

Stream geochemistry as an indicator of increasing permafrost thaw depth in an arctic watershed

Katy Keller ^{a,1}, Joel D. Blum ^{a,b,*}, George W. Kling ^b

^a Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA

^b Department of Ecology and Evolutionary Biology, University of Michigan, Ann Arbor, MI 48109, USA

ARTICLE INFO

Article history:

Received 28 October 2009

Received in revised form 9 February 2010

Accepted 11 February 2010

Editor: J. Fein

Keywords:

Permafrost

Thaw depth

Strontium isotopes

Stream water

ABSTRACT

The presence of permafrost has a strong influence on arctic hydrology, ecology, and engineering. Therefore, understanding the response of permafrost to arctic warming is critical to predicting the regional effects of global climate change. Recent research suggests that thaw depth may be increasing in response to warming, but physical thaw depth surveys in the Alaskan arctic are often not sensitive enough to detect incremental increases and cannot measure increases in the permafrost thaw bulbs beneath lakes and streams. Here we assess the use of geochemical tracers in stream water to identify changes in thaw depth in an arctic watershed. Based on marked differences in geochemistry with depth in soils and permafrost on the Alaskan North Slope, we used ⁸⁷Sr/⁸⁶Sr and elemental ratios in an arctic stream as tracers of increases in the maximum depth of soil water flow and therefore the integrated thaw depth in the watershed. From 1994 to 2004, stream water ⁸⁷Sr/⁸⁶Sr, Ca/Na, and Ca/Ba at base flow showed significant trends with time, consistent with increasing depth of soil water flowpaths. Although long time series will be necessary to identify long-term trends, stream geochemistry may be useful as a qualitative indicator of changes in thaw depth in other areas where permafrost and active layer soil geochemistry differs.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Arctic Alaskan temperature records show a mean annual increase of 2.4 °C from 1974 to 2003 (Alaska Climate Research Center, 2003). An important consequence of warming climate in these regions is increasing summer thaw depth, which is the seasonally-thawed “active layer” thickness above the permafrost. Changes in active layer thickness impact hydrology (Michel and Vaneverdingen, 1994; Rouse et al., 1997), mineral weathering and nutrient supply (Keller et al., 2007), hyporheic exchange (Greenwald et al., 2008), vegetation growth (Lloyd et al., 2003), organic carbon storage and decomposition (Waelbroek et al., 1997; Turetsky et al., 2002), and engineered structures (Nelson et al., 2001). There is considerable direct, physical evidence for increasing thaw depth and permafrost degradation in discontinuous permafrost zones (Jorgenson et al., 2001; Payette et al., 2004; Camill, 2005; Mazhitova et al., 2008). In addition, models suggest that active layer thickness in some continuous permafrost zones has already increased up to 21% over the 20th century (Chen et al., 2003), and predict further increases of up to 40% by the end of the 21st century (Stendel and Christensen, 2002).

Direct measurements of active layer thickness in some continuous permafrost regions suggest an increasing trend, but these measurements can be confounded by spatial variability and limits in methodology, which makes trends more difficult to identify. Ground-penetrating radar has been used to investigate the dependence of thaw depth on stream channel morphology (Brosten et al., 2009) but cannot detect small changes in thaw depth or measure thaw depth over an entire watershed. In the Russian arctic, a single-station measurement showed increases in active layer thickness (Pavlov and Moskalenko, 2002) and recent results from three larger thaw depth monitoring grids showed a fluctuating but generally increasing trend (Mazhitova et al., 2008). In North America, temperature increases of 2–4 °C have been observed since 1977 at still-frozen depths in the continuous permafrost of arctic Alaska (Osterkamp, 2005). Yet out of 12 thaw depth surveys from the continuous permafrost zone of arctic Alaska, only two surveys (near Barrow, Alaska, USA) showed a weak trend of increasing active layer thickness (Brown et al., 2000; Hinkel and Nelson, 2003). These large-scale thaw depth surveys are complicated by spatial heterogeneity in active layer thickness caused by variability in soil moisture content, small-scale topography, and larger landscape features (Hinkel and Nelson, 2003).

Because of the spatial variability in active layer thickness, traditional thaw depth surveys, which make many physical measurements over a large area using graduated steel probes, are not sensitive enough to detect small changes in active layer thickness over time. For example, over a 1 km² watershed near Toolik Lake in arctic Alaska,

* Corresponding author. Tel.: +1 734 615 3242.

E-mail address: jdblum@umich.edu (J.D. Blum).

¹ Current address. Shell Exploration and Production, Houston, TX 77079, USA.

mean August thaw depth from 1990 to 2005 was 38.7 cm and the mean standard deviation of these yearly measurements was 8.8 cm or about 23% of the mean ($n = 3551$ total measurements; 170–288 measurements per year) (Arctic Long Term Ecological Research Site, 2005a). Graduated probe measurements are also made relative to the ground surface elevation, which fluctuates due to freezing and thawing and locally can cause the surface to undergo permanent displacement (Hinkel and Hurd, 2006). Perhaps most importantly, increases in active layer thickness may be concentrated in areas where thaw depth is difficult to measure. For example, thaw bulbs (areas of thawed ground beneath lakes and streams) are likely locations for active layer thickness increases because hyporheic waters have been shown to be important conduits of heat transfer in permafrost zones (Conovitz et al., 2006). Here, as an alternative to traditional physical measurements of thaw depth, we report on the use of geochemical tracers in stream water that spatially integrate over the watershed, avoiding difficulties caused by small-scale spatial variation and physical barriers, and potentially allowing detection of small increases in thaw depth.

