HYDROLOGICAL PROCESSES
Hydrol. Process. **23**, 169–182 (2009)
Published online in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/hyp.7196

Impacts of permafrost degradation on arctic river biogeochemistry

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Abstract:

Over the next century, near-surface permafrost across the circumpolar Arctic is expected to degrade significantly, particularly for land areas south of 70°N. This is likely to cause widespread impacts on arctic hydrology, ecology, and trace gas emissions. Here, we present a review of recent studies investigating linkages between permafrost dynamics and river biogeochemistry in the Arctic, including consideration of likely impacts that warming-induced changes in permafrost may be having (or will have in the future) on the delivery of organic matter, inorganic nutrients, and major ions to the Arctic Ocean. These interacting processes can be highly complex and undoubtedly exhibit spatial and temporal variabilities associated with current permafrost conditions, sensitivity to permafrost thaw, mode of permafrost degradation (overall permafrost thaw, active layer deepening, and/or thermokarst processes), and environmental characteristics of watersheds (e.g. land cover, soil type, and topography). One of the most profound consequences of permafrost thaw projected for the future is that the arctic terrestrial freshwater system is likely to experience a transition from a surface water-dominated system to a groundwater-dominated system. Along with many other cascading impacts from this transition, mineral-rich groundwater may become an important contributor to streamflow, in addition to the currently dominant contribution from mineral-poor surface water. Most studies observe or predict an increase in major ion, phosphate, and silicate export with this shift towards greater groundwater contributions. However, we see conflicting accounts of whether the delivery of inorganic nitrogen and organic matter will increase or decrease with warming and permafrost thaw. It is important to note that uncertainties in the predictions of the total flux of biogeochemical constituents are tightly linked to future uncertainties in discharge of rivers. Nonetheless, it is clear that over the next century there will be important shifts in the river transport of organic matter, inorganic nutrients, and major ions, which may in turn have critical implications for primary production and carbon cycling on arctic shelves and in the Arctic Ocean basin interior. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS permafrost; Arctic; biogeochemistry; DOC; DON; nitrate

Received 2 June 2008; Accepted 14 October 2008

INTRODUCTION

Average annual surface air temperatures in the Arctic have increased at almost twice the global rate over recent decades and are predicted to increase by an additional 4–7 °C over the next century (e.g. Arctic Climate Impact Assessment, 2005). Continued climate change will likely have profound consequences for many systems throughout the region, including two significant terrestrial impacts: an increase in river discharge (Peterson *et al.*, 2002; Manabe *et al.*, 2004a,b; Wu *et al.*, 2005; Pavelsky and Smith, 2006; Smith *et al.*, 2007) as well as permafrost degradation and a reduction in permafrost extent (Stendel and Christensen, 2002; Lawrence and Slater, 2005). Both of these changes have already initiated over the past several decades (Arctic Climate Impact Assessment, 2005) and with further climate change, should combine to significantly impact river biogeochemistry across the Pan-Arctic region and the river transport of organic matter, inorganic nutrients, and major ions to the Arctic Ocean. Many studies have already observed significant biogeochemical impacts of warming in Arctic watersheds, as will be discussed here.

Previous reviews have focused on the general current state of knowledge and recent impacts of climate change on the arctic freshwater system (e.g. Hobbie *et al.*, 1999; Dittmar and Kattner, 2003; Prowse *et al.*, 2006a; White *et al.*, 2007) as well as future predictions of the impacts of continued warming (e.g. Rouse *et al.*, 1997; Prowse *et al.*, 2006b; Wrona *et al.*, 2006). Furthermore, recent studies have illuminated uncertainties surrounding the future discharge of arctic rivers (e.g. Peterson *et al.*, 2002; Manabe *et al.*, 2004a,b; Wu *et al.*, 2005), which compounds further uncertainties in predictions of the total flux of biogeochemical constituents. The aim of this paper is to review recent studies investigating impacts of climate warming on arctic river biogeochemistry as it relates to permafrost degradation specifically. To this end, we will highlight and discuss recent literature for arctic watersheds as it relates to: (a) recent trends and future predictions of permafrost degradation; (b) impacts of permafrost degradation on organic matter; (c) impacts of permafrost degradation on inorganic nutrients; and (d) impacts of permafrost degradation on major ions.

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PERMAFROST DEGRADATION: RECENT TRENDS AND FUTURE PREDICTIONS

Permafrost covers ~25% of the Northern Hemisphere land surface and ~80% of the Arctic drainage basin, and is defined as any subsurface material that remains below 0 °C for at least two consecutive years (Brown *et al.*, 1998; Zhang *et al.*, 1999). Permafrost can be partitioned by aerial extent and is typically defined as continuous (90–100%), discontinuous (50–90%), sporadic (10–50%), or isolated patches (0–10%). The thickness of permafrost can be quite variable and generally ranges from 100–800 m in continuous permafrost, 25–100 m in discontinuous permafrost, and 10–50 m in sporadic permafrost (Anisimov and Reneva, 2006), yet there is always a seasonally thawed active layer at the surface that can vary from centimetres to metres in thickness. Warming air temperatures lead to permafrost thaw and degradation (e.g. Hinkel and Nelson, 2003; Demchenko *et al.*, 2006), which can include thickening of the active layer, talik formation, thermokarst development, expansion or creation of thaw lakes, lateral permafrost thawing, and a northward migration of the southern permafrost boundary (e.g. Zhang *et al.*, 2005). These changes can have significant impacts on hydrology, ecosystems, and biogeochemical cycling (e.g. Nelson, 2003; Smith *et al.*, 2005). Permafrost warming and degradation may in turn be accelerated by positive feedbacks to include carbon release from freshly thawed soils (Zimov *et al.*, 2006a,b; Schuur *et al.*, 2008), projected expansion of shrub cover (Sturm *et al.*, 2001a,b), and wildfire occurrence (Yoshikawa *et al.*, 2003).

Permafrost currently underlies significant portions of the six largest Arctic watersheds (Ob', Yenisey, Lena, Kolyma, Mackenzie and Yukon; Figure 1) in addition to many other smaller streams and rivers entering the Arctic Ocean. As such, profound impacts will occur here with permafrost degradation, to include biogeochemical cycling within these watersheds and resulting delivery of organic matter, inorganic nutrients, and major ions to the Arctic Ocean. Studies investigating permafrost dynamics in the Arctic show observed and modelled variability in permafrost extent, permafrost temperatures, active layer depths, and freezing/thawing indices. Here, we focus on three major types of permafrost degradation: (a) overall permafrost thaw resulting in large-scale reductions of permafrost extent (which will likely take place over relatively long time scales and influence deep groundwater contributions to streams and rivers); (b) active layer deepening (which will likely increase mid- to late-season interaction between surface water and soils); and (c) thermokarst processes and surface thawing of ice-rich ground (which will likely have more localized, yet potentially more dramatic hydrological and biogeochemical impacts).

