depth on permafrost hillslopes can reach > 1 m, whereas poorly drained sites thaw to only ~0.5 m in September prior to re-freezing.

The CPCRW watershed is part of the Yukon-Tanana Terrane that consists of polydeformed and polymetamorphosed Upper Paleozoic and older metasedimentary, metavolcanic, and metaplutonic rocks collectively know as Birch Creek Schist. Specifically, CPCRW is part of the Chatanika Terrane which contains protoliths of

Devonian-Mississipian age. The Chatanika terrane contains calcareous eclogite white mica schist, biotite schist, amphibolite, and quartzite (Newberry 1996). CPCRW and the surrounding area was never glaciated during the Pleistocene, and surface soils, composed of Fairbanks silt loam, developed from fine eolian loess transported from the Alaska Range. Alluvial deposits are common in wide valleys; peat deposits are found in many low lying areas, and thick loess deposits are typically found on south-facing slopes.

Three watersheds examined in this study varied in permafrost coverage and size. The high (53.2%) and low permafrost (3.5%) watersheds had areas of 520 and 570 ha, respectively, whereas the medium permafrost watershed (18.8%) had a slightly larger area of 1040 ha (Rieger et al. 1972; Fig. 3.1).

Methods

Our study encompasses the 2000-2001 water year (October 2000 through September 2001). During the ice-free periods, stream stage was recorded every hour with a 5 psi pressure transducer and a Campbell datalogger (CR10X). Periodic discharge measurements were conducted with a Marsh-McBirney electromagnetic current meter to permit confirmation of established rating curves. Stream discharge was measured continuously during the snowmelt period in April through freeze-up in late September. We made periodic measurements of discharge and chemistry during the winter (November, February, and March). Flow recedes during the winter period from high flow in the fall season to low flow during the spring prior to snowmelt (Ray 1988, MacLean et al. 1999).

Stream water for chemical analyses was collected with an ISCO autosampler every 4 hours during snowmelt and summer storms. Samples remained in autosamplers for up to four days between collections. Samples were transferred to pre-rinsed 125 ml HDPE bottles in the field and filtered within 12 hours using glass fiber filters (Gelman A/E, 0.7 μm nominal pore size). Samples were refrigerated and analyzed within 48 hours or were frozen for later analysis. Electrical conductivity was measured in the lab using a hand-held Denver Instruments AP-50 meter. DOC was measured as non-purgeable organic carbon on a Shimadzu TOC-5000. Base cations and anions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, PO_4^{3-}, SO_4^{2-}, NO_3^-, and NH_4^+) were analyzed by Dionex ion chromatography. Total dissolved nitrogen (TDN) was measured with an Antek 720C Chemiluminescent N detector coupled with the Shimadzu TOC-5000. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN (NO_3^- plus NH_4^+).

Wet precipitation volume and chemistry for major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-, and NH_4^+) was provided by the National Atmospheric Deposition Program (NADP, site AK01; http://nadp.sws.uiuc.edu/) station located in CPCRW 1-5 km from the research watersheds. Because dry deposition was not measured at CPCRW, we used dry deposition estimates from the Clean Air Status and Trends Network Station located at Denali National Park, 200 km from CPCRW.

Soil core samples (50cm depth) were collected on 12 September 2001 in black spruce stands on adjacent hillslope and riparian sites in the medium permafrost watershed. Soil cores were separated into organic and mineral soil horizons, sieved and homogenized, and analyzed for pH, total C, total N and water extractable Cl^-, PO_4^{3-}, NO_3^-, and SO_4^{2-}.

pH was measured with a pH probe in a soil and de-ionized water slurry. Dried soil samples were analyzed on a Leco CN analyzer for total C and N. For water extractable anions, we added 10g of soil to 30ml of de-ionized water, and samples were shaken for 1 hr prior to vacuum filtration through 1μm filters. Anions were analyzed by Dionex ion chromatography.

Budget calculations were performed by comparing inputs (wet deposition from the NADP at CPCRW and dry deposition from the Denali NADP site) with stream output during the 2000-2001 water year. We used the calculated deposition rates from the NADP, which are based on precipitation estimates from a Belfort rain gage adjacent to the precipitation chemistry collector. Precipitation rates do not change appreciably with elevation at CPCRW; the NADP precipitation data (230m elevation) were very similar to those from the Remote Automated Weather Station (RAWS) operated by the Bureau of Land Management (BLM) weather station located in the medium permafrost watershed (760m elevation).

Stream chemical output was calculated as the product of discharge and concentration calculated on an hourly basis from 1 October 2000 to 31 September 2001. When chemistry or discharge were not measured directly, we linearly interpolated between sampling points. Hourly flux rates were summed for the water year to obtain an annual flux rate. The greatest source of error in our budgets is due to interpolation over winter when few samples were obtained. Previous studies in the same watersheds, however, have found a less than 10% difference between winter stream chemistry estimated by interpolation and the chemistry from actual winter samples (MacLean et al.

1999). In addition, we lacked hourly discharge measurements for the month of July for the medium permafrost watershed due to equipment malfunction, but weekly discharge measurements were still obtained.

Discharge and chemical data were analyzed by linear regression and one-way ANOVA with Statistica software (StatSoft 2000). Regression was used to examine the relationship between discharge and stream chemistry as well as the relationship between NO_3^- and SO_4^{2-} and between DOC and DON). ANOVA was used to test the difference in average chemical concentrations and regression slopes among watersheds. Normal probability plots of residuals from regressions were used to test the assumptions of normality. Annual stream data conformed to residual normality tests, but individual discharge events typically did not meet the assumptions of normality. Transformations did not significantly improve the distribution of data sets so we report raw data in all cases.

Results

Hydrologic fluxes

Stream hydrologic response to snowmelt and precipitation varied markedly among watersheds in the during summer storms (Fig 3.2). In the high permafrost watershed, storm flow was an order of magnitude higher (220 L/s) than baseflow (10-30 L/s), and was greatest among the three watersheds. Meanwhile, the low and medium permafrost watersheds showed much lower snowmelt and storm peaks, but the baseflow discharge steadily increased in both of these watersheds throughout the summer. The annual discharge patterns for the three watersheds reflected the importance of baseflow in total annual discharge with the medium (228 mm/year) and low permafrost (164mm/year) watersheds producing more water per area than the high permafrost watershed (104mm/year; Table 3.1). Winter baseflow as a percent of the annual flow was much lower in the high permafrost watershed (21%) than the medium (50%) and low (55%) permafrost watersheds, whereas runoff during the snowmelt period as a percent of total annual runoff was three times greater in high (25%) compared to low (7%) and medium (9%) permafrost basins.

Water and Soil Chemistry

Soil samples from hillslope and riparian sites did not vary significantly by site, but did vary by soil horizon. pH, total C, and total N were significantly higher in hillslope and riparian organic horizons than mineral horizons (Table 3.2; ANOVA, Tukey's multiple comparisons, $p < 0.05$). However, C/N, Cl^-, and SO_4^{2-} did not vary significantly between soil horizons or sites. NO_3^- was higher in the organic horizon of the hillslope site than any other horizon or site (Table 3.2; ANOVA, Tukey's multiple comparisons, $p < 0.05$).

Precipitation chemistry, as volume-weighted mean concentration (μeq/L), was dominated by SO_4^{2-} and NO_3^- with lesser amounts of NH_4^+ and Cl^-. Na^+, K^+, Mg^{2+} and Ca^{2+} were found in very low concentrations, typical of unpolluted continental precipitation (Table 3.3). Stream water concentrations of all ions except NH_4^+ were at least an order of magnitude higher than in precipitation. Among the major ions in stream water, Ca^{2+} and Mg^{2+} concentrations were highest, followed by Na^+ and SO_4^{2-} and NO_3^-. K^+ and Cl^- were found at relatively lower concentrations and NH_4^+ and PO_4^{3-} were often below detection limits (Table 3.3).

Temporally, Mg^{2+}, $Ca^{2+,}$ and Na^+ concentrations tended to decline during snowmelt and summer rain events in all watersheds as baseflow was diluted by the influx of snowmelt water or rain water (Fig. 3.3). In contrast, K^+ increased two-fold prior to the snowmelt peak in the medium permafrost watershed and at the same time maximum K^+ concentrations were observed in the low and high permafrost watersheds. K^+ concentration declined throughout the summer in all watersheds (Fig. 3.3).

Winter DOC concentrations were consistently low, but increased throughout the snowmelt in the high and low permafrost watersheds, whereas concentrations remained low in the medium permafrost watershed (Fig. 3.3a). The annual DOC peak in the medium permafrost watershed preceded the snowmelt discharge peak, but in the high and low permafrost watersheds the annual DOC peak coincided with snowmelt (Fig 3.3b). DOC peaks during the summer period occurred at similar times in all three watersheds and coincided with summer storms. DOC and DON concentrations were quite variable in all streams (Table 3.3). DOC:DON ratios were also variable, ranging from less than 10 to over 150 in all streams, and average DOC:DON ratios were 27.0, 23.7 and 17.1 for the high, medium and low permafrost watersheds, respectively.

Nitrate was the dominant form of dissolved nitrogen in all streams (Table 3.3), composing just over half of total dissolved nitrogen (TDN) in the high permafrost watershed and over two-thirds of TDN in the medium and low permafrost watersheds

(Table 3.3). Despite large variation in the concentration of NO_3^- and SO_4^{2-} throughout the water year in all streams, the two compounds were highly correlated (Figs. 3.4 and 3.5). For comparison, we divided the NO_3^- and SO_4^{2-} data into two periods representing winter and snowmelt (October through mid-May; top panel) and post-snowmelt (mid-May through September; bottom panel, Fig. 3.5). During the snowmelt period, the slope of the SO_4^{2-} to NO_3^- relationship was significantly greater in the high permafrost watershed than in the low and medium permafrost watersheds (95% confidence interval of slopes did not overlap, $p < 0.05$), whereas after snowmelt the slopes were not significantly different among the three watersheds (Fig. 3.5).

Chemistry and Discharge Relationships

We identified six peak discharge events during the year; the first three occurred during snowmelt and three events were generated from late spring and summer rain. According to discharge and concentration relationships, elements can be grouped into three classes: positive, negative, and both positive and negative relationships. DON and DOC always increased with flow, Mg^{2+}, Ca^{2+}, and Na^+ always declined, and Cl^-, K^+ and NO_3^- showed both positive and negative responses when relationships were significant (Table 3.4). NO_3^- was negatively correlated with higher flow in the low and medium permafrost watersheds, but in the high permafrost watershed relationships were negative early and then positive for the final two summer floods. Cl^- and K^+ were positively correlated to discharge during snowmelt but otherwise negative (Table 3.4).

Watershed Element Fluxes

Consistent patterns in watershed losses of elements were found among watersheds. The high permafrost watershed showed the lowest losses of elements on a per area basis for all solutes except for DOC, which was greatest (Table 3.5). The medium permafrost watershed had the highest output for all elements except DOC. NH_4^+ showed net retention, but because DON and NO_3^- comprised the bulk of the N flux, watersheds lost N overall, ranging from 0.38 kg ha^{-1} yr^{-1} for the high permafrost watershed to 0.92 and 1.43 kg ha^{-1} yr^{-1} for the low and medium permafrost watersheds, respectively (Fig. 3.6 and Table 3.5).

The total flux of base cations from CPCRW watersheds represents an estimation of chemical weathering rate that is related to bedrock and soil dissolution as well as biotic retention. The high permafrost catchment had the lowest output of cations (0.48 keq ha^{-1} yr^{-1}), the output in the low permafrost catchment was moderate (1.10 keq ha^{-1} yr^{-1}), and the cationic denudation rate was highest in the medium permafrost catchment (1.66 keq ha^{-1} yr^{-1}). Ca^{2+} and Mg^{2+} were greater than 80% of the total cation losses in all three watersheds and the loss of cations occurred in the following order: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$.

A seasonal analysis reveals the relative importance of the winter, snowmelt and summer flow in the annual export of nitrogen and carbon. The winter baseflow period proved to be important for the annual export of nitrate and DON for the low and medium permafrost watersheds, while in the high permafrost watershed the summer had the greatest proportion of nitrate and DON annual fluxes (Fig. 3.7). Furthermore, the snowmelt period was a dominant part of the annual flux of DOC (51% of the annual flux) in the high permafrost watershed, but otherwise was less than a 20% contribution to the annual DOC flux.

The total flux of base cations from CPCRW watersheds represents an estimation of chemical weathering rate that is related to bedrock and soil dissolution as well as biotic retention. The high permafrost catchment had the lowest output of cations (0.48 keq ha^{-1} yr^{-1}), the low permafrost catchments had moderate output (1.10 keq ha^{-1} yr^{-1}), and the medium permafrost catchment had the highest cationic denudation rate (1.66 keq ha^{-1} yr^{-1}). Ca^{2+} and Mg^{2+} were greater than 80% of the total cation losses, and all watersheds lost cations in the following order: $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$.

Discussion

Due to shallow hydrologic flow through the organic-rich active layer, the high permafrost watershed had the smallest losses of dissolved ions (NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+}), but the highest flux of DOC. Conversely, the low permafrost watershed had the lowest DOC output while the medium permafrost was intermediate. Based on this pattern of permafrost coverage and DOC loss, we would predict that the solute flux rates from the medium permafrost watershed would fall between the high and low permafrost watersheds as well. However, the medium permafrost watershed yielded the greatest flux of all solutes, which may be due to larger watershed size (Table 3.1). A larger watershed maintains longer flowpaths from hillslopes to the stream, which would tend to enrich runoff in weathered ions and release more solutes per hectare. Despite differences among sites in permafrost coverage, hydrologic flowpaths, chemical concentrations, and the extent of elemental loss, all watersheds were net sources of all individual elements (Cl^-, PO_4^{2-}, SO_4^{2-}, DOC, DON, NO_3^-, Na^+, K^+ Mg^{2+}, Ca^{2+}) except NH_4^+, which was a small fraction of the total N concentration in streams.

Solute fluxes from soils

In the early stages of snowmelt, we observed maximum concentrations of certain solutes, suggesting a temporal change in source or flowpath between early spring and the remainder of the water year. K^+ and DOC increased in the medium permafrost watershed prior to the spring discharge maxima. Early snowmelt peaks have been attributed to an ionic pulse from the initial fraction of meltwater that accumulates on the outside of ice crystals in the snowpack (Bales et al. 1989). In CPCRW, K^+ concentration is low in the snowpack (mean = 0.056 mg/L) and the high correlation between K^+ and DOC suggests an organic source of K^+ is most likely (Likens and Bormann 1995). K^+ significantly declined throughout summer in all watersheds, suggesting that either a finite pool of K^+ from an organic source is leached over the growing season, or K+ uptake is greater in the summer (Fig. 3.3). In contrast to K^+, other major cations (Ca^{2+}, Mg^{2+}, and Na^+) were diluted by snowmelt or rain water during high flows which is consistent with a weathering source.

Snowmelt is often the dominant hydrochemical event in watersheds with a seasonal snowpack in arctic (Rember and Trefry 2004), alpine (Hood et al. 2002) and temperate watersheds (Likens and Bormann 1995) when discharge reaches an annual peak. In CPCRW, greater discharge occurred in the high permafrost watershed during snowmelt while the peaks for the other watersheds occurred later in the summer during rain events. Overall, in the high permafrost watershed snowmelt generated over 25% of the annual flow and more than half of the annual DOC flux. Because much of the melt water from the snowpack likely infiltrated into deeper groundwater flowpaths on permafrost-free slopes, we observed less than 10% of the annual flow and less than 15% of the annual DOC flux during snowmelt in the medium and low permafrost watersheds (Fig. 3.7).

Elevated DOC concentrations during snowmelt or storms are a common feature of nearly all watersheds, indicating that the source area and hydrologic flowpaths change from baseflow to high flow (Buffam 2001). DOC concentration varied little over time within watersheds before snowmelt, ranging from 1-2 mg C/L. During snowmelt, DOC levels quickly rose to annual maximums from the flushing of organic matter that accumulated over the winter months. The 12-fold DOC increase from baseflow to the snowmelt peak in the high permafrost watershed was approximately twice the increase that we observed in the other watersheds, suggesting a larger DOC reservoir and flowpaths on the permafrost dominated hillslopes are more effective at delivering DOC to the stream (MacLean et al. 1997, Carey 2003). On permafrost-free hillslopes, rapid infiltration can occur in spite of seasonal frost during snowmelt, providing little direct runoff to the stream (Kane and Stein 1983, Carey and Woo 1998). Nevertheless, streamside riparian areas will often contribute to direct runoff and deliver DOC to the stream during high flows, (Petrone Chapter 2) which may supply the DOC that we observed in the low permafrost watershed during snowmelt.

Nitrogen losses

In general, stream TDN concentrations were found to be quite high in CPCRW compared to other studies in arctic, boreal, and temperate regions, and nitrate composed the majority of the TDN in stream water (Table 3.2). Dominance of NO_3^- over DON in stream chemistry in the Northeast US and Rocky Mountains has been attributed to increased atmospheric deposition of N from anthropogenic sources (Hedin 1995, Williams et al. 2001). The N saturation hypothesis predicts that increased nitrification will contribute to elevated NO_3^- concentrations in surface waters (Aber 1989). Conversely, DON has been shown to be the more important vector for N loss in low depositional ecosystems in tropical (McDowell and Asbury 1994, Lewis 1999), temperate (Hedin 1995, Campbell 2000, Perakis and Hedin 2002), and boreal regions (Kortelain 1997). Given this trend of DON dominance in low deposition ecosystems, we would expect to find low NO_3^- concentrations in CPCRW, which is among the lowest N deposition sites in the National Atmospheric Deposition Program, but DIN was greater than DON.

When compared to boreal sites in other regions, NO_3^- concentration in CPCRW streams is an order of magnitude greater (Fig. 3.8; Ford and Naiman 1989, Bayley et al. 1992, Peterson et al. 1992, Stottlemyer 1992, Kortelainen et al. 1997, Cooke and Prepas 1998, Jones et al. 2005). Although winter NO_3^- concentrations were consistently high in all watersheds in our study, NO_3^- concentrations did not decline during the growing season as has been observed elsewhere (Goodale et al. 2001). Arheimer et al. 1996 observed that stream NO_3^- was lower during growing season in 71% of boreal Swedish catchments, and catchments without seasonal patterns had high rates of N deposition. In CPCRW, NO_3^- concentrations diminished only when discharge increased in the summer, suggesting dilution by nitrate-depleted surface water (Fig. 3.4). This pattern suggests that biotic control due to utilization by primary producers or microbial immobilization during the summer does not explain the high NO_3^- concentration in CPCRW streams.

The subcatchments of CPCRW seem to be losing nitrogen based on the rate of input via deposition and export in stream flow. On-site NADP deposition totals only included input of N via precipitation; however, we can conservatively estimate dry deposition of 0.09 kg N ha^{-1} yr^{-1} that has been measured at the NADP site in Denali National Park (200 km southwest of CPCRW). Organic N deposition represents an additional potential input. Organic N deposition averages a third of total N deposition worldwide, and DON deposition is less than DIN deposition at low deposition sites (Neff et al. 2002). Assuming similar rates at CPCRW, total N deposition may be near 0.4 kg ha^{-1} yr^{-1} and N output is up to three times greater than the rate of N deposition (Table 3.4). This N loss may be derived from 1) N fixation, 2) geologic N sources, and 3) non-steady state conditions such as low or negative net ecosystem production (NEP) due to high rates of decomposition.

Nitrogen fixation from symbiotic cyanobacterial (*Nostoc* sp) is associated with feather moss (*Pleurozium schreberi*) in boreal forests of Scandinavia (1.5 to 2.0 kg N ha^{-1} yr^{-1}; DeLuca et al. 2002). Feather moss is common in permafrost underlain hillslopes at CPCRW and could potentially provide up to five times the rate of atmospheric deposition of N, although input would be mainly limited to moss communities in black spruce stands. Nitrogen fixation by alder (*Alnus crispa and A. tenufolia*) could also be a potential nitrogen source that is common in deciduous stands and valley bottoms at CPCRW (Troth et al. 1976).

Nitrogen in rock in CPCRW has not been measured directly, but the metasedimentary geology may be an N source. CPCRW is underlain by a mixture of eclogite, quartzite, muscovite schist, and unconsolidated quaternary material (Newberry 1996). Metasedimentary rock can contain nitrogen as NH_4^+ that substitutes for K^+ in micas; this NH_4^+ can be subsequently oxidized to NO_3^- during the weathering process before reaching surface waters (Holloway and Dahlgreen 2002). Weathering of N from metasedimentary and metavolcanic rocks has been shown to provide up to 30% of the N budget to streams in the Sierras of California (Holloway et al. 1998). However, the rocks present in CPCRW have not been analyzed for N and their N concentrations are unknown. SO_4^{2-} is often enriched in groundwater springs compared to surface waters. In contrast, we find that NO_3^- concentrations are similar in springs and stream waters, indicating a source that does not involve rock interaction. Since N concentration is similar in ground and surface waters, it is possible that this nitrogen was derived from non-rock sources.

Measurable quantities of nitrogen in mineral soil (0.1 to 1.0 %) in CPCRW may also provide the N source in our mass budget calculation. Total N in the mineral layer was significantly lower than in the organic soil layer, but CPCRW watersheds contain larger quantities of mineral soil. In this un-glaciated terrain, mineral soil can extend to meters in depth as it mixes with unconsolidated bedrock material. N in mineral soil (~0.5%) has been found in both mixed hardwood and black spruce stands in CPCRW (Ping unpublished data; http://lter.iab.uaf.edu/data.cfm, Lyle 2005 UAF MS thesis).

Groundwater springs have proven to be important sources of NO_3^- in a temperate watershed where NO_3^- concentrations were higher in groundwater than in unsaturated, shallow groundwater recharge areas (Burns et al. 1998). We find a similar pattern in CPCRW where surface soils are low in inorganic nitrogen and sulfate, but groundwater concentrations are equal or greater than baseflow concentrations (MacLean et al. 1998, Hinzman et al. *in press*). However, water movement through the active layer appears to be important for NO_3^- flux in the high permafrost watershed during late summer based on a positive relationship between nitrate concentrations and discharge for the final two summer storms (Table 3.4). Similar positive patterns of nitrate and discharge have been observed in the high permafrost during previous years (Petrone chapter 2). As soil temperatures increase throughout the summer and the active layer becomes thicker, more organic material becomes available for decomposition and the pool of NO_3^- may increase.