In a recent study, Keller et al. (2007) found that permafrost and infrequently thawed soils in arctic Alaska that are developed on glacial till surfaces have substantially higher concentrations of carbonate minerals than the more weathered soils in the seasonally-thawed active layer above them. Because the carbonate content increases with depth in the soil and permafrost profile, in the case of increasing active layer thickness water travelling along the deepest soil flowpath would be expected to incorporate increasing proportions of carbonate weathering products, and this should be reflected in the chemistry of stream waters. Keller et al. (2007) demonstrated that leaching of these infrequently thawed soils predominantly released carbonate weathering products and that the carbonate dissolution dominated over ion exchange and other contributions.

Strontium isotope, Ca/Na and Ca/Ba ratios have been used extensively to trace water sources and hydrologic flowpaths (Bullen and Kendall, 1998; Land and Ohlander, 2000; Aubert et al., 2002; Bailey et al., 2003; Hogan and Blum, 2003; Negrel and Petelet-Giraud, 2004) and are often more sensitive to subtle changes in mineral weathering contributions to ground water than elemental concentrations (see review by Blum and Erel, 2004). In this study we have investigated the use of these geochemical tracers in stream water as qualitative indicators of increases in the maximum depth of soil water flow and integrated thaw depth across the same arctic Alaskan watershed studied in detail for soil geochemistry by Keller et al. (2007).

2. Study area

We measured dissolved major and minor element concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of summer stream water samples collected manually over eleven summers from Toolik Inlet stream just above where it enters Toolik Lake ($68^{\circ}38'\text{N}$, $149^{\circ}36'\text{W}$, Fig. 1) in the foothills of the North Slope of the Brooks Range, Alaska, USA. Toolik Inlet stream is a third-order tundra stream draining a 46.6 km^2 watershed that includes several lakes (Kling et al., 2000). The watershed is dominated by upland tussock tundra vegetation, and includes riparian birch-willow and wet sedge vegetation.

The soils are developed on two relatively young glacial till and outwash deposits comprised primarily of sedimentary rocks, including carbonates and silicates (Mull and Adams, 1985; Hamilton, 2003; Keller et al., 2007). Glacial till of the Itkillik 1 glaciation (roughly 100–50 ka in age) is found mainly on ridges, and glacial till and outwash of the Itkillik 2 glaciation (roughly 25–10 ka in age) is found mainly in the stream valley (Fig. 1). The soils are gelisols (Munroe and Bockheim, 2001) and consist of a thick organic layer, which is the primary soil water flowpath early in the thawed season and during high-flow periods, overlying mineral soil with lower hydrologic conductivity (Hinzman et al., 1991).

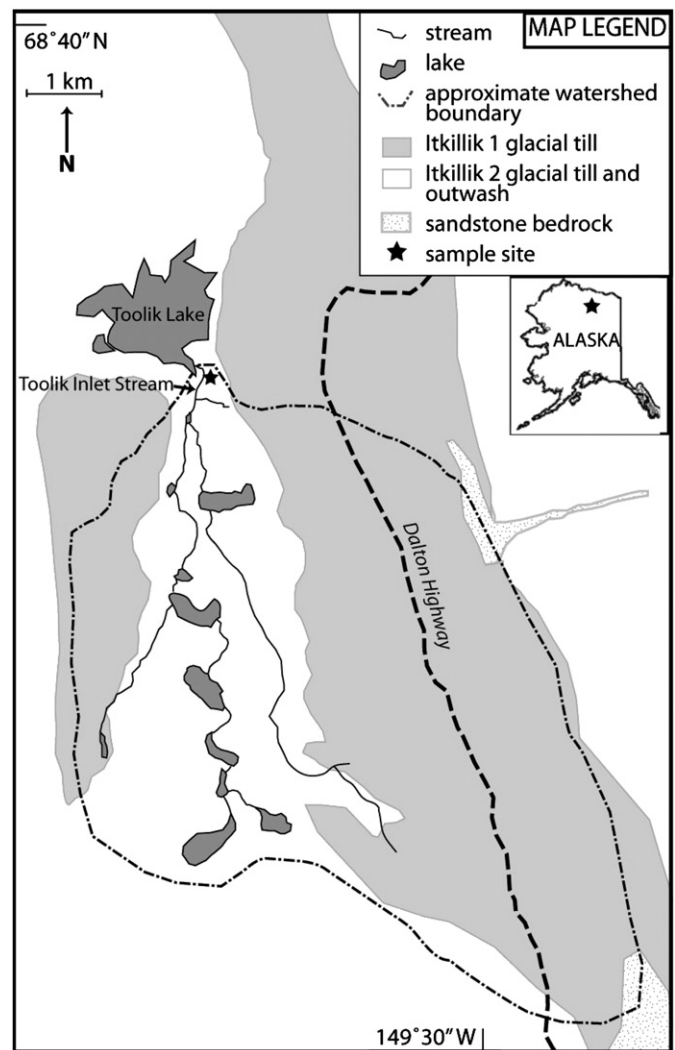


Fig. 1. Map of Toolik Inlet stream watershed and the sampling site from which water was collected weekly during the summer. The area covered by the Itkillik 1 (older) and Itkillik 2 (younger) glacial till and outwash surfaces, referred to in Fig. 2, are also shown.