First, overall 'wholesale' permafrost thaw and thermal degradation result in widespread reductions in permafrost extent, allowing connection between deep groundwaters and surface water pathways. As opposed to active

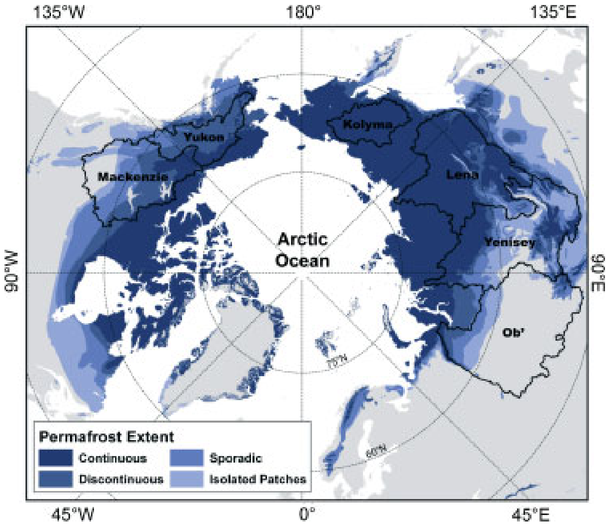

Figure 1. Drainage basins of the six largest arctic rivers and the extent of permafrost currently found within them. Delineations of continuous (90–100%), discontinuous (50–90%), sporadic (10–50%), and isolated patches of permafrost (0–10%) are from Brown *et al.* (1998)

layer and thermokarst processes, time lags involved with wholesale permafrost thaw can be significantly longer, where temperature changes at the ground surface may take from a few years to millennia to reach the bottom of permafrost layers (Osterkamp and Gosink, 1991). Not only can permafrost warm and degrade from the surface as well as from the bottom, but permafrost may also degrade internally if it contains unfrozen water, as seen in some areas of Alaska (Osterkamp, 2007). Although direct measurements of long-term permafrost dynamics are relatively rare and no real widespread pan-arctic wholesale permafrost thaw has been observed, some studies have in fact shown some substantial permafrost degradation through field observations. For example, rapid permafrost thaw has been observed to occur near the Hudson Bay in Canada, where permafrost extent began at ~82% in 1957 and declined to ~13% by 2003 (Payette *et al.*, 2004). Permafrost thaw has also accelerated significantly since 1950 across northern Manitoba, Canada (Camill, 2005). Additionally in Alaska, permafrost was observed to warm by 3–4 °C in the Arctic Coastal Plain, 1–2 °C in the Brooks Range, and 0·3–1 °C south of the Yukon River over the past several decades (Osterkamp, 2005, 2007). Many studies have also projected future overall permafrost degradation for the coming century. There have been two main approaches to modelling soil temperatures and permafrost dynamics, which include (a) utilizing climate variables determined through global climate models as input parameters for stand-alone permafrost models (e.g. Sazonova *et al.*, 2004); and (b) simulation of permafrost dynamics within a coupled global climate model that integrates the relationships between permafrost, hydrology, and climate (e.g. Stendel and Christensen, 2002; Lawrence and Slater, 2005; Anisimov and Reneva, 2006; Nicolsky *et al.*, 2007; Zhang *et al.*, 2008a). In terms of permafrost extent, more severe projections predict that pan-arctic continuous permafrost will decrease by

60–90% in the 'near surface' (when considering only the uppermost 3·43 m of the soil column) by 2100 (Lawrence and Slater, 2005). However, this has raised some concerns as to the accuracy and interpretation of models used (e.g. Burn and Nelson, 2006; Lawrence and Slater, 2006; Delisle, 2007), where criticisms of Lawrence and Slater (2005) centre around issues such as their consideration of continuous permafrost only, their neglect of thaw consolidation and the latent heat effects associated with near-surface ice-rich layers, and limitation of their model to the near surface only (<3·43 m) [i.e. temperature changes at the ground surface could take a few years up to millennia to propagate to the much deeper bottom extent of permafrost (Osterkamp and Gosink, 1991)]. More conservative models, such as Anisimov and Reneva (2006) project that by 2080, total near surface permafrost may be reduced by 19–24% (or 26–44% for continuous permafrost only). In addition, Delisle (2007) shows that permafrost may persist in areas north of 70°N (the approximate current continuous permafrost zone), but perhaps only at depth between 60 and 70°N (the approximate current discontinuous permafrost zone) (Delisle, 2007). It is important to note that the impacts of warming air temperatures on permafrost may have significant time lags (Zhang *et al*., 2008a). For instance, models for Canada specifically show that forced with a 2·8–7·0 °C increase in temperatures over the next century, reductions in permafrost extent fall within a relatively narrow range (20·5–24·4%) because the impacts on permafrost are not fully realized by the year 2100 and would continue even if air temperatures were to cease warming (Zhang *et al*., 2008b). Recent advances in permafrost modelling (e.g. Riseborough *et al*., 2008) have helped to define new, slower, and more reasonable predictions of future pan-arctic near-surface and deep permafrost degradation rates over the coming century (e.g. Lawrence *et al*., 2008) (Figure 2).

Second, active layer thaw depths are highly responsive to warming air temperatures (Hinkel and Nelson, 2003) and can be important indicators of permafrost stability. Deepening active layers may increase interaction between surface waters and soils within the newly thawed portions of the active layer, as well as liberate soluble biogeochemical constituents previously sequestered within the near-surface permafrost. Studies such as Frauenfeld *et al.* (2004) have shown that active layers across Russia deepened by ~20 cm over the period from 1956 to 1990. Because direct measurements of permafrost and active layer depths are not always available, proxies such as freezing and thawing indices (i.e. the cumulative number of degree days for a given time period) can be modelled to evaluate permafrost distribution and active layer thickness (e.g. Oelke *et al*., 2003; Frauenfeld *et al*., 2007). Over recent decades for areas north of 50°N, the freezing index has decreased by 85·6 °C-days decade^{-1} and the thawing index has increased by 44·4 °C-days decade^{-1}, indicating significant impacts on frozen ground conditions (Frauenfeld *et al*., 2007). Recent warming of soils has also been modelled and investigated over the pan-arctic region, separated by major drainage basin to more fully gauge the overall hydrological impacts of permafrost degradation. Oelke *et al*. (2004) show that from 1980 to 2002, the active layer deepened by ~0·81 cm/year in the Yenisey basin, 0·47 cm/year in the Mackenzie basin, 0·35 cm/year in the Lena basin, whereas the Ob' basin showed no significant trends (Figure 2). Other models have corroborated increased thaw depths in the Lena basin, where active layers have increased by ~32 cm from 1956 to 1990 (Zhang *et al*., 2005). Recent models predicting permafrost dynamics over the coming century have not only focused on overall permafrost extent, but also on active layer depths. For example, simulations of active layer depths indicate that thicknesses may increase by 30–40% for most permafrost areas in the Northern Hemisphere (Stendel and Christensen, 2002) and by as much as 41–104% in Canada (Zhang *et al*., 2008a) by the year 2100.