Weathering Losses

The output of Ca^{2+}, Mg^{2+}, and Na^+ reflected the weathering and dominant flowpaths in watersheds. The high permafrost watershed had the lowest output of base cations, likely due to greater flow derived from organic soil during summer, which is depleted in weathering ions. However, factors other than organic vs. groundwater flow may be important since the medium permafrost watershed had two and three times greater output of Ca^{2+}, Mg^{2+}, and Na^+ than the high and low permafrost watersheds.

Longer potential flowpaths from the hillslope to the stream in the larger watershed likely contribute to the higher element loss from this catchment. In addition, the medium permafrost watershed showed higher runoff for the year. The influence of runoff is illustrated by the output of Cl^- from the watersheds. Cl^- is typically conservative so that concentrations are similar across watersheds, but because runoff differed between watersheds the medium permafrost watershed had twice the Cl^- output of the low permafrost watershed and more than four-fold the Cl^- output of the high permafrost watershed.

Large net SO_4^{2-} losses were observed in all CPCRW watersheds, indicating that an internal S source is present or we are underestimating a potential SO_4^{2-} input. Although we have not measured S in dry deposition, we expect that it is low in CPCRW because there are no nearby anthropogenic S sources. Watershed S losses have been observed in numerous studies in North American and have been attributed to mineralization (Driscoll 1998), adsorption/desorption (Alewell 1999), oxidation of reduced S (Eimers and Dillon 2002), and S from rock weathering (Baron et al. 1995, Bailey et al. 2004). Geologic S sources are common in the CPCRW area both in and surrounding gold-bearing veins. Common sulfide minerals include arsenopyrite, stibnite, and especially, pyrite (Newberry 1996). Locally, groundwater concentrations of sulfate can reach over 300 mg/L, and are quite variable, depending on the residence time of groundwater and the rock minerals in contact with infiltrating water (Farmer et al. 1998). In the Fairbanks region, sulfate concentrations are low in waters draining granite, intermediate concentrations are found in waters draining metasedimentary rocks, and high concentrations are found in water in contact with eclogite (Goldfarb et al. 1997). The latter is a common rock type underlying CPCRW (Newberry 1995). SO_4^{2-} sources in CPCRW rock and groundwater and large SO_4^{2-} losses across all watersheds suggest that weathering sources are responsible for the SO_4^{2-} input.

Chemical dissolution is accelerated by temperature and precipitation, therefore, temperate and tropical ecosystems typically reveal higher weathering rates than alpine ecosystems (Johnson et al. 1994). Furthermore, catchments with similar climate and bedrock material can produce different weathering rates depending on water contact time with bedrock (Drever 1997). In CPCRW catchments, we found that weathering rates measured as cationic denudation (0.48 to 1.66 keq $ha^{-1}yr^{-1}$) were on par with catchments throughout northern Europe and North America (range = 0.29 to 2.29 keq $ha^{-1}yr^{-1}$, mean = 1.04 keq $ha^{-1}yr^{-1}$; Johnson et al. 1994). Despite low annual temperature, low precipitation rates, and the lack of exposed bedrock in this un-glaciated region, CPCRW watersheds had considerable losses of weathering ions. This result may reflect the lack of biotic uptake or relatively high weathering rates of primary bedrock minerals. Additionally, permafrost and dominant water flowpaths also affect weathering rates as the high permafrost catchment had the lowest weathering rate, likely due to the reduced contact time of water with bedrock.

Climate change, permafrost and solute fluxes

Climate models predict an increase in temperature at high latitudes, which may accelerate the ongoing subsidence of permafrost in interior Alaska (Osterkamp and

Romanovsky 1999, Serreze et al. 2000). Boreal soils contain large stores of organic nitrogen in frozen soils that are just below freezing and sensitive to changes in soil temperature. Improved soil conditions for decomposition and thawing of currently frozen soil are likely to increase organic N mineralization and nitrate leaching. While the majority of watersheds in temperate regions retain much of the N that enters via precipitation, other studies in interior Alaska, in the Rock Creek watershed of Denali National Park (Stottlemyer 1992), and a treeline watershed in Northwest Alaska (Stottlemyer 2001), reveal net N loss. Fundamental differences between Alaskan soils and their temperate counterparts might also exist due to an uncoupling of N mineralization and uptake. The short growing season in interior Alaska combined with soil freezing in late summer could contribute to post-senescence N leaching. Recent studies have found that soil freezing contributes to greater soil solution concentrations of nitrogen (Fitzhugh 2001). We found that much of the N loss that we observe occurs during the winter months except in the high permafrost watershed (Fig. 3.7). Winter N loss is likely driven by N leaching in surface soils that slowly infiltrates into the groundwater system before reaching the stream. While we did not measure microbial activity in this study, soil respiration has been measured when soil temperatures are below freezing in the subarctic (Schimel and Clein 1996), and net N mineralization in arctic tundra occurs during the winter when microbial activity continues, but plant uptake ceases (Hobbie and Chapin 1996).

Conclusion

Elemental budgets in watersheds in interior Alaska are influenced by the presence of permafrost, which has the greatest effect on increasing DOC output and reducing weathering ions such as Ca^{2+}, Mg^{2+}, and Na^{+}. However, weathering processes and total water runoff are also important determining factors for base cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anion (Cl^{-}, NO_3^{-}, and SO_4^{2-}) losses. Groundwater springs influence the winter chemistry of CPCRW streams in permafrost dominated watersheds where there is a clear shift in the chemistry and flow from winter through snowmelt and into summer. Snowmelt influences annual hydrologic and element fluxes to a greater degree in permafrost-dominated basins than lower permafrost basins. Active layer depth remains important for the late summer release of NO_3^{-} and DOC from surface soils, and future changes in active layer depth in a warmer climate could increase N and C loss in permafrost-dominated areas. Boreal systems are considered to be N limited, but net N losses from watersheds reveal that non-steady state conditions persist and permafrost-dominated boreal watersheds may be fundamentally different from non-permafrost boreal and temperate watersheds.

Basin Descriptions

Basin	Basin area (km^2)	Stream length (km)	Permafrost coverage %	Aspect
Burn	10.4	5	19	SSE
LoP	5.2	2.2	4	S
HiP	5.7	2.6	53	NE

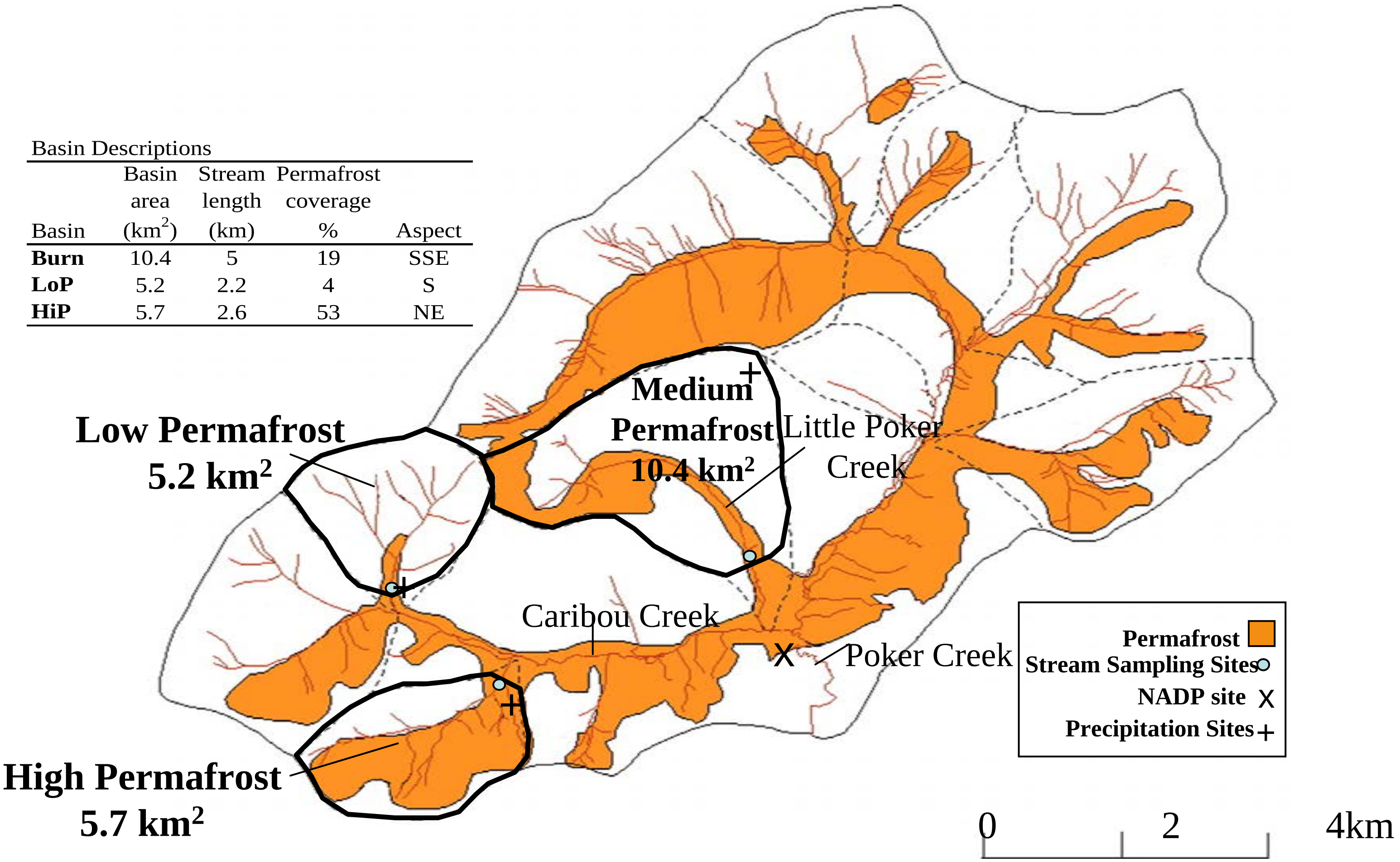


Fig. 3.1 Permafrost distribution and site descriptions at the Caribou-Poker Creeks Research Watershed (CPCRW)

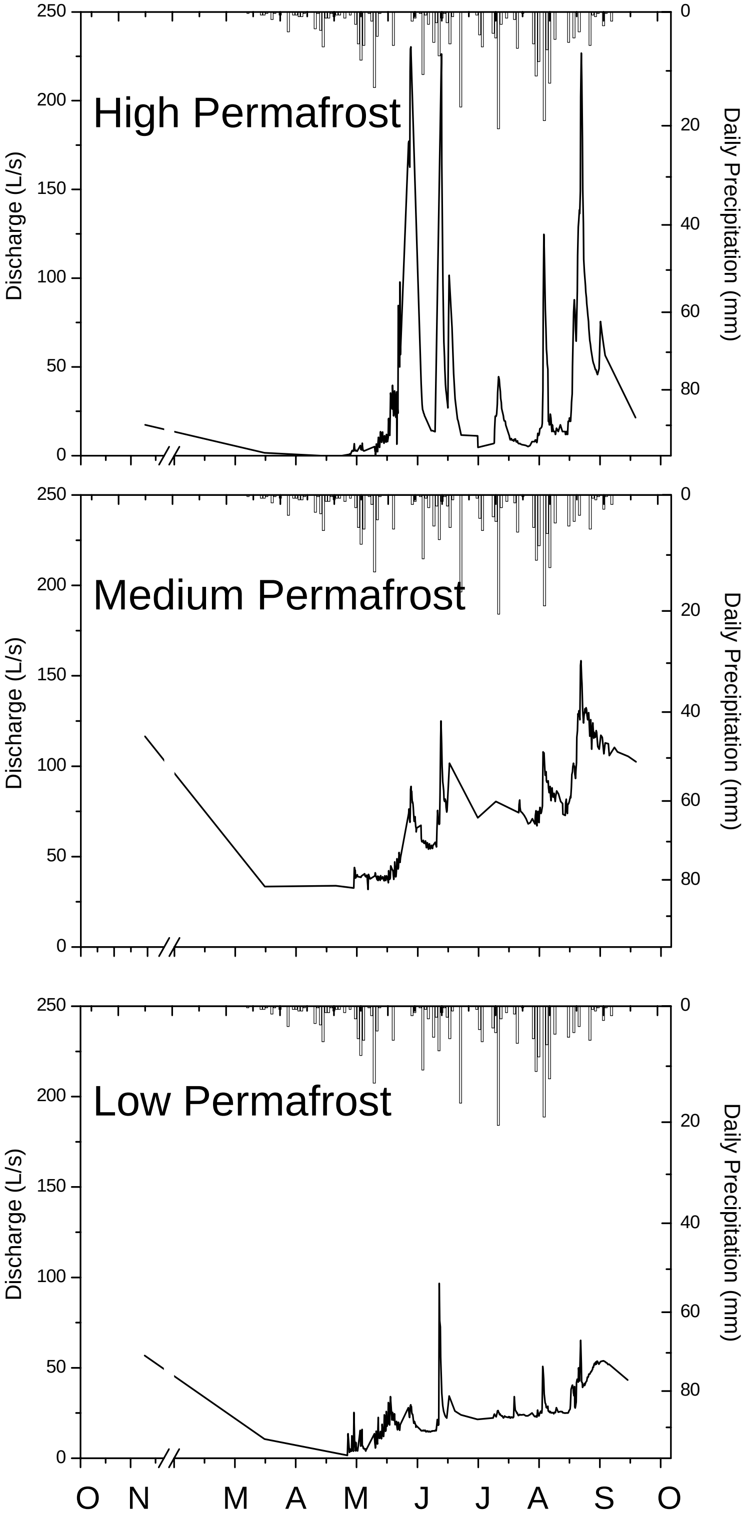


Fig. 3.2. Hydrograph and daily precipitation for the high, medium and low permafrost watersheds.

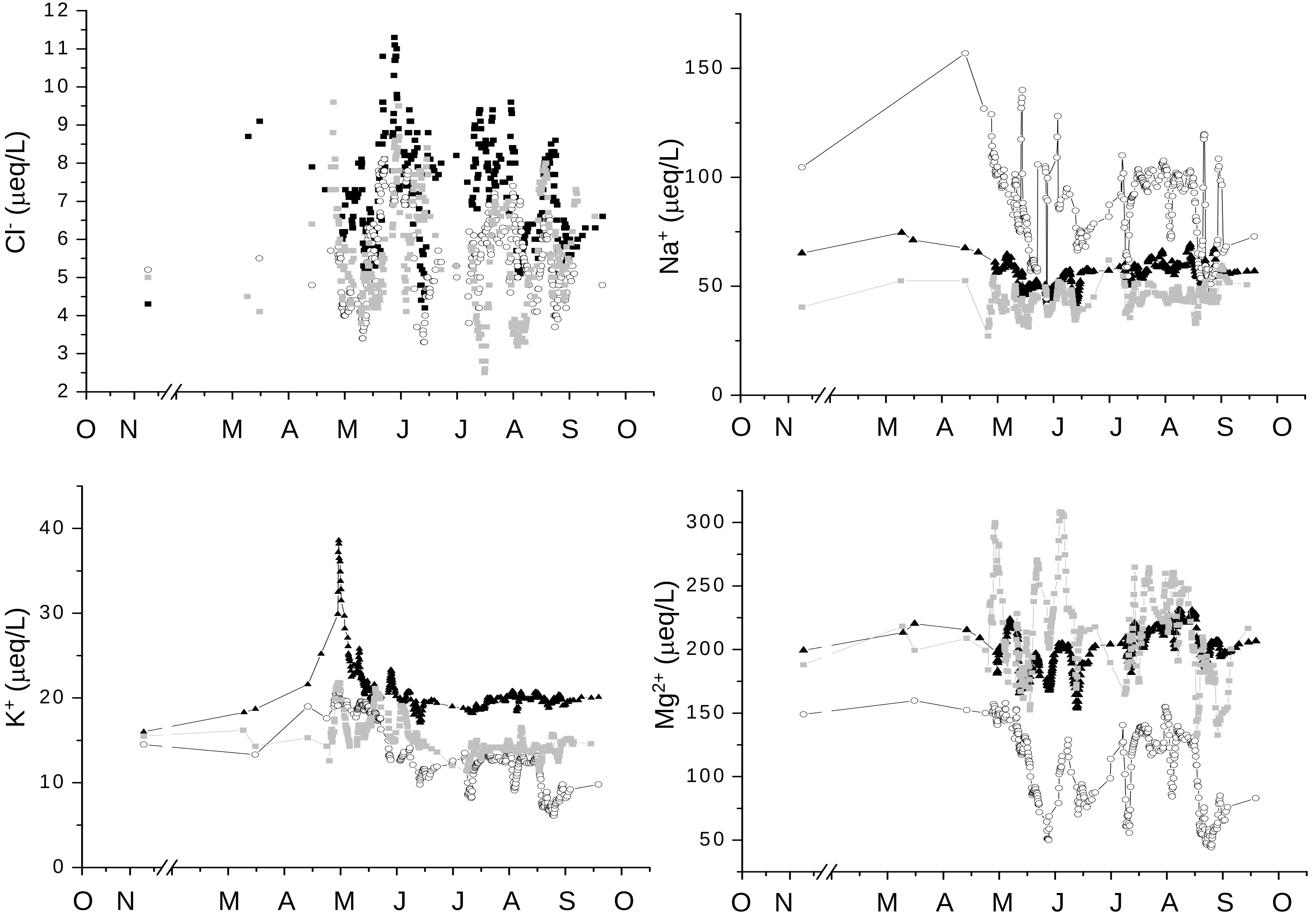


Fig. 3.3a. Time series of Cl, Na, K, and Mg for the high permafrost (open circles), medium permafrost (closed triangles), and low permafrost (gray squares). Data points are five point running averages.

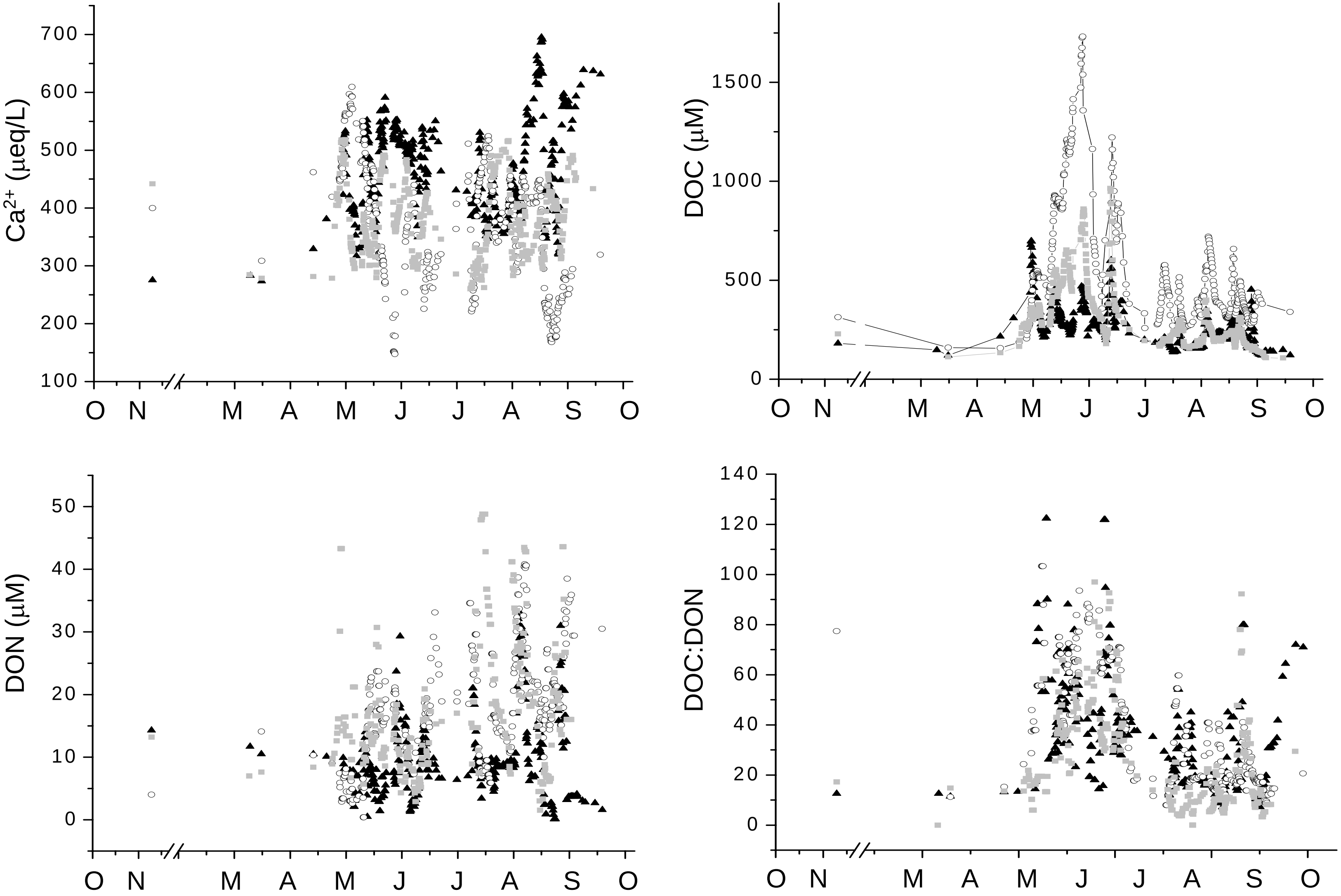


Fig. 3.3b. Time series of Ca, DOC, DON, and DOC:DON for the high permafrost (open circles), medium permafrost (closed triangles), and low permafrost (gray squares). Data points are five point running averages.