Summer thaw lasts from late May through September and during this time the active layer thickness reaches a maximum of 0.3 to 1.0 m (Kling et al., 2000). This watershed is transected by a two-lane gravel road (the Dalton Highway) and an elevated section of the Trans-Alaska Pipeline (Fig. 1), which were completed in 1977 and have been relatively unchanged since then; thus, we believe they do not have a significant influence on the time-dependent trends of interest in this study.

3. Previous work on soil chemistry

The chemistry of soils in the Toolik Inlet stream watershed has been studied extensively with emphasis on strontium isotope and cation element ratios as tracers of mineral weathering (Keller et al., 2007). The chemistry of the exchangeable soil fraction and the cold 1 M HNO_3 soil digest were shown to be well correlated across all geomorphic surfaces, and Keller et al. (2007) argued that the 1 M HNO_3 soil digest was the best estimate of the “easily weatherable,” mostly carbonate fraction of the mineral soil. In the “easily weatherable” soil fraction Ca/Na and Ca/Ba ratios generally increase, while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decrease, with depth in soil profiles and reach their extremes in the deepest soil samples collected in permafrost. The mean values for $^{87}\text{Sr}/^{86}\text{Sr}$, Ca/Na, and Ca/Ba ratios from Keller et al. (2007) for soils from the geomorphic surfaces in the Toolik Inlet

stream watershed are plotted as a function of soil depth in Fig. 2. Based on these patterns in soil chemistry, Keller et al. (2007) suggested that an increase in active layer thickness would be expected to result in increasing Ca/Na and Ca/Ba, and decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ in deep soil flowpath contributions to stream water.

4. Methods and data analysis

Toolik Inlet stream stage height and flow measurements were recorded every 30 s on a datalogger and averaged hourly to calculate discharge (Arctic Long Term Ecological Research Site, 2005b). Stream water was sampled weekly during the summers of 1994–2004, excluding 1995 when no sample collection occurred at this site. Stream water was collected manually and filtered during collection through either borosilicate glass fiber filters (1994–2001) or 0.45 μm polypropylene filters (2002–2004). Samples were acidified with trace-metal grade (1994–2001, 2004) or ultrapure HCl (2002–2003)

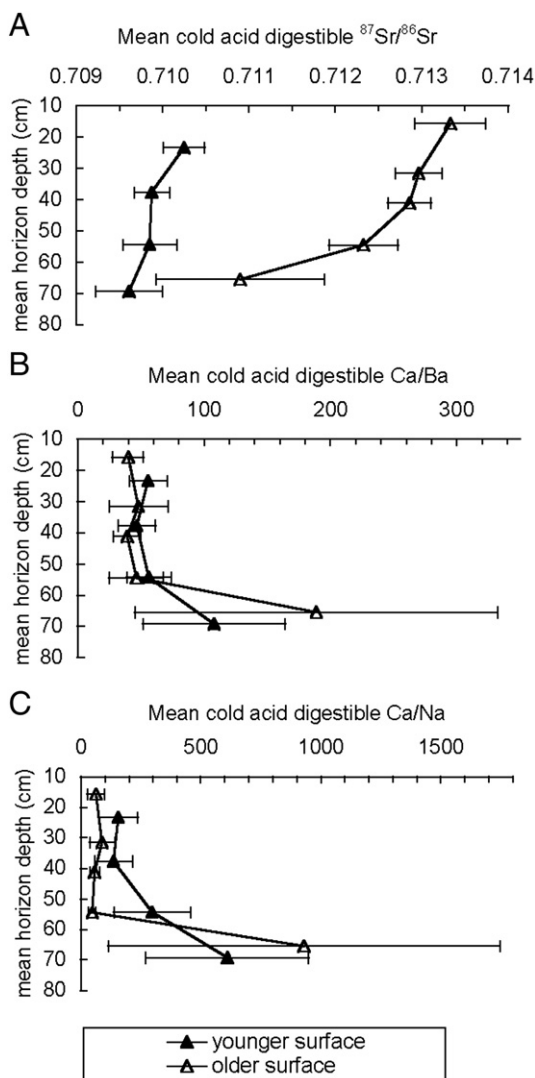


Fig. 2. Mean 1 N HNO_3 cold acid-digestible A) $^{87}\text{Sr}/^{86}\text{Sr}$, B) Ca/Ba, and C) Ca/Na of each mineral soil horizon versus mean horizon depth for the older and younger geomorphic surfaces developed on glacial till underlying the Toolik Inlet stream watershed. The lowermost points on each surface represent permafrost. Elemental ratios are calculated from measurements made in mol/g with an analytical error of $\pm 7\%$; $^{87}\text{Sr}/^{86}\text{Sr}$ analytical error (2σ) is ± 0.000040 . Error bars represent standard error ($n=3$) of three separate soil profiles collected at different locations within the watershed on each geomorphic surface. Detailed data, methods and soil sampling locations are reported in Keller et al. (2007).

immediately after collection and refrigerated at 4°C in the dark until analysis. Four replicate stream samples were taken in 2002 to test for differences in results between samples collected using borosilicate glass filters and trace-metal grade acid versus those collected using polypropylene filters and ultrapure acid. No significant differences in $^{87}\text{Sr}/^{86}\text{Sr}$ between the paired samples were found in a paired t -test ($p=0.8$); only one of the four sample pairs had $^{87}\text{Sr}/^{86}\text{Sr}$ values that differed by more than the 2σ analytical error, and they differed by less than 0.00006.