Third, it is important to address thermokarst processes in the context of permafrost degradation. Thermokarst development is the surface thawing of ice-rich ground, loss of volume from melting ice, and subsequent creation of depressions in the land surface from thaw slumping (e.g. Czudek and Demek, 1970). Compared with wholesale permafrost thaw and active layer deepening,

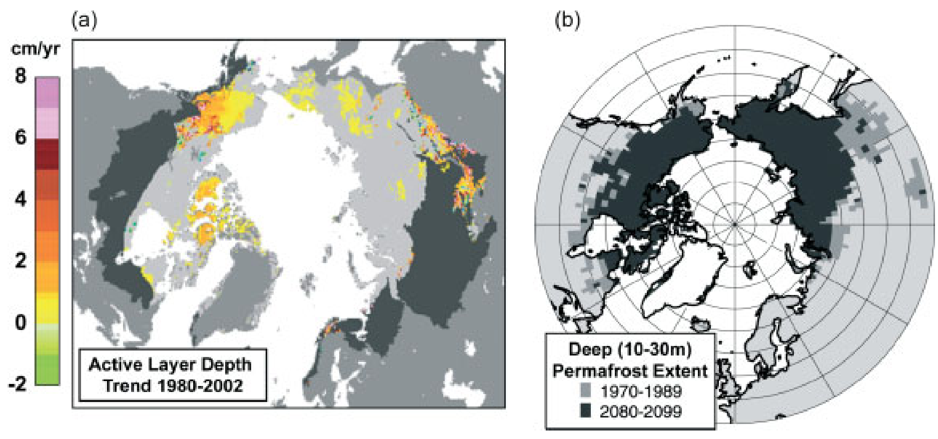

Figure 2. (a) Modelled active layer depth trends from 1980 to 2002 (adapted from Oelke *et al*., 2004). (b) Modelled extent of deep permafrost at the end of the 20th and 21st centuries (adapted from Lawrence *et al*., 2008)

DOI: 10.1002/hyp

thermokarst processes are likely to cause more localized, yet more dramatic influences on hydrological and biogeochemical systems. Although thermokarst processes are thought to be more localized, they cannot be neglected and have even been shown to be linked with globally significant emissions of methane from associated thaw lakes (e.g. Walter *et al.*, 2006, 2007). Thermokarst is associated with warming air temperatures in discontinuous and sporadic zones of permafrost extent, but it can also occur in regions of continuous permafrost and may not be directly tied to wholesale permafrost thaw. For instance, Jorgenson *et al.* (2006) found abrupt, large degradation of continuous permafrost in northern Alaska since ~1982, where massive ice wedges previously stable for thousands of years have thawed. Furthermore, both Osterkamp (2007) and Lantz and Kokelj (2008) confirm the presence of recently developed thermokarst terrain across interior/northern Alaska and northern Canada, respectively, over the past several decades. As these studies directly relate the acceleration of thermokarst processes with warming suface air temperatures, it is predicted that rates of thaw slump activity will increase with expected continued climate warming.

Although there is some variability and uncertainty in permafrost model outputs (e.g., Anisimov *et al.*, 2007), it is clear that significant reductions in permafrost extent, increases in active layer depths, and acceleration of thermokarst processes will likely transpire over the coming decades as a result of expected continued warming air temperatures. As impacts of permafrost degradation on organic matter, inorganic nutrients, and major ions in arctic rivers are discussed in the following sections, it is important to bear in mind that interacting seasonal dynamics of permafrost and hydrology have a major influence on the timing and quantity of all constituents exported from watersheds. To give greater insight into these issues, Bowling *et al.* (2000) offer an important review of hydroclimatology in the pan-arctic drainage basin. In high-latitude watersheds, a large proportion (up to 80–90%) of total annual river discharge may occur during a confined 2–3 week period when snow melt dominates at spring freshet (Linell and Tedrow, 1981). This effect does not necessarily manifest itself at small scales, but becomes increasingly apparent with watershed size (McNamara *et al.*, 1998). During the spring freshet, melt water is restricted to shallow flow paths regardless of whether areas are underlain by permafrost or seasonally frozen ground. Only later, as the summer progresses, do permafrost characteristics (e.g. active layer depth, the presence vs. absence of permafrost) strongly influence the depth of water flow through soils. A shallow active layer keeps water flow relatively near the soil surface, increasing interaction with organic-rich soils, whereas a deeper (or absent) active layer allows greater water flow through underlying mineral soils. These differences in flow paths influence water biogeochemistry through water–soil exchange reactions as well as microbial processes that vary with soil depth and water residence time. As such, throughout this review, it is critical to note that impacts of warming and permafrost degradation on river biogeochemistry are highly dependent not only on watershed environmental characteristics (e.g. land cover, soil type, and topography), but also on current permafrost conditions, sensitivity to thawing, and mode of permafrost degradation (wholesale permafrost thaw, active layer deepening, and/or thermokarst processes).

IMPACTS OF PERMAFROST DEGRADATION ON ORGANIC MATTER IN ARCTIC RIVERS

Although the Arctic Ocean constitutes only 1% of the global ocean volume, it receives more than 10% of global river discharge and river transported terrestrial dissolved organic matter (DOM) (Opsahl *et al.*, 1999; Dittmar and Kattner, 2003). Organic matter concentrations in arctic rivers are some of the highest among rivers globally (Dittmar and Kattner, 2003) and draw from carbon-rich drainage areas of the Arctic, which may contain up to half of the organic carbon (OC) stored globally in soils (e.g. Gorham, 1991; Dixon *et al.*, 1994; Smith *et al.*, 2004; MacDonald *et al.*, 2006). Owing to cool temperatures and waterlogged, anaerobic conditions, permafrost soils in particular have accumulated vast stores of OC (~400 Pg C) since the Last Glacial Maximum (Davidson and Janssens, 2006; Schuur *et al.*, 2008), representing one-fifth of global soil C and approximately equivalent to two-thirds of atmospheric CO_2 (Gruber *et al.*, 2004).

These large stocks of high-latitude carbon currently stored in permafrost are precariously situated with respect to future climate warming; carbon previously locked up in frozen permafrost soils for thousands of years (but still potentially highly labile) may become part of contemporary carbon-cycling processes from both land to atmosphere and land to ocean (e.g. Davidson and Janssens, 2006; Dutta *et al.*, 2006; Zimov *et al.*, 2006a,b; Bockheim and Hinkel, 2007; Khvorostyanov *et al.*, 2008a,b; Schuur *et al.*, 2008) that could ultimately contribute to significant positive feedbacks to climate warming (e.g. Field *et al.*, 2007). Here, we focus on DOM as both dissolved organic carbon (DOC) and dissolved organic nitrogen (DON).

Early assessments of how DOM may respond to climate warming in northern watersheds suggested that there may be overall increases in DOC export from soils and peatlands owing to drivers such as increased plant production (e.g. Rouse *et al.*, 1997; Moore *et al.*, 1998). However, it is clear that adding the consideration of permafrost dynamics causes these projections to be less straightforward, as a variety of recent studies predict both increases and decreases in DOM export with climate warming and subsequent permafrost degradation. Many of these changes are due to direct hydrological impacts, but studies also make note of indirect effects of permafrost degradation causing shifts in vegetation such as increasing shrub abundance (Sturm *et al.*, 2001a,b; Sturm *et al.*, 2005), which can in turn impact the character and concentrations of DOM (e.g. Wickland *et al.*, 2007).

DOI: 10.1002/hyp

Many studies investigating biogeochemical impacts of climate warming compare watersheds with varying permafrost extent to infer potential overall changes should there be widespread degradation of permafrost throughout that study region. For instance, in Alaska (MacLean *et al*., 1999; Striegl *et al*., 2005, 2007; Petrone *et al*., 2006, 2007), the Yukon Territory (Carey, 2003), and central Siberia (Kawahigashi *et al*., 2004; Prokushkin *et al*., 2007), the export of DOM from these watersheds is expected to decline with permafrost degradation owing to increased adsorption of DOM through new exposure to underlying mineral soils, although in some cases these long-term decreases are projected to occur only after an initial brief period of higher DOM concentrations resulting from permafrost meltwater (e.g. Striegl *et al*., 2007). Petrone *et al*. (2006), as many other studies, show both (i) positive correlations between DOC concentrations and discharge; and (ii) relatively high DOC concentrations in areas of more extensive permafrost and lower DOC concentrations in areas of less extensive low permafrost (Figure 3). In these cases, high DOC concentrations in areas underlain by permafrost are attributed to shallow flow paths of water in organic-rich soil layers. However, not all observed or predicted decreases in DOM and DOC can be attributable to permafrost dynamics; recently observed decreases in DOC export in the upper Kuparuk River (North Slope, Alaska) were primarily attributed to decreases in discharge rather than permafrost thaw and increases in active layer depths, which show no overall trend throughout North Slope region (McClelland *et al*., 2007).