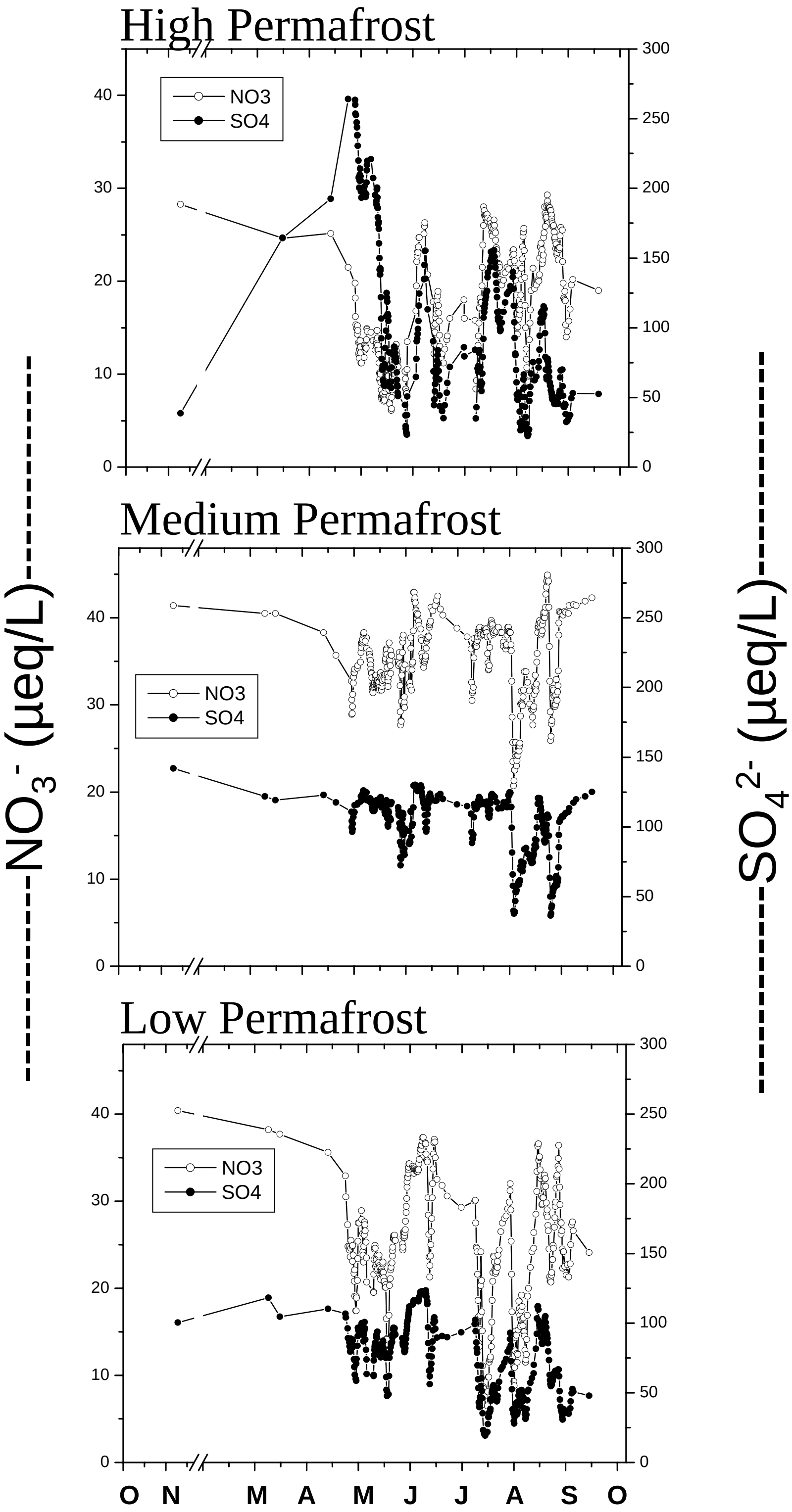


Fig. 3.4. Sulphate (open circles) and nitrate (closed circles) time series for the 2000-2001 water year in the high, medium and low permafrost watersheds. Data points are five day running averages.

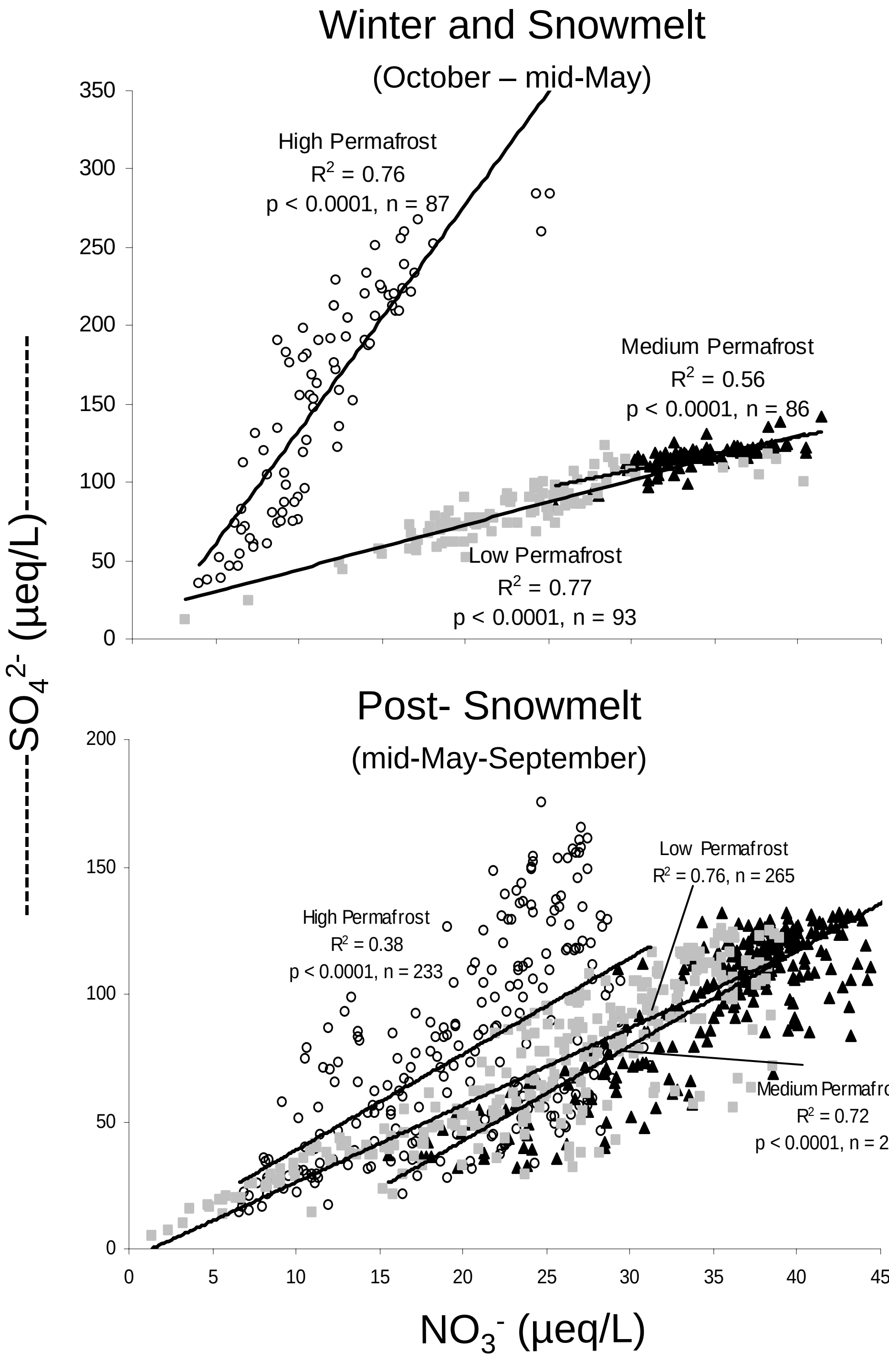


Fig. 3.5. Nitrate vs. sulphate relationships for the high permafrost (open circles), medium permafrost (closed triangles), and low permafrost (gray squares) watersheds during snowmelt (October 2000 through May 2001; top panel) and summer and fall (June 2001 through September 2001; bottom panel).

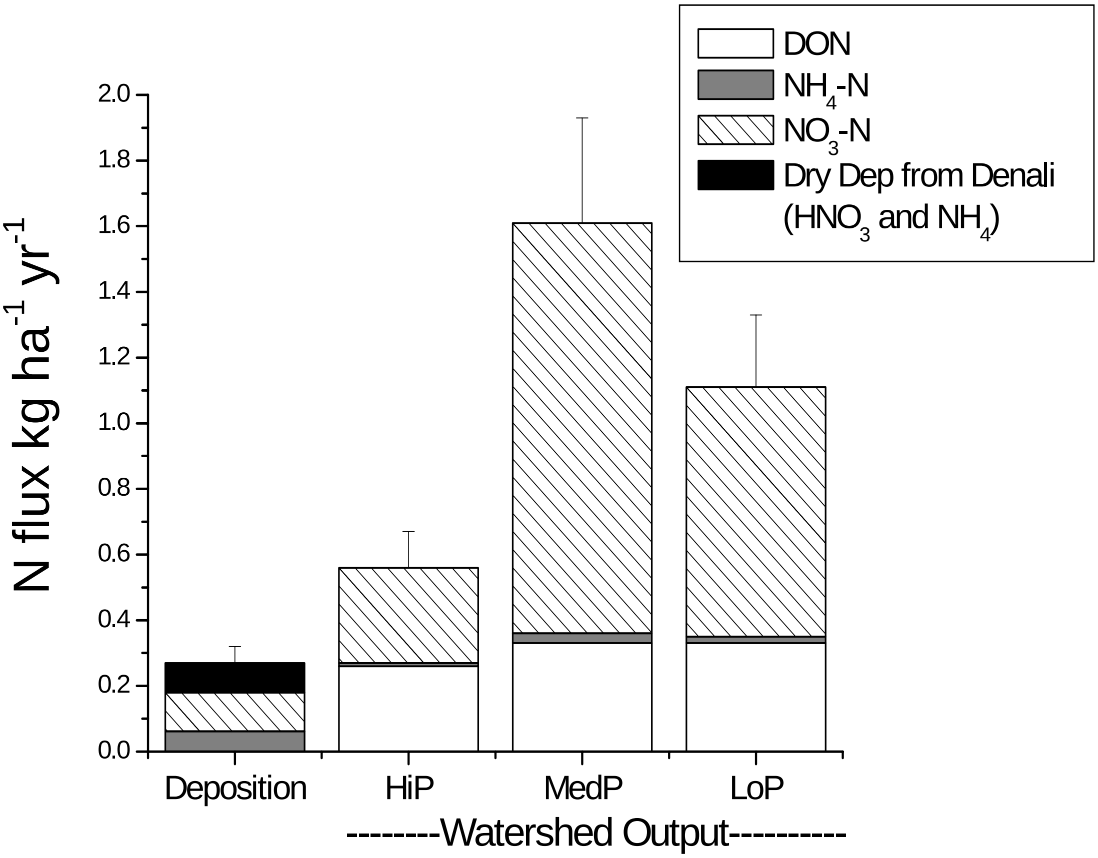


Fig.3.6. N deposition and watershed output for the three watersheds.

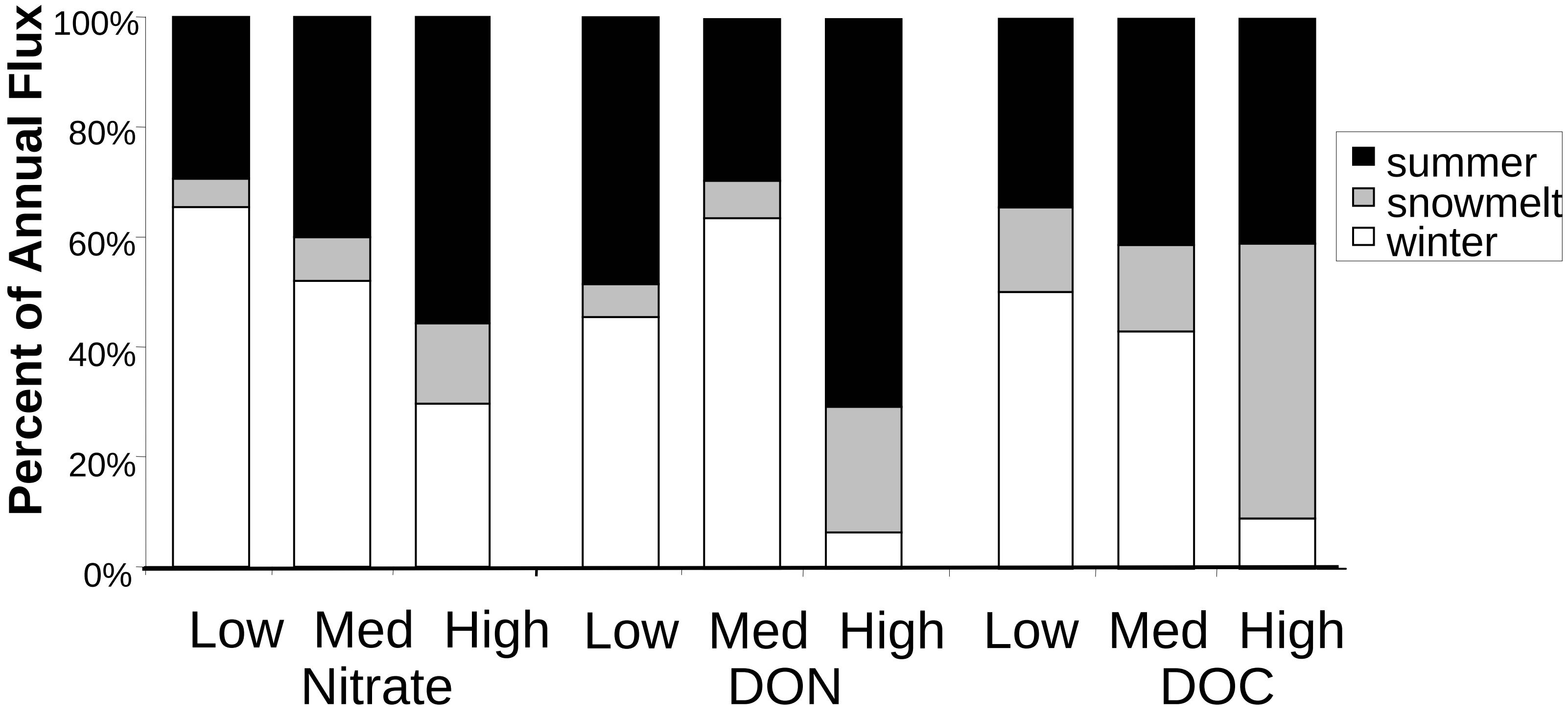


Fig. 3.7. Seasonal Nitrate, DON and DOC flux as a percentage of the annual flux.

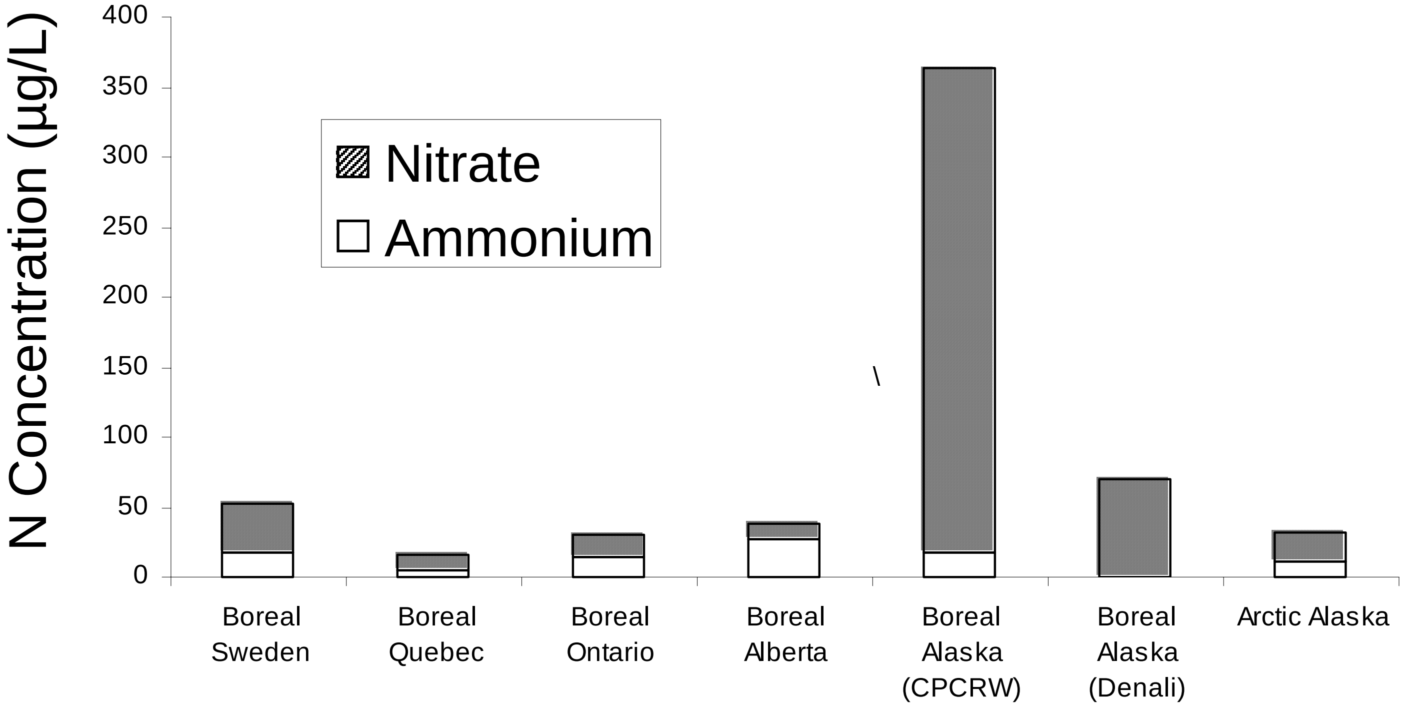


Fig. 3.8. A comparison of stream N concentrations across a range of boreal and arctic ecosystems. Boreal Sweden (Kortelainen et al. 1997), boreal Quebec (Ford and Naiman 1989), boreal Ontario (Bayley et al. 1992), boreal Alberta (Cooke and Prepas 1998), boreal Alaska (present study), boreal Denali National Park (Stottlemyer 1992), and Arctic Alaska (Peterson et al. 1992).

Table 3.1. Basin characteristic and hydrologic estimates for the 2000-2001 water year.

Characteristic	High	Medium	Low
Basin Area (ha)	570	1000	520
Aspect	N	NW	S
Permafrost Coverage %	53	18	3
Total Precipitation (mm)	367	367	367
Runoff (mm)	104	228	164
Winter %	21	50	55
Snowmelt %	25	9	7
Summer %	54	41	39

Table 3.2. Soil characteristics of organic and mineral soil horizons in adjacent hillslope and riparian black spruce stands in the medium permafrost watershed. Sites with similar letters are not significantly different, Tukey's multiple comparisons, $p < 0.05$).

	Organic Hillslope			Organic Riparian			Mineral Hillslope			Mineral Riparian		
variable	mean	SE		mean	SE		mean	SE		mean	SE	
pH	4.5	0.1	A	4.3	0.1	A	5.4	0.3	B	4.9	0.3	B
%C	19.8	2.4	A	14.7	1.3	A	5.9	1.8	B	6.3	1.0	B
%N	0.8	0.1	A	0.7	0.1	A	0.3	0.1	B	0.2	0.0	B
C/N	24.8	1.8	A	20.1	0.4	A	19.1	2.9	A	21.1	0.8	A
Cl^- (mg/kg)	4.9	0.2	A	7.8	0.1	A	1.8	0.2	A	1.5	0.0	A
NO_3^- (mg/kg)	7.0	1.7	A	2.4	0.4	B	1.2	0.4	B	1.2	0.5	B
SO_4^{2-} (mg/kg)	7.5	1.5	A	8.4	1.5	A	4.0	1.4	A	3.6	0.7	A

Table 3.3. Concentration(volume weighted mean) of DOC, DON and major solutes in precipitation and the High, Medium and Low permafrost streams. CV (coefficient of variation) = SD/mean*100. Similar letters denote that means are not significantly different, p = 0.05; Oneway ANOVA, Tukey's multiple comparisons.