Samples were analyzed for elemental concentrations by inductively coupled plasma optical emission spectrometry. One in-house standard and two NIST traceable commercial standards were used for quality control; these standards were analyzed to within $\pm 7\%$ of the known value for the base cations (Ca, Mg, Na, K) as well as the alkaline earth trace elements Ba and Sr. Strontium was separated by elution through Sr-specific resin (Eichrom) in quartz cation exchange columns and approximately 75 ng of Sr was loaded onto a tungsten filament with Ta_2O_5 powder. The Sr isotopic ratio was determined by thermal ionization mass spectrometry using a Finnigan MAT 262. Internal precision ($\pm 2\sigma$) of 100–200 ratios for each sample was less than ± 0.000035 , and replicate analyses of NBS987 yielded $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710231 ± 0.000016 ($2\sigma, n=112$) during the period of these analyses.

5. Results and discussion

When all Toolik Inlet stream water samples for July–August from 1994 to 2004 are considered, we observe a positive linear correlation between Toolik Inlet stream water $^{87}\text{Sr}/^{86}\text{Sr}$ values and the natural log of stream discharge ($R^2=0.41, p<0.0001, n=87$; Fig. 3A). When the data set is restricted to “low discharge” samples taken when discharge was less than the 1994 to 2004 summer (June 1–August 21) mean discharge of $1.1 \text{ m}^3/\text{s}$, $^{87}\text{Sr}/^{86}\text{Sr}$ is less strongly correlated to discharge ($R^2=0.24, p<0.0001, n=58$; Fig. 3B). This correlation is observed because precipitation events cause saturation of the organic mat and shallow soils, which have high acid-digestible $^{87}\text{Sr}/^{86}\text{Sr}$ ratios due to depletion of calcite from the active layer by weathering, resulting in a $^{87}\text{Sr}/^{86}\text{Sr}$ signal dominated by silicate weathering and atmospheric deposition (Keller et al., 2007; Fig. 2). The high $^{87}\text{Sr}/^{86}\text{Sr}$ signal of

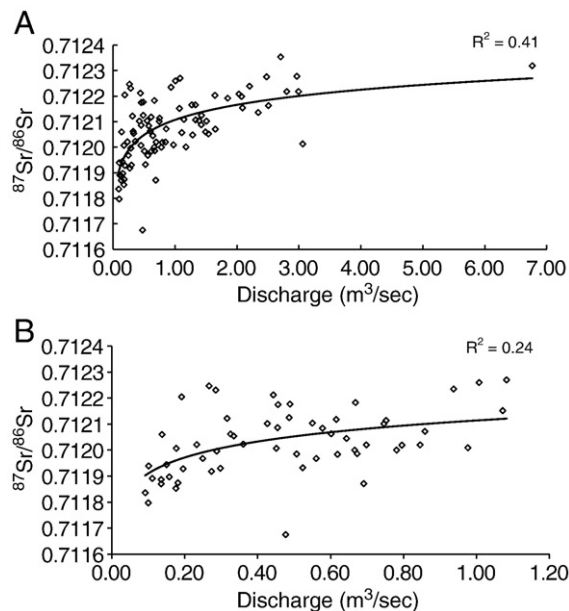


Fig. 3. Toolik Inlet stream water $^{87}\text{Sr}/^{86}\text{Sr}$ versus discharge for July–August, with regressions using log-normalized discharge. A) Samples collected at all values of discharge: $R^2=0.41, p<0.0001, n=87$ samples. B) Samples collected at below mean ($<1.1 \text{ m}^3/\text{s}$) summer discharge: $R^2=0.24, p<0.0001, n=58$ samples.

water from these shallow and overland flowpaths is believed to overwhelm the geochemical signal of deep flowpaths, which we have argued may be indicative of changes in active layer thickness.

To better isolate the potential effects of annual changes in stream water chemistry caused by increasing maximum thaw depth, and minimize the variations caused by dilution of deep flowpath geochemical signals by overland or shallow flow, we restricted the data set to samples taken during July and August during “low-discharge” ($<1.1 \text{ m}^3/\text{s}$) conditions for the purposes of determining changes in stream water chemistry over time as related to permafrost melting. As a result of this restriction, all 2003 samples are eliminated due to high discharge on each weekly sampling date. Mean values of low-discharge $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and elemental concentrations for July and August of each year of the study are summarized in Table 1.

Between 1994 and 2004, the mean values of late summer Toolik Inlet stream water $^{87}\text{Sr}/^{86}\text{Sr}$ decreases significantly (i.e., $p < 0.05$) with time as shown by linear regression (Fig. 4A; $R^2 = 0.62$, $p = 0.01$). Over the same time period, there are marginally significant increases in late summer stream water for both Ca/Ba (Fig. 4B; $R^2 = 0.46$, $p = 0.046$) and Ca/Na (Fig. 4C; $R^2 = 0.48$, $p = 0.038$). However, when the first and last years of the eleven summer time series are excluded, the correlations between $^{87}\text{Sr}/^{86}\text{Sr}$, Ca/Ba and Ca/Na with time are not significant (i.e., $p > 0.05$). This suggests that long time series (greater than the seven summers of data from 1996 to 2002) are needed to draw conclusions about changing stream water chemistry in the Toolik Inlet stream, and also points out the equivocal nature of the potential long-term chemical trends and their interpretation. Over the eleven summer period sampled, there are statistically significant changes in stream water chemistry, but this may or may not be related to long-term changes in climate. The maximum active layer thickness is influenced by seasonal temperature patterns and snowpack properties as well as annual mean temperature. It is therefore possible that the long-term trend we observe is actually a result of 1994 and 2004 being unusual years with anomalously shallow and deep thaw layers, respectively; however, what is clear is the relationship between deeper flowpaths and lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Ca/Sr ratios for the same stream water samples do not show a significant trend with time over the eleven summer study period ($p \gg 0.05$); there is generally no change in mean Ca/Sr except for the year 2002, which has a highly anomalous value. We note that both Ca and Sr inputs are dominated by carbonate weathering and their ratio generally remains constant. In contrast, Na and Ba are dominated by silicate weathering (Keller et al., 2007) and the increasing Ca/Na and Ca/Ba ratios indicate an increasing ratio of carbonate to silicate

weathering over time, which is consistent with the idea that water flowpaths are increasingly reaching deeper, more carbonate-rich mineral soils.

