DISSOLVED ORGANIC MATTER BIOAVAILABILITY AND COMPOSITION IN STREAMS DRAINING CATCHMENTS WITH DISCONTINUOUS PERMAFROST

By

Kelly L. Balcarczyk

Recommended: ______________________________

____

____

____
Advisory Committee Chair

____
Chair, Department of Biology and Wildlife

APPROVED: ______________________________
Dean, College of Natural Science and Mathematics

____
Dean of the Graduate School

____
Date

DISSOLVED ORGANIC MATTER BIOAVAILABILITY AND COMPOSITION IN STREAMS DRAINING CATCHMENTS WITH DISCONTINUOUS PERMAFROST

A

THESIS

Presented to the faculty
of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

By

Kelly L. Balcarczyk, B.S.

Fairbanks, Alaska

May 2008

ABSTRACT

We examined the influence of permafrost on dissolved organic matter (DOM) in Caribou Poker Creeks Research Watershed (CPCRW). We analyzed long-term data from watersheds underlain with varying degrees of permafrost, sampled springs and thermokarsts to capture the range of DOM concentration and quality, used fluorescence spectroscopy to examine DOM composition, and measured DOM bioavailabity. Permafrost hydrology influenced DOM patterns, with the stream draining the high permafrost watershed having the highest dissolved organic carbon and nitrogen (DOC and DON) concentrations, higher DOC:DON, and greater specific ultraviolet absorbance (SUVA). Streams, springs, and thermokarsts exhibited a wide range of DOC and DON concentrations (1.5 – 37.5 mgC/L and 0.14 – 1.26 mgN/L), DOC:DON (7.08 – 42.8), and SUVA (1.5 – 4.7 L mgC^{-1} m^{-1}). All sites had fluorescence index values (1.3 – 1.4) consistent with DOM derived from terrestrial sources. Principal components analysis revealed distinct groups in our fluorescence data determined by diagenetic processing and DOM source. Bioavailability of DOM ranged from 2 – 35% and was correlated with the proportion of tyrosine and tryptophan. Our results indicate that the degradation of permafrost in CPCRW will result in a decrease in DOC and DON concentrations, a decline in DOC:DON, and a reduction in SUVA, accompanied by a change in bioavailability.

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

PREFACE

This thesis is in manuscript format. Chapter One is in an introduction to permafrost, hydrology and dissolved organic carbon chemistry. Chapter Two is formatted for submission to the peer-reviewed journal *Ecology*.

I would like to gratefully acknowledge my advisor, Jay Jones, for his guidance throughout this study and the writing of this manuscript. Thanks to the members of my committee, Rich Boone and Dan White, for their valuable comments on the research and manuscript. Thank you to Rudolf Jaffé and Nagamitsu Maie for fluorescence analysis and help with the interpretation of the PARAFAC data. Many thanks to Emma Betts, Hannah Clilverd, Amanda Rinehart, Emily Schwing and Julia Taylor for their help in the field and laboratory. Finally, a special thanks to Aaron Hall for his endless support and encouragement.

This research was supported Bonanza Creek Long-Term Ecological Research program (funded jointly by NSF grant DEB-0423442 and USDA Forest Service, Pacific Northwest Research Station grant PNW01-JV11261952-231). The EEM-PARAFAC work was supported through a NSF funded inter-LTER collaboration between the Bonanza Creek and Florida Coastal Everglades Long-Term Ecological Research sites.

CHAPTER 1: INTRODUCTION

Permafrost and Hydrology

Permafrost is defined as ground that is below 0°C for at least two consecutive years (Davis 2001). Permafrost is present beneath the surface of approximately one-fifth of the earth's land area and is extensive in high latitudes and mountainous regions (Davis 2001). Within Alaska, continuous permafrost spans the northern portion of the state with the zone of discontinuous permafrost extending over much of the interior, including the boreal forest (Fig. 1; Davis 2001).

In interior Alaska, permafrost is warming and thawing with extensive thermokarsts developing (Osterkamp and Romanovsky 1999). Thermokarsts are topographic depressions due to the thawing of permafrost and may act as a source of dissolved organic matter to streams. In interior Alaska, the surface temperature of discontinuous permafrost is estimated to have warmed 0.5 – 1.5 °C, with an estimated warming rate of 0.05 – 0.2 °C/yr (Hinzman et al. 2005). Permafrost thawing and thermokarst formation have been observed in several locations in interior Alaska. In Caribou Poker Creeks Research Watershed (CPCRW; Fig. 2), near Fairbanks, Alaska, over a third of the permafrost is just below 0°C and at least 2% of the permafrost was lost during the 20th century (Hinzman et al. 2005).

The primary control of hydrology in northern regions is the presence or absence of permafrost (Woo 1986). Permafrost acts as an aquatard, preventing water from infiltrating deep soil horizons. This inhibition of percolation results in decreased ground water recharge and increased surface runoff compared with permafrost-free areas (Bolton et al. 2004). In areas lacking permafrost, water can infiltrate into deeper soil horizons and the infiltration capacity of the soils must be exceeded before runoff generation can occur (Bolton et al. 2004).

In CPCRW, differences in stream flow among sub-catchments are dramatic and dependent upon the extent of underlying permafrost. Comparing among streams, as the extent of permafrost underlying the sub-basin increases, peak specific discharge increases, specific baseflow declines and response time to precipitation increases (Bolton et al. 2004). These differences in sub-basin hydrology in CPCRW result in variation in stream chemistry (Fig. 3). Stream chemistry in a permafrost dominated watershed is tightly coupled to the chemistry of the organic horizons, having high dissolved organic carbon (DOC) and nitrogen (DON) concentrations. In contrast, the chemistry of streams draining watersheds lacking permafrost is controlled by contact between water and the mineral soils; these streams have lower DOC and DON concentrations due to adsorption and higher concentrations of cations due to weathering (MacLean et al. 1999).

Stream DOC patterns

DOC constitutes the largest pool of organic carbon in most streams. DOC serves as a microbial energy source (Findlay et al. 1993, Raymound and Bauer 2000), influences the availability of nutrients (Qualls et al. 1991), affects the transport and degradation of pollutants (Morris and Hargreaves 1997), and alters stream pH (McKnight et al. 1985). DOC transport in streams is also an important pathway for carbon loss from terrestrial ecosystems.

The transport of DOC in streams and rivers from terrestrial to marine and estuarine ecosystems is an important link in global biogeochemical cycles. Stream DOC fluxes from watersheds ranges from 1 to 140 kgC $ha^{-1}y^{-1}$ (Aitkenhead and McDowell 2000), and mean annual DOC concentrations range from 0.1 – 36.6 mgC/L (Mulholland 1997). Watersheds in tropical wetlands tend to have the highest DOC export rates, with streams in temperate and boreal regions having intermediate export rates, and tundra or savannah ecosystems having the lowest (Meybeck 1993). DOC export from the low (C2), medium (C4), and high (C3) permafrost watersheds in CPCRW ranges from 4.34 to 8.34 kgC ha^{-1} y^{-1}, and is not consistent with overall global patterns of DOC flux (Petrone et al. 2006). The low DOC export values in CPCRW may be a result of recalcitrant pools of carbon in watersheds due to low runoff and cold soil temperatures (Petrone et al. 2006).

Over the last 15 years, much research has focused on the factors controlling DOC concentration and flux in streams. Studies in small watersheds have shown that DOC production rate in organic soils, rates of DOC sorption in mineral soils, and the flow path of water through soil horizons to the stream influence stream water DOC concentration and flux (Aitkenhead and McDowell 2000). On a larger scale, the concentration and export of DOC has been shown to be related to watershed characteristics, indicating that the major source of stream DOC is terrestrial ecosystems (Mulholland 1997). Watershed characteristics influencing DOC concentration and flux include channel slope, discharge, rainfall, vegetation, and permafrost and wetland composition of the drainage (Rasmussen et al. 1989, Esser and Kohlmaier 1991, Clair et al. 1994, Mulholland 1997, MacLean et al. 1999). Thus far, the predominant watershed characteristics used to predict annual DOC flux have been the carbon content of the watershed (Hope et al. 1997) and soil carbon:nitrogen ratio (Aitkenhead and McDowell 2000).

In CPCRW, flow through organic soil in an important source of DOC to streams. DOC concentration in the stream draining the watershed with the greatest extent of permafrost (C3) is approximately two-fold greater than in the streams draining the low and medium permafrost watersheds (C2 and C4; Petrone et al. 2006). In all CPCRW streams, DOC concentration is highest during snowmelt and storms when flow through the organic layer and saturated riparian zone is greatest. In the streams draining the high and low permafrost watersheds (C3 and C2) the annual peak in DOC concentration coincides with snowmelt, whereas in the stream draining the medium permafrost watershed (C4) DOC concentration peak precedes the snowmelt discharge peak (Petrone et al. 2006). Peaks in DOC concentration throughout the summer coincide with storms in all three streams and are affected by changes in depth of thaw (Petrone et al. 2007). As depth of thaw deepens from July through September, the contribution to stream flow from ground water increases, and flow from the organic soils declines. As thaw depth reaches mineral soils, water infiltration to deeper horizons and DOC sorption increase (Petrone et al. 2007).

Studies by Petrone et al. (2006 and 2007) supported and expanded upon the conceptual model proposed by MacLean et al. (1999), whereby permafrost restricts flow to the organic layer, resulting in increased DOM delivery to streams. Petrone et al. (2006 and 2007) demonstrated that flowpath and the mechanism for water movement to the stream influence stream chemistry during storms and snowmelt. In addition, the hydrologic and chemical response seen in streams is attenuated by an increase in active layer thickness and water storage throughout the summer (Petrone et al. 2006 and 2007). The conceptual model can be further expanded upon by characterizing long-term DOM patterns across years and the determining the influence of hydrologic flowpath on DOM composition and bioavailability in CPCRW.

DOM fluorescence and Excitation Emission Spectroscopy

Over the past 50 years, fluorescence has been used to investigate dissolved organic matter (DOM) composition, concentration and distribution in a range of aquatic habitats. Organic matter fluorescence occurs when a molecule absorbs light (energy) and a loosely bound electron is excited and promoted to an unoccupied orbital, which, in turn, relaxes to a ground state resulting in an emission of energy and fluorescence (Fig. 4; Lakowicz 1983, Stedmon et al. 2003). The energy difference between the ground state and the excited states determines the wavelength at which light is absorbed and emitted. Wavelength absorption and emission are specific to molecules (Lakowicz, 1983).

Aromatic compounds in DOM tend to be fluorescent because of the energy sharing, unpaired electron structure of the carbon ring (Hudson et al. 2007). The optically active portion of DOM is called colored dissolved organic matter (CDOM), which fluoresces when excited by light in the ultraviolet and blue region of the spectrum (Stedmon et al. 2003). The most widely studied fluorescent compounds in DOM include humic substances (a blue fluorescence) and amino acids in proteins or peptides (UV fluorescence; Coble et al. 1998, Cory and McKnight 2005).

Recently, the use of excitation emission matrix fluorescence spectroscopy (EEMS) has become common in studies of DOM composition in aquatic ecosystems. The principle of EEMS is that excitation, emission and fluorescence intensity can be scanned over a range of wavelengths synchronously and plotted on a single chart. This chart is a three dimensional "map" of optical space, or an excitation-emission matrix (EEM; Hudson et al. 2007). Excitation-emission matrices provide information on the number and type of fluorophores present, and their relative position in optical space (Stedmon et al. 2003). Relative concentrations of fluorophores can be determined based upon calibration of fluorescence intensity against standards. A fluorescence index (FI), based on the concentration of fluorophores, can be used to distinguish whether DOM is derived from aquatic microbial material or terrestrial material (McKnight et al. 2001). In addition, statistical analysis such as parallel factor analysis (PARAFAC) can be applied to the excitation-emission matrices to identify and quantify the relative concentration of DOM components based on their unique excitation and emission patterns (Stedmon et al. 2003, Cory and McKnight 2005).

EEMS is a rapid (~1 minute per sample), non-destructive method that requires little or no sample preparation. The EEMS approach provides a vast amount of data available for interpretation within an excitation-emission matrix. However, EEMS has the potential to be constrained by lack of understanding of the effects of inner filtering (the absorption and re-emission of emitted energy at a longer wavelength by surrounding molecules), scatter by particulates and larger colloids, and the scattering properties of water (Raman line and Rayleigh-Tyndall features; Hudson et al. 2007).

DOM bioavailability

DOM is a heterogeneous mixture of molecules that range from labile to recalcitrant. As DOM moves through a watershed, a number of biogeochemical factors influence DOM uptake by bacteria including availability of electron acceptors, inorganic nutrients, temperature, pH and meiofaunal grazing (Sobczak and Findlay 2002). Diagenetic alterations, such as oxidation, reduction, hydration or dehydration also influence the availability of DOM by changing the elemental composition (Sun et al. 1997, Volk et al. 1997, Cleveland et al. 2004, Hood et al. 2005).

Concentrations of bioavailable DOM can be estimated from changes in DOC concentrations following the exposure of water samples to microorganisms (Kaplan and Newbold 1995). One approach is to use in-lab mesocosms, with the difference between initial DOC concentration and DOC concentration after incubation being an estimate of bioavailable DOC. In-lab mesocosms require an extended period of colonization and incubation, but can be used to measure bioavailable DOM concentrations quite accurately.

Although in-lab mesocosms are an accurate way to measure labile DOC, there are a few drawbacks to this method. First, the bioassay for labile organic carbon assumes carbon limitation and in some cases may require nutrient amendment or aeration (Kaplan and Newbold 1995). In addition, mesocosm measurements are net measurements because they include both DOC uptake and excretion by microorganisms, which may result in an underestimation of DOM bioavailability. In contrast, abiotic absorption of DOC in the mesocosms may result in an overestimation of DOM bioavailability. In spite of these potential caveats, approximately 90% of the DOC removed in a mesocosm is attributable to biological activity and microorganisms equilibrate within hours of exposure to new DOC (Kaplan and Newbold 1995).

Previous research on dissolved organic matter in CPCRW has focused on the influence of permafrost on the concentration and flux of DOM in streams throughout the summer or in response to storms, fire, and snowmelt (MacLean et al. 1999, Petrone et al. 2006 and 2007). Our research expands on previous studies by analyzing differences in DOM concentration and quality among streams and across years, and by examining the influence of hydrologic flowpath on DOM composition and bioavailabity. Long-term stream chemistry and hydrologic data from streams draining the low, medium and high permafrost watersheds were analyzed to calculate differences in DOM concentration and composition, and DOC response to change in discharge. Fluorescence spectroscopy was used in combination with long-term indicators of DOM quality to determine the composition of DOM in streams, springs and thermokarsts. To establish if differences in DOM composition, temperature, or nutrient availability influence the bioavailability of DOC in streams, springs, and thermokarsts we used a laboratory mesocosm experiment.

Literature cited

Aitkenhead, J.A. and W.H McDowell. 2000. Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. Global Biogeochemical Cycles **14**: 127-138.

Bolton, W. R., L. Hinzman, and K. Yoshikawa. 2004. Water balance dynamics of three small catchments in a Sub-Arctic boreal forest. Northern Research Basins Water Balance (Proceedings of a workshop held at Victoria Canada 2004) IAHS Published 290.

Clair, T.A., T.L Pollock, and J.M. Ehrman. 1994. Exports of carbon and nitrogen from river basins in Canada's Atlantic Provinces. Global Biogeochemical Cycles **8**: 441-450.

Cleveland, C., J. Neff, A. Townsend, and E. Hood. 2004. Composition, dynamics, and fate of leached dissolved organic matter in terrestrial ecosystems: results from a decomposition experiment. Ecosystems **7**: 275-285.

Coble, P. G., C.E. Del Castillo, and A. Bernard. 1998. Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon. Deep-Sea Research II **45**: 2195-2223.

Cory, R. M. and D.M McKnight. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environmental Science and Technology **39**: 8142-8149.

Davis, N. 2001. Permafrost: a Guide to Frozen Ground in Transition. University of Alaska Press, Fairbanks, Alaska, USA.

Esser, G. and G. H. Kohlmaier. 1991. Modelling terrestrial sources of nitrogen, phosphorus, sulphur and organic carbon in rivers. Degens, E.T., Kempe, S., and Richey, J.E. (editors), Biogeochemistry of Major World Rivers, SCOPE 42. John Wiley, Chichester: 297-322.

Findlay, S., D. Strayer, C. Goumbala, and K. Gould. 1993. Metabolism of streamwater dissolved organic carbon in the shallow hyporheic zone. Limnology and Oceanography **38**: 1493-1499.