Contrary to these predictions of reduced DOM and DOC with permafrost degradation in Alaska, the Yukon Territory, and central Siberia are projections of significant increases in DOC export from West Siberia with expected permafrost thaw over the next century. In the West Siberian Lowland, which contains the most extensive peatlands in the world (Sheng *et al*., 2004; Smith *et al*., 2004), current observations show that permafrost-influenced watersheds contain low concentrations of DOC and permafrost-free watersheds contain significantly higher concentrations of DOC that rise sharply as a function of peatland cover (Frey and Smith, 2005) (Figure 4). Utilizing a space-for-time substitution approach, these data show that up to ~700% increases in DOC concentrations for individual watersheds and up to ~46% increases in annual DOC export from the entire West Siberian region are possible by the year 2100 (Frey and Smith, 2005). Variations in DOC and DON concentrations are highly correlated across watersheds in West Siberia, leading to predictions of concomitant (~53%) increases in DON export by 2100 (Frey *et al*., 2007a). As opposed to the findings for DOC (where DOC concentrations and permafrost extent are positively correlated in Alaska, yet negatively correlated in West Siberia), patterns in river water DON across a wide geographical range in Alaska were remarkably similar to those found in the West Siberia region (Figure 5a). This implies that as permafrost degrades across the Arctic, future changes in DON may be more uniform (where export to rivers may show consistent increases) than changes in DOC (where export to rivers may either increase or decrease).

In permafrost areas of West Siberia, hydrological transport of DOM from peatlands and organic-rich soils to their outlet streams may be limited by the presence of permafrost. High-latitude northern soils have been shown to export recently fixed DOM of plant and near-surface soil origin (e.g. Benner *et al*., 2004), suggesting little hydrological interaction at depth. This contrasts with studies of DOC export at lower latitudes, where radiocarbon dating has shown riverine DOM to be much older (Raymond and Bauer, 2001). While relatively deep peat soils in West Siberia are a potential source of old DOM to streams and rivers (Smith *et al*., 2004), permafrost may present a physical barrier to infiltration and subsurface flow through the older and deeper peat

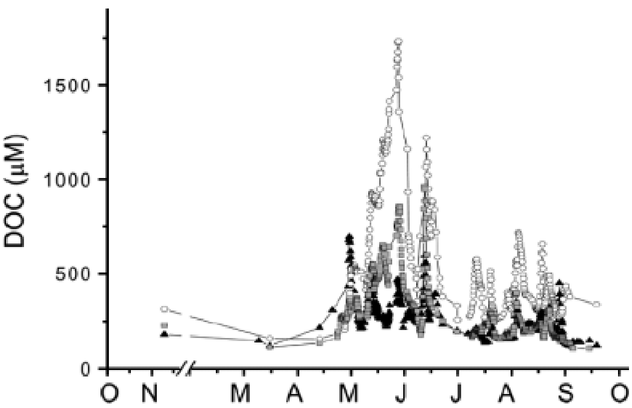

Figure 3. Time series of dissolved organic carbon (DOC) for high permafrost (53·2% permafrost extent, open circles), medium permafrost (18·5% permafrost extent, closed triangles), and low permafrost (3·5% permafrost extent, grey squares) for watersheds in Alaska (from Petrone *et al*., 2006)

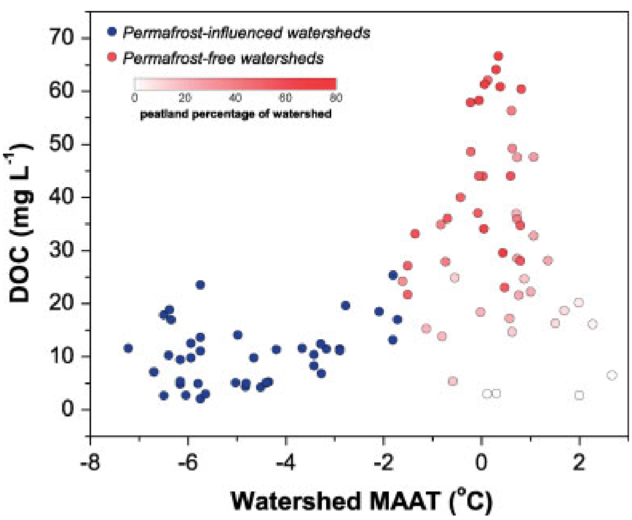

Figure 4. Dependence of DOC concentration on watershed mean annual air temperature (MAAT) in West Siberia. A sharp increase in concentrations occurs in watersheds not impacted by permafrost. Low concentrations in these permafrost-free watersheds are due to sparse peatland coverage (adapted from Frey and Smith, 2005)

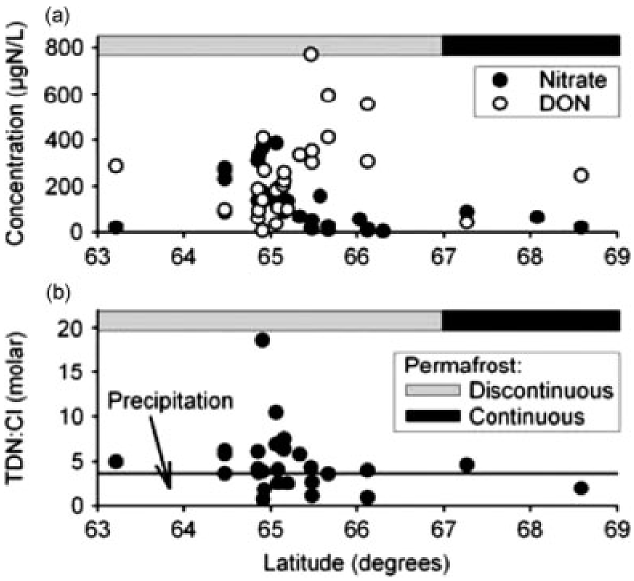

Figure 5. (a) Stream water nitrate and dissolved organic nitrogen (DON) concentrations and (b) total dissolved nitrogen (TDN) to chloride ratios along a latitudinal gradient of varying permafrost extent in interior Alaska (from Jones *et al*., 2005)