One possible alternate explanation for the observed geochemical trends with time is that they are related to changing patterns of stream discharge. But this explanation seems unlikely because there is no correlation between year and discharge when samples were taken, either for the low-discharge sample set ($p \gg 0.05$) or for the entire July–August sample set ($p \gg 0.05$). Another possible alternate explanation for the observed geochemical trends is that runoff from the younger geomorphic surface has become a proportionally more important component of base flow than runoff from the older surface. We cannot, however, think of any reason why this would occur over the eleven summer time span and we consider this explanation to be unlikely.

The observed geochemical trends with time are, however, consistent with a greater influence of carbonate dissolution (compared to silicate dissolution and atmospheric input) on stream geochemistry as a result of increasing depth of water flowpaths, indicating increasing thaw depth with time. When glacial deposits containing carbonate and silicate materials are exposed to water, carbonate dissolution is highly accelerated relative to silicate dissolution (Blum et al., 1998; Anderson et al., 2000; Jacobson et al., 2002). Enhanced carbonate versus silicate dissolution has also been observed experimentally in the early stages of weathering, even for silicate rocks with only a small amount of carbonate (Erel et al., 2004; White et al., 2005).

The trends in stream geochemistry suggest that seasonally and spatially integrated thaw depth has increased in the Toolik Inlet stream watershed from 1994 to 2004, but they do not indicate where in the watershed or to what extent. Thaw depth increases could be relatively uniform across the watershed or spatially patchy, occurring predominantly in the thaw bulbs under surface water bodies or other places where the insulating soil organic mat is thin. It is also possible that some of the observed geochemical trend is due to an earlier and longer seasonal thaw of deep active layer soils; however, this scenario could not explain the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios over time, and it would also likely result in an increase in thaw depth due to a longer time for heat transfer through these soils into the upper permafrost.

The geochemical changes we observe in stream water suggest that thaw depth has increased over the eleven summer observation period, although we cannot rule out the possibility that 1994 and 2004 were anomalous years. The years when stream chemistry suggest deep thaw layers could result from either a thin layer of previously unfrozen material that is reacting extensively with soil

Table 1
Yearly mean cation and Sr isotope values in low-discharge ($<1.1 \text{ m}^3/\text{s}$) Toolik Inlet stream water.

Year	Ba $\mu\text{mol/L}$ $\pm 1\text{SD}$	Ca mmol/L $\pm 1\text{SD}$	K mmol/L $\pm 1\text{SD}$	Mg mmol/L $\pm 1\text{SD}$	Na mmol/L $\pm 1\text{SD}$	Si mmol/L $\pm 1\text{SD}$	Sr $\mu\text{mol/L}$ $\pm 1\text{SD}$	$^{87}\text{Sr}/^{86}\text{Sr}$ $\pm 1\text{SD}$
1994	0.201 0.051	0.269 0.042	0.00400 0.00058	0.0570 0.0109	0.0150 0.0014	0.0280 0.0030	0.224 0.037	0.712190 0.000070
1996	0.095 0.009	0.273 0.047	0.00400 0.00089	0.0580 0.0107	0.0130 0.0015	0.0260 0.0067	0.226 0.035	0.712079 0.000103
1997	0.128 0.062	0.275 0.024	0.00400 0.00102	0.0580 0.0047	0.0140 0.0011	0.0290 0.0100	0.229 0.021	0.712066 0.000064
1998	0.165 0.056	0.367 0.035	0.00400 0.00058	0.0760 0.0075	0.0170 0.0015	0.0340 0.0044	0.299 0.027	0.711946 0.000089
1999	0.156 0.091	0.338 0.032	0.00400 0.00067	0.0730 0.0051	0.0170 0.0007	0.0340 0.0036	0.279 0.025	0.711984 0.000080
2000	0.128 0.033	0.333 0.094	0.00500 0.00062	0.0660 0.0112	0.0180 0.0077	0.0270 0.0039	0.258 0.045	0.711927 0.000148
2001	0.091 0.006	0.272 0.029	0.00500 0.00069	0.0580 0.0074	0.0130 0.0010	0.0220 0.0031	0.226 0.022	0.712025 0.000069
2002	0.103 0.018	0.318 0.046	0.00400 0.00031	0.0670 0.0100	0.0160 0.0044	0.0230 0.0012	0.261 0.036	0.711992 0.000094
2004	0.091 0.009	0.282 0.032	0.00500 0.00128	0.0590 0.0064	0.0120 0.0012	0.0280 0.0091	0.236 0.026	0.711924 0.000092