Hinzman, L. D., N.D. Bettez, W.R. Bolton, F.S. Chapin, M.B. Dyurgerov, C.L. Fastie, B. Griffith, R.D. Hollister, A. Hope, H.P Huntington, A.M. Jensen, G.J. Jia, T. Jorgenson, D.L. Kane, D.R. Klein, G. Kofinas, A.H. Lynch, A.H. Lloyd, D. McGuire, F.E. Nelson, M. Nolan, W.C. Oechel, T.E. Osterkamp, C.H. Racine, V.E. Romanovsky, R.S. Stone, D.A. Stow, M. Sturm, C.E. Tweedie, G.L. Vourlitis, M.D. Walker, D.A. Walker, P.J. Webber, J. Welker, K.S. Winker, and K. Yoshikawa. 2005. Evidence and implications of recent climate change in Northern Alaska and other arctic regions. Climatic Change **72**: 251-298.

Hood, E., M.W. Williams, and D.M. Mcknight. 2005. Sources of sissolved organic matter in a Rocky Mountain stream using chemical fractionation and stable isotopes. Biogeochemistry **74**: 231-255.

Hope, D., M.F. Billett, R. Milne, and T. Brown. 1997. Exports of organic carbon in British rivers. Hydrological Processes **11**: 325-344.

Hudson, N., A. Baker, and D. Reynolds. 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters – a review. River Research and Applications DOI: 10.1002/rra.1005.

Kaplan, L.A. and J.D. Newbold. 1995. Measurement of streamwater biodegradable dissolved organic carbon with a plug-flow bioreactor. Water Resources **29**: 2696-2706.

Lakowicz, J.R. 1983. Principles of Fluorescence Spectroscopy. Plenum Press, New York, NY, USA.

MacLean, R., M.W. Oswood, J.G Irons III, and W.H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: A case study of two streams in the Alaskan taiga. Biogeochemistry **47**: 239-267.

McKnight, D.M., E.M. Thurman, R.L. Wershaw, and H. Hemond. 1985. Biogeochemistry of aquatic humic substances in Thoreau's Bog, Concord, Massachusetts. Ecology **66**: 1339-1352.

McKnight, D.M., E.W. Boyer, P.K. Westerhoff, P.T. Doran, T. Kulbe, and D.T. Anderson. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromacticity. Limnology and Oceanography **46**: 38-48.

Meybeck, M. 1993. Riverine transport of atmospheric carbon: sources, global typology and budget. Water Air and Soil Pollution **70**: 443-464.

Morris, D.P. and B.R. Hargreaves. 1997. The role of photochemical degradation of dissolved organic carbon in regulating the UV transparency of 3 lakes on Pocono Plateau. Limnology and Oceanography **42**: 239-249.

Mulholland, P.J. 1997. Dissolved organic matter concentration and flux in streams. J.R. Webster and J.L. Meyer (editors). Stream organic matter budgets. Journal of the North American Benthological Society. **16**: 122-131.

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

Petrone, K.C., J.B. Jones, L.D. Hinzman, and R.D. Boone. 2006. Seasonal export of carbon , nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost. Journal of Geophysical Research **111**: G02020.

Petrone, K.C., L. D. Hinzman, H. Shibata, J.B. Jones, and R.D. Boone. 2007. The influence of fire and permafrost on sub-arctic stream chemistry during storms. Hydrological Processes **21**: 423-434.

Péwé, T.L., R.D. Reger. 1983. Richarson and Glenn Highways, Alaska, guidebook to permafrost and quaternary geology. Fairbanks, Alaska: Alaska Department of Natural Resources, Division of Geological and Geophysical Surveys: 263.

Qualls, R.G., B.L. Haines, and W.T. Swank. 1991 Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecology **72**: 254-266.

Rasmussen, J.B., L. Godbout, and M. Schallenberg. 1989. The humic content of lake water and its relationship to watershed and lake morphometry. Limnology and Oceanography **34**: 1336-1343.

Raymound, P.A. and J.E. Bauer. 2000. Bacterial consumption of DOC during transport through a temperate estuary. Aquatic Microbial Ecology **22**: 1-12.

Stedmon, C.A., S. Markager, and B. Rasmus. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Marine Chemistry **82**: 239-254.

Sobczak, W.V. and S. Findlay. 2002. Variation in bioavailabilty of dissolved organic carbon among stream hyporheic flowpaths. Ecology **83**: 3194-3209.

Sun, L., M. Perdue, J.L. Meyer, and J. Weis. 1997. Use of elemental composition to predict bioavailability of dissolved organic matter in a Georgia river. Limnology and Oceanography **42**: 714-721.

Volk, C.J., C.B. Volk, and L.A. Kaplan. 1997. Chemical composition of biodegradable organic matter in streamwater. Limnology and Oceanography **42**: 39-44.

Woo, M-K. 1986. Permafrost hydrology in North America. Atmosphere-Ocean **24**: 201-234.

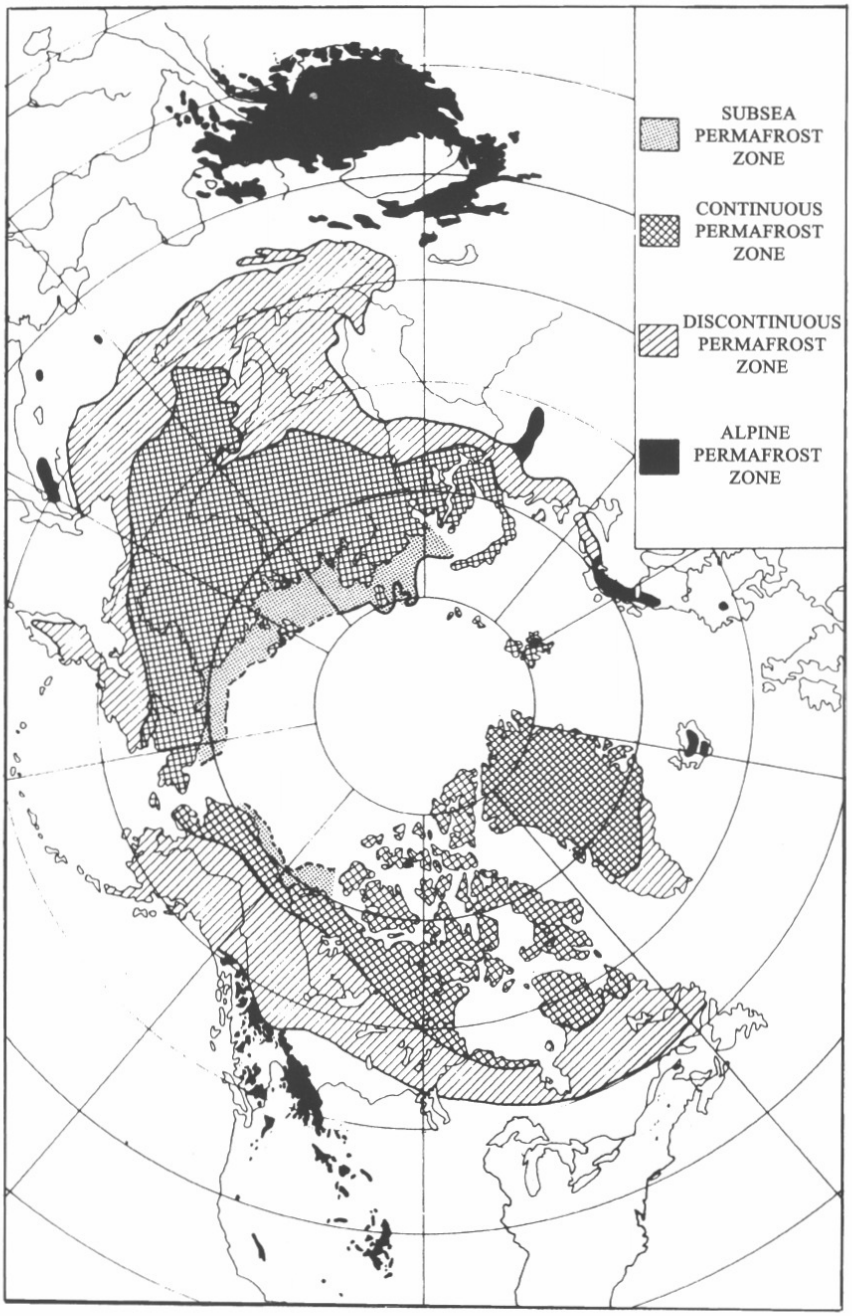

Figure 1. Map of permafrost in the northern hemisphere (Davis 2001; modified from Péwé 1975). The boreal forest of interior Alaska is underlain with discontinuous permafrost.

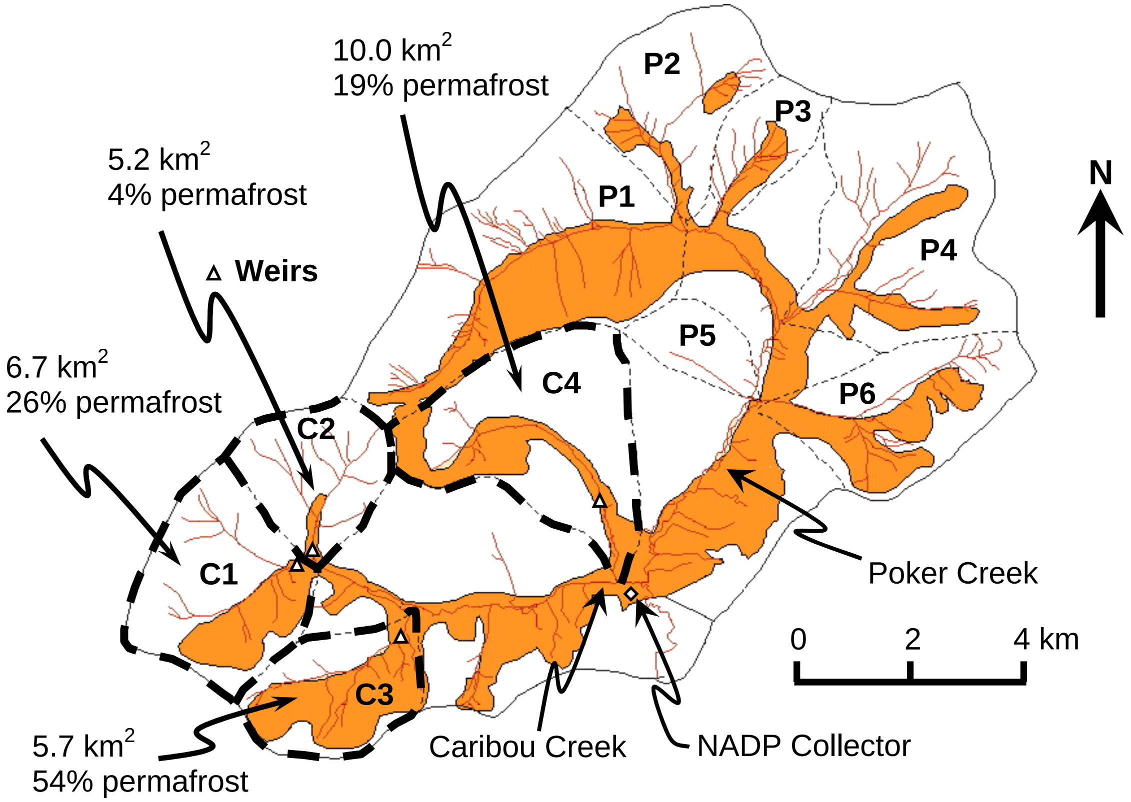

Figure 2. Map of Caribou Poker Creeks Research Watershed. C is used to denote a sub-basin in the Caribou creek catchment and P is used to denote a sub-basin in the Poker creek catchment. Shaded areas indicate the presence of permafrost.

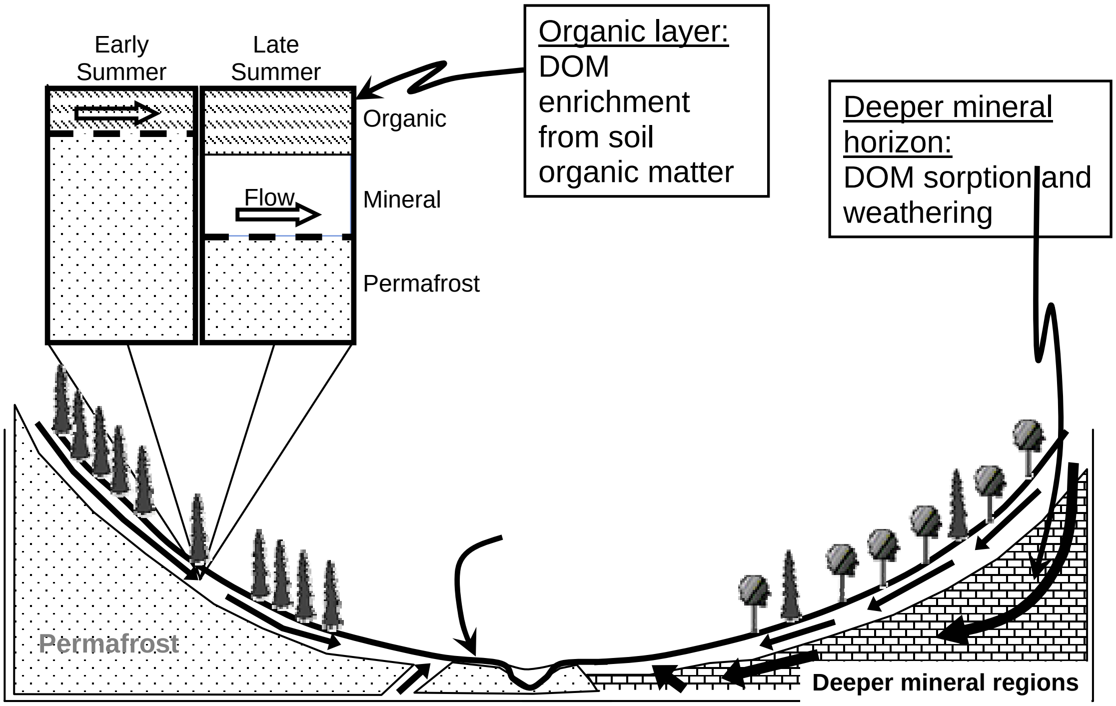

Figure 3. Conceptual model of permafrost, hydrology and biogeochemistry in Caribou Poker Creeks Research Watershed modified from MacLean et al. (1999). Permafrost in watersheds promotes the movement of runoff rich in DOC to the stream. DOC transfer is reduced in streams draining permafrost-free watersheds due to DOC sorption in mineral soils.

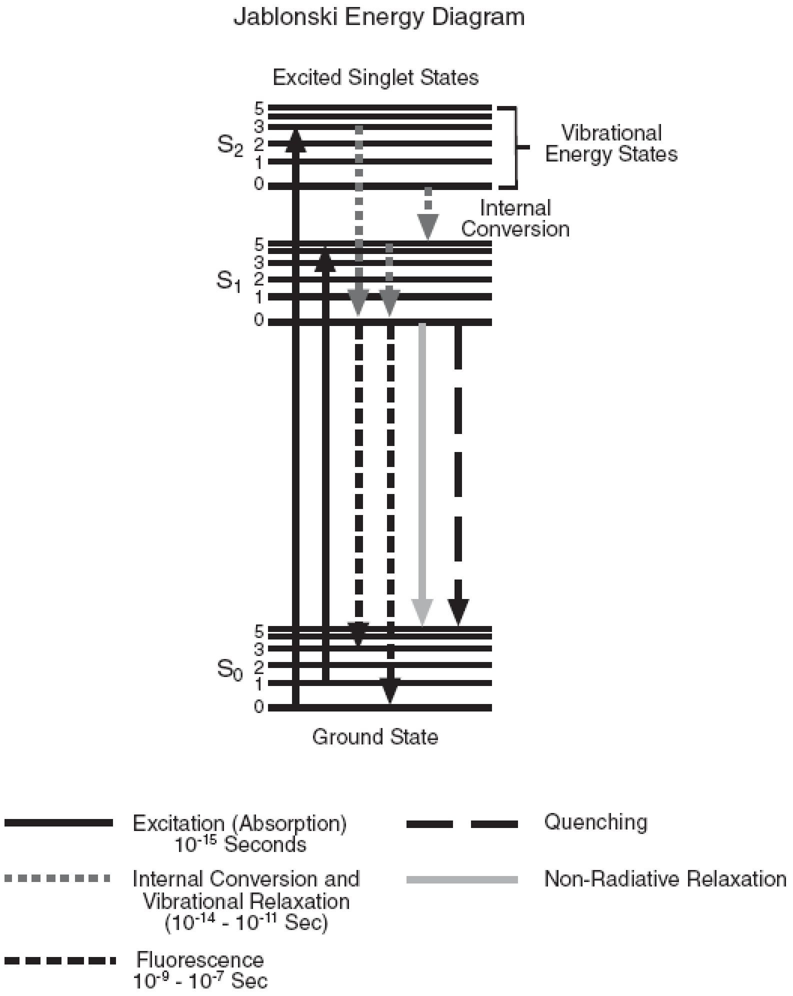

Figure 4. The Jablonski diagram from Hudson et al. (2007). The energy-level diagram suggested by A. Jablonski illustrates the absorption and emission of light. The ground, first and second electronic states are depicted by S_0, S_1 and S_2, respectively. Each of these electronic energy levels can exist in a number of vibrational energy levels (0, 1, 2, etc.). Following light absorption, a fluorophore is usually excited to a higher vibrational level of either S_1 or S_2. Relaxation to the ground state occurs through energy dissipation in non-radiative decay or via quenching.