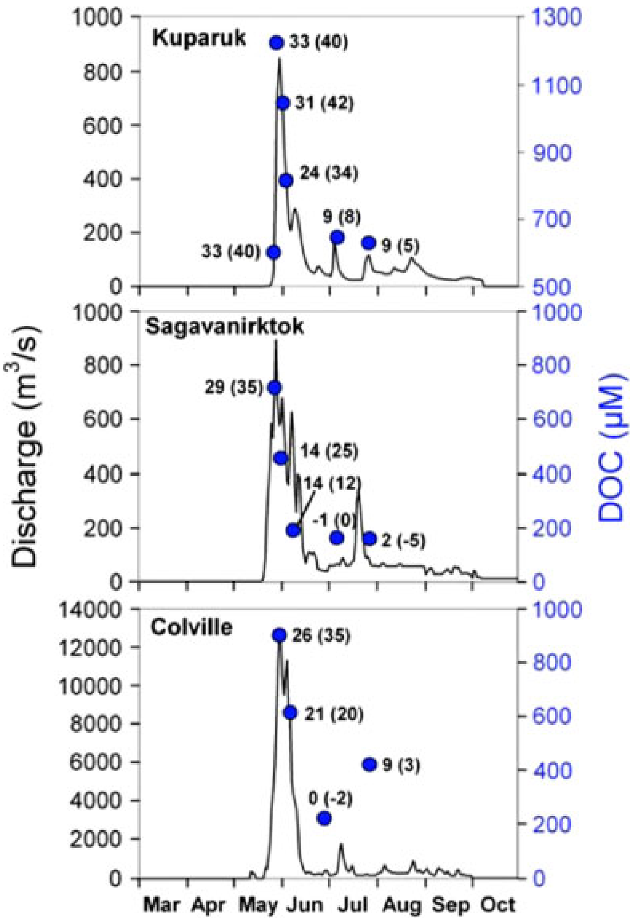

Figure 6. DOC concentration and percent loss of DOC after 3 months of incubation in the dark at 20 °C. Values in parentheses show loss with nutrient amendment. DOC lability tends to be high (20–40%) during the freshet period, declining substantially during summer low-flow conditions (from Holmes *et al*., 2008)

layers. As observed in Alaska and Siberia, we would expect flow through organic-rich soils of the shallow active layer to result in higher DOC concentrations than flow through deeper mineral soils (e.g. MacLean *et al*., 1999; Carey, 2003; Kawahigashi *et al*., 2004; Striegl *et al*., 2005, 2007; Petrone *et al*., 2006, 2007; Prokushkin *et al*., 2007). However, in West Siberia the organic-rich peat layer averages ~1–5 m deep (Sheng *et al*., 2004) and thus provides a continued (indeed even richer) source of organic matter as permafrost thaws and flow paths deepen. Thus, degradation of permafrost and increases in active layer depths may introduce a new source pool of organic material for DOM production and cause increases in delivery of this material to adjacent streams and rivers. Additionally, the fact that peat has relatively low hydraulic conductivity may also maintain waters with long residence times in these organic-rich soils, even in the complete absence of permafrost. This increased residence time potentially allows for increases in both decomposition and leaching/production of DOM, but low oxygen conditions in waterlogged soils often lead to anoxic conditions which limit decomposition rates and thus result in net increases in DOM. Therefore, it is critical to consider soil substrate when determining future DOM release to streams and rivers with warming and permafrost degradation, where deep, anoxic, low hydraulic conductivity peat soils may result in greater release of DOM when compared with mineral soils overlain with only a thin layer of organic-rich material.

In addition to overall concentrations and fluxes, the lability and age of DOM found in rivers may also be impacted by the degradation of permafrost. Although it is difficult to predict the lability of DOM that would be liberated as a consequence of warming and permafrost degradation, new evidence suggests that such DOM may be more labile than previously thought; until recently, DOM exported from arctic rivers was considered to be largely recalcitrant (Opsahl *et al*., 1999; Dittmar and Kattner, 2003; Rachold *et al*., 2003; Amon and Meon, 2004), but a newer study suggests that ~30% may be rapidly processed in the nearshore marine environment (Cooper *et al*., 2005). This shift in our understanding may be partly due to previously restricting sampling to summer only; a recent study in the Kupark, Sagavanirktok, and Colville rivers in Alaska shows there is a substantial seasonal variability in the lability of DOC (Holmes *et al*., 2008), where DOC associated with spring freshet is relatively labile and DOC associated with summer low-flow conditions is relatively refractory (Figure 6). This may be explained by short residence times and cold temperatures limiting microbial processing in the spring, but increased thaw depths in the summer months limiting interaction with shallow organic soils and slowing movements of water, which allow for more processing of groundwater DOC (Hobbie *et al*., 2000; Striegl *et al*., 2005; O'Donnell and Jones, 2006; Wickland *et al*., 2007; Holmes *et al*., 2008). This suggests that with permafrost thaw and degradation, although the source of soil organic material currently locked up in permafrost may be highly labile (e.g. Uhlirova *et al*., 2007), residence times of

DOI: 10.1002/hyp

waters may increase and the DOC ultimately delivered to the Arctic Ocean may become more refractory overall. As discussed in the previous paragraph, however, this would be mediated (at least in part) by oxygen conditions of the soil waters. Further understanding of the processes related to lability will allow for utilization of this parameter to monitor hydrological and biogeochemical changes on a watershed scale. For instance, the lability of DOC has already been shown to be a predictor of flow paths in the Caribou Poker Creeks Research Watershed (CPCRW), where labile DOC that has undergone a low degree of biological processing indicates that water has been transported through cracks in bedrock rather than a loess layer that would have led to biological decomposition of the organic matter (White *et al.*, 2008).

Given the large amounts of old carbon stored in permafrost soils (e.g. Smith *et al.*, 2004; MacDonald *et al.*, 2006; Zimov *et al.*, 2006a,b), the age of OC in rivers may be used as an integrative measure of future changes in permafrost. If the age of OC found in rivers does not change with warming temperatures, we cannot necessarily rule out the occurrence of permafrost thaw because OC production may be limited to surface layers only, and thus retain the *status quo* even if permafrost were to thaw completely. However, if OC in rivers becomes older, it does imply mobilization of older carbon at depth in the soil or peat column. While earlier discussion of old carbon focused on West Siberia, there is also abundant evidence of old carbon stored in permafrost in other regions of the Arctic (MacDonald *et al.*, 2006; Zimov *et al.*, 2006a,b). Thus, large quantities of aged, potentially reactive (e.g. Dutta *et al.*, 2006; Uhlirova *et al.*, 2007) OC could be released around the pan-arctic domain as permafrost thaws, including mobilization through river networks. This premise is supported by seasonal trends of DOC age in the Kolyma River basin (Figure 7a and b), where early season DOC is relatively young and late-season DOC is relatively old as active layer thaw depths increase through the spring and summer months (Neff *et al.*, 2006). Raymond *et al.* (2007) also show that for five of the largest arctic rivers (Yenisey, Lena, Ob', Mackenzie, and Yukon), DOC is generally relatively young during spring flood and slightly older during winter baseflow periods. However, these patterns are not always straightforward; many studies of the radiocarbon age of arctic river DOC show late summer DOC ages also to be modern [e.g. Amon and Meon, 2004; Benner *et al.*, 2004; Neff *et al.*, 2006 (Figure 7c)], suggesting a relatively continuous source of modern DOC throughout the entire growing season. Furthermore, studies in the Yukon, Sagavanirkok, and Mackenzie Rivers also show that while particulate organic carbon (POC) may increase in age with permafrost thaw and resulting river-bank erosion, future variability in DOC may be more reliant on altered plant ecology (Guo and MacDonald, 2006; Guo *et al.*, 2007). Although studies to date are not entirely consistent, a warming climate, degradation of permafrost, and increases in active layer depths may in fact result in a larger proportion of older OC released to rivers and ultimately to the Arctic Ocean, suggesting a new, large source pool of potentially reactive soil organic matter should permafrost thaw from these regions. These issues may be elucidated with future studies of relatively small, homogenous watersheds, comparing those with stable permafrost to those with actively degrading permafrost. Studies separating the impacts of different modes of permafrost degradation (wholesale permafrost thaw, active layer deepening, and/or thermokarst processes) would also give further insight into the implications of future warming on DOM delivery to arctic streams and rivers.