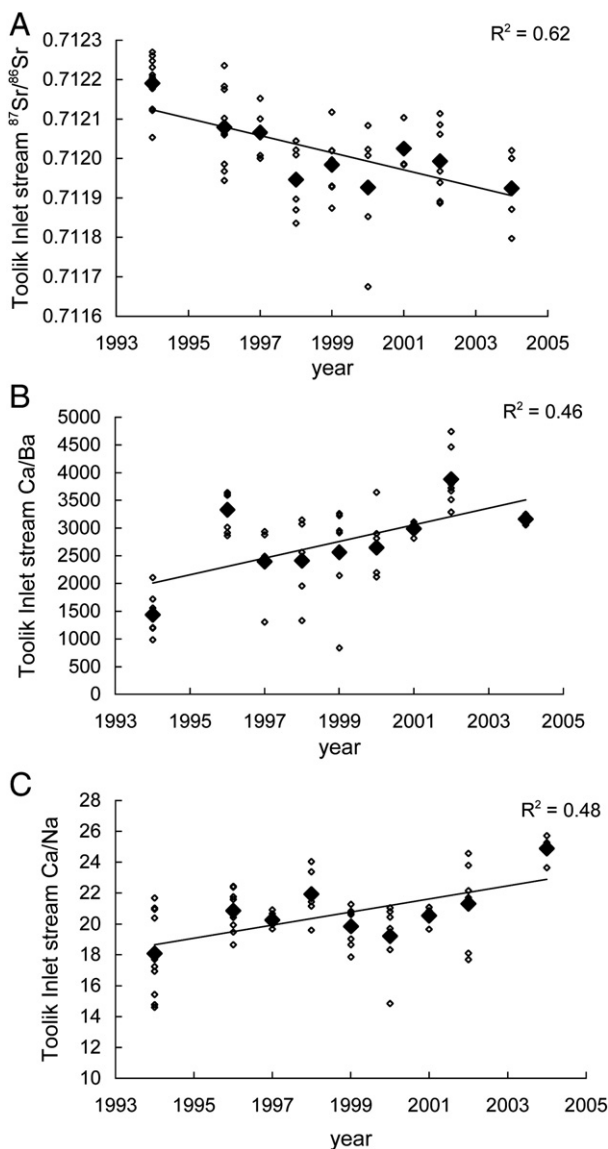


Fig. 4. Toolik Inlet stream July–August low-discharge ($<1.1 \text{ m}^3/\text{s}$) stream water geochemistry versus year. A) $^{87}\text{Sr}/^{86}\text{Sr}$: $R^2 = 0.36$, $p < 0.0001$, $n = 58$ total samples shown by small open diamonds; $R^2 = 0.62$, $p = 0.012$, $n = 9$ yearly means shown by large filled diamonds; B) Ca/Ba: $R^2 = 0.32$, $p < 0.0001$, $n = 58$ total samples (open diamonds); $R^2 = 0.46$, $p = 0.046$, $n = 9$ yearly means (filled diamonds); and C) Ca/Na: $R^2 = 0.26$, $p < 0.0001$, $n = 58$ total samples (open diamonds); $R^2 = 0.48$, $p = 0.038$, $n = 9$ yearly means (filled diamonds). Elemental ratios are calculated from measurements made in mol/L. $^{87}\text{Sr}/^{86}\text{Sr}$ error (2σ) is less than ± 0.000035 . Propagated analytical error for elemental ratios is less than $\pm 10\%$.

solution, or a thicker layer that is reacting incompletely. We constrained the minimum thickness of active layer increase needed to cause the observed stream water $^{87}\text{Sr}/^{86}\text{Sr}$ changes with a simple mass balance calculation based on the end-member assumption that all newly thawed soil carbonate completely reacted with soil water each season. We estimated the July and August flux of Sr from Toolik Inlet stream (for July–August mean $Q = 1.2 \text{ m}^3/\text{s}$, $[\text{Sr}] = 0.23 \mu\text{mol}/\text{L}$). We then calculated the amount of Sr with the $^{87}\text{Sr}/^{86}\text{Sr}$ of the upper permafrost necessary to produce the observed trend, assuming that the younger surface covers 34% of the watershed, and the remainder is covered by the older surface (Hamilton, 2003). The amount and $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by a 1 M HNO_3 digest of soil and permafrost (Keller et al., 2007) was used to estimate the maximum effect of soil thawing on stream chemistry. Averaging over the entire watershed (46.6 km^2) we find that only 0.6 mm of permafrost would have to thaw between 1994 and 2004 and completely react with soil water to produce the

observed chemical effect on stream water. Because natural waters are far less acidic than the laboratory digest used for the calculations, this is clearly a minimum estimate of the newly thawed layer thickness. The data could also be explained by, for instance, 60 mm of permafrost from which only 1% of the calcite has been leached over the observation period. Because there are still carbonate minerals present in active layer soils that are thousands of years old (Keller et al., 2007), a thicker layer almost certainly has thawed and only partially reacted with soil waters, but it is not possible at this time to estimate its thickness. In addition, thaw is likely to be spatially heterogeneous and perhaps concentrated beneath lakes and streams or in other areas with reduced organic mat thickness. Despite the simplified nature of our calculation, it illustrates that a small amount of permafrost thaw could produce changes in stream geochemistry, yet be too small or physically inaccessible to detect by traditional measurements of thaw depth.