CHAPTER 2: DISSOLVED ORGANIC MATTER BIOAVAILABILITY AND COMPOSITION IN STREAMS DRAINING CATCHMENTS WITH DISCONTINUOUS PERMAFROST[1]

Abstract

We examined the impact of permafrost on dissolved organic matter (DOM) concentration and quality in Caribou Poker Creeks Research Watershed (CPCRW), a watershed underlain with discontinuous permafrost, in interior Alaska. We analyzed long term data from watersheds underlain with varying degrees of permafrost, sampled springs and thermokarsts to capture the range of DOM concentration and quality throughout the watershed, used fluorescence spectroscopy to examine DOM composition, and measured the bioavailabity of dissolved organic carbon (DOC) using in-lab mesocosms. Permafrost driven patterns in hydrology and vegetation played a significant role in determining DOM patterns in streams and across years, with the stream draining the high permafrost watershed having higher DOC and dissolved organic nitrogen (DON) concentrations, higher DOC:DON and greater specific ultraviolet absorbance (SUVA) than the streams draining the low and medium permafrost watersheds. Streams, springs and thermokarsts exhibited a wide range of DOC and DON concentrations (1.5 – 37.5 mgC/L and 0.14 – 1.26 mgN/L, respectively), DOC:DON (7.1 – 42.8) and SUVA (1.5 – 4.7 L mgC^{-1} m^{-1}). All sites had a high proportion of humic components, a low proportion of protein components, and a low fluorescence index value (1.3 – 1.4), consistent with terrestrially derived DOM. Principal component analysis

---

[1] Balcarczyk, K.L., J.B. Jones Jr., R. Jaffé, and N. Maie. Dissolved organic matter bioavailability and composition in streams draining catchments with discontinuous permafrost. Prepared for submittal to the journal Ecology.

revealed three distinct groups in our fluorescence data, which were likely determined by the extent of diagenetic processing and DOM source. The bioavailability of DOC in stream, spring and thermokarst samples ranged from 2 – 35% after forty days of incubation. DOC loss was highly correlated with the proportion of tyrosine- and tryptophan-like fluorophores in the fluorescing DOM ($p < 0.05$, $R^2 = 0.99$). Our results indicate that the degradation of permafrost in CPCRW will result in a decrease in DOC and DON concentrations, a decline in DOC:DON of DOM, and a reduction in SUVA, possibly accompanied by an increase in DOC bioavailability if the contribution of water from deeper flowpaths to streams increases. If thermokarsts become more prevalent as permafrost degrades, the contribution of highly recalcitrant thermokarst DOM to streams will likely increase.

Key words: dissolved organic matter, bioavailability, boreal forest, discontinuous permafrost, dissolved organic carbon, fluorescence, ground water, thermokarst

Introduction

Dissolved organic carbon (DOC) constitutes the largest pool of organic carbon in most streams. DOC serves as a microbial energy source (Findlay et al. 1993, Baker et al. 2000, Raymound and Bauer 2000), influences the availability of nutrients (Qualls et al. 1991), affects the transport and degradation of pollutants (Morris and Hargreaves 1997) and alters stream pH (McKnight et al. 1985). DOC transport in streams is also an important pathway for carbon loss from terrestrial ecosystems. In headwater streams of the boreal forest, DOC originates primarily from allochtonous (terrestrial) sources (Boyer et al. 1996). Allochthonous DOC is transported to streams from a number of sources including ground water, soil water, riparian zones and overland flow (Hood et al. 2005). Stream DOC derived from these different sources can have unique chemical characteristics, which influence its use by microbes (Michaelson et al. 1998, Kalbitz et al. 2000, Kawahigashi et al. 2004).

Much of the northern boreal forest is underlain with discontinuous permafrost, which has a large effect on catchment hydrology and the resulting delivery of dissolved organic matter (DOM) to streams (MacLean et al. 1999). In areas underlain with permafrost, flow is largely restricted to organic horizons and leaches DOM from soil. In areas lacking permafrost, flow can infiltrate into deeper organic layers and mineral soil where DOM can be adsorbed (MacLean et al. 1999, Carey 2003). Increased contact time with mineral soil in watersheds lacking permafrost decreases the concentration and alters the composition of DOM that reaches a stream (Kawahigashi et al. 2004). Thus, streams draining catchments underlain with permafrost typically have a higher concentration of

DOM and DOM that is chemically different from DOM in streams draining catchments lacking permafrost (MacLean et al. 1999, Kalbitz et al. 2000, Carey 2003).

Discontinuous permafrost in the boreal forest of Alaska is thawing in response to climatic warming, which, in turn, is influencing the movement of dissolved material from upland soils to streams by altering watershed hydrology and vegetation (Striegl et al. 2005). In the Caribou Poker Creeks Research Watershed (CPCRW) in interior Alaska over a third of the permafrost is just below 0°C, and at least 2% of the permafrost was lost during the 20th century (Hinzman et al. 2005). As ice-rich permafrost thaws, topographic depressions (thermokarsts) can form and may act as a source of DOC to streams.

In our study, we addressed the following questions in catchments underlain with varying degrees of permafrost: 1) how does permafrost and the associated hydrology affect the DOM concentration and quality in streams, and 2) what controls the decomposition of DOC in the streams, springs and thermokarsts? We hypothesized that differences in watershed hydrology influence the chemical composition and bioavailability of DOM in streams, and that the influence of substrate quality on decomposition is large relative to the effects of temperature or nutrients. In order to address these questions, we used three approaches. First, longer-term stream chemistry and hydrologic data from streams draining a low, medium and high permafrost watershed were analyzed for variation in DOM concentration and composition, and DOC response to discharge. Second, fluorescence spectroscopy was used in combination with longer-term indicators of DOM quality to determine the composition of DOM in streams, springs and thermokarsts. Finally, we used a laboratory mesocosm experiment to establish if differences in DOM composition influence the bioavailability of DOC in streams, springs and thermokarsts.

Methods

Study Site

Our study was conducted in the Caribou Poker Creeks Research Watershed (CPCRW), which is located approximately 50 km NE of Fairbanks, Alaska (65.15°N, 147.5°W) and is approximately 104 km^2 in size. The climate of CPCRW is continental, with warm summers (mean = 16.4°C in July), cold winters (mean = −29°C in January), and low precipitation (411 mm, of which 31% falls as snow). The watershed is located in a region of discontinuous permafrost, with the extent of permafrost underlying sub-catchments ranging from 4 to 53%. The distribution of permafrost in interior Alaska is largely a function of aspect and winter temperature, with north-facing slopes and valley bottoms generally underlain by permafrost (Viereck et al. 1983).

Vegetation types in the watershed are typical of interior Alaska. South facing slopes are dominated by hardwood forests of paper birch (*Betula paprifera*) and quacking aspen (*Populous tremuloides*), whereas north facing slopes are dominated by black spruce (*Picea mariana*), white spruce (*Picea glauca*) and feathermoss (*Pleurozium schreberi*). Soil in the valley bottoms is covered with mosses (*Sphagnum spp., Hylocomium*) and dwarf shrubs *(B. nana, Salix spp., Vaccinium uliginosum*), with a patchy coverage of alder (A*lnus tenuifolia*).

For this study, data were used from four streams draining catchments that varied in permafrost coverage and size: C2 (4% permafrost and 5.2 km^2), C4 (19% permafrost and 10.4 km^2), C3 (53% permafrost and 5.7 km^2) and CJ (28% permafrost and 41.7 km^2; Fig. 1, Table 1). The C4 catchment was partially burned in 1999 by a prescribed fire to assess fire and climate feedbacks in the boreal forest (FROSTFIRE project; Hinzman et al. 2003). The prescribed burn was of moderate intensity, covered 28% of the watershed area, and was largely restricted to the black spruce-dominated north-facing slopes with the riparian zone left mostly unburned. CJ is below the confluence of C2, C3, C4 and several other streams. In addition, we sampled two springs in the C3 watershed (S-C3a and S-C3b), one spring in the C4 watershed (S-C4a) and two thermokarsts located near the CJ sampling station (K1 and K2; Fig. 1). The thermokarsts sampled are shallow bodies of freshwater that formed in a topographic depression by meltwater from thawing permafrost.

Field methods

In June through August of 2002 – 2006 stream water samples were collected daily from C2, C4 and C3 using ISCO autosamplers. Additionally, in 2006 weekly grab samples were collected from all streams, springs and thermokarsts. Spring and thermokarst samples were taken at the point of discharge, where water reaches the surface, so that they were minimally influenced by surface biotic and abiotic transformation. Samples were collected in acid-washed 125 ml high density polyethylene (HDPE) bottles and filtered within 24 hours using glass fiber filters (Gelman A/E, 0.7 µm pore size). Samples were refrigerated until analysis (< 48 hours) or frozen until processing. We found no significant difference in chemistry between autosampler and grab samples.

From 2002 – 2006, stream stage height was measured continuously from June through August using pressure transducers and Campbell Scientific dataloggers (CR10X) at Parshall flumes in the C2, C3 and C4 streams. For each stream, rating curves were developed to translate stage height to discharge.

Laboratory analyses

Samples were analyzed for DOC, dissolved organic nitrogen (DON), DOC:DON, specific ultraviolet absorbance (SUVA) and DOC fluorescence. In the laboratory, electrical conductance was measured using an Accument portable ASPSO conductivity meter. DOC concentration was measured as non-purgeable organic carbon using a Shimadzu TOC 5000 analyzer plumbed to an Antek 7050 nitric oxide chemiluminescent detector to quantify total dissolved nitrogen (TDN). Anions (Cl^-, Br^-, NO_3^-, SO_4^{2-}) and cations (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+) were determined using a Dionex DX-320 Ion Chromatograph. Dissolved organic nitrogen (DON) was calculated as TDN – (NH_4^+ + NO_3^-). SUVA is defined as UV absorbance at $\lambda = 254$ nm divided by DOC concentration (mg/L) and is a measure of DOM aromaticity (Weishaar et al. 2003). SUVA was quantified using a Beckman DU 640B spectrophotometer set to $\lambda = 254$ nm and a 1 cm cell path.

DOC optical properties

In 2006, 100 ml grab samples were collected from streams, springs and thermokarsts in pre-rinsed amber HDPE bottles for fluorescence analysis and sent to Florida International University within 48 hours for analysis. Bulk water samples were submitted for fluorescence and UV-Vis absorption analyses after filtration using standard procedures reported in the literature (McKnight et al. 2001, Jaffé et al. 2004). UV-Vis absorption spectra were measured with a Shimadzu UV-2102PC spectrophotometer between 250 and 800 nm in a 1 cm quartz cuvette to determine UV absorbance at 254 nm ($SUVA_{254}$).

Fluorescence spectra were determined with a Horiba Jobin Yvon Fluoromax-3 spectrofluorometer equipped with a 150 W continuous output xenon arc lamp (Maie et al. 2006). Single emission fluorescence scans were obtained at an excitation wavelength of 370 nm and the fluorescence intensity was recorded at emission wavelengths ranging from 385 – 500 nm. The band pass was set at 5 nm for excitation and emission wavelengths. The fluorescence index (FI) was calculated using the ratio of fluorescence intensities at 470 and 520 nm (Cory and McKnight 2005). The FI was used to distinguish whether DOM was derived from aquatic microbial material or terrestrial material with a difference of at least 0.1 being indicative of a difference in the source of DOM (McKnight et al. 2001). Excitation-Emission Matrices (EEMs) were determined at excitation wavelengths (λ_{ex}) between 240 and 455 nm at 5 nm intervals. The emission wavelengths were scanned from λ_{ex} + 10 nm to λ_{ex} + 250 nm at 2 nm intervals. The sample (emission signal, S) and reference (excitation lamp output, R) signals of the fluorescence spectra were collected and the ratio (S/R) was calculated. Post acquisition, several steps were taken to correct the fluorescence spectra. First, an inner filter correction was applied to the fluorescence data according to McKnight et al. (2001). After inner filter corrections, the sample EEM underwent spectral subtraction of the Milli-Q water to remove most of the effects of Raman scattering. Instrument bias due to wavelength dependent efficiencies of the specific instrument's optical components (gratings, mirrors, etc) were then corrected by applying multiplication factors (supplied by the manufacturer) for both excitation and emission wavelengths.

Parallel-factor analysis (PARAFAC) statistically decomposes EEMs into distinct fluorescent components without any assumptions on their spectral shape or the number of components (Stedmon et al. 2003). Since the number of the spectra in our study was not large enough to run a specific PARAFAC model for this data set, we combined the EEMs from our study with an already existing database of over 2000 EEMs. For PARAFAC modeling, EEMs with excitation wavelengths from 260 nm to 450 nm and emission wavelengths from 300 nm to 500 nm were used to minimize the influence from noise signal. The PARAFAC analysis was carried out in MATLAB (The MathWorks Inc.) software using the "N-way toolbox for MATLAB". Split-half analysis and residual analysis (Stedmon et al. 2003, Cory and McKnight 2005) were used to validate the identified components. A total of ten fluorescent components were identified (Fig. 2, Table 2).

DOC bioavailability

In June of 2007, grab samples were collected from four streams, three springs and two thermokarsts for an incubation experiment to measure DOC bioavailability. Four liters of sample were collected in acid washed cubitainers. All samples were transported in a cooler to the lab, filtered and refrigerated until analysis (< 24 hours).

The incubation experiment followed a factorial design that included *in situ* and elevated levels of temperature and nutrients. The various treatment combinations resulted in a total of four treatments: (1) 4°C with *in situ* nutrients (2) 4°C with nutrients added (3) room temperature with *in situ* nutrients, and (4) room temperature with nutrients added. Nutrients were added to elevate the nutrient concentration by 1.0 mgN/L and 0.1 mgP/L. Temperature was maintained at 4°C by placing samples in a refrigerator. Five replicates were run for each treatment combination.

For each replicate, a mason jar was filled with 190 ml of sample, and a piece of glass fiber filter was added to promote bacterial growth (Kawahigashi et al. 2004). Nutrient stock solution or nanopure water was added (10 ml), so each treatment had a final volume of 200 ml. For DOC analysis, 5 ml of sample was filtered using a peristaltic pump through 0.2 μm pore size membrane filters into vials, and 100 μl of 2 N HCl was added. DOC was measured at 0 and 40 days. Labile DOC was calculated as the loss of DOC after 40 days of incubation.

Statistical analysis

Regression analysis was used to examine relationships between stream chemistry and discharge. Regressions were compared among streams using a t-test on regression slopes. Analysis of Covariance (ANCOVA) was used to test for differences in average chemical concentrations among streams and years. One-way analysis of variance (ANOVA) was used to test for differences among treatments and sites in the incubation experiment. If a significant difference was found ($p < 0.05$), we used Tukey's tests to determine which sites were significantly different ($p < 0.05$).

The PARAFAC data were analyzed using principal components analysis. The PARAFAC data consisted of ten components expressed as percent of fluorescent DOM. These components were standardized into a covariance matrix such that components with greater magnitude would not exert more influence on the model than those with less magnitude. The first two PCA factor scores were further analyzed using ANOVA, and when there were significant effects Tukey's tests were used to determine significant differences among groups. Regression analysis was used to determine significant relationships between stream chemistry and the first two principal components.