IMPACTS OF PERMAFROST DEGRADATION ON INORGANIC NUTRIENTS IN ARCTIC RIVERS

As discussed with respect to organic matter, there is considerable uncertainty about how changes in permafrost may impact inorganic nitrogen in arctic rivers. Experimental work on organic matter lability and nutrient cycling in tundra soils demonstrates that nitrogen remineralization is likely to increase as the Arctic warms (Shaver *et al.*, 1998; Weintraub and Schimel, 2003; Uhlirova *et al.*, 2007). However, variations in soil moisture and water flow paths which are tightly linked to

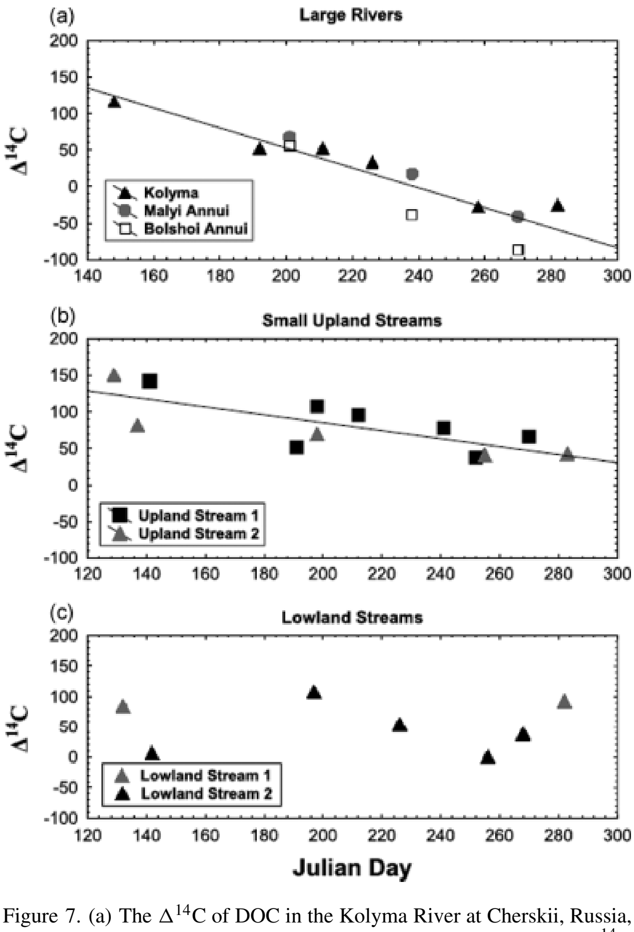

Figure 7. (a) The $\Delta^{14}C$ of DOC in the Kolyma River at Cherskii, Russia, and two large upstream tributaries; (b) seasonal changes in the ^{14}C content of DOC in two upland first-order streams that drain permafrost underlain basins; (c) $\Delta^{14}C$ of DOC in two lowland streams that drain seasonally flooded, non-permafrost areas around the Kolyma (from Neff *et al.*, 2006)

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permafrost dynamics have a profound influence on the concentrations of dissolved inorganic nitrogen (DIN) that ultimately enter a river from the surrounding landscape. Studies comparing river water nitrogen among catchments with different amounts of permafrost coverage in interior Alaska (MacLean *et al*., 1999; Jones *et al*., 2005; O'Donnell and Jones, 2006; Petrone *et al*., 2006) and West Siberia (Frey *et al*., 2007a) can be used to investigate how nitrogen export may change in the future. Results have not been entirely consistent among these studies, leading to competing hypotheses about the dominant mechanisms controlling nitrogen export under different permafrost conditions. Comparisons among subcatchments of the CPCRW lead MacLean *et al*. (1999) to hypothesize that longer soil water residence time in areas of less extensive permafrost facilitates greater DIN removal, whereas later studies in the CPCRW support the alternative hypothesis that deeper flow paths in areas of less extensive permafrost facilitate nitrate export (Jones *et al*., 2005; Petrone *et al*., 2006). This second hypothesis is corroborated by a broader comparison of nitrate in Alaskan rivers between 63°12′N and 68°5′N (Figure 5). Nitrate concentrations are, on average, greater at lower latitude sites with discontinuous permafrost as compared with higher latitude sites with continuous permafrost (Figure 5a). Furthermore, elevated total dissolved nitrogen (TDN) : Cl in stream water relative to TDN : Cl of rain water indicates net nitrogen export from many watersheds with discontinuous permafrost, particularly at intermediate latitudes (Figure 5b). However, comparison of 96 rivers in West Siberia over a similarly wide latitudinal range found no differences in nitrate concentrations linked to variations in permafrost coverage (Frey *et al*., 2007a). The difference in findings for West Siberia and interior Alaska may be explained by greater remineralization (and subsequent nitrification) of organic nitrogen in the Alaskan watersheds with intermediate permafrost coverage (i.e. note how nitrate concentrations increase as DON concentrations decrease towards lower latitudes in Figure 5a). Remineralization of organic nitrogen in the Siberian watersheds may be limited by soil water saturation (i.e. the West Siberian Lowland contains the most extensive peatlands in the world (Sheng *et al*., 2004; Smith *et al*., 2004)). In addition, denitrification facilitated by wet conditions may help account for the consistently low nitrate concentrations in the Siberian study.

Expected impacts of degrading permafrost on dissolved silicate and phosphate concentrations in arctic rivers are more predictable. Mineral weathering is the primary source of both dissolved silicate and phosphate in soil waters, and deeper flow paths through previously frozen mineral soils as permafrost thaws would lead to an increase in the concentrations of these inorganic nutrients. Increases in dissolved silicate with decreases in permafrost coverage have been identified through cross-site comparisons in the CPCRW (MacLean *et al*., 1999) as well as the West Siberian watersheds (Frey *et al*., 2007b). Very low absolute concentrations of phosphate (measured as soluble reactive phosphorus) in the CPCRW and the West Siberian watersheds make it difficult to confirm expected differences related to permafrost coverage. However, Hobbie *et al*. (1999) do report anomalously high concentrations of soluble reactive phosphorus in a stream on the North Slope of Alaska that has been attributed to permafrost degradation. Although there is no evidence of widespread permafrost thawing on the North Slope of Alaska, the catchment of this particular stream was impacted by excavation work in the 1970s associated with road development. Furthermore, analyses of permafrost and active layer soils on the North Slope of Alaska show that exchangeable phosphorus is greater in the permafrost soils (Keller *et al*., 2007). While there have been many important studies of nutrient chemistry in active layer soils, Keller *et al*. (2007) provides a rare comparison of phosphorus between active layer and permafrost soils. More such studies, including comparisons of inorganic nitrogen as well as phosphorus would be very helpful for thinking about future changes in arctic river biogeochemistry.