6. Implications and conclusions

The geochemical method we used here to detect a change in thaw depth across the Toolik Inlet stream watershed may be applicable to other permafrost areas where streams are (or were) sampled regularly. Soil geochemical profiles of different landscape surfaces on the North Slope have increasing carbonate content with depth (Keller et al., 2007), and in the Canadian Arctic on a contrasting type of parent material, soils also have been shown to have depth-dependent geochemical profiles (Kokelj et al., 2002). Less-intensely weathered soil at depth may provide geochemical gradients in many permafrost regions sufficient to cause changes in stream geochemistry as a result of changes in active layer thickness. Based on the results of this study, we propose that (1) thaw depth has increased in this part of the Arctic and has influenced surface water chemistry, although we do not know the extent to which the eleven summer observation period represents a “long-term” trend, and (2) stream geochemistry provides a sensitive, albeit qualitative, indicator of thaw depth that may be useful in many areas as a compliment or an alternative to physical thaw depth surveys.

Acknowledgements

This study was supported by the National Science Foundation grants DEB-0423385, DEB 97-26837, ATM-0439620, and ARC-0435893. Field work was supported by a student grant from the Geological Society of America to K. Keller. We thank two anonymous reviewers of this manuscript and B. Kennedy and T. Bullen for thoughtful comments on an earlier version of this manuscript.

References

- Alaska Climate Research Center, 2003. Temperature Change in Alaska 1974–2003. <http://climate.gi.alaska.edu/ClimTrends/Change/7403Change.html>.
- Anderson, S.P., Drever, J.I., Frost, C.D., Holden, P., 2000. Chemical weathering in the foreland of a retreating glacier. *Geochimica et Cosmochimica Acta* 64, 1173–1189.
- Arctic Long Term Ecological Research Site, 2005a. Biannual Thaw Depth Survey Data. <http://ecosystems.mbl.edu/ARC/>.
- Arctic Long Term Ecological Research Site, 2005b. Toolik Lake Inlet Stream Discharge Measurements. <http://ecosystems.mbl.edu/ARC/>.
- Aubert, D., Probst, A., Stille, P., Viville, D., 2002. Evidence of hydrologic control of Sr behavior in stream water (Strengbach catchment, Vosges mountains, France). *Applied Geochemistry* 17, 285–300.
- Bailey, S.W., Buso, D.C., Likens, G.E., 2003. Implications of sodium mass balance for interpreting the calcium cycle of a northern hardwood ecosystem. *Ecology* 84, 471–484.
- Blum, J.D., Erel, Y., 2004. Radiogenic isotopes in weathering and hydrology. In: Drever, J.I. (Ed.), *Surface and Ground water: Weathering, and Soils*, Volume 5: Treatise on Geochemistry. Elsevier-Perigamon, Oxford, pp. 365–392.
- Blum, J.D., Gazis, C.A., Jacobson, A., Chamberlain, C.P., 1998. Carbonate versus silicate weathering rates in the Raikot Watershed within the High Himalayan Crystalline Series. *Geology* 26, 411–414.