Results

Hydrology

Stream discharge responses to precipitation varied among the watersheds in relation to the extent of permafrost (Fig. 3). The stream draining the high permafrost watershed (C3) had larger and more frequent spates than the streams draining the low

(C2) and medium (C4) permafrost watersheds (Fig. 3). The summers of 2002, 2003 and 2006 were relatively high flow years compared to 2004 and 2005 with the largest and most frequent spates occurring in 2003 (Fig. 3). Mean discharge for 2002, 2003 and 2006 ranged from 24.6 – 79.4 L/s. In contrast, 2004 and 2005 were relatively low flow years with mean discharge ranging from 28.4 – 69.2 L/s.

Stream DOM concentration and quality

DOC concentration was always highest in the stream draining the watershed with the greatest extent of permafrost, whereas the streams draining the low and medium permafrost catchments had similar DOC concentrations ($p < 0.05$, Fig. 4a). Mean summer DOC concentrations were 3.0, 2.9 and 6.2 mgC/L in the streams draining the low, medium and high permafrost watersheds, respectively. Comparing across years, all streams had significantly lower DOC concentration in 2004 ($p < 0.05$, Fig. 4a).

Mean DON concentration was highest in the stream draining the high permafrost watershed (0.35 mgN/L) and slightly lower in the streams draining the low and medium permafrost watersheds (0.31 and 0.29 mgN/L, respectively; Fig. 4b). Among streams, DON concentration did not significantly vary in higher flow years (2002, 2003 and 2006; Fig. 4b). However, in years with lower flow (2004 and 2005) DON concentration was highest in the stream draining the high permafrost watershed ($p < 0.05$, Fig. 4b). Comparing across years, DON concentration was lower in all streams during the low flow years of 2004 and 2005 ($p < 0.05$, Fig. 4b).

Mean DOC:DON in the streams draining the low, medium and high permafrost watersheds was 13.7, 13.8 and 20.8, respectively (Fig. 4c). In most years (except 2005) DOC:DON was significantly higher in the stream draining the high permafrost watershed than in the streams draining the low and medium permafrost watersheds ($p < 0.05$). DOC:DON across years was lower in 2006 in all streams ($p < 0.05$, Fig. 4c). Although not significantly different ($p < 0.05$), SUVA values tended to be highest in the stream draining the watershed with the greatest extent of permafrost. Mean summer SUVA in the stream draining the high permafrost watershed was 3.0 L mgC^{-1} m^{-1} followed by the streams draining the low and medium permafrost watersheds with 2.6 and 2.4 L mgC^{-1} m^{-1}, respectively (Fig. 4d).

DOC and discharge relationships

DOC concentration in all streams was positively correlated with discharge in nearly every year (Table 3). The slope of DOC versus discharge was significantly different among watersheds in all years ($p < 0.05$, Table 3). The stream draining the low permafrost watershed had the largest mean slope of DOC versus discharge with 0.071 mgC/s, followed by the streams draining the high and medium permafrost watersheds with 0.048 and 0.025 mgC/s, respectively (Table 3).

DOM concentration and quality in springs and thermokarsts

Springs and thermokarsts in CPCRW exhibited a wide range of DOC and DON concentrations, DOC:DON and SUVA (Fig. 5, Table 4). The range of DOC and DON concentrations in springs and thermokarsts was 1.5 – 37.5 mgC/L and 0.29 – 1.26 mgN/L (Fig. 5a and b). Along with having the highest DOC and DON concentrations, the thermokarsts had the highest DOC:DON and SUVA values with 42.8 and 4.7 L mgC^{-1} m^{-1}. In contrast, springs S-C3b and S-C4a had the lowest DOC:DON and SUVA values with 7.2 and 1.5 L mgC^{-1} m^{-1}, respectively (Fig. 5c and d).

DOM optical properties

All sites had similar fluorescence index values ranging from 1.3 – 1.4 (Table 5). Fluorescence index values were negatively correlated with both SUVA and DOC:DON (Fig. 6, $p < 0.05$).

The analysis of DOM fluorescence characteristics, based on EEM-PARAFAC analysis, using PCA revealed distinct differences among sites (Fig. 7). The first two PCA axes explained 85% of the variance in the PARAFAC data. PCA axis one was positively related with component eight and negatively related with component two, both of which are terrestrial humic-like components (Fig. 7). PCA axis two was positively related with component one (terrestrial humic-like) and negatively related with components nine and ten (tyrosine and tryptophan; Fig. 7). Tukey’s test revealed three distinct groups in the PCA results, with the thermokarst samples as a separate group along PCA axis one and spring S-C3b samples as a separate group along PCA axis two (Fig. 7). PCA axis one was positively correlated with conductivity, whereas PCA axis two was negatively correlated with conductivity (Figs. 8e and 9b). PCA axis one was negatively correlated with DOC, DON, DOC:DON and SUVA (Fig. 8). PCA two was positively correlated with DOC:DON (Fig. 9a).

DOC bioavailability

Like DOC concentration and quality, streams, springs and thermokarsts exhibited a wide range of DOC bioavailability ranging from 2 – 35% of the initial DOC after forty days of incubation under 4°C and *in situ* nutrient conditions (Fig. 10). The proportion of DOC lost from springs S-C3b and S-C4a was significantly higher than the proportion lost from all other sites. Despite thermokarsts having the highest DOC concentration (Fig. 5, Table 4), most of the DOC was not biodegradable under the incubation conditions (Fig. 10). DOC bioavailability in stream samples was intermediate between springs and thermokarsts, with the stream draining the high permafrost watershed having the lowest proportion of DOC lost among the streams. Temperature and nutrients had variable effects on the decomposition of DOC (Fig. 10). In general, temperature and nutrients did not affect DOC decomposition. However, DOC loss from the stream draining the high permafrost watershed and spring S-C3a significantly increased with an increase in both temperature and nutrients. When expressed as absolute concentration, the loss of DOC after forty days of incubation under 4°C and *in situ* nutrient conditions ranged from 0 – 1.1 mgC/L (Fig. 11). The loss of DOC was significantly higher in thermokarsts than all other sites in the room temperature with *in* *situ* nutrients treatment ($p < 0.05$). The percent of tyrosine and tryptophan in the sample was a major predictor of DOC loss (Fig. 12, $p < 0.05$, $R^2 = 0.99$).

Discussion

Permafrost, hydrology and stream DOM

The indicators of DOM quality (DOC:DON and SUVA) suggest that even though the stream draining the high permafrost watershed had a greater concentration of DOM than the streams draining the low and medium permafrost watersheds, the DOM may be of lower quality. These patterns in DOM composition in streams are most likely due to differences in watershed vegetation and hydrologic flow paths.

Differences in DOM quality among streams are undoubtedly due in part to differences in vegetation and soil in watersheds. South facing watersheds with little permafrost are dominated by hardwood forests of paper birch and quacking aspen, whereas north facing watersheds with extensive permafrost are dominated by black and white spruce. Deciduous litter has higher nitrogen content, lower aromatic carbon content and decomposes faster than coniferous litter (Hobbie et al. 2000, Berg and Meentemeyer 2002, Prescott et al. 2004). In addition, the cold, wet soil of permafrost dominated watersheds has a slower decomposition rate, reduced plant activity, and a lower rate of nitrogen mineralization than the drier, warmer soil of watersheds lacking permafrost (Van Cleve et al. 1983, Hobbie et al. 2000). Vegetation with higher aromatic carbon content and higher C:N, coupled with slower nutrient mineralization in soil may result in stream DOM with higher C:N and SUVA in the higher permafrost watershed.

Differences in flowpaths among watersheds also impact the quality of DOM in CPCRW streams. As water percolates through soil, not only the concentration but also the composition of DOM changes due to the selective sorption of hydrophobic compounds in the mineral soil leaving hydrophilic compounds in solution (Qualls and Haines 1991, Kaiser and Zech 1998, Ussiri and Johnson 2004). Therefore, the concentration of hydrophobic compounds would be greater in the stream draining the high permafrost watershed than in the streams draining the low and medium permafrost watersheds. These hydrophobic compounds have higher C:N than hydrophilic compounds and contain humic substances that can be highly aromatic (Qualls and Haines 1991, Kaiser et al. 1997, Ussiri and Johnson 2004).

The increase in DOC concentration with discharge in CPCRW streams is similar to patterns observed in forested headwater catchments in temperate and boreal regions (Hinton et al. 1998, Buffman et al. 2001, Hood et al. 2006, Petrone et al. 2006 and 2007) and in desert, alpine and wetland drainages (Jones et al. 1996, Boyer et al. 1997, Mulholland 1997). DOC concentration in the streams draining the low (C2), medium (C4), and high (C3) permafrost watersheds increases with snowmelt and storm flow, with the low permafrost watershed typically having the most rapid response to increased flow, although the total change in discharge and DOC is smaller (Petrone et al. 2006 and 2007). In our study, the slope of DOC versus discharge averaged over five summers was greatest in the low permafrost watershed. This quick, short response of DOC during periods of increased flow in the low permafrost watershed may be a result of a smaller contributing area and greater confinement of flow to saturated riparian soils compared to other catchments (Petrone et al. 2007). The riparian zone is flushed more rapidly and frequently of DOC than higher points on the hill slope because of a larger throughput of subsurface water (Boyer et al. 1997).

Variation in flow across years resulted in differences in DOC and DON concentrations and DOC:DON in all streams. DOC and DON concentrations were lower in years with smaller and less frequent spates (Fig. 2) likely due to decreased hydrologic connectivity between the stream and organic soil (Stieglitz et al. 2003, Bolton et al. 2004). During periods of base flow, stream flow is mostly sustained by ground water, which is depleted in DOM relative to soil water (Boyer et al. 1997, Hinton et al. 1998, O'Donnell and Jones 2006). In this study, 2002, 2003 and 2006 were higher flow years. However, unlike 2002 and 2003, 2006 was preceded by two unusually low flow years. The lower DOC:DON in 2006 may be a legacy of low precipitation in 2004 and 2005. Poor drainage and high soil moisture have been shown to slow decomposition in high latitude soils (Hobbie et al. 2000). A decrease in precipitation in 2004 and 2005 could have led to a decrease in soil moisture and an increase in decomposition in the watersheds. As the soil organic matter decomposed, C:N would have declined as carbon was respired leaving DOM with lower C:N to be flushed by the more frequent spates and increased discharge in 2006.

DOM composition and bioavailability

Fluorescent, freshwater DOM is primarily composed of humic fractions from the breakdown of organic material in water, riparian zones and other soils (McKnight et al.

2001, Katsuyama and Ohte 2002). Increases in the protein fraction of DOM in freshwaters result from increases in anthropogenic inputs, urbanization (Baker and Spencer 2004), glacial inputs (Battin et al. 2004, Lafreniére and Sharp 2004), decreases in flow from organic soil (Mladenov et al. 2005, Hood et al. 2006), and are likely due to increased primary productivity (Lu et al. 2003). Fluorescence index values of terrestrially derived DOM in streams typically range from 1.2 – 1.5 (McKnight et al. 2001, Mladenov et al. 2005, Hood et al. 2006) with FI values of DOM in lakes and rivers dominated by microbially derived DOM ranging from 1.6 – 2.0 (McKnight et al. 2001, Baker and Spencer 2004, Battin et al. 2004, Lafreniére and Sharp 2004). Fluorescent DOM in streams, springs and thermokarsts in CPCRW had high proportions of humic components, low proportions of protein components, and low fluorescence index values (1.3 – 1.4) consistent with DOM derived from predominantly terrestrial sources rather than microbially derived DOM. In further support that DOM in CPCRW is from terrestrial sources, FI values were inversely related with DOC:DON and SUVA. Terrestrially derived DOM typically has a high aromatic carbon content and higher C:N reflecting the presence of tannin-like and humic-like substances originating from higher plants and soil organic matter (Battin 1998).

The PCA analysis of DOM fluorescence revealed distinct groups among streams, springs and thermokarsts. The PCA one axis was associated with an increase in component eight and a decrease in component two, it is likely controlled by diagenetic processing (photodegradation). Based on its fluorescence spectrum, component two may represent an oxidized quinone, whereas component eight is a reduced version of the quinone (Cory and McKnight 2005). Thermokarst samples formed a distinct group along the PCA one axis. Surprisingly, even with often anoxic conditions (based increased methane concentration relative to streams and springs; Jones unpublished data), thermokarst samples contained a higher proportion of the oxidized quinone than streams and springs. The enhanced presence of component two in thermokarst DOM is most likely controlled by photochemical exposure and processing of DOM. Photodegradation can change the structure (Waiser and Robarts 2004) and fluorescence properties (Moran et al. 2000) of DOM. In fact, during photodegradation studies of DOM, a component with spectral characteristics similar to component two was reported to increase in abundance at the expense of the other DOM components (Stedmon et al. 2007). The extent of DOM photodegradation may be greater in thermokarsts than in springs and streams due to shallower water (Skoog et al. 1996), greater terrestrial input of DOC (Skoog et al. 1996), and a higher incidence of irradiation (Waiser and Robarts 2004). The presence of an oxidized quinone-type component in thermokarst samples may also be attributable to the heterogeneous structure of thermokarsts and anaerobic respiration. Thermokarsts are heterogeneous in structure and likely have a complex matrix of oxidized and reduced regions, which may favor the oxidation of reduced quinones produced in anoxic environments. Additionally, reduced humics and other extracellular quinones have been shown to donate electrons for the microbial reduction of electron acceptors during anaerobic respiration (Lovely et al. 1999).

The separation on PCA axis two was likely related with DOM source. Components nine and ten (tyrosine and tryptophan) are proteins most likely of microbial origin (Amon et al. 2001), whereas component one is a terrestrial humic-like component (Coble et al. 1998). Spring S-C3b formed a distinct group along PCA axis two. Spring S-C3b had a high electrical conductance, associated with deeper groundwater flow and long groundwater residence time (White et al. 2008), and a low DOC:DON, associated with a high percentage of proteinaceous carbon. Thus, S-C3b likely represents a deeper groundwater spring with increased microbial production relative to streams and thermokarsts.

The proportion of DOC lost from CPCRW streams, springs and thermokarsts (2 – 35%) is similar to the percent of DOC mineralized in samples from streams along a gradient from discontinuous to continuous permafrost (5 – 28%; Kawahigashi et al. 2004), and in temperate (16.5 – 34.4%, Volk et al. 1997; 7 – 15%, Sobczak and Findlay 2002) and tropical (22%; Kim et al. 2006) regions. Bioavailability of DOM in CPCRW streams was intermediate between springs and thermokarsts, indicating multiple sources contribute to DOM in streams. The higher conductivity due to weathering, higher proportion of proteinaceous carbon due to increased microbial primary production, and greater proportion of DOC lost in springs S-C3b and S-C4a suggest that deeper groundwater flows are a source of relatively bioavailable DOM to streams in CPCRW. In contrast, thermokarsts have high concentrations of relatively unavailable DOC and are a source of recalcitrant DOM to streams. The absolute concentration of bioavailable DOM did not vary among CPCRW streams, springs, and thermokarsts indicating that the lower proportions of bioavailable DOM in streams and thermokarsts were compensated for by higher overall DOM concentration.

The present study examined DOM bioavailability on one sampled date, however, the similarity among the absolute concentration of bioavailable DOM in streams, springs, and thermokarsts likely varies throughout the year. In a related study in CPCRW, the bioavailable DOM varied from a low of < 1 mgC/L during summer baseflow to nearly 7 mgC/L during snowmelt (White et al. 2008).

The proportion of tyrosine and tryptophan was highly correlated with the proportion of DOC lost from CPCRW samples. Amino acid/protein carbon has been shown to be an excellent indicator of bioavailability of DOM (Amon et al. 2001, Cammack et al. 2004) and is thought to be diagenetically young DOM with high energy content (Amon et al. 2001). The small proportion of proteinaceous carbon in streams, springs and thermokarsts suggests that most of the DOM exported from soils in CPCRW may not be readily used for microbial respiration/production along the stream reach and is probably transported unaltered downstream.

DOM and climate change

DOM input to streams will likely decrease with the degradation of permafrost in CPCRW based on differences in DOM concentration and composition in streams draining watersheds differing in permafrost coverage. Changes may include a decrease in DOC and DON concentrations, DOC:DON and SUVA, possibly accompanied by an increase in the proportion of bioavailable DOM if the contribution of deeper groundwater flow to streams increases. Interestingly, the absolute concentration of bioavailable DOM may not substantially change in spite of the increased proportion of bioavailable DOM because the concentration of DOM in deeper ground water is lower than in shallower, soil flowpaths. Moreover, superimposed on changing watershed flowpaths is the input of DOM from thermokarst formation. Thermokarst formation will likely increase with permafrost thaw and accordingly the contribution of recalcitrant DOM to streams will likely increase.