	Deposition				High				Medium				Low		
	Mean				Mean				Mean				Mean		
	mg/L	μeq/L	CV		mg/L	μeq/L	CV		mg/L	μeq/L	CV		mg/L	μeq/L	CV
Cl^-	0.030	0.8	(84)	A	0.20	5.5	(16)	B	0.25	7.1	(26)	B	0.20	5.6	(26)
PO_4^{3-}	--	--	--	A	0.05	1.6	(61)	A	0.05	1.6	(67)	A	0.05	1.7	(75)
SO_4^{2-}	0.190	4.0	(61)	A	4.73	98.5	(48)	B	5.58	116.3	(15)	C	3.58	74.5	(27)
DOC	--	--	--	A	7.03	--	(73)	B	3.33	--	(49)	C	3.94	--	(63)
DON	--	--	--	A	0.26	--	(63)	B	0.14	--	(46)	A	0.23	--	(52)
NO_3-N	0.117	8.4	(56)	A	0.25	17.7	(24)	B	0.48	34.0	(10)	C	0.34	24.6	(25)
NH_4-N	0.020	1.4	(68)	A	0.02	1.1	(39)	A	0.02	1.1	(29)	A	0.01	0.9	(39)
Na^+	0.007	0.3	(135)	A	1.96	85.3	(53)	B	1.26	54.7	(52)	C	1.00	43.7	(60)
K^+	0.006	0.2	(72)	A	0.53	13.5	(18)	B	0.81	20.7	(16)	C	0.60	15.4	(7)
Mg^{2+}	0.003	0.2	(73)	A	1.30	107.1	(23)	B	2.42	199.0	(6)	C	2.61	214.6	(12)
Ca^{2+}	0.004	0.2	(64)	A	7.35	367.0	(20)	B	9.40	469.0	(35)	A	7.63	380.9	(18)

Table 3.4. Discharge and chemical relationships for six storm events for the high, medium and low permafrost watersheds. ns = non significant

		SO_4^{2-}			NO_3^-			DOC			Mg^{2+}		
Event	day of water year	slope	R	P	slope	R	P	slope	R	P	slope	R	P
HighP-melt 1	207-215	-10.91	0.67	<0.0001	-1.27	0.71	<0.0001	ns	ns	ns	-5.20	0.79	<0.0001
HighP-melt 2	220-229	-1.77	0.46	<0.0001	ns	ns	ns	10.95	0.67	<0.0001	-1.64	0.87	<0.0001
HighP-melt 3	230-243	-0.35	0.90	<0.0001	-0.06	0.78	<0.0001	4.53	0.84	<0.0001	-0.27	0.92	<0.0001
HighP-summer 4	247-255	-0.25	0.77	<0.001	-0.05	0.83	<0.0001	3.65	0.88	<0.0001	-0.18	0.83	<0.0001
HighP-summer 5	300-308	ns	ns	ns	0.07	0.38	<0.05	1.54	0.37	<0.05	-0.56	0.84	<0.0001
HighP-summer 6	315-328	-0.17	0.32	<0.05	0.04	0.33	<0.01	0.88	0.40	<0.005	-0.24	0.49	<0.001
MedP-melt 1	199-215	-5.00	0.68	<0.001	-1.61	0.72	<0.01	67.73	0.56	<0.01	-6.19	0.62	<0.01
MedP-melt 2	220-230	-1.04	0.35	<0.01	ns	ns	ns	14.40	0.49	<0.001	-1.72	0.37	<0.01
MedP-melt 3	230-243	ns	ns	ns	ns	ns	ns	4.49	0.84	<0.0001	-0.67	0.69	<0.0001
MedP-summer 4	250-254	-0.63	0.91	<0.0001	ns	ns	ns	8.41	0.92	<0.0001	-0.72	0.78	<0.01
MedP-summer 5	300-308	-2.38	0.76	<0.0001	-0.51	0.72	<0.0001	6.16	0.84	<0.0001	ns	ns	ns
MedP-summer 6	315-328	ns	ns	ns	ns	ns	ns	ns	ns	ns	-0.43	0.60	<0.0001
LowP-melt 1	207-214	-1.52	0.37	<0.05	-0.48	0.46	<0.01	4.48	0.41	<0.05	ns	ns	ns
LowP-melt 2	220-230	-1.73	0.52	<0.001	-0.54	0.62	<0.0001	4.67	0.35	<0.05	ns	ns	ns
LowP-melt 3	230-243	-2.53	0.91	<0.0001	-0.54	0.63	<0.0001	36.85	0.93	<0.0001	-6.59	0.82	<0.0001
LowP-summer 4	250-255	-0.87	0.85	<0.0001	-0.26	0.86	<0.0001	10.42	0.84	<0.0001	-0.87	0.88	<0.0001
LowP-summer 5	300-308	ns	ns	ns	ns	ns	ns	9.17	0.76	<0.0001	ns	ns	ns
LowP-summer 6	318-321	-1.97	0.64	<0.0001	-0.21	0.28	<0.05	ns	ns	ns	-1.17	0.27	<0.05

Table 3.4. (continued)

		Ca^{2+}			K^+			DOC vs. DON			NO_3^- vs. SO_4^{2-}		
Event	day of water year	slope	R	P	slope	R	P	slope	R	P	slope	R	P
HighP-melt 1	207-215	ns	ns	ns	-0.38	0.54	<0.01	ns	ns	ns	3.34	0.86	<0.0001
HighP-melt 2	220-229	-5.97	0.81	<0.0001	-0.06	0.72	<0.0001	ns	ns	ns	3.66	0.95	<0.0001
HighP-melt 3	230-243	-1.05	0.95	<0.0001	ns	ns	ns	0.02	0.78	<0.001	2.72	0.85	<0.0001
HighP-summer 4	247-255	-0.73	0.87	<0.0001	-0.02	0.95	<0.0001	0.01	0.63	<0.05	2.45	0.97	<0.0001
HighP-summer 5	300-308	-1.37	0.76	<0.0001	-0.04	0.90	<0.0001	ns	ns	ns	3.21	0.94	<0.0001
HighP-summer 6	315-328	-0.97	0.61	<0.0001	-0.02	0.50	<0.0001	ns	ns	ns	2.57	0.64	<0.0001
MedP-melt 1	199-215	ns	ns	ns	2.03	0.54	<0.05	ns	ns	ns	7.39	0.82	<0.0001
MedP-melt 2	220-230	ns	ns	ns	ns	ns	ns	ns	ns	ns	10.85	0.72	<0.0001
MedP-melt 3	230-243	ns	ns	ns	0.08	0.84	<0.0001	0.01	0.86	<0.001	4.43	0.91	<0.0001
MedP-summer 4	250-254	-1.89	0.53	<0.05	ns	ns	ns	ns	ns	ns	5.89	0.99	<0.0001
MedP-summer 5	300-308	ns	ns	ns	ns	ns	ns	ns	ns	ns	2.72	0.75	<0.0001
MedP-summer 6	315-328	-2.36	0.32	<0.05	-0.01	0.30	<0.05	ns	ns	ns	2.91	0.61	<0.0001
LowP-melt 1	207-214	ns	ns	ns	0.19	0.36	<0.05	ns	ns	ns	3.02	0.92	<0.0001
LowP-melt 2	220-230	ns	ns	ns	0.14	0.35	<0.05	ns	ns	ns	2.3	0.6	<0.0001
LowP-melt 3	230-243	-8.79	0.72	<0.0001	-0.27	0.52	<0.001	ns	ns	ns	3.76	0.96	<0.0001
LowP-summer 4	250-255	-1.20	0.73	<0.001	ns	ns	ns	0.02	0.76	<0.05	ns	ns	ns
LowP-summer 5	300-308	-3.36	0.38	<0.05	ns	ns	ns	0.11	0.65	<0.01	4.12	0.93	<0.0001
LowP-summer 6	318-321	ns	ns	ns	ns	ns	ns	ns	ns	ns	3.68	0.84	<0.0001

Table 3.5. Flux and net output of carbon, nitrogen and major solutes in precipitation and stream export from the High, Medium and Low permafrost watersheds. CV (coefficient of variation) = SD/mean*100 for the uncertainty analysis.

element	Deposition		High		Medium		Low		High	Medium	Low
	flux kg ha-1 yr-1								*net output kg ha-1 yr-1*		
	total	*CV*	*total*	*CV*	*total*	*CV*	*total*	*CV*			
Cl^-	0.12	(21)	0.21	(5)	0.52	(3)	0.31	(3)	0.09	0.40	0.19
PO_4^{3-}	--	--	0.05	(5)	0.12	(3)	0.09	(3)	0.05	0.12	0.01
SO_4^{2-}	0.68	(20)	4.37	(3)	13.39	(3)	6.69	(3)	3.69	12.71	6.01
DOC	--	--	8.34	(7)	5.32	(3)	4.34	(3)	8.34	5.32	4.34
DON	--	--	0.26	(5)	0.33	(3)	0.33	(3)	0.26	0.33	0.33
NO_3-N	0.12	(21)	0.29	(4)	1.25	(3)	0.76	(3)	0.17	1.13	0.64
NH_4-N	0.07	(20)	0.02	(4)	0.03	(3)	0.02	(3)	-0.05	-0.03	-0.05
total N	0.19	(20)	0.56	(4)	1.62	(3)	1.11	(3)	0.38	1.43	0.92
Na^+	0.03	(21)	1.40	(5)	5.96	(3)	2.44	(2)	1.37	5.93	2.42
K^+	0.02	(21)	0.48	(4)	1.66	(3)	0.95	(3)	0.46	1.64	0.93
Mg^{2+}	0.01	(20)	1.19	(3)	5.66	(3)	3.92	(3)	1.18	5.64	3.91
Ca^{2+}	0.08	(20)	6.22	(3)	17.94	(3)	13.04	(3)	6.14	17.86	12.96

References

Aber JD, Nadelhoffer KJ, Steudler P, and Melillo JM. 1989. Nitrogen saturation in northern forest ecosystems. Bioscience. 39: 378-386.

Alewell C, Mitchell MJ, Likens GE, and Krouse HR. 1999. Sources of stream sulphate at the Hubbard Brook Experimental Forest: Long-term analyses using stable isotopes. Biogeochemistry. 44: 284-299.

Arheimer B, Andersson L, and Lepisto A. 1996. Variation of nitrogen concentration in forest streams – influences of flow, seasonality, and catchment characteristics. Journal of Hydrology. 179: 281-304.

Bales RC, Davis RE, and Stanley DA. 1989. Ion elution through shallow homogeneous snow. Water Resour. Res. 25: 1869-1877.

Baron JS, Allstott EJ, and Newkirk BK. 1995. Analysis of long term sulfate and nitrate budgets in a Rocky Mountain basin. *In*: Tonnessen K, Williams MW, and Tranter M (Eds) Biogeochemistry of seasonally snow covered catchments. IAHS Pub. No.228 p 255-261.

Bailey SW, Mayer B, and Mitchell MJ. 2004. Evidence for influence of mineral weathering on stream water sulphate in Vermont and New Hampshire .USA.. Hydrological Processes. 18:1639-1653.

Bayley SE, Schindler DW, Beaty KG, Parker BR, & Stainton MP. 1992. Effects of multiple fires on nutrient yields form streams draining boreal forest and fen watersheds. Can J. Fish. Aquat. Sci. 49: 584-596.

Buffam I, Galloway JN, Blum LK, and McGlathery KJ. 2001. A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochemistry. 53: 269-306.

Burns DA, Murdoch PS, Lawrence GB, and Michel RL. 1998. Effect of groundwater spring on NO_3^- concentrations during summer in Catskill Mountain streams. Water Resources Research. 34: 1987-1996.

Campbell JL, Hornbeck JW, McDowell WH, Buso DC, Shanley JB, and Likens GE. 2000. Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry. 49: 123-142.

Carey SK. 2003. Dissolved organic carbon fluxes in a discontinuous permafrost subarctic alpine catchment. Permafrost Periglac. Process. 14: 161-171.

Carey SK and Woo WK. 1998. Snowmelt hydrology of two subarctic slopes, Southern Yukon, Canada. Nordic Hydrology 29: 331-346.

Cooke SE and Prepas EE. 1998. Stream phosphorus and nitrogen export from agricultural and forested watersheds on the Boreal Plain. Can. J. Fish. Aquat. Sci. 55: 2292-2299.

DeLuca TH, Zackriss O, Nilsson M-C, and Sellstedt A. 2002. Quantifying nitrogen-fixation in feather moss carpets of boreal forests. Nature. 419: 917-920.

Drever JI. 1997. The Geochemistry of Natural Waters: Surface and Groundwater Environments. Prentice Hall, NJ, U.S.A.

Driscoll CT, Likens GE, and Church MR. 1998. Recovery of surface waters in the northeastern US from decreases in atmospheric deposition of sulfur. Water Air Soil Pollution. 105: 319-329.

Eimers MC and Dillon PJ. 2002. Climate effects on sulphate flux from forested catchments in south-central Ontario. Biogeochemistry 61: 337-355.

Farmer GL, Goldfarb RJ, Lilly MR, Bolton B, Meier AL, Sanzolone RF. 1998. The chemical characteristics of ground water near Fairbanks, Alaska. U.S. Geological Survey Professional Paper 1615, 12p.

Fitzhugh RD, Driscoll CT, Groffman PM, Tierney GL, Fahey TJ, and Hardy JP. 2001. Effects of soil freezing disturbance on soil solution nitrogen, phosphorus, and carbon chemistry in a northern hardwood system. Biogeochemistry. 56: 215-238.

Ford TE, and Naiman RJ. 1989. Groundwater-surface water relationships in boreal forest watersheds: Dissolved organic carbon and inorganic nutrient dynamics, Can. J. Fish. Aquat. Sci. 46: 41-49.

Goldfarb RJ, Farmer GL, Cieutat BA, and Meier AL. 1997. Major-element, trace-element, and strontium-Isotope systematics of natural waters in the Fairbanks mining district: constraints from local geology. U.S. Geological Survey Professional Paper 1614, 12p.

Goodale CL, Aber JD, McDowell WH. 2001. The long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire. Ecosystems. 3: 433-450.

Hedin LO, Armesto JJ, and Johnson AH. 1995. Patterns of nutrient loss from unpolluted old-growth temperate forests: evaluation of biogeochemical theory. Ecology. 76: 493-509.

Hinzman LD, Bolton BW, Jones JB & Petrone KC. Hydrological Processes in Alaska's Boreal Forest. In M.W. Oswood and F.S. Chapin [Eds]. BNZ LTER synthesis chapter: Alaska's Changing Boreal Forest, in press.

Hobbie, SE, and Chapin FS III. 1996. Winter regulation of tundra litter carbon and nitrogen dynamics. Biogeochemistry. 35:327-338.

Holloway JM, Dahlgren RA, Hansen B, Casey WH. 1998. Contribution of bedrock nitrogen to high nitrate concentrations in stream water. Nature. 395: 785-788.

Holloway JM, Dahlgreen RA. 2002. Nitrogen in rock: occurrences and biogeochemical implications. Global Biogeochemical Cycles. 16: 1118- 1126.

Hood EW, Williams MW, and Caine N. 2002. Yields of dissolved organic C, N and P. from three high-elevation catchments, Colorado Front Rance, U.S.A. Water Air. Soil. Poll. 2: 165-180.

Johnson CE, Litaor MI, Billett MF, and Bricker OP. 1994. Chemical weathering in small catchments: climate and anthropogenic influences. *In*: Cerny J and Moldan B (Eds) Biogeochemistry of Small Catchments: A Tool for Environmental Research. New York, Wiley.

Jones JB, Petrone KC, Finlay JC, Hinzman LD, and WR Bolton. 2005. Nitrogen loss from watersheds of interior Alaska underlain with discontinuous permafrost. Geophysical Research Letters. 32, L02401, doi:10.1029/2004GL021734.

Kane DL, and Stein J. 1983. Water movement into seasonally frozen soils. Water Res. Res. 19: 1547-1557.

Kortelainen PS, Saukkonen S, and Mattsson T. 1997. Leaching of nitrogen from forested catchments in Finland. Global. Biogeochem. Cycles. 11: 627-638.

Lewis WM, JM Melack, WH McDowell, M McClain, and Richey J. 1999. Nitrogen yields from undisturbed watersheds in the Americas. Biogeochemistry. 46: 149-162.

Likens GE, and Bormann FH. .1995. Biogeochemistry of a forested ecosystem. Springer-Verlag, New York, NY.

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

McDowell WH, and Asbury CE. 1994. Export of carbon, nitrogen, and major ions from three tropical montane watersheds. Limnol. Oceanogr. 39: 111-125.

Neff JC, Holland EA, Dentener FJ, McDowelll WH, and Russell KM. 2002. The origin, composition, and rates of organic nitrogen deposition: a missing piece of the nitrogen cycle? Biogeochemistry 57/58: 99-136.

Newberry, RJ, Bundtzen TK, Clautice KH, Combellick RA, Douglas T, Laird GM, Liss SA, Pinney DS, Reifenstuhl RR, and Solie DN. 1996. Preliminary Geologic Map of the Fairbanks Mining District, Alaska. State of Alaska Division of Geological and Geophysical Surveys, Public-Data File. 14p.

Osterkamp, T.E., and V.E Romanovsky. 1999. Evidence for warming and thawing of discontinuous permafrost in Alaska. Permafrost and Periglacial Proc. 10:17-37.

Perakis SS, and Hedin LO. 2002. Nitrogen loss from unpolluted South American forests mainly via dissolved organic nitrogen compounds. Nature. 415: 416-419.

Peterson BJ, Corliss T, Kriet K, and Hobbie JE. 1992. Nitrogen and phosphorus concentrations and export for the upper Kuparuk River on the North Slope of Alaska in 1980. Hydrobiologia 240: 61-69.

Ray S. 1988. Physical and Chemical Characteristics of Headwater Streams at Caribou-Poker Creeks Research Watershed, Alaska. MS Thesis University of Alaska Fairbanks, 170p.

Rember RD, and Trefry JH. 2004. Increased concentrations of dissolved trace metals and organic carbon during snowmelt in rivers of the Alaskan Arctic. Geochem. Cosmoch. Acta. 68: 477-489.

Rieger S, Furbush CE, Schoephorster DB, Summerfield H, and Geiger LC Jr. 1972. Soils of the Caribou-Poker creeks research watershed, Interior Alaska. CRREL Technical Report 236, US Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.A.

Serreze MC, Walsh JE, Chapin FS, Osterkamp T, Dyurgerov M, Romanovsky V, Oechel WC, Morison J, Zhang T, and Barry RG. 2000. Observational evidence of recent change in the northern high-latitude environment. Climatic Change. 46: 159-207

Schimel JP, and Clein JS. 1996. Microbial response to freeze-thaw cycles in tundra and taiga soils. Soil Biology Biochemistry. 28: 1061-1066.

StatSoft. 2000. STATISTICA for Windows. 2300 East 14th Street, Tulsa, OK 74104, StatSoft, Inc.

Stottlemyer R. 1992. Nitrogen mineralization and streamwater chemistry, Rock Creek Watershed, Denali National Park, Alaska, USA. Arc. Alp. Res. 24: 291-303

Stottlemyer R. 2001. Biogeochemistry of a treeline watershed, northwestern Alaska, J. Environmen. Qual. 30: 1990-1998.

Troth JL, Deneke FJ, Brown LM. 1976. Upland aspen/birch and black spruce stands and their litter and soil properties in interior Alaska. For. Sci. 22: 33-44.

Williams MW, Hood E, and Caine N. 2001. Role of organic nitrogen in the nitrogen cycle of a high-elevation catchment, Colorado Front Range. Water Res. Res. 37: 2569-2581.

Woo MK. 1986. Permafrost hydrology in North America. Atmos. Ocean 24: 201-234.

Yoshikawa K, Hinzman LD, Gogineni P. 2002. Ground temperature and permafrost mapping using an equivalent latitude/elevation model. Journal of Glaciology and Geocryology 24: 526-531.

CHAPTER FOUR

CHEMICAL EXPORT AND HYDROGRAPH SEPARATION DURING SNOWMELT IN A SUB-ARCTIC WATERSHED

Abstract

Hydrologic tracers, organic, and inorganic solutes were used to determine source areas and flowpaths for the spring snowmelt periods from 2000-2002 in a sub-arctic watershed in interior Alaska. Runoff was variable during the study period, ranging from 18.2 mm in 2001 to 51.8 and 85.9 mm in 2000 and 2002, and significantly related to the contribution of new water to discharge (17% in 2001, 46% in 2000, and 64% in 2002). However, total runoff was not linearly related to snowpack water equivalent (SWE) as 2001 was intermediate in SWE, but lowest in total runoff, suggesting that rainfall, soil moisture conditions, and the timing of snow ablation are more important than SWE in generating runoff. High flow during snowmelt was associated with elevated concentrations of Cl^-, K^+, DOC, DON, total P, total Al, and total Fe, but reduced levels of NO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+}. Correlation coefficients between subsets? of ions indicated that dominant flowpaths or source areas for solutes changed over the snowmelt period. K^+ and total P levels were highly correlated and preceded the increase of correlated DOC, DON, total Al and total Fe concentrations. Base cations (Na^+, Mg^{2+}, Ca^{2+}) and anions (NO_3^- and SO_4^{2-}) were also highly correlated since they were all diluted by the influx of snowmelt water. When compared to the input from snowpack solutes, the watershed was a net source of all solutes during the snowmelt period (April 10-May 31) except Cl^-, which showed net retention in 2000 and 2001.

Keywords: boreal, snowmelt, nitrogen, DOC, hydrograph separation

Introduction

Snowmelt is an important hydrochemical event in the boreal region, where more than a third of the annual precipitation typically falls as snow, and snow cover extends for over half of the year. At the start of snowmelt, the ground is commonly frozen, limiting the interaction between runoff and soil horizons. During cold Alaskan winters, the active layer (the portion of soil above permafrost that freezes and thaws annually) completely freezes. In permafrost-free soil, ice formation, which is dependent on soil water content, decreases infiltration capacity by orders of magnitude (Kane and Stein 1983). Where soil pores are not saturated with ice, however, infiltration may occur on permafrost-free slopes during snowmelt, resulting in little runoff from meltwater (Kane and Stein 1984, Carey and Quinton 2004). On permafrost slopes, however, water flow is limited to surface soils, and rapid runoff may occur during the snowmelt period (MacLean et al. 1999, McNamara et al. 1997, Carey and Woo 2001). While we have a good understanding of the hydrometric properties of discontinuous permafrost watersheds in the boreal region (Carey and Woo 1999), we know less about how soils influence the chemistry of runoff (e.g. MacLean et al. 1999, Carey and Quinton 2004).

Surface water chemistry during snowmelt is influenced by solutes deposited from precipitation, accumulated in the snowpack, and flushed from soils along flowpaths to the stream. Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations often increase during snowmelt due to dissolution in surface soils (Hruska 2001), and solute transport in meltwater can enrich (Williams and Melack 1991, Campbell et al. 1995, Williams et al. 1995) or dilute (Stottlemyer and Toczydlowski 1996) stream concentrations of NO_3^-, Cl^-, and SO_4^{2-} in snowmelt-dominated watersheds. Further, biological processes can attenuate or accentuate the release of N from the snowpack through immobilization, denitrification, or mineralization during the winter and snowmelt periods (Schimel and Clein 1996, Brooks et al. 1998).