Few long-term datasets are available to directly examine trends in nutrient concentrations and export from arctic rivers. One rare example comes from the North Slope of Alaska, where nutrients have been measured in the upper Kuparuk River since ~1980 as part of the Arctic Long Term Ecological Research (ARC LTER, http://ecosystems.mbl.edu/ARC/default.html) effort. A recent analysis of these data by McClelland *et al*. (2007) identified a major increase in nitrate concentrations and export beginning in the 1990s (Figure 8) that may be linked to accelerated warming of permafrost in the region (Osterkamp and Romanovsky, 1999; Stieglitz *et al*., 2003). There is no conclusive evidence of increasing active layer depths in the Kuparuk River basin in parallel with this warming, but many new thermokarst features are evident (Bowden *et al*., 2008). Long-term data on nutrient concentrations also exist for several major rivers in the Russian Arctic, but uncertainties about data quality limit their utility (Holmes *et al*., 2000, 2001; Zhulidov *et al*., 2000). Existing river nutrient data from Russia and elsewhere around the Arctic are also limited with respect to seasonal coverage. Although it is widely recognized that the spring freshet (in response to snowmelt) accounts for a large percentage of total annual export from arctic rivers, sampling of these rivers has occurred primarily during summer. The Pan-Arctic River Transport of Nutrients, Organic Matter and Suspended Sediments (PARTNERS) project, focusing on the six largest arctic rivers, has greatly improved our understanding and appreciation for the seasonal dynamics of arctic river biogeochemistry and provided a more robust baseline for detecting future changes (McClelland *et al*., 2008). However, there is still a pressing need to establish long-term sampling programmes on smaller arctic rivers, particularly outside of Alaska. Changes in river export as a consequence of thawing permafrost as well as other drivers are likely to differ markedly across spatial scales. Not only must patterns and modes of permafrost degradation be considered, but also spatial variations in

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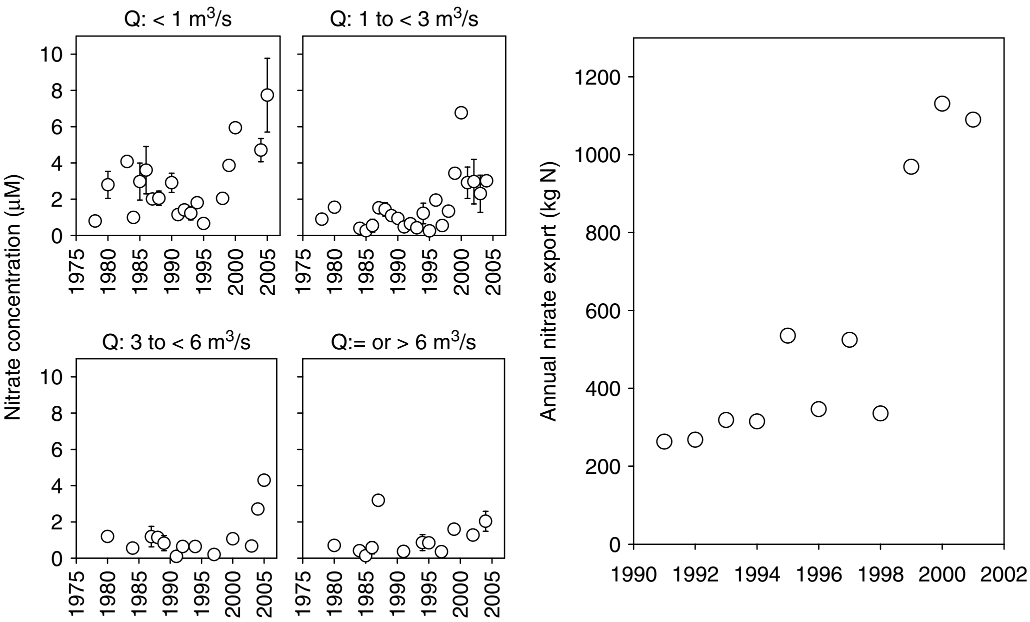

Figure 8. Long-term measurements of nitrate concentrations in the upper Kuparuk River, North Slope, Alaska, from the Arctic LTER database (left) and modelled estimates of annual nitrate export between 1991 and 2001 (right). Concentrations are separated into four discharge (Q) categories to demonstrate that changes are evident over a wide range of flow conditions (adapted from McClelland *et al.*, 2007)

the chemical composition and soil structure of thawing permafrost.

IMPACTS OF PERMAFROST DEGRADATION ON MAJOR IONS IN ARCTIC RIVERS

In addition to organic matter and nutrients, degradation of permafrost is also expected to have significant impacts on major ions in rivers, with these changes projected to be relatively consistent across the pan-arctic region. However, it is again important to note that the mode of permafrost degradation (wholesale permafrost thaw, active layer deepening, and/or thermokarst processes) may determine how and where new flow paths are formed, thus impacting the concentrations and types of major ions delivered to streams and rivers. In general, concentrations of major ions (e.g. Ca^{2+}, Mg^{2+}, K^+, Na^+) are predicted to increase markedly with permafrost degradation and lowering of water tables, resulting from less interaction with organic shallow soils and enhanced interaction with deep mineral horizons. For example, total inorganic solutes (TIS, defined as the sum of eight solutes: $Ca^{2+} + K^+ + Mg^{2+} + Na^+ + Si + Cl^- + HCO_3{}^- + SO_4{}^{2-}$) in West Siberian streams and rivers average $\sim$289 mg l^{-1} in permafrost-free watersheds in contrast with only $\sim$48 mg l^{-1} in permafrost-influenced watersheds (Frey *et al.*, 2007b) (Figure 9). This currently observed divergence in solutes may be driven by permafrost-controlled hydrological processes, with permafrost forming a confining barrier that inhibits the infiltration of surface water through deep mineral horizons (limiting water–rock interaction and weathering) and restricts mineral-rich subpermafrost groundwater from reaching surface water pathways (e.g. Woo and Winter, 1993; Michel and van Everdingen, 1994; Woo *et al.*, 2000). This hypothesis is corroborated by MacLean *et al.* (1999), who found that the presence of permafrost significantly reduces the dissolution and transport of dissolved inorganic mineral loads (particularly Ca^{2+} and Mg^{2+}) in streams of the Alaskan taiga by confining runoff to upper soil horizons.

Many studies in Alaska show that by investigating watersheds with variable permafrost extent, permafrost degradation will likely result in increased delivery of carbonate and Ca^{2+} (Keller *et al.*, 2007); Ca^{2+} and $SO_4{}^{2-}$ (Stottlemyer, 2001); and Ca^{2+}, Mg^{2+}, K^+, and Na^+ (Petrone *et al.*, 2006, 2007). In some cases, permafrost thaw and water table lowering may cause oxidation of the soil itself, which may in turn cause the mobilization