Acknowledgements

We would like to thank Rich Boone and Dan White for their valuable comments on the research and manuscript. Thanks to Emma Betts, Hannah Clilverd, Amanda Rinehart, Emily Schwing and Julia Taylor for their help in the field and laboratory. This research was supported by Bonanza Creek Long-Term Ecological Research program (funded jointly by NSF grant DEB-0423442 and USDA Forest Service, Pacific Northwest Research Station grant PNW01-JV11261952-231). The EEM-PARAFAC work was supported through a NSF funded inter-LTER collaboration between the Bonanza Creek and Florida Coastal Everglades Long-Term Ecological Research sites.

Literature cited

Amon, R.M.W., H. Fitznar, and R. Benner. 2001. Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter. Limnology and Oceanography **46**: 287-297.

Baker, M., M. Valett, and C. Dahm. 2000. Organic carbon supply and metabolism in a shallow groundwater ecosystem. Ecology **81**: 3133-3148.

Baker, A. and Spencer. 2004. Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy. Science of the Total Environment **333**: 217-232.

Battin, T.J. 1998. Dissolved organic materials and its optical properties in a blackwater tributary of the upper Orinoco River, Venezuela. Organic Geochemistry **28**: 561-569.

Battin, T.J., A. Wille, R. Psenner, and A. Richter. 2004. Large-scale environmental controls on microbial biofilms in high-alpine streams. Biogeosciences **1**: 159-171.

Berg, B. and V. Meentemeyer. 2002. Litter quality in a northern European transect versus carbon storage potential. Plant and Soil **242**: 83-92.

Bolton, W.R., L. Hinzman, and K. Yoshikawa. 2004. Water balance dynamics of three small catchments in a Sub-Arctic boreal forest. Northern Research Basins Water Balance (Proceedings of a workshop held at Victoria Canada 2004) IAHS Published 290.

Boyer, E.W., G.M. Hornberger, K.E. Bencala, and D.M. Mcknight. 1996. Overview of a simple model describing variation of dissolved organic carbon in an upland catchment. Ecological Modelling **86**: 183-188.

Boyer, E.W., G.M. Hornberger, K.E. Bencala, and D.M. Mcknight. 1997. Response characteristics of DOC flushing in an alpine catchment. Hydrological Processes **11**: 1635-1647.

Buffman, I., J.N. Galloway, L.K. Blum, and K.J. McGlathery. 2001. A stormflow/baseflow comparison of dissolved organic matter and bioavailability in an Appalachian stream. Biogeochemistry **53**: 269-306.

Cammack, W.K., J. Kalff, Y.T. Prairie, and E.M. Smith. 2004. Fluorescent dissolved organic matter in lakes: Relationships with heterotrophic metabolism. Limnology and Oceanography **49**: 2034-2045.

Carey, S.K. 2003. Dissolved organic carbon fluxes in a discontinuous permafrost subarctic alpine catchment. Permafrost and Periglacial Processes **14**: 161-171.

Coble, P.G. 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry **51**: 325-346.

Coble, P.G., C.E. Del Castillo, and A. Bernard. 1998. Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon. Deep-Sea Research II **45**: 2195-2223.

Cory, R.M. and D.M. McKnight. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environmental Science and Technology **39**: 8142-8149.

Findlay, S., D. Strayer, C. Goumbala, and K. Gould. 1993. Metabolism of streamwater dissolved organic carbon in the shallow hyporheic zone. Limnology and Oceanography **38**: 1493-1499.

Hinton, M.J., S.L. Schiff, and M.C. English. 1998. Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. Biogeochemistry **41**: 175-197.

Hinzman, L. D., M. Fakuda, D.V. Sandberg, F. S. Chapin III, and D. Dash. 2003. FROSTFIRE: An experimental approach to predicting the climate feedbacks from the changing boreal fire regime. Journal of Geophysical Research. **108:** 8153, doi:10.1029/2001JD000415.

Hinzman, L.D., N.D. Bettez, W.R. Bolton, F.S. Chapin, M.B. Dyurgerov, C.L. Fastie, G. Griffith, R.D. Hollister, A. Hope, H.P. Huntington, A.M. Jensen, G.J. Jia, T. Jorgenson, D.L. Kane, D.R. Klein, G. Kofinas, A.H. Lynch, A.H. Lloyd, A.D. McGuire, F.E. Nelson, M. Nolan, W.C. Oechel, T.E. Osterkamp, C.H. Racine, V.E. Romanovsky, R.S. Stone, D.A. Stow, M. Sturm, C.E. Tweedie, G.L. Vourlitis, M.D. Walker, D.A. Walker, P.J. Webber, J. Welker, K.S. Winker, and K. Yoshikawa. 2005. Evidence and implications of recent climate change in northern Alaska and other arctic regions. Climatic Change **72**: 251-298.

Hobbie, S.E., J.P. Schimel, S.E. Trumbore, and J.R. Randerson. 2000. Controls over carbon storage and turnover in high-latitude soils. Global Change Biology **6**: 196-210.

Hood, E., M.W. Williams, and D.M. Mcknight. 2005. Sources of dissolved organic matter in a Rocky Mountain stream using chemical fractionation and stable isotopes. Biogeochemistry **74**: 231-255.

Hood, E., M.N. Gooseff, and S.L. Johnson. 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. Journal of Geophysical Research **111**: 1-8.

Jaffé, R., J.N. Boyer, X. Lu, N. Maie, C. Yang, N.M. Scully, and S. Mock. 2004. Source characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by fluorescence analysis. Marine Chemistry **84**: 195-210.

Jones, J.B., S.G. Fisher, and N.B. Grimm. 1996. A long-term perspective of dissolved organic carbon transport in Sycamore Creek, Arizona, USA. Hydrobiologia **317**: 183-188.

Kaiser, K., G. Guggenberger, L. Haumaier, and W. Zech. 1997. Dissolved organic matter sorption on subsoils and minerals studied by C-13-NMR and DRIFT spectroscopy. European Journal of Soil Science **48**: 301-310.

Kaiser, K. and W. Zech. 1998. Soil dissolved organic matter sorption as influenced by organic and sesquioxide coatings and sorbed sulfate. Soil Science Society of American Journal **62**: 129-136.

Kalbitz, K., S. Solinger, J.H. Park, B. Micahlzik, and E. Matzner. 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Science **165**: 277-304.

Katsuyama, M. and Ohte. 2002. Determining the sources of stormflow from the fluorescence properties of dissolved organic carbon in a forested headwater catchment. Journal of Hydrology **268**: 192-202.

Kawahigashi, M., K. Kaiser, K. Kalbitz, A. Rodionov, and G. Guggenberger. 2004. Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost. Global Change Biology **10**: 1576-1586.

Kim, S., L.A. Kaplan, and P.G. Hatcher. 2006. Biodegradable dissolved organic matter in a temperate and a tropical stream determined from ultra—high resolution mass spectrometry. Limnology and Oceanography **51**: 1054-1063.

Lakowicz, J.R. 1983. Principles of Fluorescence Spectroscopy. Plenum Press, New York, NY, USA.

Lafreniére, M.J. and M.J. Sharp. 2004. The concentration and fluorescence of dissolved organic carbon (DOC) in glacial and nonglacial catchments: interpreting hydrological flow routing and DOC sources. Arctic, Antarctic, and Alpine Research **36**: 156-165.

Lovely, D.R., J.L. Fraga, J.D. Coates, and E.L. Blunt-Harris. 1999. Humics as an electron donor for anaerobic respiration. Environmental Microbiology **1**: 89-98.

Lu, X.Q., N. Maie, D.L. Childers, and R. Jaffé. 2003. Molecular characterization of dissolved organic matter in freshwater wetlands of the Florida Everglades. Water Research **37**: 2599-2606.

Maie, N., J.N. Boyer, C. Yang, and R. Jaffé. 2006. Spatial, geomorphological, and seasonal variability of CDOM in estuaries of the Florida Coastal Everglades. Hydrobiologia **569**: 135-150.

MacLean, R., M.W. Oswood, J.G. Irons III, and W.H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: A case study of two streams in the Alaskan taiga. Biogeochemistry **47**: 239-267.

McKnight, D.M., E.M. Thurman, R.L. Wershaw, and H. Hemond. 1985. Biogeochemistry of aquatic humic substances in Thoreau’s Bog, Concord, Massachusetts. Ecology **66**: 1339-1352.

McKnight, D.M., E.W. Boyer, P.K. Westerhoff, P.T. Doran, T. Kulbe, and D.T. Anderson. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromacticity. Limnology and Oceanography **46**: 38-48.

Michaelson, G.J., C.L. Ping, G.W. Kling, and J.E. Hobbie. 1998. The character and bioactivity of dissolved organic matter at thaw and in the spring runoff waters of the arctic tundra north slope, Alaska. Journal of Geophysical Research **103**: 28939-28946.

Mladenov, N., D.M. McKnight, P. Wolski, and L. Ramberg. 2005. Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango Delta, Botswana. Wetlands **25**: 622-638.

Moran, M.A., W.M. Sheldon, and R.G. Zepp. 2000. Carbon loss and optical property change during long-term photochemical and biological degradation of estuarine organic matter. Limnology and Oceanography **45**: 1254-1264.

Morris, D.P. and B.R. Hargreaves. 1997. The role of photochemical degradation of dissolved organic carbon in regulating the UV transparency of 3 lakes on the Pocono Plateau. Limnology and Oceanography **42**: 239-249.

Mulholland, P.J. 1997. Dissolved organic matter concentration and flux in streams. Pages 122-131 in J.R. Webster and J.L. Meyer (editors). Stream organic matter budgets. Journal of the North American Benthological Society 16: 3-161.

O'Donnell, J.A. and J.B. Jones. 2006. Nitrogen retention in the riparian zone of catchments underlain by discontinuous permafrost. Freshwater Biology **51**: 854-864.

Petrone, K.C., J.B. Jones, L.D. Hinzman, and R.D. Boone. 2006. Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost. Journal of Geophysical Research **111**: G02020, doi: 10.1029/2005JG000055.

Petrone, K.C., L.D. Hinzman, H. Shibata, J.B. Jones, and R.D. Boone. 2007. The influence of fire and permafrost on sub-arctic stream chemistry during storms. Hydrological Processes **21**: 423-434.

Prescott, C.E., L. Vesterdal, C.M. Preston, and S.W. Simard. 2004. Influence of initial chemistry on decomposition of foliar litter in contrasting forest types in British Columbia. Canadian Journal of Forest Research **34**: 1714-1729.

Qualls, R.G. and B.L. Haines. 1991. Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. Soil Science Society of America Journal **55**: 1112-1123.

Raymound, P.A. and J.E. Bauer. 2000. Bacterial consumption of DOC during transport through a temperate estuary. Aquatic Microbial Ecology **22**: 1-12.

Skoog, A., M. Wedborg, and E. Fogelqvist. 1996. Photobleaching of fluorescence and the organic carbon concentration in a coastal environment. Marine Chemistry **55**: 333-345.

Sobczak, W.V. and S. Findlay. 2002. Variation in bioavailability of dissolved organic carbon among stream hyporheic flowpaths. Ecology **83**: 3194-3209.

Stedmon, C.A., S. Markager, and B. Rasmus. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Marine Chemistry **82**: 239-254.

Stedmon, C.A., and S. Markager. 2005a. Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis. Limnology and Oceanography **50**: 686-697.

Stedmon, C.A., and S. Markager. 2005b. Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis. Limnology and Oceanography **50**: 1415-1426.

Stedmon, C.A., S. Markager, L. Tranvik, L. Kronberg, T. Slätis, and W. Martinsen. 2007. Photochemical production of ammonium and transformation of dissolved organic matter in the Baltic Sea. Marine Chemistry **104**: 227-240.

Stieglitz, M., J. Shaman, J. McNamara, V. Engel, J. Shanley, and G.W. Kling. 2003. An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. Global Biogeochemical Cycles **17**: doi:10.1029/2003GB002041.

Striegl, R.G., G.R. Aiken, M.M. Dornblaser, P.A. Raymond, and K.P. Wickland. 2005. A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. Geophysical Research Letters **32**: L21413.

Ussiri, D. and C. Johnson. 2004. Sorption of organic carbon fractions by spodosol mineral horizons. Soil Science Society of American Journal **68**: 253-262.

Van Cleve, K., L. Oliver, R. Schlentner, L.A. Viereck, and C.T. Dyrness. 1983. Productivity and nutrient cycling in taiga forest ecosystems. Canadian Journal of Forest Research **13**: 747-767.

Viereck, L., C. Dyrness, K. Van Cleve, and M.J. Foote. 1983. Vegetation, soils and forest productivity in selected forest types in interior Alaska. Canadian Journal of Forest Research **13**: 703-720.

Volk, C.J., C.B. Volk, and L.A. Kaplan. 1997. Chemical composition of dissolved organic matter in streamwater. Limnology and Oceanography **42**: 39-44.

Waiser, M.J. and R.D. Robarts. 2004. Photodegradation of DOC in a shallow prairie wetland: evidence from seasonal changes in DOC optical properties and chemical characteristics. Biogeochemistry **69**: 263-284.

Weishaar, J.L., G.R. Aiken, B.A. Bergamaschi, M.S. Fram, R. Fujii, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science and Technology **37**: 4702-4708.

White, D., V. Autier, K. Yoshikawa, J.B. Jones, and S. Seelen. 2008. Using DOC to better understand local hydrology in a subarctic watershed. Cold Regions Science and Technology **51**: 68-75.

Yamashita, Y., and E. Tanoue. 2003. Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids. Marine Chemistry **82**: 255-271.

Table 1. Stream and watershed characteristics in Caribou Poker Creeks Research Watershed.

Watershed/ stream	Stream length (km)	Basin area (km^2)	Permafrost coverage (%)	Aspect
C2	2.2	5.2	4	S
C3	2.6	5.7	53	NE
C4	5	10.4	19	SSE
CJ	19	41.7	28	E

Table 2. Characteristics of the fluorescent components identified in the EEMs of DOM in streams, springs and thermokarsts.

Component	Assignment/region			Description
	Coble (1996) Coble et al. (1998)	Stedmon and Markager (2005a)	Cory and McKnight (2005)	
1	Visible-humic (C)	3	C10	Terrestrial origin, humic-like component; absent in wastewater (Stedmon and Markager 2005a)
2	UV-humic (A)	1	Q1/C11	Terrestrial origin, humic-like component; formed during photodegradation (Stedmon et al. 2007); absent in wastewater (Stedmon and Markager (2005 a)
3	Marine-humic (M)	6	Q3/C12 or C3	Microbial component; abundant in wastewater (Stedmon and Markager 2005a)
4	-	2	SQ1/C6	High in humic acids (Maie et al. unpublished data); very sensitive to microbial and photochemical degradation (Stedmon et al. 2007); decreases fluorescence index (Cory and McKnight 2005)
5	N	-	-	Autochtonous, biologically labile component

Table 2 continued...

Component	Assignment/region			Description
	Coble (1996) Coble et al. (1998)	Stedmon and Markager (2005a)	Cory and McKnight (2005)	
6	-	4	C1	Microbial processing of algae-derived DOM (Component 5, Stedmon & Maekager 2005b); increases fluorescence index (Cory and McKnight 2005)
7	-	-	HQ/C4	Microbial processing of algae-derived DOM (Component 1, Stedmon & Markager 2005b)
8	-	5	C6	
9	Tyrosine (B)	8	Tyrosine/C13	Significantly weakened large protein molecules (Lakowicz 1983); Peptides (Yamashita and Tanoue 2003)
10	Tryptophan (T)	7	Tryptophan/C8	Proteins (Yamashita and Tanoue 2003)

Table 3. Slopes (mgC/s) of DOC versus discharge for 2002 – 2006 for the streams draining the low, medium and high permafrost watersheds.

	Streams		
	C2 (4%)	C4 (19%)	C3 (53%)
2002	0.0751*	0.0414*	0.0455*
2003	0.0137*	0.0156*	0.0352*
2004	0.1191*	0.0419*	0.0635*
2005	0.0625*	0.0105	0.0632*
2006	0.0823*	0.0246*	0.0336*
Mean Slope	0.0705	0.0247	0.0482

***** denotes a statistically significant slope ($p < 0.05$). In all years, slopes were significantly different among streams ($p < 0.05$).