In order to understand how snow meltwater affects stream chemistry, the components of flow during the snowmelt discharge peak need to be determined. Numerous studies have separated source components of flow (new water vs. old water) using oxygen isotopes, whereas chemical tracers (e.g., Si, Na, Cl, and electrical conductivity) typically delineate flow pathways (Hooper and Shoemaker 1996). Melt water from snow and pre-existing soil water that mix during snowmelt may be indistinguishable by electrical conductivity, but different in terms of $\delta^{18}O$ signature (Carey and Quinton 2004). In this context, electrical conductivity would delineate surface flowpaths and $\delta^{18}O$ would distinguish the source. Other studies, however, have found similar results using electrical conductivity and $\delta^{18}O$ for hydrograph separation (McNamara et al. 1997). In any case, the use of $\delta^{18}O$ isotopes for tracing water sources is prone to error during snowmelt if the isotopic signature of melt water is not measured (Laudon 2002), and chemical tracers may introduce errors if they change along hydrologic flowpaths or if source waters are similar.

The purpose of this study was to better understand the factors controlling organic and inorganic solutes during snowmelt in a sub-arctic watershed. Specifically, our objectives were to 1) compare the use of oxygen and electrical conductivity tracers for determining the role of new water (snowmelt water) and old water (pre-existing water in the catchment) to the snowmelt hydrograph peak, 2) identify flowpaths of organic and inorganic solutes to stream flow, and 3) determine the importance of snowmelt to the flux of solutes in the spring season.

Study Site

The Caribou Poker Creeks Research Watershed (CPCRW), part of the Bonanza Creek Long Term Ecological Research (LTER) program, is located 50 km northeast of Fairbanks, Alaska and covers 10,620 ha. The climate is continental with low winter temperature, high summer temperature, and an annual mean temperature of -2.5°C. Roughly one-third of annual precipitation (400 mm) falls as snow, snow cover extends from mid-October to late April. Snowmelt begins on south-facing slopes that receive greater radiation in mid-April and continues for up to five weeks.

The CPCRW boundary includes several sub-basins that differ in permafrost coverage due to aspect. In this study, we focused on a watershed of 10.0 km^2 that has approximately 18% permafrost coverage overall. Low sun angle throughout the year results in less energy reaching slopes with northern aspects than southern aspects. Consequently, permafrost is found on north-facing slopes and in valley bottoms while south-facing slopes are permafrost-free. Vegetation is closely related to soil type and permafrost distribution. North-facing slopes are dominated by a black spruce (*Picea mariana*) and feather moss (*Pleurozium schreberi* and others) community, whereas southern slopes are deciduous with a mixture of quaking aspen (*Populus tremuloides*) and paper birch (*Betula neoalaskana*). Permafrost upland and valley bottom soils are classified as gelisols and histosols, respectively, and soils of permafrost-free south-facing slopes are classified as inceptisols. Maximum depth of thaw on permafrost hillslopes can reach > 1 m whereas poorly drained sites thaw to only 0.5 m in September prior to re-freezing.

The CPCRW watershed is part of the Yukon-Tanana Terrane that consists of polydeformed and polymetamorphosed Upper Paleozoic and older metasedimentary, metavolcanic, and metaplutonic rocks formerly known as Birch Creek Schist. Specifically, CPCRW is part of the Chatankia Terrane which contains protoliths of Devonian-Mississipian age. The Chatanika terrane contains calcareous eclogite white mica schist, biotite schist, amphibolite, and quartzite (Newberry 1996). CPCRW and the surrounding area were never glaciated, and thin loess caps occur on south-facing slopes. Alluvial deposits are common in wide valleys, and peat deposits are found in many low lying areas where soils are saturated and ice lenses may form in the winter months.

Methods

Stream stage was recorded every hour with a 5 psi pressure transducer and a Campbell datalogger (CR10X). Periodic discharge measurements were conducted with a

Marsh-McBirney electromagnetic current meter to permit confirmation of established rating curves. Stream water for chemical analyses was collected with an ISCO autosampler every 4 hours during snowmelt from early April through late May, 2000, 2001, and 2002. Samples were transferred to pre-rinsed 125 ml HDPE bottles in the field and filtered within 12 hours using glass fiber filters (Gelman A/E, 0.7 μm nominal pore size). Samples were refrigerated until analysis (<48 hours) or frozen for subsequent analyses. Electrical conductivity was measured in the lab using a hand-held Denver Instruments AP-50 meter. Dissolved organic carbon (DOC) was measured as non-purgeable organic carbon on a Shimadzu TOC-5000. Base cations and anions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-, and NH_4^+) were analyzed by Dionex ion chromatography. Total P, total Al, and total Fe were analyzed using induced coupled plasma optical emission spectrometry (Jarrel Ash Inc., IRIS) at the North Research Station of Hokkaido University Forests (NR-HUF), Japan. Total dissolved nitrogen (TDN) was measured with an Antek 720C chemiluminescent N detector coupled with the Shimadzu TOC-5000. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and dissolved inorganic nitrogen (DIN; NO_3^- plus NH_4^+).

Oxygen isotope samples were collected in 60 ml HDPE bottles. $\delta^{18}O$ analyses were performed in the International Arctic Research Center stable isotope facility at the University of Alaska Fairbanks. Isotopic values are expressed as a ratio to Vienna-standard mean ocean water, where R is the ratio of $^{18}O/^{16}O$:

$$\delta^{18}{}_{sample} = [(R_{sample}/R_{VSMOW})-1] \times 1000 \qquad (1)$$

Wet precipitation chemistry for major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^- , and NH_4^+) in fresh snow was provided by the National Atmospheric Deposition Program (NADP, site AK01; http://nadp.sws.uiuc.edu/) station located in CPCRW 1 km from the sub-basin. We also measured major ions of bulk snowpack samples prior to snowmelt in 2002. In late March, cumulative snow water equivalent was estimated from extensive snow surveys using measurements of snow depth and snow density (n=20 per site, 10 sites in the watershed; Rovansek et al., 1993). Budget calculations were performed by comparing inputs from bulk snow chemistry with stream output during the snowmelt period each year (defined as April 10 – May 31). We used the product of chemistry (mg L-1) and water volume (mm snow water equivalent x watershed area) in the watershed to estimate elemental inputs. Stream chemical output was calculated as the product of discharge (L hr-1) and concentration (mg L-1) conducted on an hourly basis. When chemistry or discharge was not measured directly, we linearly interpolated between sampling points. Hourly flux rates were summed for the study period to obtain a total flux rate.

During the 2000 snowmelt season, we obtained simultaneous measurements of $\delta^{18}O$ and conductivity. Runoff was separated into new (melt water) and old water (water in the catchment prior to melt) components using a two-component end-member mixing model,

$$C_oQ_o\ C_nQ_n = C_tQ_t \tag{2}$$

where C is the tracer concentration, Q is discharge, and the subscripts o, n and t refer the old water component, new water component and total discharge, respectively. The specific proportion of flow components at any particular time can be calculated from the mass balance equation,

$$Q_t = Q_n + Q_o \tag{3}$$

Results

The spring snowmelt period started in mid-April and continued through late May across the three years of the study period. The timing and magnitude of peak flow was variable across years. In 2000 and 2002, peak flow was an order of magnitude greater (1763 and 1250 L/s, respectively) than peak flow in 2001 (87.2 L/s; Fig. 4.1). Discharge peaks occurred during periods of mean daily above freezing temperature in 2000 and 2002, but little discharge variation was observed in response to above freezing temperatures during 2001. In 2000, a large snowpack water equivalent (197.9 mm), combined with rain during the snowmelt period (35.4 mm), resulted in peak flow in late April coinciding with 90 mm of melt. A later but smaller flow peak occurred after a rain event in late May (Fig 4.2a). In 2001, snow ablation did not increase flow, and maximum flow was observed during a rain event in late May (Fig. 4.2b). In 2002, snowpack water equivalent (53.2 mm) was low, but total rain during the snowmelt period was greatest among study years (48.9 mm). Peak flow in 2002 coincided with snow ablation and was preceded by four consecutive days of rain (15.7 mm; Fig 4.2c). Total runoff from 2000-2002 was 51.8, 18.2, and 85.9mm, respectively (Table 4.1). The runoff ratio (total runoff/total precipitation) was similar in 2000 and 2001 (0.22 and 0.18), but much high higher in 2002 (0.84).

Soils were completely frozen from early October though early April (Figs. 2 a, b and c). Soils began thawing at the 23cm depth each spring and began earliest in 2001 (April 10th), a week later in 2002 (April 17th), and latest in 2000 (April 24th). Overwinter soil moisture was similar across years, averaging near 0.05 % volumetric moisture content (VMC). Maximum soil moisture was lower during the low flow year in 2001 (0.31 VMC) than higher flow years 2000 (0.39 VMC) and 2002 (0.41 VMC). In 2000 and 2001, maximum soil moisture occurred during snow ablation in late April. However, maximum soil moisture in 2002 coincided with snow ablation and heavy rains (30.5 mm total between April 28th and 29th) when soils were still frozen (compare rain and soil temperature panels; Fig. 4.2 c).

Oxygen Isotopes and Conductivity as Hydrologic Tracers

During baseflow prior to snowmelt, conductivity and δ^{18}O were stable, averaging 126 μS/cm and -19.50‰, respectively (range = 126 to 128 μS/cm, and -19.48 to 19.51‰, Fig. 4.2). Conductivity and δ^{18}O both decreased at the onset of snowmelt to a minimum of 56 μS/cm and -22.59 ‰, respectively, at peak flow. On the receding limb of the hydrograph, conductivity and δ^{18}O increased to 87.7μS/cm and -20.63‰, respectively. The relationship between conductivity and δ^{18}O can be expressed by two regression lines representing the ascending and descending limb of the hydrograph peak. Both regression lines are significant ($p < 0.0001$) with the ascending relationship revealing a steeper slope than the descending relationship (Fig. 4.3).

Using constant old-water signatures, which minimized the initial difference in the two methods during baseflow (4µs/cm and -25.15‰), we found good agreement between the estimation of the new water contribution to streamflow in 2000 (Fig. 4.4, top panel). The overall new water contribution was estimated at 53 and 54 % using conductivity and oxygen isotopes, respectively. However, the results from the two tracers differed over the course of snowmelt (Fig. 4.4, bottom panel). The oxygen isotope method estimated a greater new water component during the ascending limb of the hydrograph, but thereafter estimated a lower component of new water relative to the conductivity method.

The large variation in runoff among the three years of this study provided a good test for the use of conductivity as a tracer in hydrograph separation. For all years, we used the stream conductivity value prior to snowmelt as an old water signature. Mean snowpack conductivity was used for the new water signature. The contribution of new water to streamflow increased during peaks in the hydrograph for each snowmelt period (Fig. 4.5). The contribution of new water to flow increased with greater runoff during the study period shown by the significant relationship between the contribution of new water and total runoff ($p = 0.014$, $R^2 = 0.94$, Table 4.1 and Fig 4.6).

Solute Chemistry - Snowmelt 2000

Solutes can be divided into two groups according to their response to the hydrologic input of snowmelt water: 1) solutes that decrease with flow (baseflow dominant chemistry), and 2) solutes that increase with flow (snowmelt dominant chemistry).

Baseflow dominant solutes included NO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+} as well as the hydrologic tracers $\delta^{18}O$ and conductivity. Snowmelt dominant solutes included Cl^-, K^+, DOC, DON, total P, total Al, and total Fe (Table 4.2). Additional chemical groupings are shown by the strength of the correlation coefficients between specific ions. For instance, Mg^{2+}-Ca^{2+}, Ca^{2+}-EC, Mg^{2+}-EC, and NO_3^--EC showed near perfect correlations (all correlation coefficients = 0.99, $p < 0.001$). Various other correlations with Mg^{2+}, Ca^{2+} and conductivity with $\delta^{18}O$, NO_3^-, SO_4^{2-}, and Na^+ were also highly significant (all correlation coefficients from 0.96 to 0.90, $p < 0.001$). Among the snowmelt dominant solutes, total-P and K^+ were most highly correlated (0.97), followed by DOC-DON (0.94), total Al-total P (0.93), DOC- total Al (0.90), DON-total Fe (0.87), and DON-total Al (0.83, $p < 0.005$).

Solute Chemistry - Snowmelt 2000-2002

By comparing stream solute concentrations during three snowmelt seasons, we were able to examine chemical response across a range of hydrologic conditions. Total runoff was variable among the study years, being high in 2000 and 2002, but much lower in 2001 (Fig. 4.5). Similarly, maximum concentrations of snowmelt dominant ions, DOC, DON and K^+, were higher in 2000 and 2002 than 2001 (Fig. 4.7). When averaged over the entire snowmelt period, DOC and DON were significantly higher in 2000 and 2002 compared to 2001 (ANOVA, $p < 0.05$, Table 4.3). In contrast, the minimum concentrations of baseflow dominant solutes, NO_3^- and SO_4^{2-}, were lower in 2000 and 2002 than 2001 (Fig. 4.8). Similarly, average concentrations of baseflow dominant solutes (NO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+}) were significantly higher in the low flow year of 2001 compared to 2000 and 2002 (ANOVA, $p < 0.05$, Table 4.3).

The correlative relationships between specific solutes also changed among snowmelt years. The correlation between DOC and DON was significant in 2000 ($p < 0.001$, R2 = 0.89) and 2002 ($p < 0.001$, R2 = 0.85), but the lower DOC and DON concentrations in 2001 were not significantly related (Fig. 4.8). NO_3^- and SO_4^{2-} were significantly correlated in 2000 ($p < 0.001$, R2 = 0.66), 2001 ($p < 0.001$, R2 = 0.60), and 2002 ($p < 0.001$, R2 = 0.47; Fig. 4.10). The slope in 2002 was significantly lower than slopes in 2000 and 2001, which were not significantly different from each other (95% confidence interval of slopes did not overlap, $p < 0.05$).

Solute Mass Balance

All ions were enriched in the snowpack compared to fresh snow (Table 4.4). This enrichment was an order of magnitude for Ca^{2+} and Na^+, approximately five-fold for Mg^{2+}, K^+, Cl^- and SO_4^{2-}, and two-fold for NO_3^-. Because the total snowpack chemistry is a more direct measure of the ion load into the watershed during melt, we used this measurement as input into the mass balance calculation.

For all ions except Cl^-, stream export was greater than snowpack input during the snowmelt period from 2000 to 2002 (Table 4.5). Cl^- was retained in 2000 and 2001, but showed a net loss in 2002. Ca^{2+}, SO_4^{2-} and Mg^{2+} had the greatest net loss among ions, and NO_3^- and Na^+ had the smallest net loss.

Discussion

The large variation in runoff in this study was not linearly related to the water content of the snowpack, suggesting that rainfall, soil moisture, and the timing of snow ablation can be more important than the snowpack water equivalent in determining the hydrologic response during snowmelt. The lack of hydrologic response in 2001 may be explained by the timing of soil thawing and snow ablation. Soils thawed early in 2001, but little snow ablation occurred until two weeks after the initial thawing. During this period between soil thawing and snow ablation, any ice present in the soils would have disappeared and soils would be better able to store additional water inputs from the snowpack. Soil moisture conditions support this pattern as soil moisture increased to a moderate level in 2001 and remained elevated for an extended period. Over this time, water may gradually drain into deeper soils on north- and south-facing slopes.

In contrast to the low flow in 2001, high flow in 2002 may be explained by a combination of snow ablation and intense rainfall during the snowmelt period when surface soils were still frozen. These conditions generated the greatest soil moisture content observed over the study period. During a subsequent rain event, flow increased rapidly, indicating that surface soils were primed to generate rapid flow.

Hydrograph Separation

Numerous studies have warned against using bulk snowpack δ^{18}O as a new water signature during hydrograph separation as fractionation that tends to enrich meltwater as snowmelt proceeds is ignored (Cooper 1993, 1998, Laudon et al. 2002, Rodhe 1998, Taylor 2001, Liu et al. 2004). Although we did not measure the temporal variation in meltwater during the snowmelt period method, the good agreement between models based on $\delta^{18}O$ and conductivity suggests that snowpack fractionation had a small effect on $\delta^{18}O$ stream signature. Nevertheless, systematic differences in the response of the two tracers over snowmelt suggest that the tracer concentrations were changing in source waters.

We suggest two possible explanations for the shift in the $\delta^{18}O$ and conductivity relationship that caused the conductivity estimate to be lower than the $\delta^{18}O$ estimate at peak flow, but greater than the $\delta^{18}O$ estimate after peak discharge. First, as snowmelt water (new water) mixes with soil water or groundwater (old water), the conductivity may rapidly increase at the start of snowmelt followed by a more gradual change after equilibration (Pilgrim et al. 1979, McNamara et al. 1997). In this case, conductivity would behave conservatively and decrease quickly as snowmelt water first reaches the stream, but thereafter conductivity would remain lower relative to $\delta^{18}O$ after snowmelt water equilibrates with soil and groundwater. Since oxygen isotopes are not affected by reactions of the meltwater and soil water, $\delta^{18}O$ can respond more quickly to maximum discharge and hydrograph recession. Second, if the snowpack meltwater becomes progressively heavier during latter stages of melt, the $\delta^{18}O$ stream signature would also become enriched and we would underestimate the contribution of new water to stream flow (Rodhe 1998, Liu et al. 2004).

Despite potential errors involved with using conductivity as a tracer in hydrograph separation, this technique proved to be useful in describing the contribution of new water to streamflow during the course of this study. The increase in the new water component with greater runoff suggests that the simple two-end member model using conductivity as a hydrologic tracer was a useful tool for hydrograph separation in this sub-arctic watershed. Reports of hydrograph separation in permafrost catchments using conductivity have found either dominance of old (Carey and Quinton 2004) or new water (McNamara 1997) during the snowmelt peak. We found that the contribution of new water changed through the course of the study period from dominance (64 % in 2002) to only a fraction (17% in 2001) of total flow. The variability in the new water contribution underscores the importance of interannual variation in the delivery of snowmelt water to the stream.

Solute Chemistry and Flow

Intraannual variation in stream solute concentrations during snowmelt can be largely explained by input of new water from the snowpack either diluting baseflow dominant solutes or leaching highflow dominant solutes along hydrologic flowpaths. High correlation coefficients among ions demonstrate that flowpaths changed temporally during the snowmelt period or the dissolution of the source material occurred at similar rates in relation to the influx of snowmelt water. For instance, in 2000 total P and K were highly correlated and peaked earlier than other highflow dominant ions. In order for these ions to precede others, they must be more soluble or the flowpath that generates these ions must be dominant only at the onset of snowmelt. Similarly, DOC, DON, total Al and total Fe were all highly correlated (all correlation coefficients > 0.90), suggesting that these solutes had a similar source material or flowpaths. For baseflow dominant ions, Ca and Mg responded very similarly to flow, indicating that they were similarly diluted by snowmelt water and originated from the same parent material.

In contrast to observations in temperate (Cadle et al. 1984, Likens and Bormann 1985, Rascher et al. 1987, Stottlemeyer 1987, Creed et al. 1996, Semkin et al 2002, Detenbeck et al. 2003), and alpine (Williams and Melack 1991, Campbell et al. 1995, Sickman et al. 2002, Sickman et al. 2003) ecosystems where NO_3^- or SO_4^{2-} concentrations increase with flow during snowmelt, we found that NO_3^- and SO_4^{2-} were consistently diluted by snowmelt water. This difference may be attributable to the low NO_3^- and SO_4^{2-} concentrations in the snowpack due to low rates of N and S deposition (less than 1 kg ha^{-1} yr^{-1}) in our study watershed. Deposition rates in interior Alaska are low compared to midwestern and northeastern U.S. temperate watersheds and alpine watersheds in the Rocky Mountain and Sierra Nevada Ranges that receive greater anthropogenic inputs (Likens and Bormann 1995, Campbell et al. 2000, NADP regional data; http://nadp.sws.uiuc.edu/).

Soil microbial processes can influence stream concentrations of biologically active solutes during snowmelt. Soil provided more than half of the stream nitrate flux during snowmelt in an alpine ecosystem (Sickman et al. 2003), and microbial activity can occur below freezing in boreal soils in interior Alaska (Schimel and Clein 1996). Although we did not measure microbial processes during snowmelt, early spring would favor microbial immobilization since C:N ratios are high in surface soils (C:N = 20-30, Lyle unpublished data). In any case, baseflow stream NO_3^- and SO_4^{2-} concentrations were high compared to snowpack concentrations, so an influx of snowmelt water would reduce stream concentrations if additional flowpath sources had not been present.

Interannual Chemistry Variation

Stream chemistry response over the study period was highly influenced by interannual variations in peak flow and runoff. The higher average concentrations of DOC and DON in the higher flow years, 2000 and 2002, compared to 2001, indicate that organic matter flushing is related to overall flow in a snowmelt season. Studies have reported that finite sources of organic matter are leached during the onset of snowmelt because maximum DOC concentration occurs on the ascending hydrograph and DOC concentrations subside during peak flow (Hornberger 1994, Hood et al. 2003). While we observed such a pattern during the low runoff in 2001, DOC and DON concentrations remained elevated for a longer period in 2000 and 2002, suggesting that high runoff can flush the large pools of organic matter typical of boreal watersheds and generate high DOC and DON concentrations. Therefore, high flow during snowmelt may be particularly important in the retention of organic solutes in boreal forest watersheds as organic flux is related to the magnitude of hydrologic flux.

The ratio of DOC:DON changed among snowmelt years, suggesting that different sources contributed to flow. The slope of the relationship between DOC and DON was similar in 2000 and 2002, but DOC:DON ratios were much lower in 2000. This result may be explained by changes in source area due to the timing of hydrograph peaks between years. In 2000, early peak flow in April likely originated from south-facing slopes and was followed by a smaller peak in May from north-facing slopes. In 2002, there was only one large discharge peak in early May that included water generated from north and south-facing slopes. C/N ratio of soil organic matter is lower in birch stands on south-facing slopes (C/N = 20) than soil in black spruce stands (C/N = 30) on north-facing slopes (Lyle 2005). A greater proportion of water from the south-facing slopes in 2000 may have produced runoff with a lower DOC:DON ratio than the mixture of water from north and south slopes in 2002. The lack of relationship between DON and DOC in 2001 may be due to a different source area or flowpath in low-flow years. In 2001, the DOC peak was lower, appeared early in the spring, and was not coupled to a corresponding DON peak, suggesting that early spring organic matter sources were different from those occurring later in snowmelt

In contrast to organic solutes that increase with discharge, interannual concentrations of baseflow dominant solutes (NO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+}) appear to be controlled by dilution of snowmelt water. Volume-weighted mean concentrations were all significantly higher for these ions in 2001 compared to 2000 and 2002. Although biological processes may be important during the winter months, we postulate that variations in these solutes are best explained by simple mixing of dilute snowmelt water with enriched baseflow water.