- Brosten, T.R., Bradford, J.H., McNamara, J.P., Gooseff, M.N., Zarnetske, J.P., Bowden, W.B., Johnston, M.E., 2009. Estimating 3D variation in active-layer thickness beneath arctic streams using ground-penetrating radar. *Journal of Hydrology* 373, 479–486.
- Brown, J.G., Kling, G.W., Hinkel, K.M., Hinzman, L.D., Nelson, F.E., Romanovsky, V., Shiklomanov, N.I., 2000. Arctic Alaska and Seward Peninsula. In: Brown, J.G., Hinkel, K.M., Nelson, F.E. (Eds.), *The Circumpolar Active Layer Monitoring (CALM) Program: Research Designs and Initial Results*. Polar Geography, 24, pp. 165–258.
- Bullen, T.D., Kendall, C., 1998. Tracing of weathering reactions and water flowpaths: a multi-isotope approach. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier Science, Amsterdam, The Netherlands, pp. 611–646.
- Camill, P., 2005. Permafrost thaw accelerates in boreal peatlands during late-20th century climate warming. *Climatic Change* 68, 135–152.
- Chen, W., Zhang, Y., Cihlar, J., Smith, S., Riseborough, D., 2003. Changes in soil temperature and active layer thickness during the twentieth century in a region in western Canada. *Journal of Geophysical Research-Atmospheres* 108 Art. No. 4696.
- Conovitz, P.A., MacDonald, L.H., McKnight, D.M., 2006. Spatial and temporal active layer dynamics along three glacial meltwater streams in the McMurdo Dry Valleys, Antarctica. *Arctic Antarctic and Alpine Research* 38, 42–53.
- Erel, Y., Blum, J.D., Roueff, E., Ganor, J., 2004. Lead and strontium isotopes as monitors of experimental granitoid mineral dissolution. *Geochimica et Cosmochimica Acta* 68, 4649–4663.
- Greenwald, M.J., Bowden, W.B., Gooseff, M.N., Zarnetske, J.P., McNamara, J.P., Bradford, J.K., Brosten, T.R., 2008. Hyporheic exchange and water chemistry of two arctic tundra streams of contrasting geomorphology. *Journal of Geophysical Research* 113, G02029.
- Hamilton, T.D., 2003. *Glacial Geology of Toolik Lake and the Upper Kuparuk River Region*. Alaska Geobotany Center, Institute of Arctic Biology, University of Alaska Fairbanks, Fairbanks, Alaska. 24 p.
- Hinkel, K.M., Hurd, J.K., 2006. Permafrost destabilization and thermokarst following snow fence installation, Barrow, Alaska, U.S.A. *Arctic, Antarctic, and Alpine Research* 38, 530–539.
- Hinkel, K.M., Nelson, F.E., 2003. Spatial and temporal patterns of active layer thickness at Circumpolar Active Layer Monitoring (CALM) sites in northern Alaska, 1995–2000. *Journal of Geophysical Research-Atmospheres* 108 Art. No. 8168.
- Hinzman, L.D., Kane, D.L., Gieck, R.E., Everett, K.R., 1991. Hydrologic and thermal-properties of the active layer in the Alaskan Arctic. *Cold Regions Science and Technology* 19, 95–110.
- Hogan, J.F., Blum, J.D., 2003. Tracing hydrologic flow paths in a small forested watershed using variations in $^{87}\text{Sr}/^{86}\text{Sr}$, $[\text{Ca}]/[\text{Sr}]$, $[\text{Ba}]/[\text{Sr}]$ and $\delta^{18}\text{O}$. *Water Resources Research* 39.
- Jacobson, A.D., Blum, J.D., Chamberlain, C.P., Poage, M., Sloan, V., 2002. The Ca/Sr and Sr isotope systematics of a Himalayan glacial chronosequence: carbonate versus silicate weathering rates as a function of landscape surface age. *Geochimica et Cosmochimica Acta* 66, 13–27.
- Jorgenson, M.T., Racine, C.H., Walters, J.C., Osterkamp, T.E., 2001. Permafrost degradation and ecological changes associated with a warming climate in central Alaska. *Climatic Change* 48, 551–579.
- Keller, K., Blum, J.D., Kling, G.W., 2007. Geochemistry of soils and streams on surfaces of varying ages in arctic Alaska. *Arctic, Antarctic, and Alpine Research* 39, 84–98.
- Kling, G.W., Kipphut, G.W., Miller, M.M., O'Brien, W.J., 2000. Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. *Freshwater Biology* 43, 477–497.
- Kokelj, S.V., Smith, C.A.S., Burn, C.R., 2002. Physical and chemical characteristics of the active layer and permafrost, Herschel Island, western Arctic Coast, Canada. *Permafrost and Periglacial Processes* 13, 171–185.
- Land, M., Ohlander, B., 2000. Chemical weathering rates, erosion rates and mobility of major and trace elements in a boreal granitic till. *Aquatic Geochemistry* 6, 435–460.
- Lloyd, A.H., Yoshikawa, K., Fastie, C.L., Hinzman, L.D., Fraver, M., 2003. Effects of permafrost degradation on woody vegetation at arctic treeline on the Seward Peninsula, Alaska. *Permafrost and Periglacial Processes* 14, 93–101.
- Mazhitova, G., Malkova, G., Chestnykh, O., Zamolodchikov, D., 2008. Recent decade thaw-depth dynamics in the European Russian Arctic, based on the Circumpolar Active Layer Monitoring (CALM) data. Ninth international conference on Permafrost Proceedings, 9, pp. 1155–1160.
- Michel, F.A., Vanoverdingen, R.O., 1994. Changes in hydrogeologic regimes in permafrost regions due to climatic-change. *Permafrost and Periglacial Processes* 5, 191–195.
- Mull, C.G., Adams, K.E., 1985. *Bedrock Geology of the Eastern Koyukuk Basin, Central Brooks Range, and East Central Arctic Slope along the Dalton Highway, Yukon River to Prudhoe Bay*. Department of Natural Resources, Division of Geological and Geophysical Surveys, Anchorage, Alaska. 309 p.
- Munroe, J.S., Bockheim, J.G., 2001. Soil development in low-arctic tundra of the northern Brooks Range, Alaska, USA. *Arctic and Alpine Research* 33, 78–87.
- Negrel, P., Petelet-Giraud, E., 2004. Strontium isotopes as tracers of ground-water-induced floods: the Somme case study (France). *Journal of Hydrology* 305, 99–119.
- Nelson, F.E., Anisimov, O.A., Shiklomanov, N.I., 2001. Subsidence risk from thawing permafrost. *Nature* 410, 889–890.
- Osterkamp, T.E., 2005. The recent warming of permafrost in Alaska. *Global and Planetary Change* 49, 187–202.
- Pavlov, A.V., Moskalenko, N.G., 2002. The thermal regime of soils in the north of Western Siberia. *Permafrost and Periglacial Processes* 13, 43–51.
- Payette, S., Delwaide, A., Caccianiga, M., Beauchemin, M., 2004. Accelerated thawing of subarctic peatland permafrost over the last 50 years. *Geophysical Research Letters* 31 Art.No. L18208.
- Rouse, W.R., Douglas, M.S.V., Hecky, R.E., Hershey, A.E., Kling, G.W., Lesack, L., Marsh, P., McDonald, M., Nicholson, B.J., Roulet, N.T., Smol, J.P., 1997. Effects of climate change on the freshwaters of arctic and subarctic North America. *Hydrological Processes* 11, 873–902.
- Stendel, M., Christensen, J.H., 2002. Impact of global warming on permafrost conditions in a coupled GCM Art. No. 1632 *Geophysical Research Letters* 29.
- Turetsky, M.R., Wieder, R.K., Vitt, D.H., 2002. Boreal peatland C fluxes under varying permafrost regimes. *Soil Biology and Biochemistry* 34, 907–912.
- Waelbroek, C., Monfray, P., Oechel, W.C., Hastings, S., Vourlitis, G., 1997. The impact of permafrost thawing on the carbon dynamics of tundra. *Geophysical Research Letters* 24, 229–232.
- White, A.F., Schulz, M.S., Lowenstern, J.B., Vivit, D.V., Bullen, T.D., 2005. The ubiquitous nature of accessory calcite in granitoid rocks: implications for weathering, solute evolution, and petrogenesis. *Geochimica et Cosmochimica Acta* 69, 1455–1471.