Table 4. DOM characteristics and conductivity in the 2006 grab samples from streams, springs and thermokarsts. All values are means (± SE) for six sampling dates

	C2	C3	C4	CJ	S-C3a	S-C3b	S-C4a	K1	K2
Site type	Stream	Stream	Stream	Stream	Spring	Spring	Spring	Thermokarst	Thermokarst
DOC	2.6	6.3	2.3	5.5	14.3	1.5	1.6	37.5	32.2
(mgC/L)	(0.31)	(0.84)	(0.18)	(0.90)	(4.36)	(0.26)	(0.38)	(1.2)	(1.15)
DON	0.36	0.41	0.35	0.37	0.66	0.29	0.35	1.03	1.26
(mgN/L)	(0.08)	(0.07)	(0.08)	(0.05)	(0.12)	(0.07)	(0.08)	(0.05)	(0.16)
DOC:DON	10.1	19.6	9.4	18.2	22.4	7.2	7.6	42.8	30.4
	(2.15)	(3.59)	(2.15)	(3.42)	(4.79)	(1.52)	(2.61)	(2.47)	(2.54)
SUVA	2.74	3.44	2.56	3.79	4.50	1.54	2.23	4.66	3.91
(L mgC^{-1} m^{-1})	(0.23)	(0.15)	(0.11)	(0.16)	(0.49)	(0.21)	(0.51)	(0.11)	(0.23)
Conductivity	77.9	63.1	103.7	80.6	106.4	115.8	107.0	52.1	77.0
(µS/cm)	(2.09)	(4.99)	(2.46)	(4.47)	(21.52)	(2.43)	(3.51)	(3.47)	(4.36)

Table 5. DOC fluorescence data for the 2006 biweekly stream, spring and thermokarst samples. All values are a mean (± SE) of six samples.

			Component (%)									
Site	Site Type	FI	1	2	3	4	5	6	7	8	9	10
C2	Stream	1.38	14.5	17.2	7.2	20.4	3.1	15.8	1.8	13.7	2.3	4.0
		(0.01)	(0.9)	(0.4)	(0.4)	(0.3)	(0.0)	(0.4)	(0.1)	(0.5)	(0.4)	(0.3)
C3	Stream	1.37	18.4	17.3	8.0	20.9	2.8	15.7	0.9	11.8	1.4	2.8
		(0.01)	(0.4)	(0.3)	(0.2)	(0.3)	(0.1)	(0.2)	(0.3)	(0.5)	(0.1)	(0.2)
C4	Stream	1.39	14.4	16.8	7.9	18.7	3.6	15.2	1.4	13.7	3.4	4.9
		(0.01)	(0.7)	(0.4)	(0.2)	(0.2)	(0.1)	(0.3)	(0.1)	(0.7)	(0.2)	(0.4)
CJ	Stream	1.37	20.3	17.6	10.7	18.5	2.9	14.6	1.3	9.0	2.0	3.1
		(0.01)	(0.5)	(0.2)	(0.4)	(0.6)	(0.1)	(0.2)	(0.1)	(0.5)	(0.4)	(0.3)
S-C3a	Spring	1.33	18.6	20.1	8.8	19.3	2.3	14.0	3.2	9.6	1.3	2.8
		(0.01)	(0.3)	(0.9)	(0.6)	(0.4)	(0.2)	(0.5)	(0.4)	(0.4)	(0.3)	(0.3)
S-C3b	Spring	1.37	12.7	17.1	9.2	16.1	4.4	12.5	2.5	11.5	5.7	8.3
		(0.02)	(0.7)	(0.9)	(0.8)	(0.7)	(0.3)	(0.5)	(0.4)	(0.8)	(1.2)	(0.9)
K1	Thermokarst	1.32	17.7	27.3	9.7	15.7	2.7	11.1	5.4	7.4	0.9	2.1
		(0.02)	(0.6)	(1.1)	(0.5)	(0.3)	(0.2)	(0.4)	(0.4)	(0.5)	(0.2)	(0.2)
K2	Thermokarst	1.36	16.7	27.9	11.9	13.9	3.3	10.7	5.0	7.4	0.4	2.8
		(0.01)	(0.4)	(0.9)	(0.6)	(0.6)	(0.2)	(0.2)	(0.1)	(0.3)	(0.2)	(0.1)

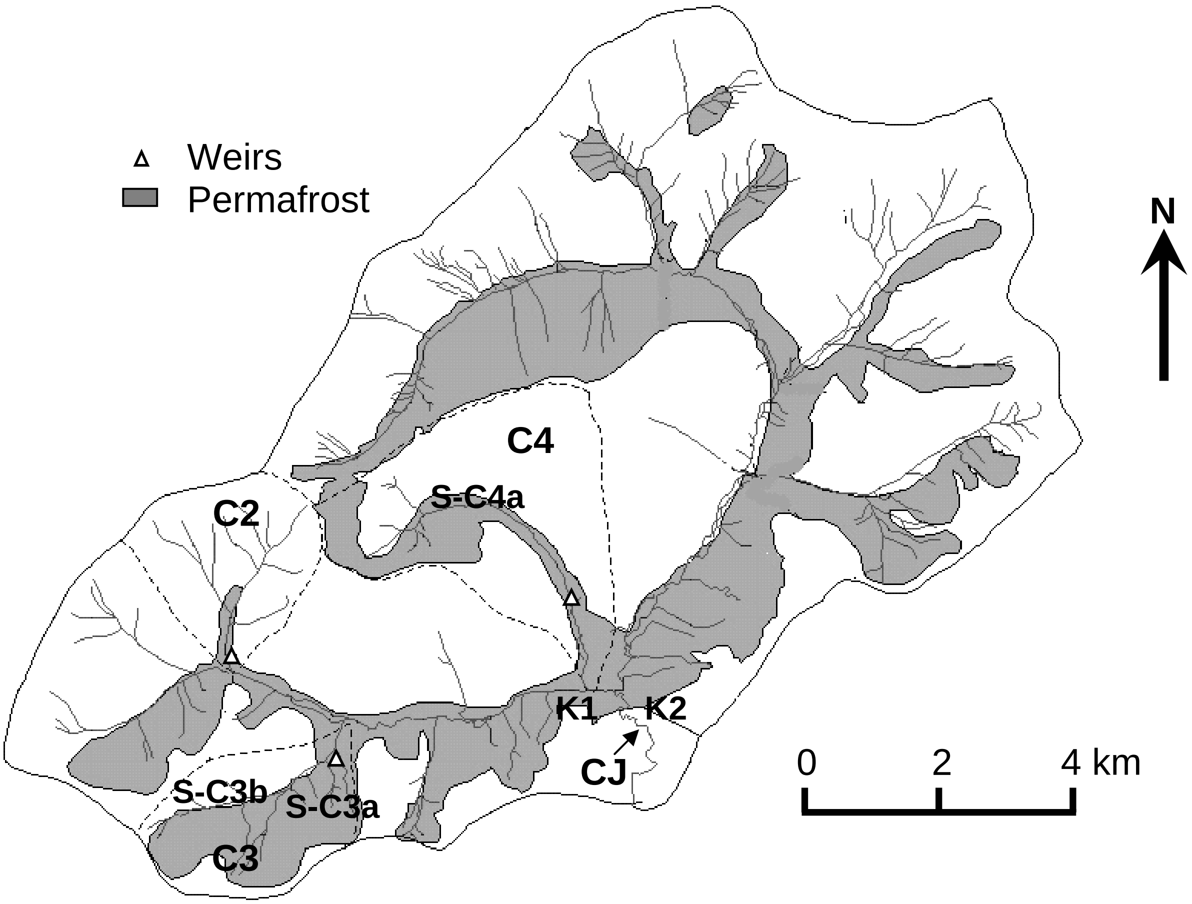

Figure 1. Map of the Caribou Poker Creeks Research Watershed with sampling sites. C denotes streams sampled within the Caribou watershed, S- denotes a spring followed by the watershed in which the spring was located, and K denotes a thermokarst.

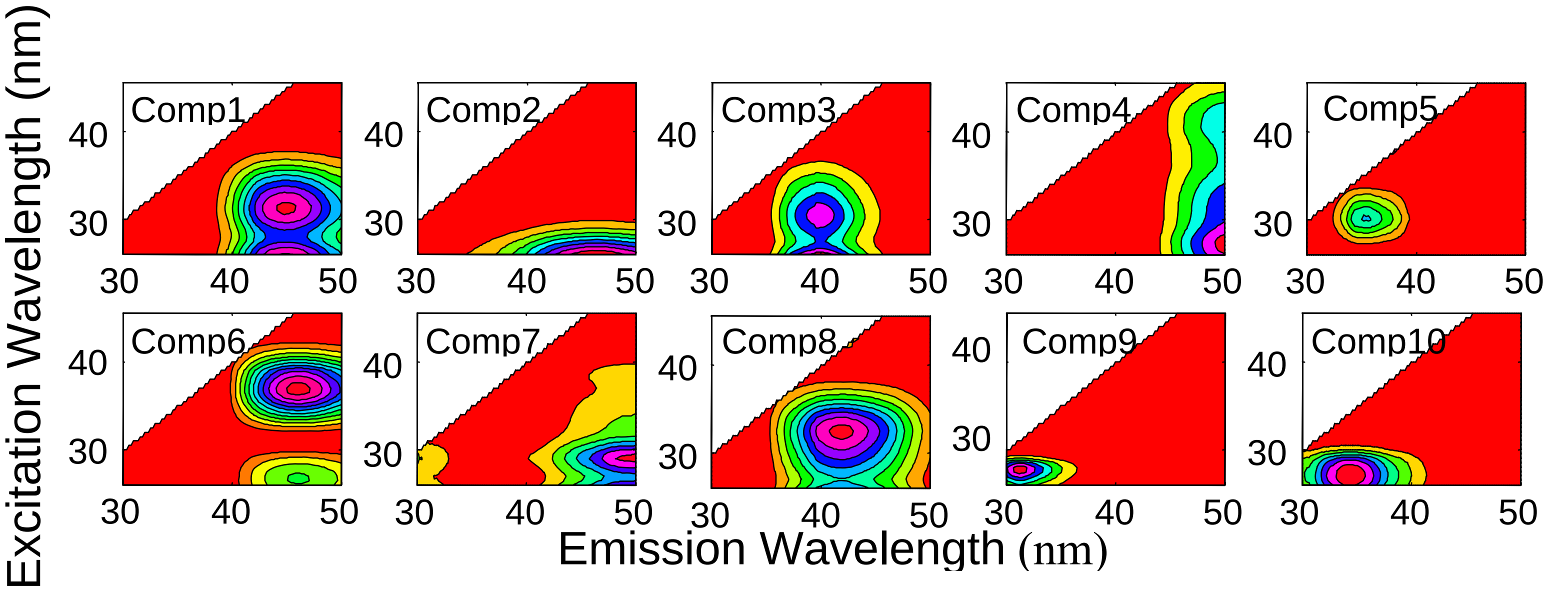

Figure 2. Excitation-Emission Matrices for the PARAFAC modeled components identified in DOM in streams, springs, and thermokarsts.

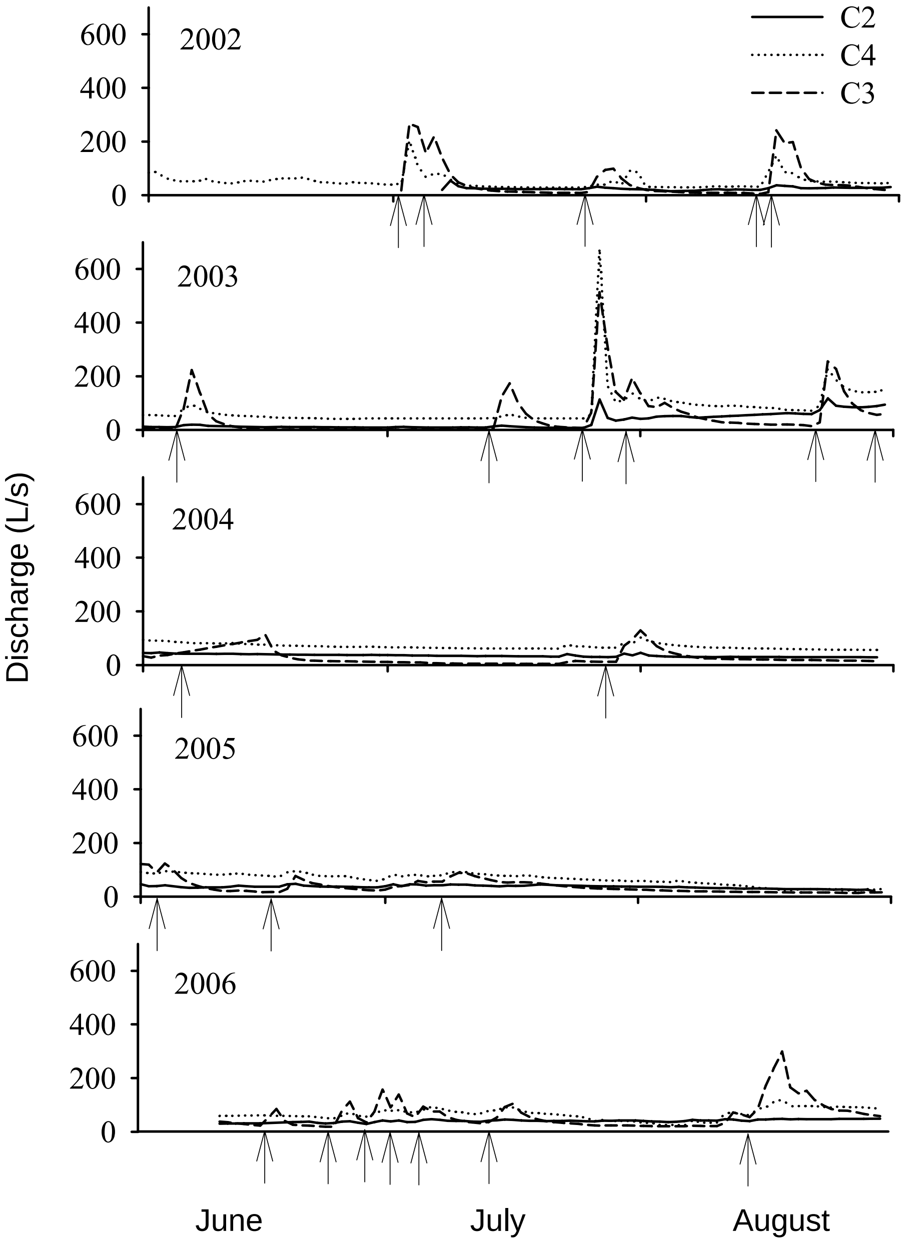

Figure 3. Hydrographs for the summers of 2002 – 2006 for the streams draining the low (C2), medium (C4) and high (C3) permafrost watersheds. Significant precipitation events are denoted with arrows.