Solute Mass Balance

Enrichment of bulk snowpack compared to fresh snow may represent the addition of dry deposition and plant material into the snowpack that occurred over the winter.

Enrichment of snowpack solutes from plant material is common in temperate regions (Likens and Bormann 1985), and enrichment of snowpack SO_4^{2-} has been reported in arctic regions of Alaska, due to arctic haze pollution (Douglas and Sturm 2004). We do not know the origin of the additional solutes that we measured in the snowpack, but the subject warrants more attention.

Although the snowpack accumulates atmospherically derived solutes from both dry and wet deposition for almost half of the year, the stream output was greater than the snowmelt input for all major cations and anions except Cl^- in 2000 and 2001. This result indicates that the input of snowpack solutes is small relative to hydrologic fluxes and watershed sources of elements. Cl^- retention was surprising given that the snowpack concentrations were lower than the average volume weighted mean concentrations that we observed in streams. However, we did not measure Cl^- in soils during the snowmelt period, and high concentrations of Cl^- due to evaporation of surface soil layers could be a factor. The large temperature gradient between warm soils and cold ambient air during the winter may generate water vapor migration from the soil to the snowpack, which could enrich soil Cl^- concentration (Friedman 1991).

Snowmelt solute fluxes may only represent a small proportion of the annual flux in low flow years. In 2001, we obtained annual flux rates and the snowmelt period was a fraction of the annual output of solutes. However, if we assume similar annual flux rates as we found in 2001 for 2000 and 2002, snowmelt solute fluxes could be a larger proportion of the annual flux as solute output was up to several-fold greater in the high flow years. This interannual variation in solute flux rates underscores the importance of antecedent soil moisture, rainfall, and melt processes in delivering water and solutes to the stream. We found that high flow years (2000 and 2002) produced larger solute fluxes despite similar snowpack water content. Variation in flow and solute flux across snowmelt seasons may be explained by soil conditions prior to snow ablation and rainfall during the snowmelt period.

Conclusions

During the three snowmelt years of this study, we observed considerable variation in runoff and consequent stream chemistry during spring snowmelt. It appears that boreal watersheds in interior Alaska are especially sensitive to processes that regulate melt and infiltration into permafrost-dominated and permafrost-free soils. Variation in runoff and peak discharge is important to stream chemistry in the spring as the magnitude of organic solute concentration (DOC and DON) increased with discharge over the study period. Furthermore, these solutes remained elevated during the broad discharge peaks during the high flow years (2000 and 2002), indicating that a large pool of organic matter became available for flushing at this time of year. At the same time, high spring flows consistently reduced inorganic solute concentrations through dilution since the snowpack and surface soils are depleted in these ions.

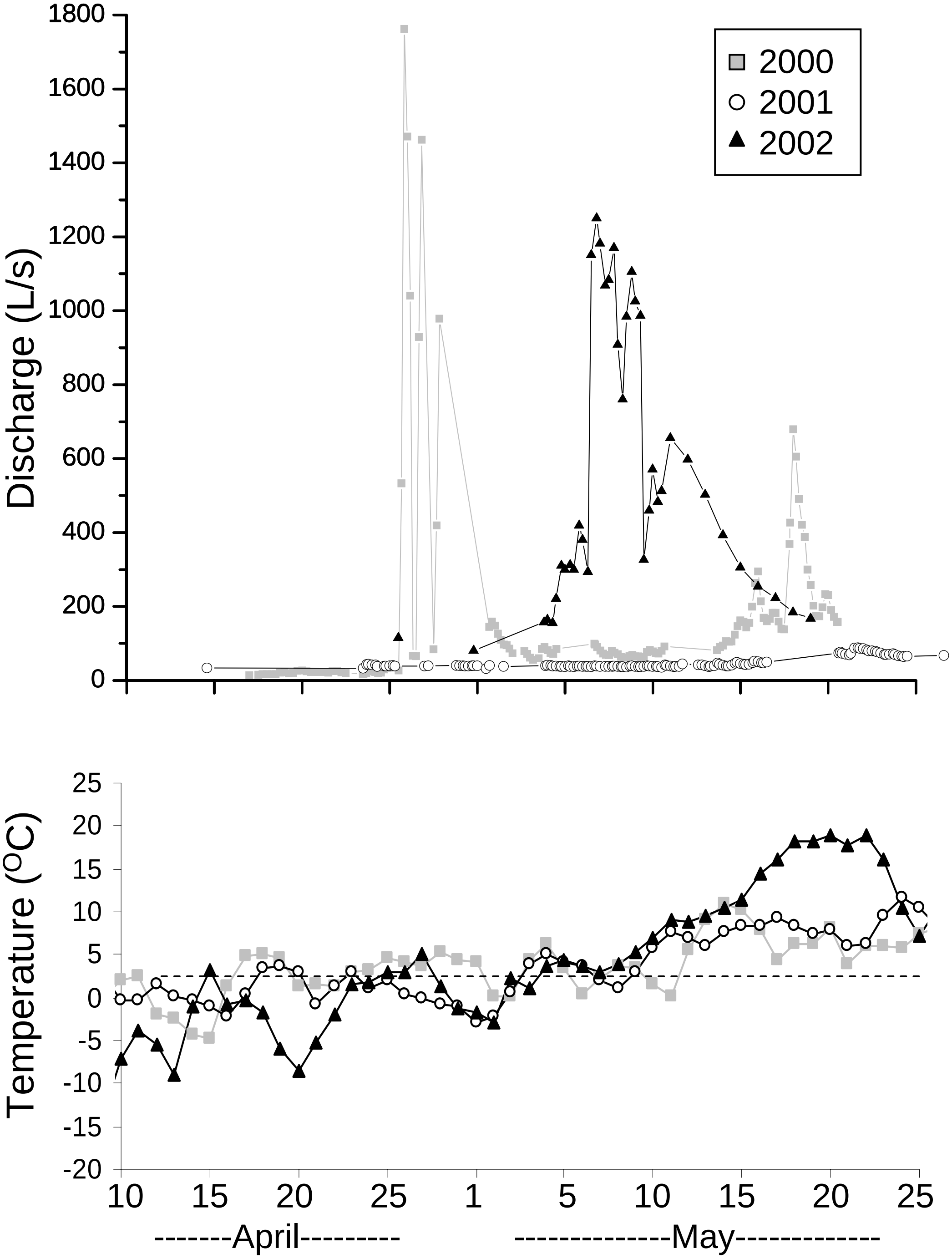


Fig. 4.1. Discharge and temperature during the snowmelt period (April 10- May 31) in 2000 (gray squares), 2001 (open circles), and 2002 (closed triangles).

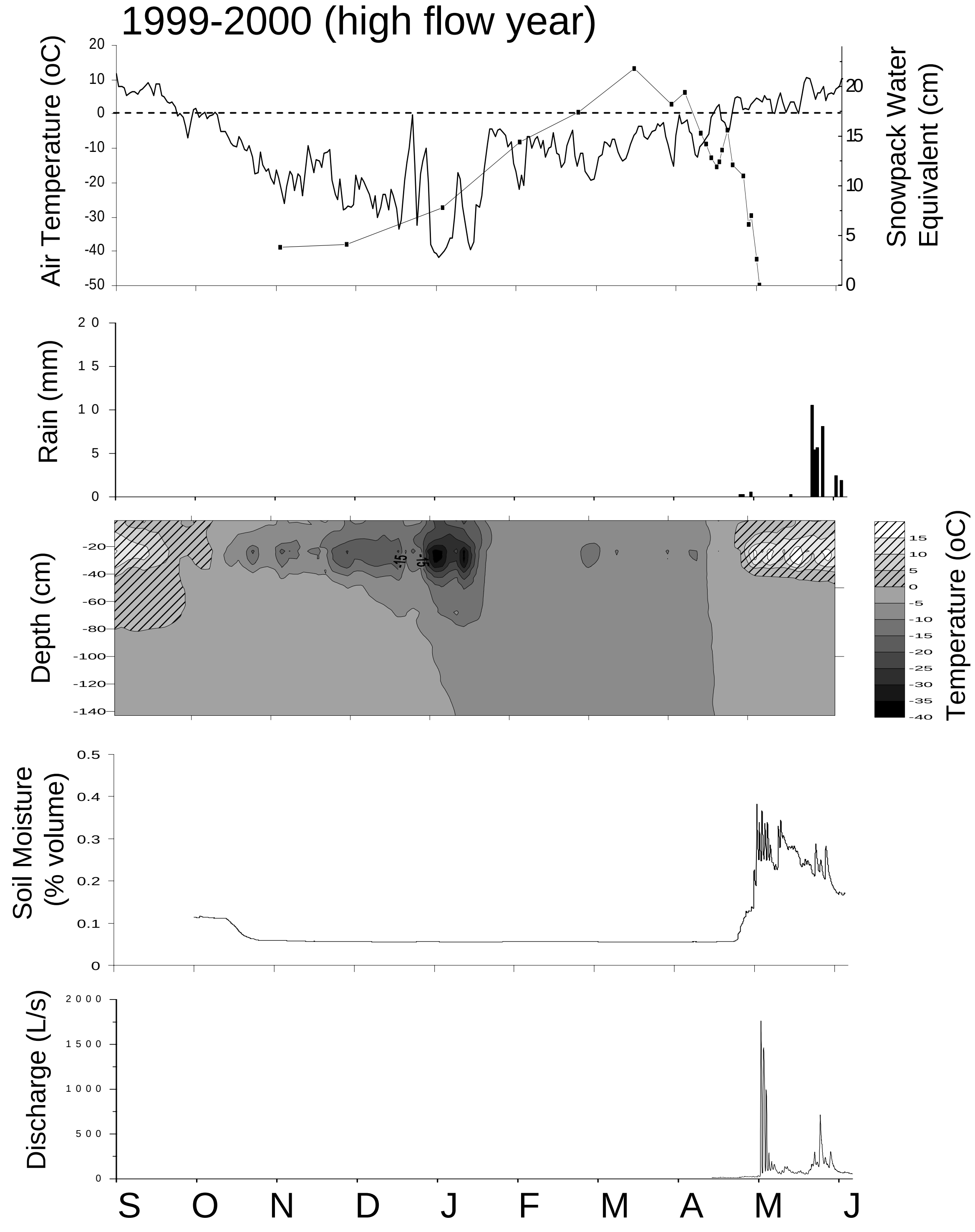


Fig. 4.2a. Time series of air temperature, snowpack water equivalent, rain, soil temperature, soil moisture at 15cm depth, and discharge between September 1999 and May 2000.

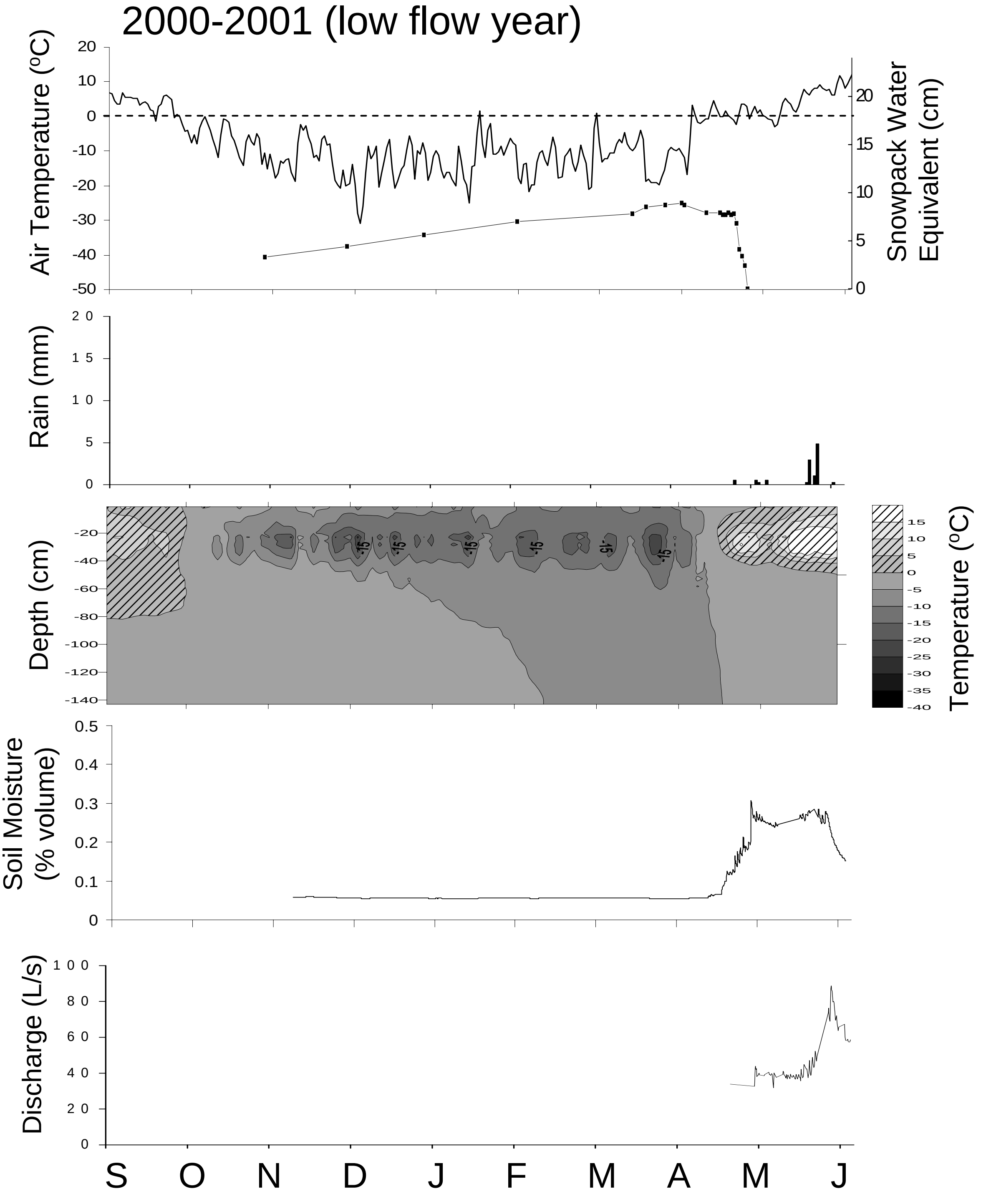


Fig. 4.2b. Time series of air temperature, snowpack water equivalent, rain, soil temperature, soil moisture at 15cm depth, and discharge between September 2000 and May 2001.

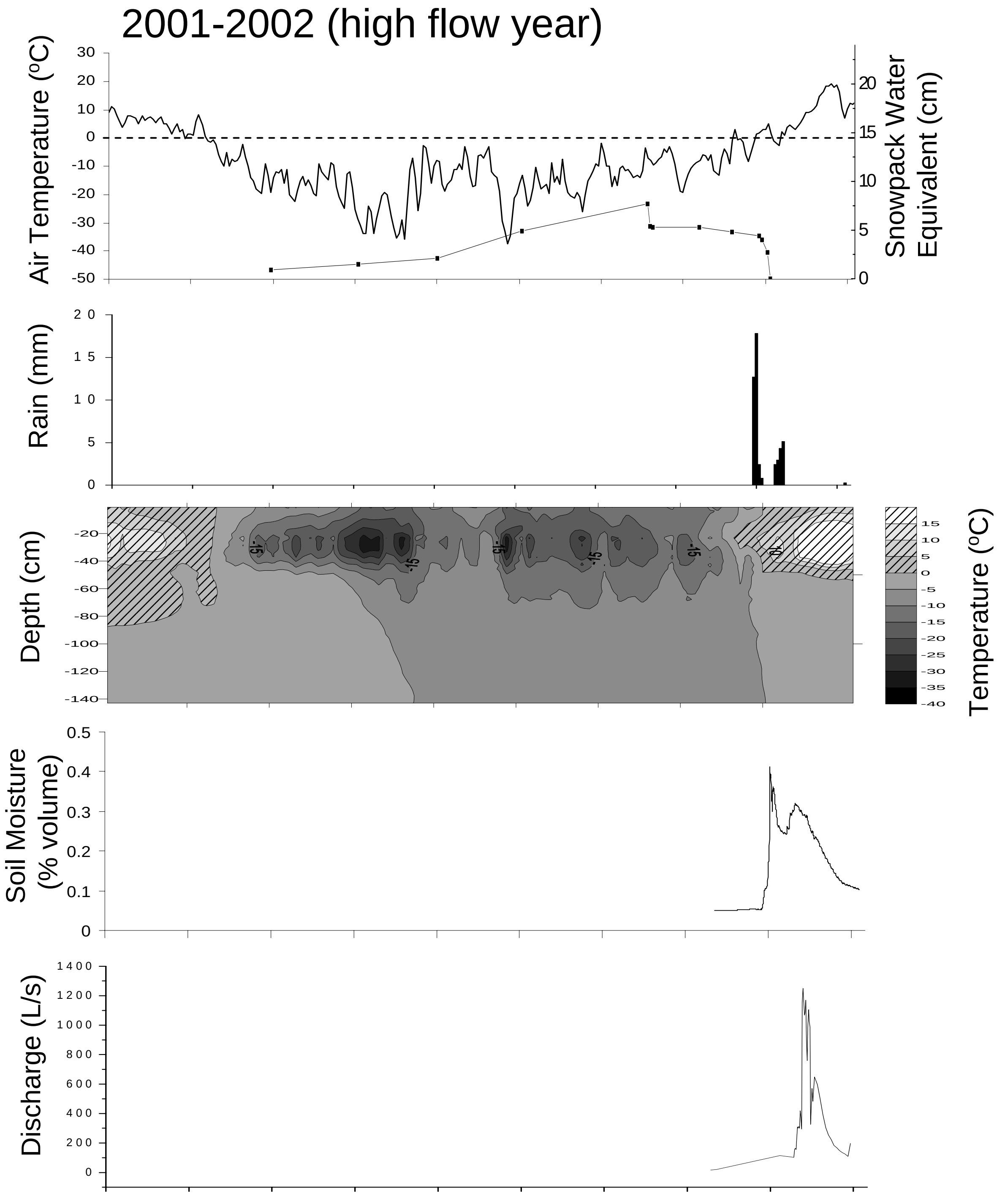


Fig. 4.2c. Time series of air temperature, snowpack water equivalent, rain, soil temperature, soil moisture at 15cm depth, and discharge between September 2001 and May 2002.

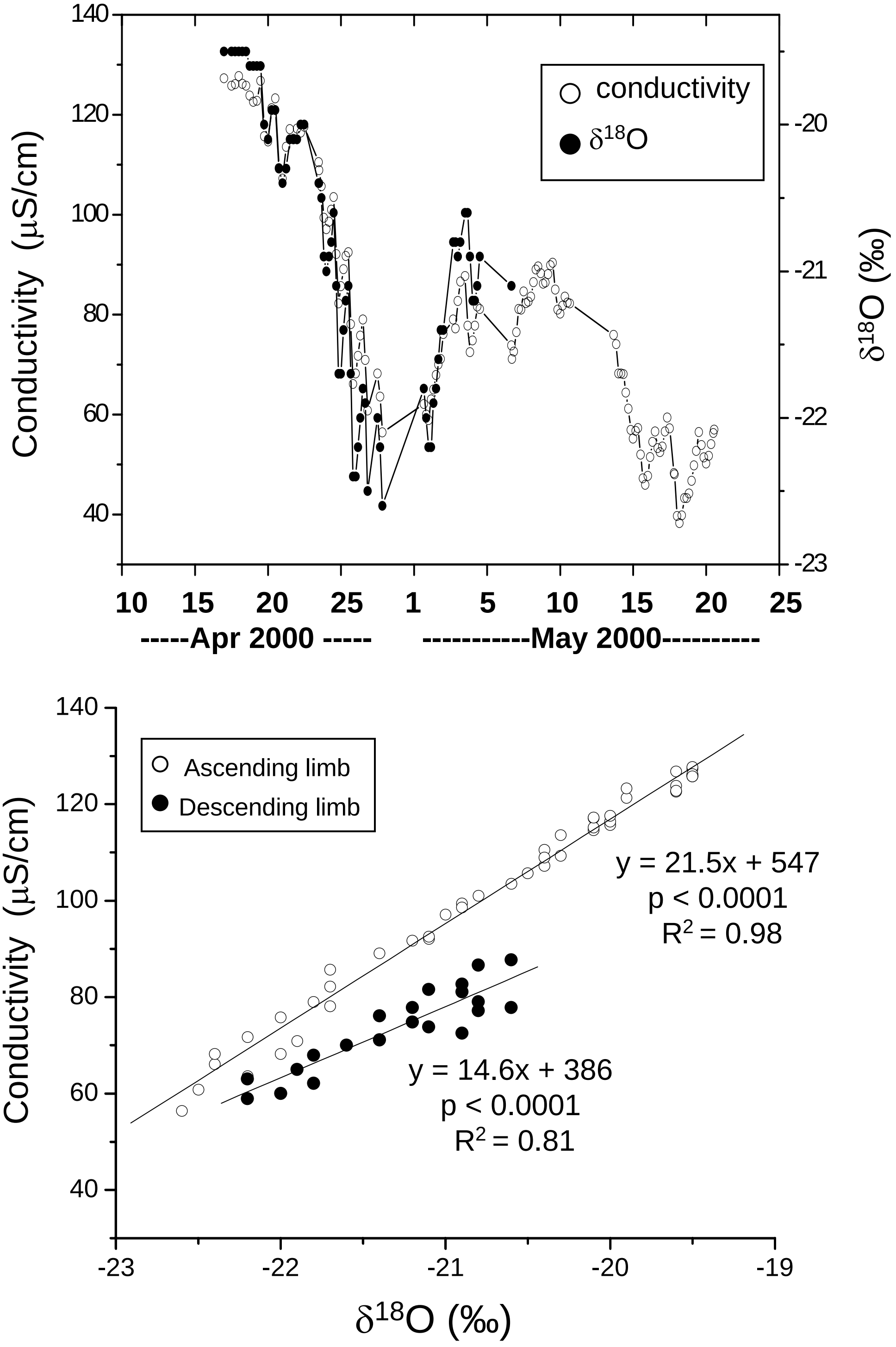


Fig. 4.3. Conductivity and $\delta^{18}O$ during the snowmelt period (April 10-May 31) in 2000 (top panel), and the relationship between conductivity and $\delta^{18}O$ in 2000 (bottom panel).