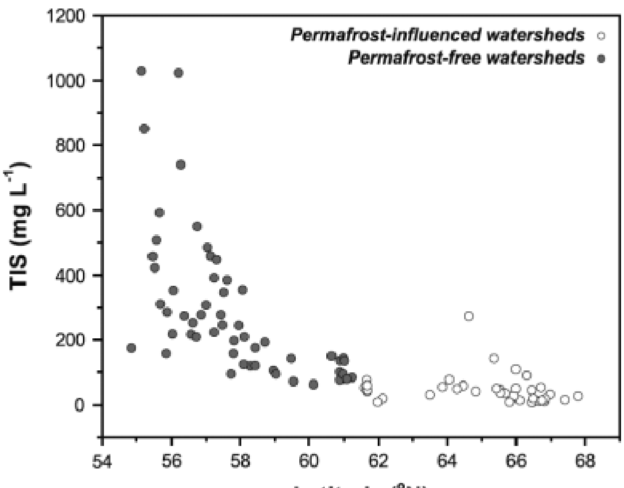

Figure 9. Total inorganic solutes (TIS) as a function of latitude for 94 streams and rivers in West Siberia. TIS rises considerably northward of $\sim$61 °N, which is approximately coincident with the southern limit of permafrost (from Frey *et al.*, 2007b)

and release of major and trace elements accumulated during soil and peatland development (Chagué-Goff and Fyfe, 1997). Predictions of future release of major ions may also be elucidated by direct investigations of the geochemical characteristics of the current active layer versus underlying permafrost layers (e.g. Kokelj and Lewkowicz, 1999; Kokelj *et al.*, 2002; Kokelj and Burn, 2005a,b). Kokelj and Burn (2005a) find near-surface permafrost to be solute-rich compared with the overlying active layer (attributed to progressive removal of solutes from the active layer) and may contribute a pulse of increased solute delivery to streams and rivers upon new degradation of permafrost. Thermokarst processes may cause localized and dramatic release of salts to streams and rivers from surface salt accumulations in coastal areas such as those on the Canadian Arctic Archipelago (Kokelj and Lewkowicz, 1999). If studies are geographically expansive and incorporate sufficient variability in permafrost, one may also quantify expected future increases in solute loads to the Arctic Ocean by taking a space-for-time substitution approach: TIS export from the West Siberian region to the Kara Sea and Arctic Ocean would increase by ~59% (~46 Tg year^{-1} to ~73 Tg year^{-1}) should permafrost from the region completely disappear (Frey *et al.*, 2007b).

One of the most profound changes to occur with future arctic warming may be the transition of the Arctic System from a surface water-dominated system to a groundwater-dominated system, with resulting cascading impacts on hydrology, ecosystems, and biogeochemical cycling (e.g. Nelson, 2003; Smith *et al.*, 2005). Although this transition may be difficult to assess over large areas, the relatively consistent and straightforward relationship between concentrations of major ions and groundwater contribution to rivers may allow the geochemistry of river waters to be utilized as a monitor of watershed-scale changes in permafrost extent and thaw depth. For example, Keller *et al.* (2007) suggest that their $^{87}Sr/^{86}Sr$ and Ca/Sr trends in soils and streams on the North Slope of Alaska may reflect increases in thaw depth, particularly if the parent material and soil geochemistry are variable with depth. Furthermore, an end-member mixing analysis utilizing variability in dissolved major ion concentrations has enabled the quantitative separation of relative groundwater versus surface water influences in watersheds throughout West Siberia (Frey *et al.*, 2007b). However, it must be noted that although impacts of permafrost degradation on major ions in streams and rivers may be relatively simple, predicted concentrations and fluxes of these major ions may be confounded by future uncertainties in river discharge. Many studies show a positive relationship between DOM concentrations and discharge owing to the flushing of carbon and organic matter when moist conditions return to previously aerated soils (Christ and David, 1996; Evans *et al.*, 2002). However, the opposite is typically the case for major ions, where discharge is negatively correlated with concentrations of major ions because of dilution effects (e.g. MacLean *et al.*, 1999; Petrone *et al.*, 2006, 2007). Future potential increases in discharge and resulting dilution effects may therefore somewhat temper potential increases in major ion concentrations that are expected to occur from permafrost degradation, lowered water tables, and enhanced source water interaction with deep mineral horizons.

SUMMARY AND CONCLUSIONS

Near-surface permafrost is expected to exhibit significant degradation over the coming century, although this process may somewhat lag trends in warming surface air temperatures. Already, the thawing of near-surface permafrost and ground ice has been observed in continuous and discontinuous permafrost zones across the pan-arctic region over the past several decades. One of the most important changes to the Arctic System caused by ongoing and future warming will be the shift from a surface water-dominated system to a groundwater-dominated system. As the degradation of permafrost thaws previously frozen soils and significantly changes the flow paths of waters through the system, this may in turn have profound consequences for biogeochemical cycling in arctic watersheds. These consequences can be highly complex and undoubtedly exhibit spatial and temporal variabilities associated with current permafrost conditions, sensitivity to permafrost thaw, mode of permafrost degradation (wholesale permafrost thaw, active layer deepening, and/or thermokarst processes), and environmental characteristics of watersheds (e.g. land cover, soil type, topography).

The simplest and most consistent of these consequences across the Arctic region involves impacts of permafrost degradation on major ions in streams and rivers. In general, concentrations of major ions (e.g. Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) are predicted to increase markedly with permafrost degradation and lowering of water tables, resulting from less interaction with organic shallow soils and enhanced interaction with deep mineral horizons. Likewise, concentrations of phosphate and silicate in rivers are expected to increase. In contrast, considerable uncertainty exists about how DIN and organic matter in arctic rivers will respond to permafrost degradation. Deeper flow paths under lower permafrost conditions seem to facilitate nitrate export for sites in Alaska, but the presence or absence of permafrost shows little influence on nitrate export in watersheds in West Siberia. Impacts of permafrost degradation on organic matter in rivers are of particular interest because concentrations of organic matter in arctic rivers are some of the highest among rivers globally, owing to large-stores of organic-rich soils in the pan-arctic watershed. While organic matter export is expected to decrease in Alaskan watersheds with permafrost degradation and increased active layers depths (largely attributed to increased adsorption of DOM in mineral soils), the presence of deep, anoxic, organic-rich peat soils in West Siberia may be the reason for projections of increased organic matter export in watersheds in

DOI: 10.1002/hyp

this region. The lability and age of organic matter found in rivers are also expected to show marked changes with permafrost degradation, and may in fact be utilized as integrative measures of permafrost variability. Regardless of the uncertainties in future predictions, however, it is clear that significant impacts on biogeochemical cycling in rivers will transpire with continued warming and permafrost degradation. All of these changes in the delivery of organic matter, inorganic nutrients, and major ions to arctic rivers and ultimately to coastal waters may have important consequences for primary production and carbon cycling on arctic shelves and in the Arctic Ocean basin interior.

Although the cross-watershed comparisons emphasized throughout much of this review are helpful for thinking about potential changes in organic matter, inorganic nutrient, and major ion concentrations and export from arctic rivers as a consequence of degrading permafrost, it is important to remember that these studies may not capture key transitional dynamics. Each watershed is in a (quasi) steady state, representing concentrations and export of biogeochemical constituents under current conditions, and we cannot necessarily assume a linear trajectory between states. Increasing the number of watersheds representing different conditions (e.g. permafrost extent, topography, land cover, soil type) in a space-for-time substitution improves the chances of capturing non-linear behaviour, but logistical and analytical constraints ultimately limit temporal resolution of sampling. Important transient effects may in fact happen on very short time scales. Continued year-round sampling of the major arctic rivers as part of the Arctic Observing Network (McClelland *et al*., 2008) and establishment of long-term sampling programmes on smaller arctic rivers across the pan-arctic domain would greatly facilitate our ability to detect future changes. Changes in river export of organic matter, inorganic nutrients, and major ions as a consequence of degrading permafrost as well as other drivers are likely to differ markedly across spatial scales and geographical regions.

ACKNOWLEDGEMENTS

Funding for this research was provided to K. Frey by the NSF Arctic Sciences Division (grants 0804773 and 0732586) and to J. McClelland by the NSF Arctic System Science Program (grants 0229302 and 0436118). The authors wish to thank two anonymous reviewers for their constructive comments and suggestions.

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