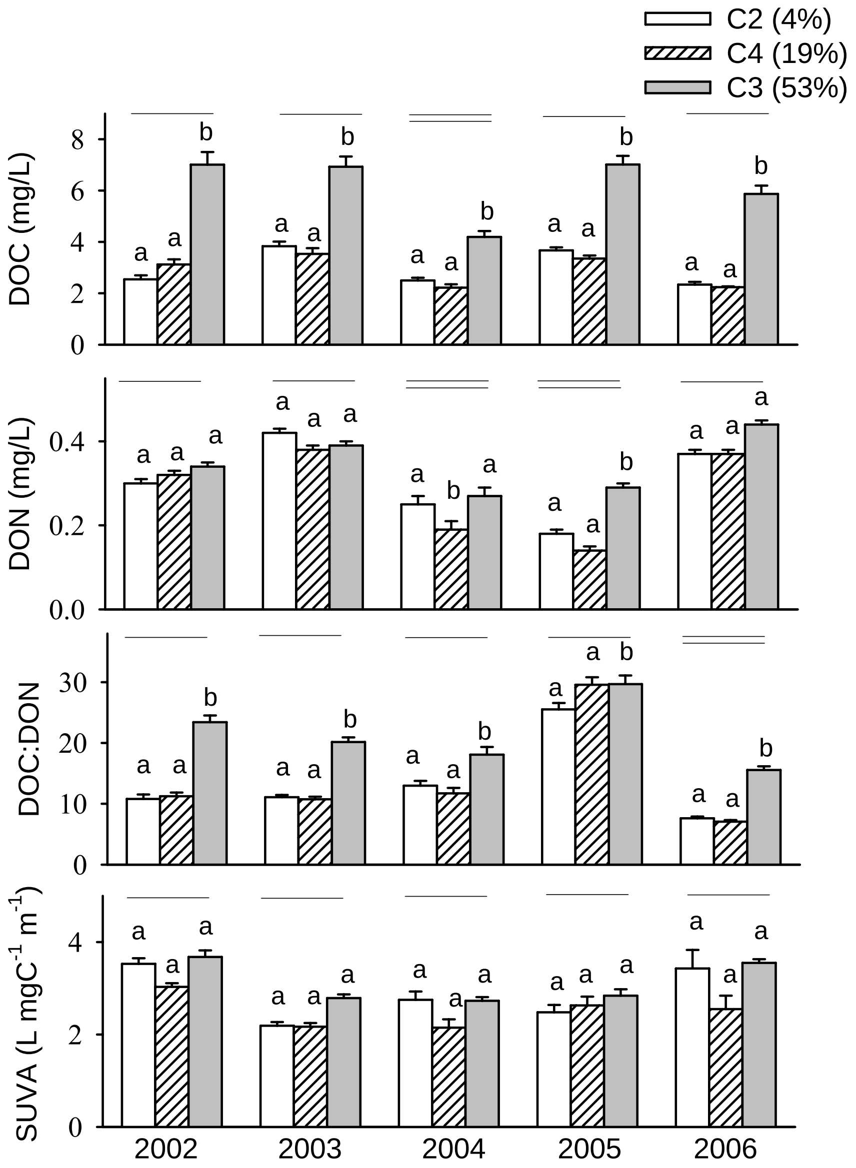

Figure 4. DOC (a), DON (b), DOC:DON (c) and SUVA (d) for the streams draining the low, medium and high permafrost watersheds for 2002 – 2006. Values are means ± SE. The letters denote significant differences among streams for a given year ($p < 0.05$). Single or double lines above the bars denote significant differences among years in a given stream ($p < 0.05$).

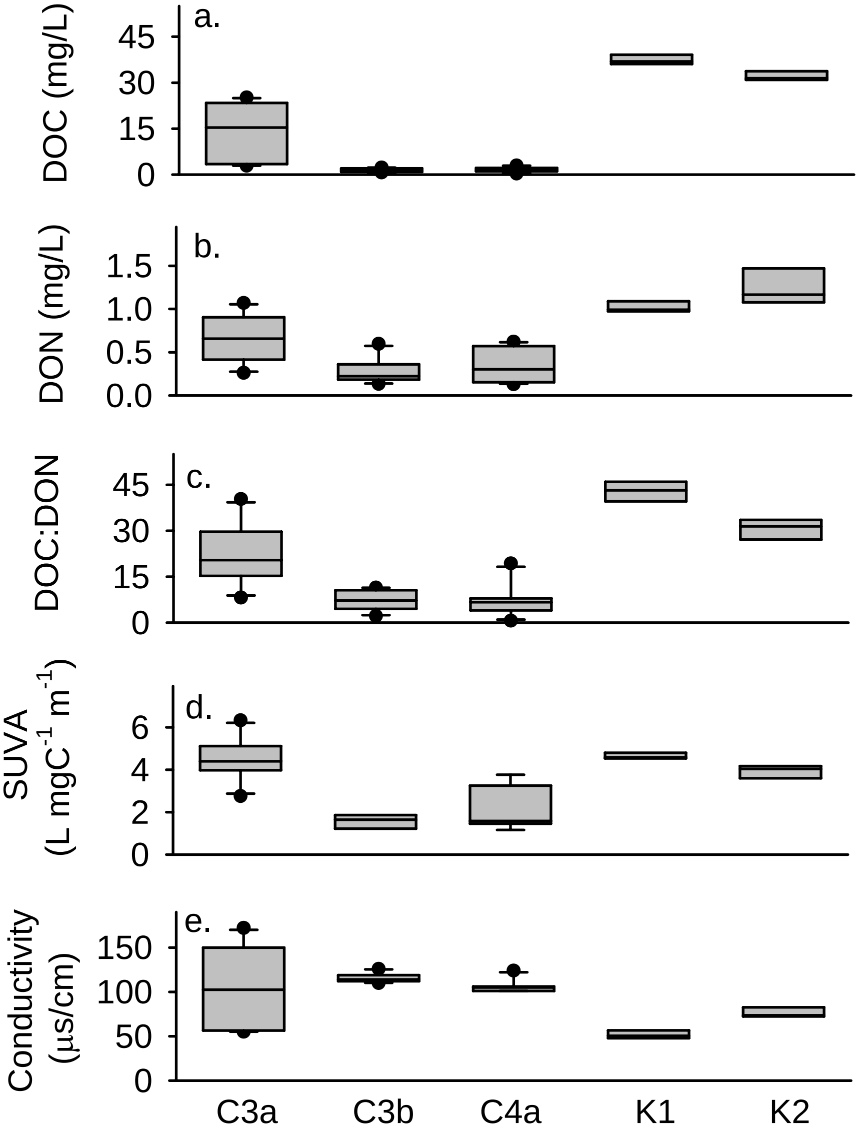

Figure 5. DOC (a), DON (b), DOC:DON (c), SUVA (d) and conductivity (e) in springs and thermokarsts for six sampling dates in 2006. S- denotes a spring followed by the watershed in which the spring was located and K denotes a thermokarst. The center line, box extent, error bars and circles represent the median, 25th and 75th, 10th and 90th, and 5th and 95th percentiles, respectively.

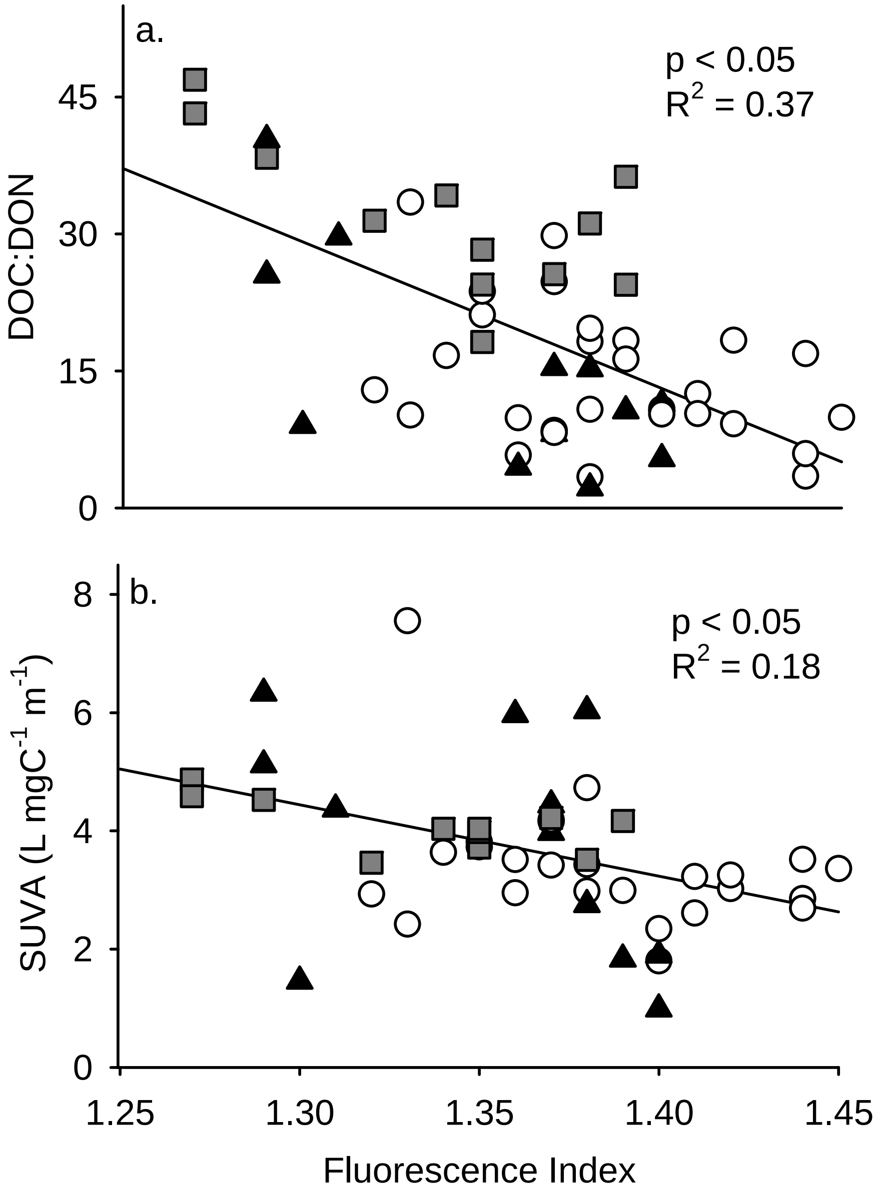

Figure 6. DOC:DON (a) and SUVA (b) versus Fluorescence Index for the 2006 grab samples taken from streams (open circles), springs (closed triangles) and thermokarsts (grey squares). FI is used to distinguish whether DOC is derived from aquatic microbial material (FI ≈ 1.9) or terrestrial material (FI ≈ 1.3; McKnight et al. 2001).

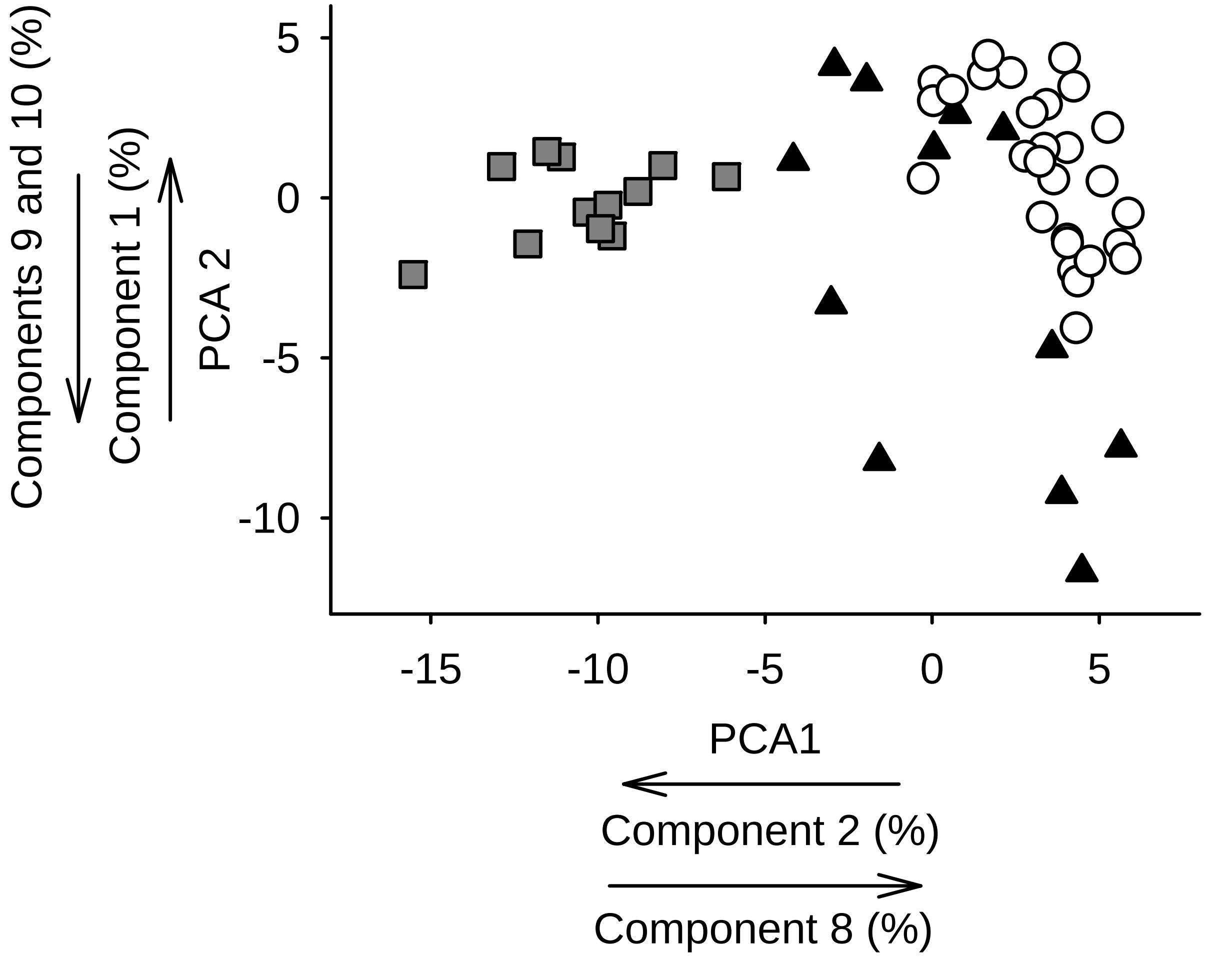

Figure 7. The first two line vectors from the principal components analysis (PCA) using the 2006 PARAFAC data from streams (open circles), springs (closed triangles) and thermokarsts (grey squares). The percent of each of the 10 fluorescing DOC components was used in the model. The two axes shown explained 85% of the variance in the data.

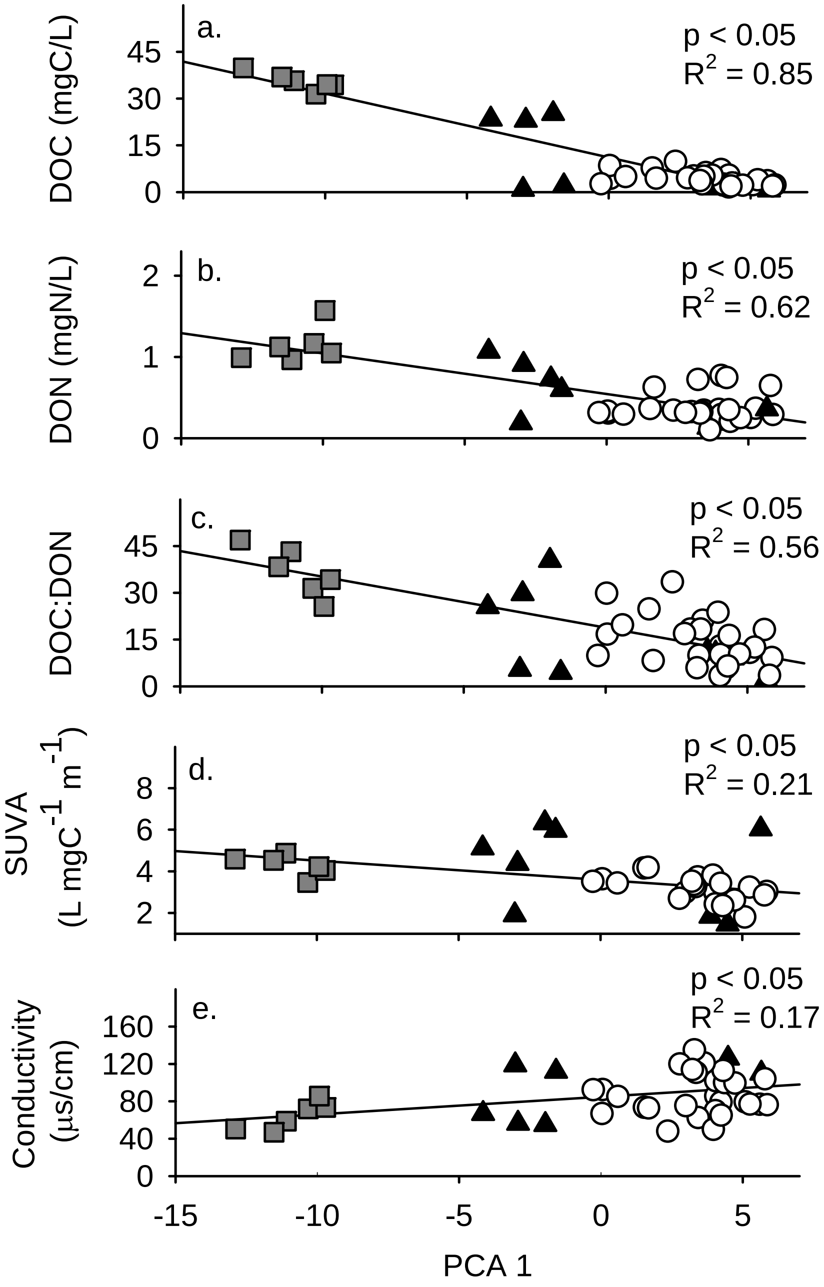

Figure 8. Stream (open circles), spring (closed triangles) and thermokarst (grey squares) DOC (a), DON (b), DOC:DON (c), SUVA (d) and conductivity (e) versus PCA axis one. All relationships were significant ($p < 0.05$).