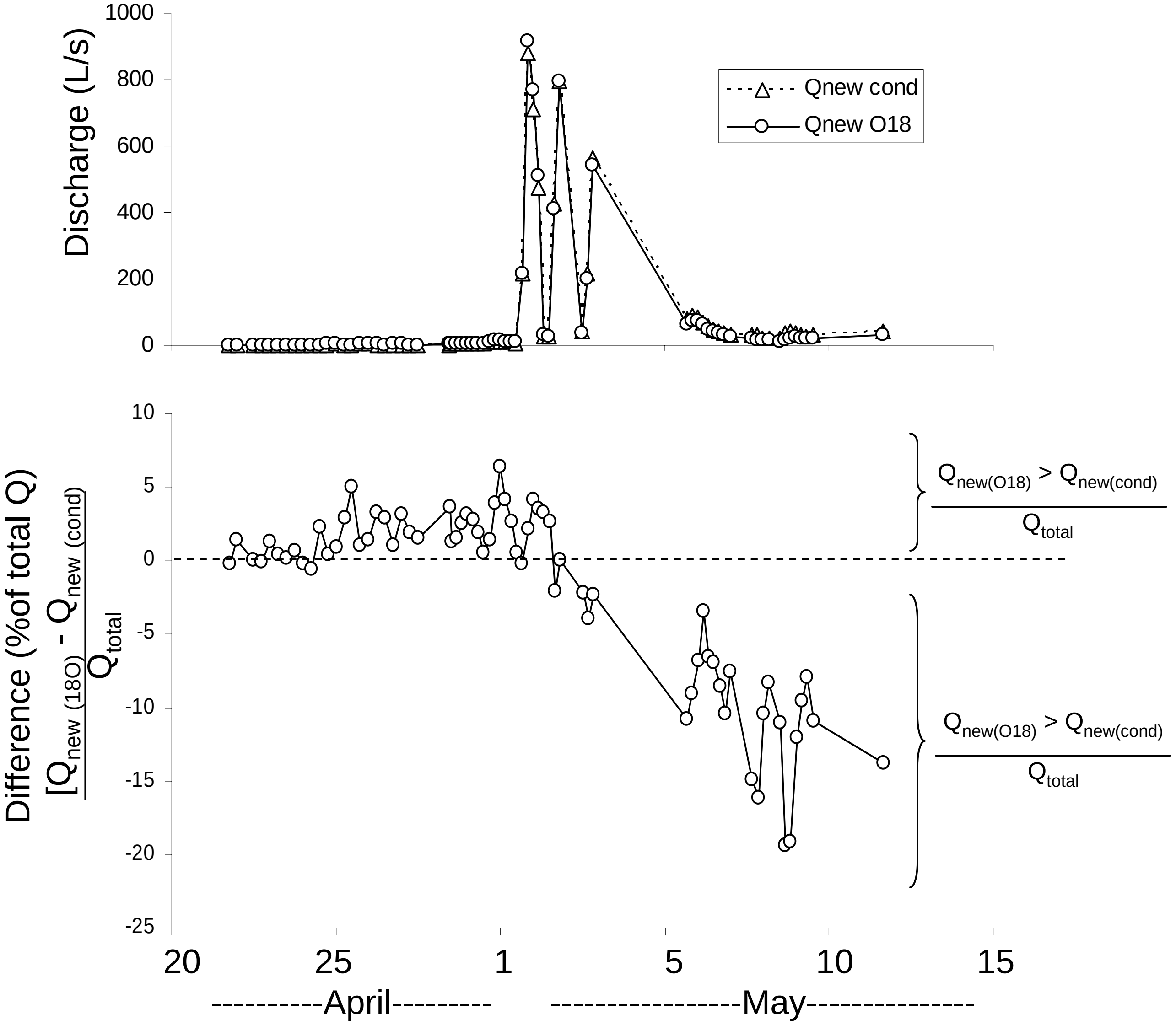


Fig. 4.4. Estimate of the new water contribution using conductivity and δ^{18}O as hydrologic tracers to the snowmelt hydrograph peak in 2000 (top panel), and the difference between new water from δ^{18}O and new water from conductivity represented as a fraction of the total discharge (Q_{total}; bottom panel).

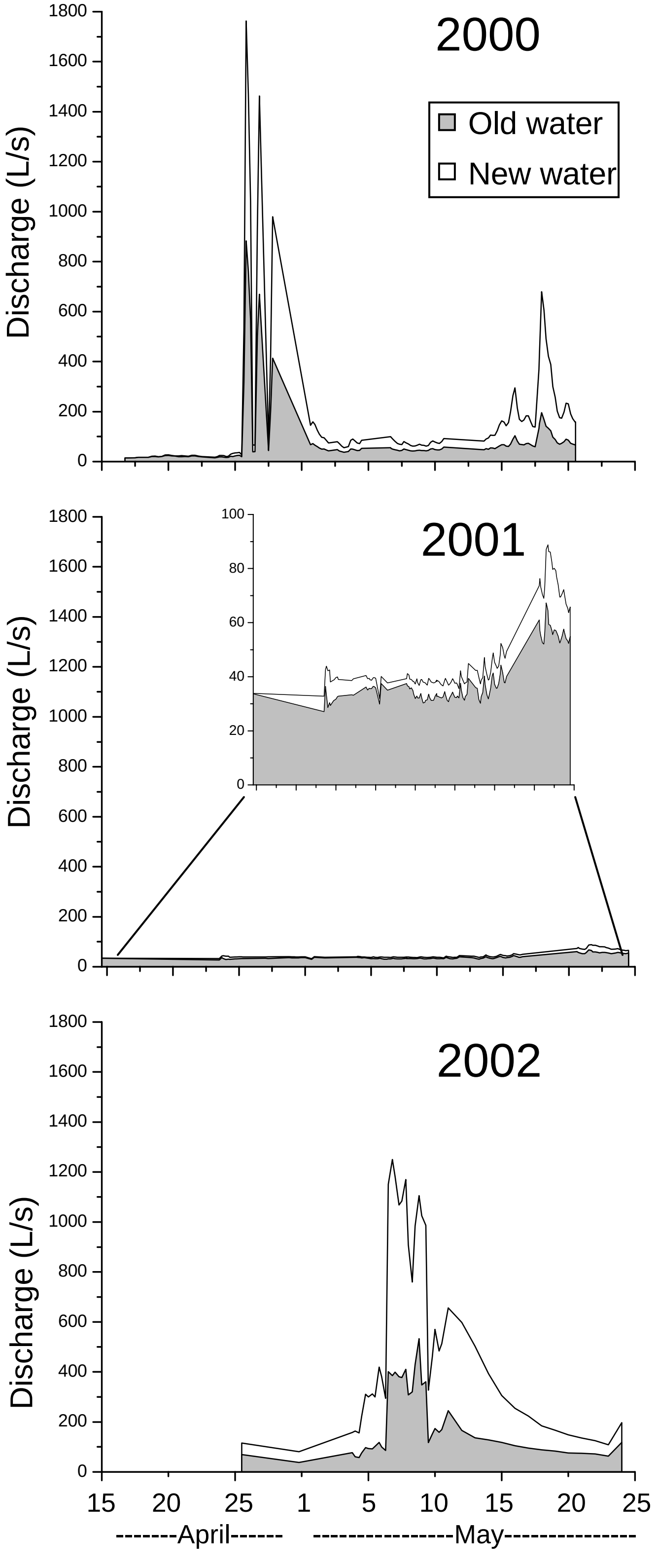


Fig. 4.5. Estimates of old water and new water to snowmelt hydrograph peaks in 2000, 2001 and 2002.

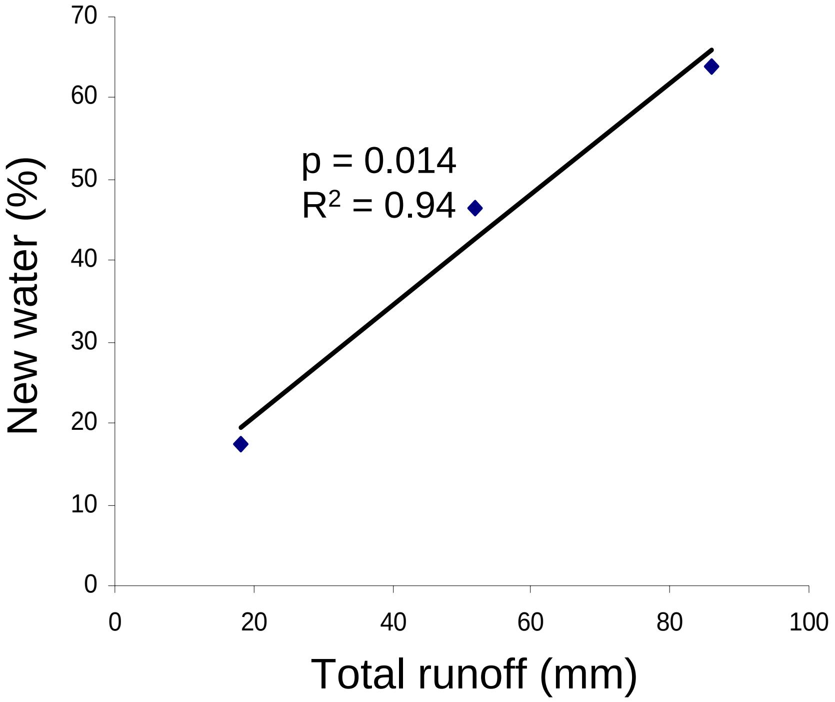


Fig. 4.6. The relationship between % new water and total runoff from 2000-2002.

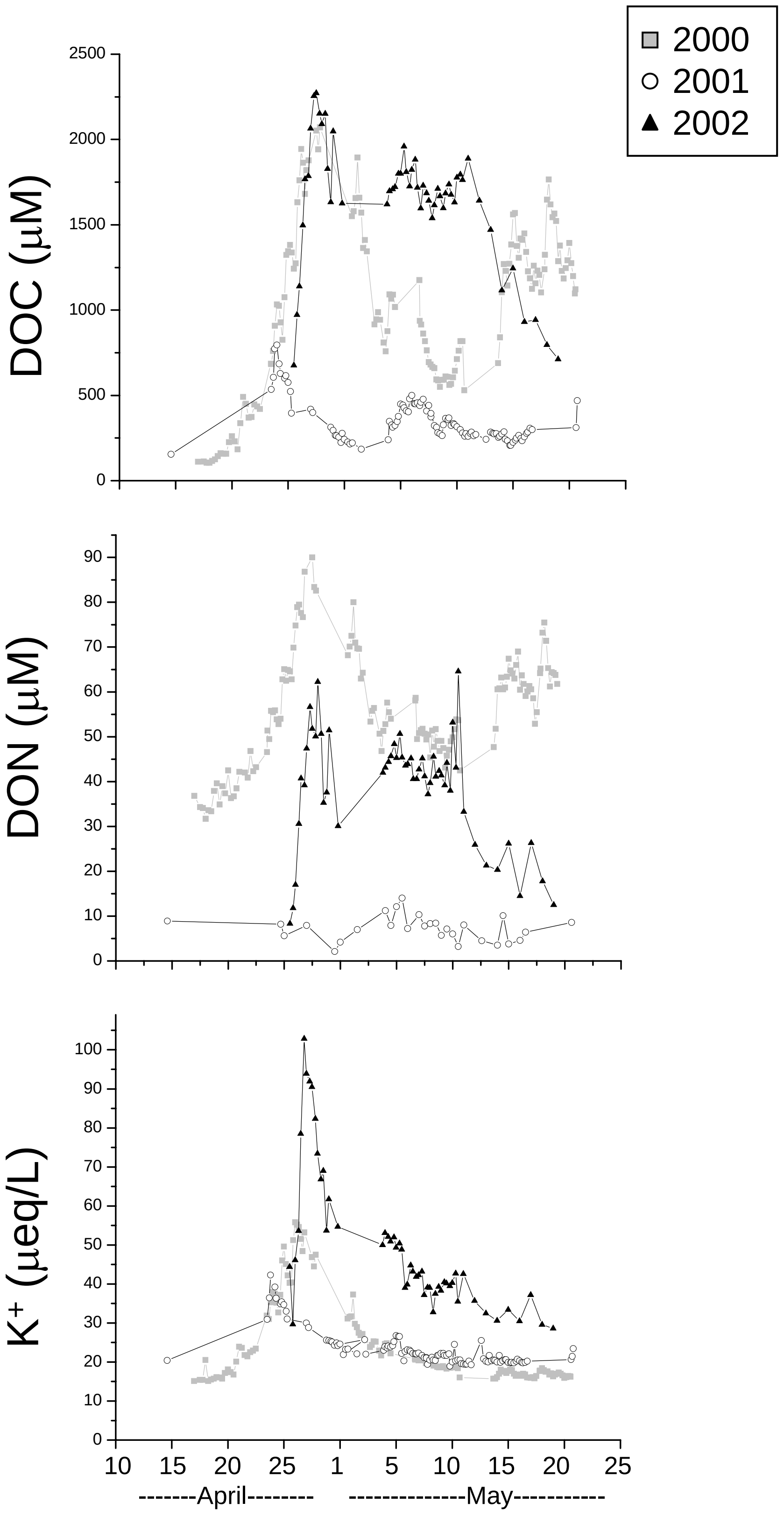


Fig. 4.7. Time series of DOC, DON and K+ in 2000 (gray squares), 2001 (open circles), and 2002 (closed triangles).

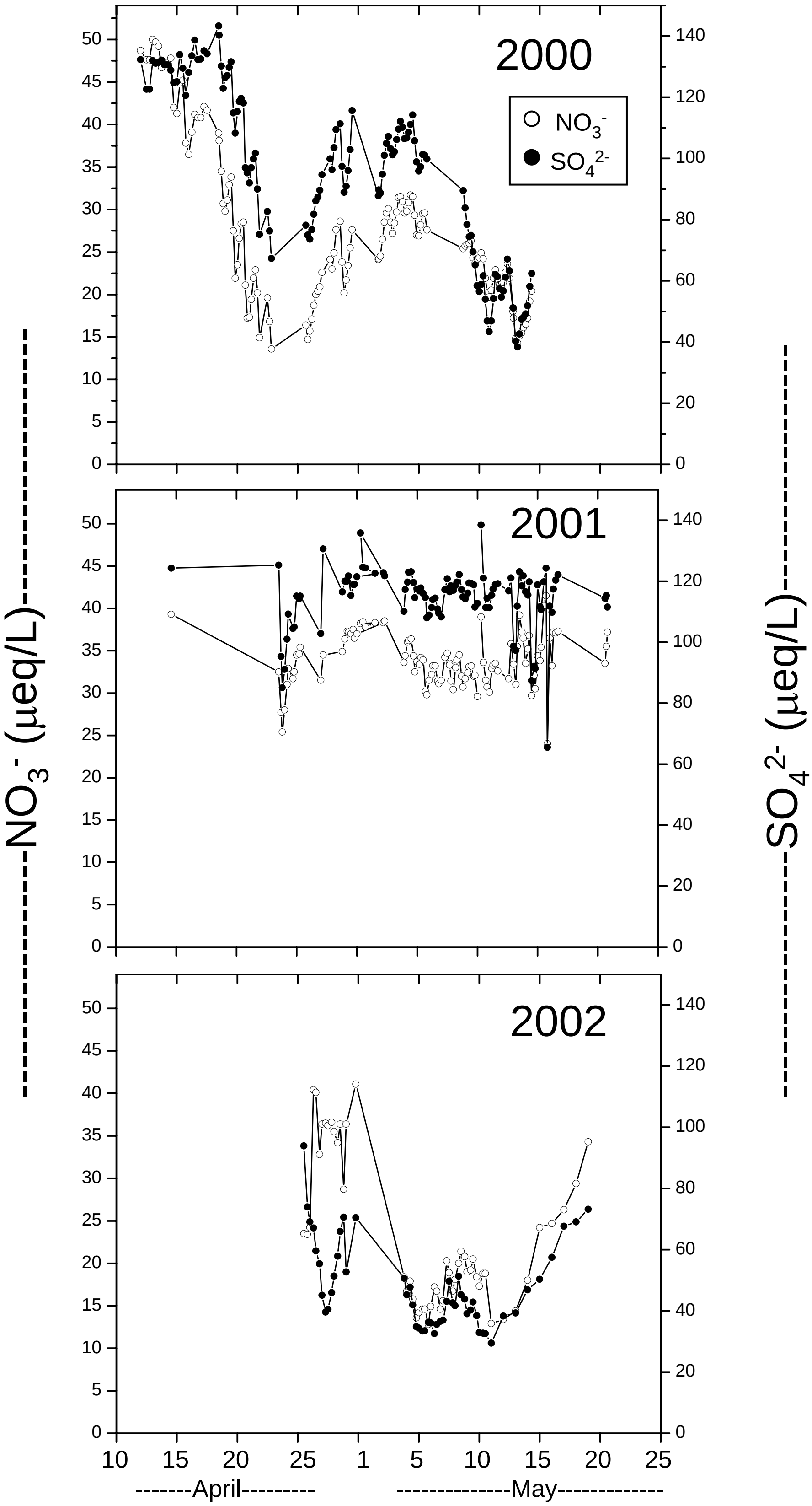


Fig. 4.8. Time series of SO_4^{2-} and NO_3^- in 2000 (top panel), 2001 (middle panel), and 2002 (bottom panel).

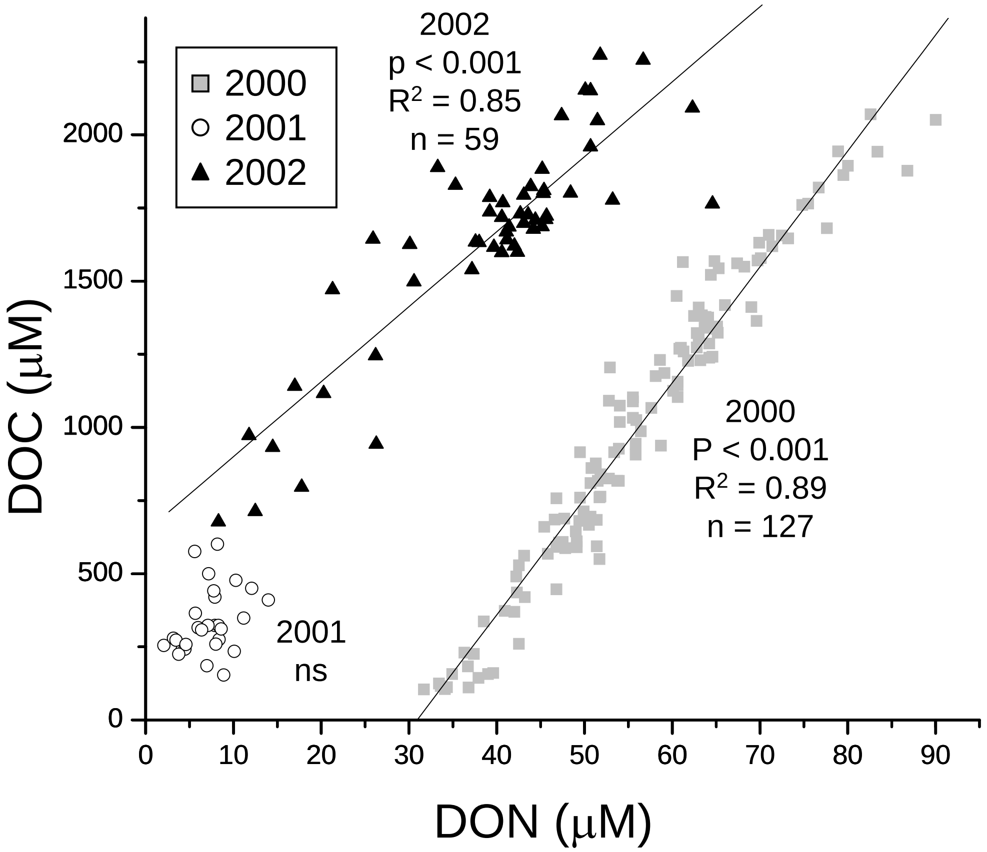


Fig. 4.9. The relationship between DON and DOC in 2000 (gray squares), 2001 (open circles), and 2002 (closed triangles).

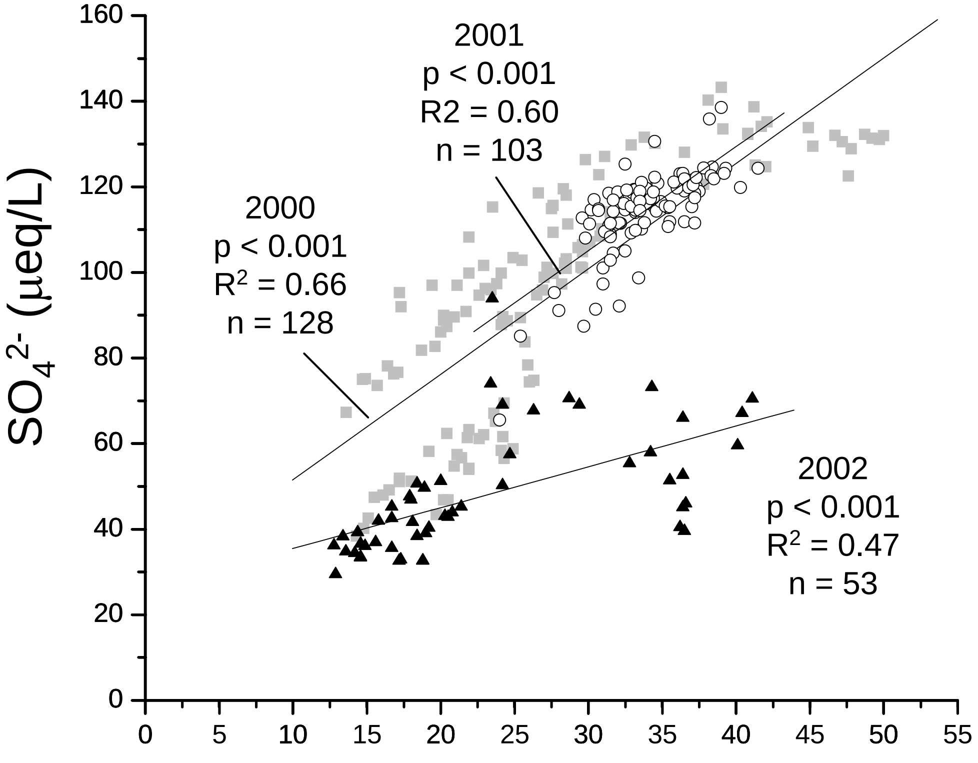


Fig. 4.10. The relationship between SO_4^{2-} and NO_3^- in 2000 (gray squares), 2001 (open circles), and 2002 (closed triangles).

Table 4.1. Hydrograph separation from snowmelt 2000-2001 using conductivity as a tracer. Runoff ratio = total runoff/total precipitation (rain and snow).

Year	snow water equivalent (mm)	rain (mm)	rain + snow (mm)	total runoff (mm)	runoff ratio	old water discharge (mm)	new water discharge (mm)	old water (%)	new water (%)
2000	197.9	35.4	233.3	51.8	0.22	28	13	54	46
2001	91.6	11.3	102.9	18.2	0.18	15	3	83	17
2002	53.2	48.9	102.1	85.9	0.84	31	20	36	64

Table 4.2. Correlation matrix for baseflow and highflow elements during snowmelt in 2000. All correlations are significantly different from zero, t test p<0.001, unless otherwise noted. EC = conductivity, Q = discharge.

	Baseflow							
	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	Ca^{2+}	$\delta^{18}O$	EC	Q
NO_3^-	1.00	0.81	0.87	0.93	0.95	0.96	0.99	-0.47
SO_4^{2-}		1.00	0.87	0.96	0.94	0.84	0.93	-0.46
Na^+			1.00	0.90	0.89	0.84	0.90	-0.42
Mg^{2+}				1.00	0.995	0.95	0.99	-0.51
Ca^{2+}					1.00	0.95	0.99	-0.51
$\delta^{18}O$						1.00	0.94	-0.58
Conductivity							1.00	-0.47
Discharge								1.00

	Highflow							
	Cl^-	K^+	DOC	DON	total P	total Al	total Fe	Q
Cl^-	1.00	0.61	0.60	0.51	0.61	0.46	0.56	0.53
K^+		1.00	0.52	0.55	0.97	0.36	0.26*	0.60
DOC			1.00	0.94	0.60	0.90	0.94	0.52
DON				1.00	0.60	0.83	0.87	0.47
total P					1.00	0.44	0.37	0.66
total Al						1.00	0.93	0.49
total Fe							1.00	0.50
Discharge								1.00

*p < 0.005

Table 4.3. A comparison of volume-weighted mean solute concentrations during snowmelt (April 10-May31), 2000-2002. Values with similar letters are not significantly different, ANOVA, Tukey's multiple comparison, $p < 0.05$. Units are as follows: major ions, μeq/L; DOC and DON, μM; and EC (conductivity), μS/cm.

Solute	2000		2001		2002	
Ca^{2+}	418.5	A	521.4	B	397.7	C
Mg^{2+}	128.5	A	192.1	B	126.5	C
K^{+}	31.5	A	22.8	A	41.4	B
Na^{+}	26.4	A	50.0	B	42.7	C
NO_3^{-}	18.8	A	34.4	B	19.5	C
Cl^{-}	8.5	A	6.1	A	11.9	B
SO_4^{2-}	72.0	A	110.6	B	43.9	C
DOC	1451.3	A	285.3	B	1611.4	C
DON	63.3	A	13.2	B	39.1	C
EC	62.9	A	100.8	B	46.9	C

Table 4.4. Major cation and anion chemistry of fresh snow (mean NADP 2000-2002) and the bulk snowpack (2002).

	Fresh Snow				Snowpack			
	mean	SE	mean	SE	mean	SE	mean	SE
Solute	mg/L	mg/L	μeq/L	μeq/L	mg/L	mg/L	μeq/L	μeq/L
Ca^{2+}	0.023	0.009	1.2	0.4	0.304	0.001	15.2	0.0
Mg^{2+}	0.003	0.001	0.2	0.1	0.030	0.004	2.5	0.3
K^+	0.002	0.000	0.1	0.0	0.032	0.002	0.8	0.1
Na^+	0.008	0.003	0.4	0.2	0.109	0.010	4.7	0.4
NO_3^-	0.035	0.064	2.5	4.5	0.072	0.003	5.2	0.2
Cl^-	0.027	0.007	0.8	1.8	0.140	0.001	4.0	0.0
SO_4^{2-}	0.057	0.012	1.2	0.1	0.223	0.035	4.6	0.7

Table 4.5. Mass balance of major ions for the snowmelt period (April 10- May 31) in 2000, 2001 and 2002. In 2001, % of annual = snowmelt output/annual export*100. All units are kg/ha.

	2000			2001				2002		
Solute	Input	Output	Net	Input	Output	Net	% of Annual	Input	Output	Net
Ca^{2+}	0.60	4.51	-3.91	0.28	1.64	-1.36	9.2	0.16	7.67	-7.51
Mg^{2+}	0.06	0.84	-0.78	0.03	0.44	-0.41	7.8	0.02	1.45	-1.43
K^+	0.06	0.61	-0.55	0.03	0.16	-0.13	9.7	0.02	1.24	-1.22
Na^+	0.22	0.32	-0.10	0.10	0.23	-0.13	3.9	0.06	1.04	-0.98
NO_3^-	0.14	0.15	-0.01	0.07	0.09	-0.02	7.8	0.04	0.26	-0.22
Cl^-	0.28	0.16	0.12	0.13	0.05	0.08	12.4	0.07	0.37	-0.29
SO_4^{2-}	0.44	1.93	-1.49	0.20	0.98	-0.78	7.7	0.12	2.15	-2.03

References

Brooks PD, Williams MW, and Schmidt SK. 1998. Inorganic nitrogen and microbial biomass dynamics before and during spring snowmelt. Biogeochemistry. 43: 1-15.

Cadle SH, Dasch JM, and Grossnickle NE. 1984. Retention and release of chemical species by a northern Michigan snowpack. Water Air Soil Pollution. 22: 303-319.

Campbell DH, Clow DW, Ingersoll GP, Mast MA, Spahr NE, and Turk JT. 1995. Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains. Water Resources Research. 31: 2811-2821.

Campbell DH, Baron JS, Tonnessen KA, Brooks PD, and Schuster PF. 2000. Controls on nitrogen flux in alpine/subalpine watersheds of Colorado. Water Resources Research. 36: 37-47.

Carey SK, and Woo M-K. 1999. Hydrology of two slopes in subarctic Yukon, Canada. Hydrological Processes. 13: 2549-2562.

Carey SK, and Woo M-K. 2001. Spatial variability of hillslope water balance, Wolf Creek basin, subarctic Yukon. Hydrological Processes. 15: 3113-3132.

Carey SK, and Quinton WL. 2004. Evaluating snowmelt runoff generation in a discontinuous permafrost catchment using stable isotope, hydrochemical and hydrometric data. Nordic Hydrology. 35: 309-324.

Cooper LW, Solis C, Kane DL, and Hinzman LD. 1993. Application of oxygen-18 tracer techniques to Arctic hydrological processes. Arctic and Alpine Research. 25: 247-255.

Cooper LW. 1998. Isotopic fractionation in snow cover. In: C Kendall and JJ McDonnell (Eds) Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam, NL, pp 119-136.

Creed IF, Band LE, Foster NW, Morrison IK, Nicholson JA, Semkin RS, and Jeffries DS. 1996. Regulation of nitrate-N release from temperate forests: A test of the N flushing hypothesis. Water Resources Research. 32: 3337-3354.

Detenbeck NE, Elonen CM, Taylor DL, Anderson LE, Jicha TM, and Batterman SL. Effects of hydrogeomorphic region, catchment storage and mature forest on baseflow and snowmelt stream water quality in second-order Lake Superior Basin tributaries. Freshwater Biology. 28: 912-927.

Douglas TA and Sturm M. 2004. Arctic haze, mercury and the chemical composition of snow across northwestern Alaska. Atmospheric Environment 38: 805-820.

Friedman I, Benson C, and Gleason J. 1991. Isotopic changes during snow metamorphism. In: HP Taylor, JR O'Neil, IR Kaplan. (Eds) Stable Isotope Geochemistry: A Tribute to Samuel Epstein. The Geochemical Society, San Antonio, pp 211-221.

Hood E, McKnight DM, and Williams MW. 2003. Sources and chemical character of dissolved organic carbon across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range, United States. Water Resources Research. 39: 1188, doi:10.1029/2002WR001738

Hooper RP, and Shoemaker CA. 1986. A comparison of chemical and isotopic hydrograph separation. Water Resources Research. 22: 1444-1454.

Hornberger GM, Bencala KE, and McKnight DM. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry. 25: 147-165.

Hruška J, Laudon H, Johnson CE, Köhler S, and Bishop K. 2001. Acid/Base character of organic acids in a boreal stream during snowmelt. Water Resources Research. 37: 1043-1056.

Johnson DW, Susfalk RB, Dahlgren RA, Caldwell TG, and Miller WW. 2001. Nutrient fluxes in a snow-dominated, semi-arid forest: Spatial and temporal patterns. Biogeochemistry. 55: 219-245.

Jones HG and Pomeroy JW. 2001. Early spring snowmelt in a small boreal forest watershed: Influence of concrete frost on the hydrology and chemical composition of streamwaters during rain-on-snow events. 58th Eastern Snow Conference, Ottowa, Ontario, CA, 2001.

Kane DL, and Stein J. 1983. Water movement into seasonally frozen soils. Water Resources Research. 19: 1547-1557.

Kane DL & Stein J. 1984. Plot measurements of snowmelt runoff for varying soil conditions. Geophysica. 20: 123-135.

Laudon H, Hemond HF, Krouse R, and Bishop KH. 2002. Oxygen 18 fractionation during snowmelt: Implications for spring flood hydrograph separation. Water Resources Research 38: 1252-1262.

Likens GE and Bormann FH. 1995. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York.

Liu FL, Williams MW, Caine N. 2004. Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. Water Resources Research. doi: 10.1029/2004WR003076

Lyle S. 2005. Soil nitrogen dynamics after fire in a Boreal forest of interior Alaska. MS Thesis, Univ. of Alaska Fairbanks.

McNamara JP, Kane DL, Hinzman LD. 1997. Hydrograph separations in an Arctic watershed using mixing model and graphical techniques. Water Resources Research 33: 1707-1719.

Pilgrim DH, Huff DD, and Steele TD. 1979. Use of specific conductance and contact time relations for separating flow components in storm runoff. Water Resources Research. 15: 329-339.

Rascher CM, Driscoll CT, and Peters NE. 1987. Concentration and flux of solutes from snow and forest floor during snowmelt in the West-Central Adirondack region of New York. Biogeochemistry. 3: 209-224.

Rodhe A. 1998. Snowmelt-dominated systems. In: C Kendall and JJ McDonnell (Eds) Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam, NL, pp 391-433.

Rovansek RJ, Kane DL, and Hinzman LD. 1993. Improving estimates of snowpack water equivalent using double sampling. In Ferrick M and Pangburn T (Eds) Proceedings of the 50th Eastern Western Snow Conference (Joint Meeting with the 61st Western Snow Conference, Quebec City, Quebec, Canada, June 1993), 157-163.

Schimel JP, and Clein JS. 1996. Microbial response to freeze-thaw cycles in tundra and taiga soils. Soil Biology Biochemistry. 28: 1061-1066.

Semkin RG, Hazlett PW, Beall FD, and Jeffries DS. 2002. Development of stream water chemistry during spring melt in a northern hardwood forest. Water Air Soil Pollution: Focus. 1: 37-61.

Sickman JO, Melack JM, and Stoddard JL. 2002. Regional analysis of inorganic nitrogen yield and retention in high-elevation ecosystems of the Sierra Nevada and Rocky Mountains. Biogeochemistry. 57/58: 341-374.

Sickman JO, Leydecker A, Chang CC, Kendall C, Melack JM, Lucero DM, and Schimel J. 2003. Mechanisms underlying export of N from high-elevation catchments during seasonal transitions. Biogeochemistry. 64: 1-24.

Stottlemeyer R. 1987. Snowpack ion accumulation and loss in a basin draining to Lake Superior. Can. J. Fish. Aquat. Sci. 44:1812-1819.

Taylor S, Feng X, Kirchner JW, Osterhuber R, Klaue B, and Renshaw CE. 2001. Isotopic evolution of a seasonal snowpack and its melt. Water Resources Research. 37: 759-769.

Wels C, Cornett RJ, and LaZerte BD. 1990. Hydrograph separation: A comparison of geochemical and isotopic tracers. Journal of Hydrology. 122: 253-274.

Williams MW, and Melack JM. 1991. Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. Water Resources Research. 27: 1575-1588.

Williams MW, Brooks PD, Mosier A, and Tonnessen K. 1996. Mineral nitrogen transformations in and under seasonal snow in a high-elevation catchment in the Rocky Mountains, United States. Water Resources Research. 32: 3161-3171.

Williams MW, Leydecker A, Brown AD, and Melack JM. 2001. Processes regulating the solute concentrations of snowmelt runoff in two subalpine catchments of the Sierra Nevada, California. Water Resources Research. 37: 1993-2008.

CHAPTER FIVE

CONCLUSIONS

General Findings

This dissertation expands upon our current knowledge of the hydrochemistry of subarctic catchments by incorporating the effects of fire, permafrost, and snowmelt on the chemistry of hydrologic flowpaths and the annual and seasonal budgets of major elements.

The FROSTFIRE prescribed burn had a short-term effect on the chemistry of a receiving stream, demonstrating that low-severity fires may not affect stream chemistry greatly if the riparian zones remain intact. The immediate influence of fire on stream chemistry depends on the source area for flow during storms. Since permafrost hillslopes and riparian zones are the predominant source areas during storms, fire must occur in these areas in order to affect stream chemistry. Much of the FROSTFIRE prescribed burn occurred on hillslopes distant from the contributing areas for stream flow. While the short-term effects of the prescribed burn were addressed in chapter two, one might ask of the fire could affect stream chemistry in subsequent years, since conditions for decomposition may improve after the fire. Long-term measurements may reveal a trend in the chemistry due to the fire, but it was difficult in the present study to differentiate the effects of interannual variation in runoff and chemistry from fire effects. However, during the three years of this study, the fire did not distinctly elevate nitrate or sulfate concentrations, as has been observed in other studies (Bayley and Schindler 1991, Bayley et al. 1992, Chorover et al. 1994, Williams et al. 1997, Williams and Melack 1997). . This result may be due in part to the hydrogeology of the CPCRW basins. After water infiltrates beneath the rooting zone on permafrost-free hillslopes, it takes a long path to the stream through unconsolidated bedrock that does not confine infiltration at depth.

In attempting to detect the influence of the prescribed burn on stream chemistry, I learned a great deal about the importance of water flowpaths on stream chemistry. Storm chemistry in low-permafrost watersheds is influenced mainly by the saturated riparian soils and precipitation while watersheds with greater permafrost coverage are affected by flow from more distant hillslopes underlain by permafrost that reaches the stream following saturation. Active layer dynamics were also important in the high permafrost watershed, resulting in a lag response of flow from the organic soils during late summer as soils must become saturated before generating hillslope runoff. Overall, organic soils can serve as a source for not only DOC and DON, but also DIN, mainly nitrate during the summer storms.

On a seasonal and annual scale, the greatest effect of permafrost was increasing DOC output and reducing weathering ions such as Ca^{2+}, Mg^{2+}, and Na^{+}. These findings support earlier studies (Ray 1988, MacLean et al. 1999), but expand on this model by demonstrating the importance of seasonal transitions and active layer dynamics in governing C, N and major solute export. Groundwater springs influence the winter chemistry of CPCRW streams in permafrost-dominated watersheds where there is a clear shift in the chemistry and flow from winter through snowmelt and into summer. Snowmelt influences annual hydrologic and element fluxes to a greater degree in permafrost-dominated basins than in lower permafrost basins. As demonstrated in chapter two, active layer depth remains important for the late summer release of NO_3^- and DOC from surface soils. Consequently, future changes in active layer depth in a warmer climate could increase N and C loss in permafrost-dominated areas.

Early in the development of my thesis questions, I was intrigued by the nitrogen composition of subarctic streams at CPCRW. I consistently found that streams had high levels of nitrate compared to catchments in temperate and boreal regions. This led to the question: Why does an N limited ecosystem leak NO_3^- that is readily available for biotic uptake? Dominance of NO_3^- over DON in stream chemistry in the Northeast US and Rocky Mountains has been attributed to increased atmospheric deposition of N from anthropogenic sources (Williams et al. 2001), whereas in pristine ecosystems DON is the dominant form of nitrogen in streams (Hedin 1995). More recently, researchers have begun to apply this model of DON vs. DIN dominance in nitrogen chemistry as an indicator of anthropogenic impact on catchments throughout North America (Williams et al. 2004; AGU fall meeting). While this model may work in some ecosystems across similar climate regimes, it may not be applicable to catchments of interior Alaska.

At first glance, it does appear to be paradoxical that an N-limited boreal ecosystem can be a net source of nitrogen. However, in the context of the interaction between hydrologic and biologic systems, N leaching and N limitation can occur simultaneously if N supplied from decomposition is unavailable to biota, either spatially or temporally. In the currently and previously unglaciated region of interior Alaska, decomposition of deep nitrogen stores in permafrost or buried organic layers could supply nitrogen that is too deep for plant uptake. On the other hand, the short growing season in this region may allow soil mineralization and nitrification to occur when plants are dormant, thereby temporally separating nitrogen supply by decomposition and uptake by plants.

Climate Change

Despite low rates of atmospheric deposition in interior Alaska, anthropogenic sources of ammonium and nitrate are evident as an enrichment relative to seawater solute ratios and contrasting seasonal patterns relative to other solutes (Hinzman et al. in press). In the future, atmospheric deposition of nitrogen is likely to increase as human activity adds approximately twice the amount of naturally occurring nitrogen to the global nitrogen cycle each year (Vitousek et al. 1997). What will be the response in boreal ecosystems of interior Alaska to this added nitrogen? This answer to this question may in turn shed light on the watershed nitrogen dynamics discussed in this dissertation. Soils in temperate regions can be sinks for added nitrogen (Nadelhoffer 1999), but will soils in boreal systems also retain additional nitrogen? If nitrogen flux rates from CPCRW catchments remain unchanged as deposition rates increase (and additional nitrogen is retained in soils and plants), then the nitrogen that we are currently observing as a loss may be a relict of older stores of nitrogen in deep soils that do not reflect current plant-microbe interactions in surface soils.

Climate change is expected to be most pronounced at high latitudes where a 3.5 to 7^{O}C increase in average annual air temperature is estimated by the end of this century (IPCC 2001). Such a rise in temperature will likely change the current hydrochemistry of boreal watersheds in the region of discontinuous permafrost. The outcome at the watershed scale is difficult to predict because it is the sum of many climate and biotic factors with concurrent positive and negative feedbacks. Fire will likely play a strong role in the region as a whole through direct effects on stream chemistry during severe fires and indirectly by changing soil conditions for decomposition. Additionally, climate change models predict higher summer temperatures at high-latitudes (IPCC 2001). The most immediate effect of higher summer temperatures will be to increase the seasonally frozen active layer. In this study, the active layer proved to be an important source of organic (DOC) and inorganic (NO_3^-) solutes during late summer storms. Further thawing of the active layer in the summer will involve greater interaction of infiltrating water with mineral soils which may be a source of nitrate to CPCRW streams. Conversely, greater infiltration through mineral soils in permafrost-dominated slopes may attenuate the DOC flux to streams as greater adsorption is likely in mineral soils.

The impact of future changes in winter conditions are also difficult to predict, but in this study we found that snowmelt runoff and solute fluxes were sensitive to soil conditions that affect infiltration. Currently, the active layer completely freezes back and soils remain frozen throughout the winter. Warmer conditions that induce freeze-thaw cycles or incomplete re-freezing of the active layer may dramatically affect water and solute fluxes during snowmelt. Freeze-thaw cycles are more likely to create ice layers in soils, thereby reducing infiltration and increasing runoff and solute fluxes. On the other hand, incomplete freezing and talik formation could facilitate infiltration during the winter and snowmelt periods.

References

Hinzman LD, Bolton BW, Jones JB & Petrone KC. Hydrological Processes in Alaska's Boreal Forest. In M.W. Oswood and F.S. Chapin [Eds]. BNZ LTER synthesis chapter: Alaska's Changing Boreal Forest, in press.

IPCC 2001. Climate Change 2001: Synthesis Report. A Contribution of Working Groups I, II, and III to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Watson RT and the Core Writing Team (Eds.). Cambridge University Press, Cambridge, United Kingdom, and New York, NY, USA, 398 pp.

Nadelhoffer KL, and Downs MR. 1999. Sinks for 15N-enriched additions to an oak forest and a red pine plantation. Ecological Applications 9: 72-86.

Vitousek PM., Aber JD, Howarth RW, Likens GE, Matson PA, Schindler DW, Schlesinger WH and Tilman DG. 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications. 7: 737-750.