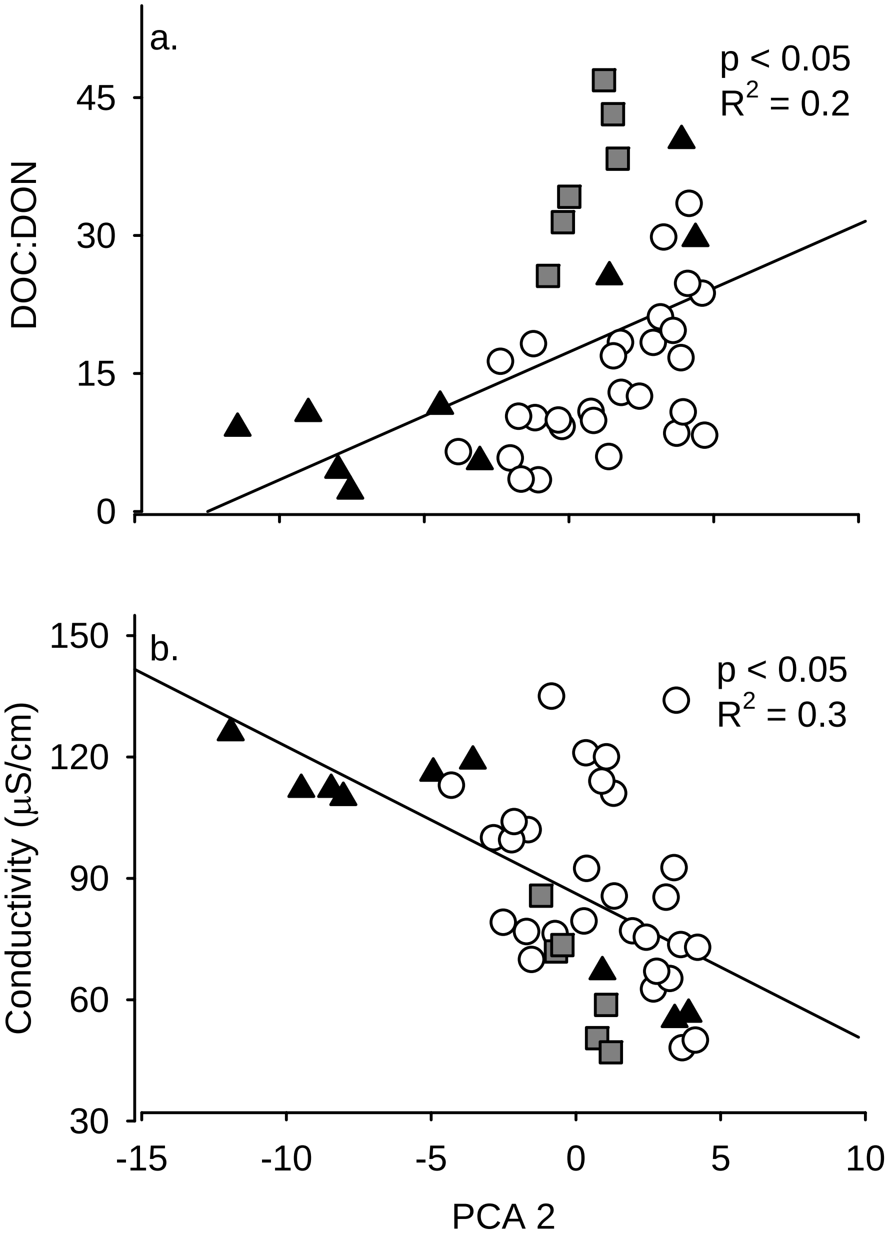

Figure 9. Stream (open circles), spring (closed triangles) and thermokarst (grey squares) DOC:DON (a) and conductivity (b) versus PCA axis two. Both relationships were significant ($p < 0.05$).

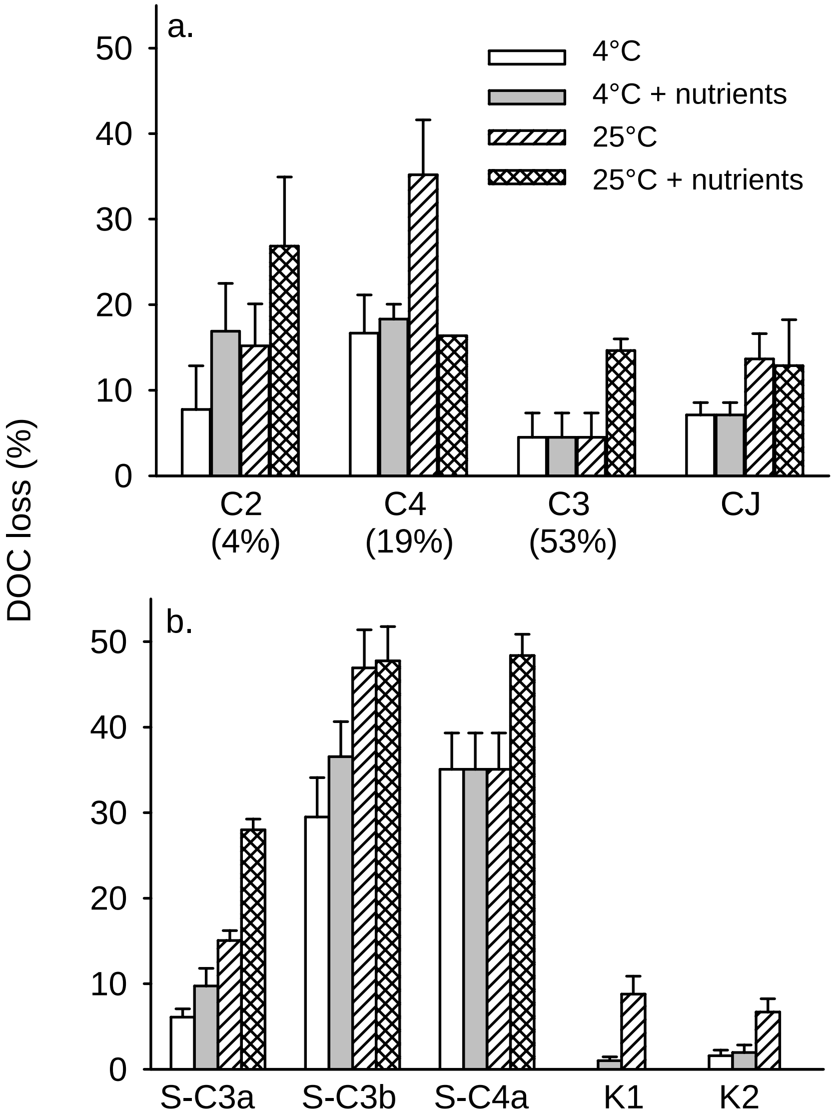

Figure 10. Proportion of DOC reduction (± SE) for streams (a), and springs and thermokarsts (b) after a 40 day incubation. S- denotes a spring followed by the watershed in which the spring was located and K denotes a thermokarst. Each sample received one of four treatments: 4°C and *in situ* nutrients, 4°C plus nutrients, room temperature *in situ* nutrients and room temperature plus nutrients

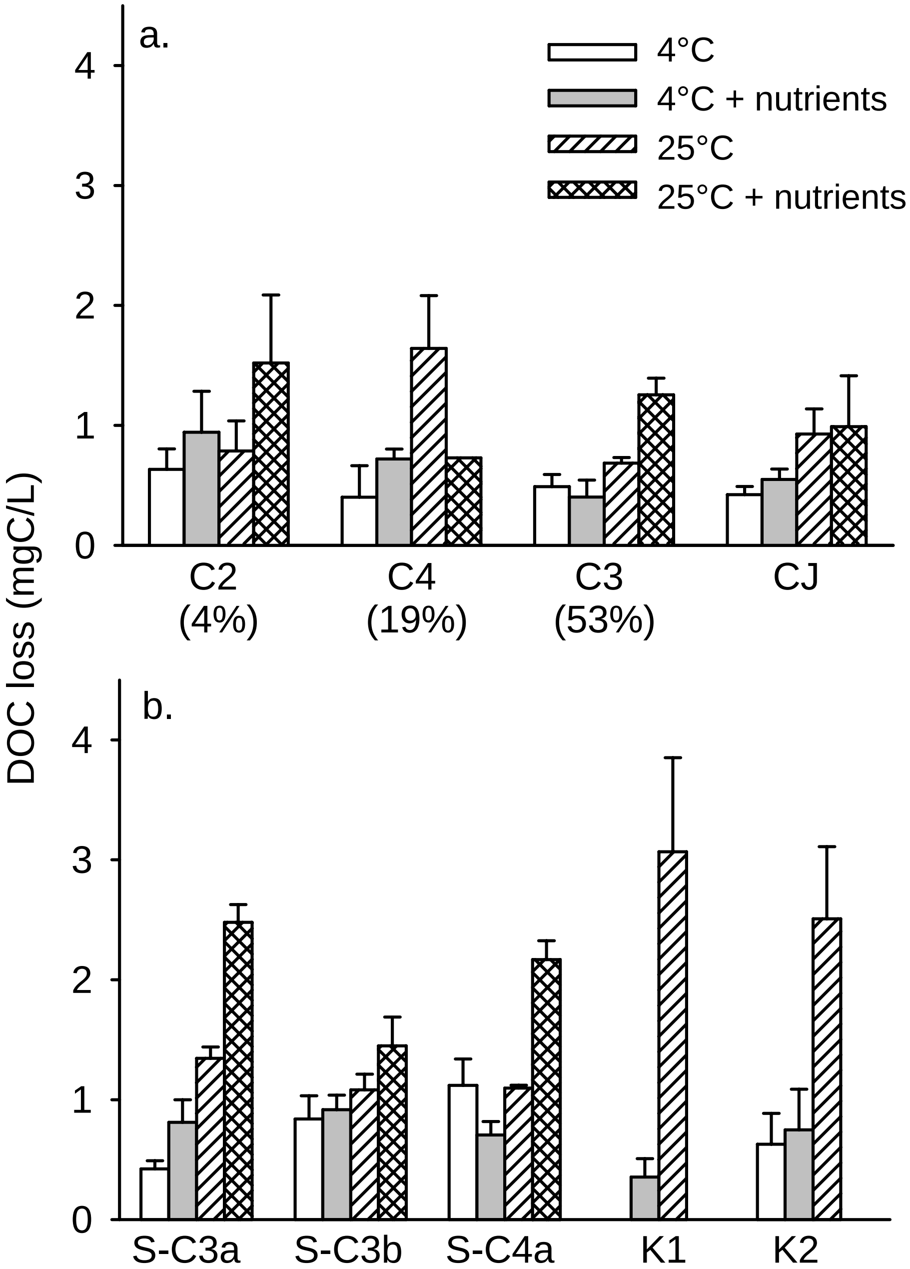

Figure 11. DOC loss (mg ± SE) for streams (a) and springs and thermokarsts (b) after 40 days of incubation. Treatments and codes as in figure 9.

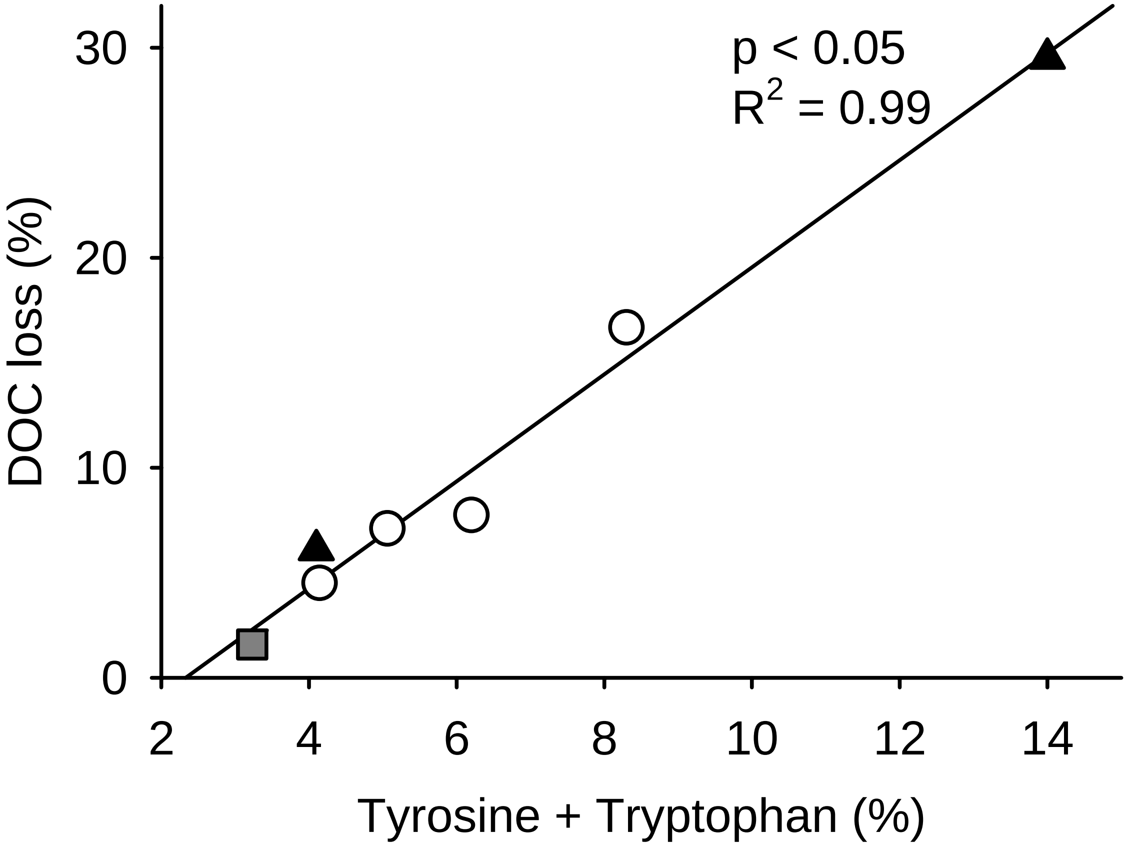

Figure 12. The proportion of DOC lost after a 40 days incubation at 4°C and *in situ* nutrients in stream (open circles), spring (closed triangles) and thermokarst (grey squares) samples versus the proportion of tyrosine (component 9) and tryptophan (component 10) in the fluorescing DOC ($p < 0.05$). Each point is the mean of five replicates samples.

CHAPTER 3: CONCLUSIONS

Much of the northern boreal forest is underlain with discontinuous permafrost, which has a large effect on catchment hydrology and the resulting delivery of dissolved organic matter (DOM) to streams (MacLean et al. 1999). This research examined the impact of permafrost and hydrology on DOM concentration, composition and bioavailability in steams draining watersheds underlain with discontinuous permafrost. The patterns in hydrology and DOM in Caribou Poker Creeks Research Watershed streams were typical of streams draining watersheds underlain with discontinuous permafrost.

Permafrost driven patterns in hydrology and vegetation resulted in the stream draining the high permafrost watershed having a higher concentration of lower quality DOM than the streams draining the low and medium permafrost watersheds. DOM in streams, springs and thermokarsts in CPCRW had high percentages of humic components, low percentages of protein components and low fluorescence index values consistent with DOM derived from terrestrial sources rather than microbial sources. In CPCRW, the influence of DOM composition over decomposition was large relative to the effects of DOM concentration, temperature and nutrients, with the percent proteinaceous dissolved organic carbon (DOC) predicting the percent DOC lost during incubation. Our results suggest that as permafrost degrades, DOC and dissolved organic nitrogen (DON) concentration, DOC:DON and specific ultraviolet absorbance in CPCRW streams will decrease and the proportion of bioavailable DOM will increase if the contribution of deep ground water flow to streams increases. Interestingly, the absolute concentration of bioavailable DOM may not substantially change in spite of the increased proportion of bioavailable DOM because the concentration of DOM in deeper ground water is lower than in shallower, soil flowpaths. Moreover, superimposed on changing watershed flowpaths is the input of DOM from thermokarst formation. Thermokarst formation will likely increase with permafrost thaw and accordingly the contribution of recalcitrant DOM to streams will likely increase.

Literature cited

MacLean, R., M.W. Oswood, J.G. Irons III, and W.H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: A case study of two streams in the Alaskan taiga. Biogeochemistry **47**: 239-267.