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Effect of atmospheric deposition and weathering on trace element concentrations in glacial meltwater at Grand Teton National Park, Wyoming, U.S.A.

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A B S T R A C T

Glaciers are reservoirs of atmospherically deposited trace elements that are released during melt. Weathering in glacial environments also contributes solutes to proglacial streams. To investigate the relative importance of atmospheric deposition and weathering on trace element chemistry of glacial streams, we sampled supraglacial and proglacial meltwater at two glacierized catchments in Grand Teton National Park, Wyoming, which is located downwind of agricultural/industrial emissions and dust sources. Concentrations of major ions (Mg^{2+} , K^+ , Na^+ , Ca^{2+} , SO_4^{2-}), alkalinity, conductivity, and a subset of trace elements (U, Mo, Sr, Rb, Li, Ba) were low in supraglacial meltwater but increased in proglacial streams because of water-rock interactions. In contrast, concentrations of the trace metals Mn, Co, Zn, Pb, Cd, and Hg had relatively high concentrations in supraglacial meltwater and decreased downstream. These metals are not abundant in the local bedrock and thus are likely sourced from atmospheric deposition. Stable isotopes indicated different water sources in July (snowmelt-dominated) and August (ice melt-dominated), but water chemistry was similar during both months, indicating similar composition of recent snowfall and older ice. These findings have implications for evaluating the relative impacts of atmospheric deposition and weathering in glacier- and snow-dominated catchments.

INTRODUCTION

The retreat of glaciers worldwide may lead to the rapid release of trace metals that are stored in the ice (Schuster et al., 2002; Barbante et al., 2004; Hong et al., 2004; Fortner et al., 2005, 2009). Metals and other solutes released from the thawing cryosphere can impact the hydrologic system, resulting in changing water chemistry because of melting glaciers (Salerno et al., 2016), permafrost (Schuster et al., 2011; Todd et al., 2012), and rock glaciers (Thies et al., 2007). Trace metals are deposited in alpine environments via wet and dry atmospheric deposition, with important contributions from windblown dust (Reynolds et al., 2010; Carling et al., 2012) and industrial activities

(Hong et al., 2004). For example, maximum Hg concentrations in an ice core from the Wind River Range, Wyoming, were found in ice from the 1960s to 1980s because of mining and industrialization (Schuster et al., 2002). Thus, glaciers may act as a reservoir of anthropogenically derived elements that are released during melt (Fortner et al., 2009). Receding glaciers also expose readily weathered fresh bedrock and glacial till that may contribute to elevated metal concentrations in proglacial streams (Fortner et al., 2011). As the rate of glacier melt continues to accelerate, trace metal concentrations in meltwater need to be evaluated for contributions from atmospheric deposition and interactions with freshly weathered bedrock in the proglacial environment.

Glacierized watersheds are under increasing stress from the combined effects of climate change and atmospheric deposition of anthropogenic aerosols. For example, glacier runoff can cause enrichment of reactive N in high elevation lakes (Saros et al., 2010) and may be a source of Hg for osprey that live at high elevations of the Canadian Rockies (Guigueno et al., 2012). Glaciers on the Tibetan Plateau are currently an important sink in the global Hg cycle, but with a warming climate they may become a Hg source that could endanger ecosystems and human health in the region (Huang et al., 2012). Glacier dynamic models project future increases in contaminant releases from glacier melt (Hodson, 2014).

In this study we sampled water chemistry of supraglacial meltwater and proglacial streams at two glacierized catchments in Grand Teton National Park (GTNP), Wyoming, U.S.A. (Fig. 1). We assumed that solute chemistry of supraglacial meltwater is dominated by inputs from wet and dry atmospheric deposition, whereas chemistry of the proglacial streams is dominated by weathering of minerals in local bedrock. GTNP is a Class 1 federal protection area under the Clean Air Act that is located in the arid western United States downwind of agricultural, industrial, and natural dust sources (Benedict et al., 2013; Brahney et al., 2014). Enhanced deposition of anthropogenically reactive N beginning in the 1960s caused a shift in the diatom community composition

in alpine lakes in GTNP (Spaulding et al., 2015), suggesting the importance of atmospheric deposition to this otherwise pristine protected area. Similarly, in the nearby Wind River Range enhanced dust deposition due to human activities beginning in the 1940s caused a two- to threefold increase in P deposition in remote alpine lakes (Brahney et al., 2014, 2015). Increased dust deposition due to human activities is well documented across the western United States (Ballantyne et al., 2011; Brahney et al., 2013).

Specific objectives of this study were to (1) evaluate relative contributions of trace elements from atmospheric deposition and bedrock weathering and (2) compare water chemistry between snowmelt-dominated early summer conditions to glacier-melt-dominated late summer conditions. To investigate downstream implications of glacial meltwater, we sampled longitudinal transects from supraglacial meltwater channels to meltwater in fresh moraines and proglacial streams. Studies of water chemistry in glacial watersheds typically rely on temporal sampling of proglacial streams to infer changes in water chemistry from ice melt, snowmelt, and groundwater contributions on diurnal or seasonal timescales (Mitchell et al., 2001, 2006; Mitchell and Brown, 2007; Dragon et al., 2015). This study presents a spatial “snapshot” of water chemistry across early season and late season melt conditions along transects from supraglacial meltwater to proglacial streams to provide a

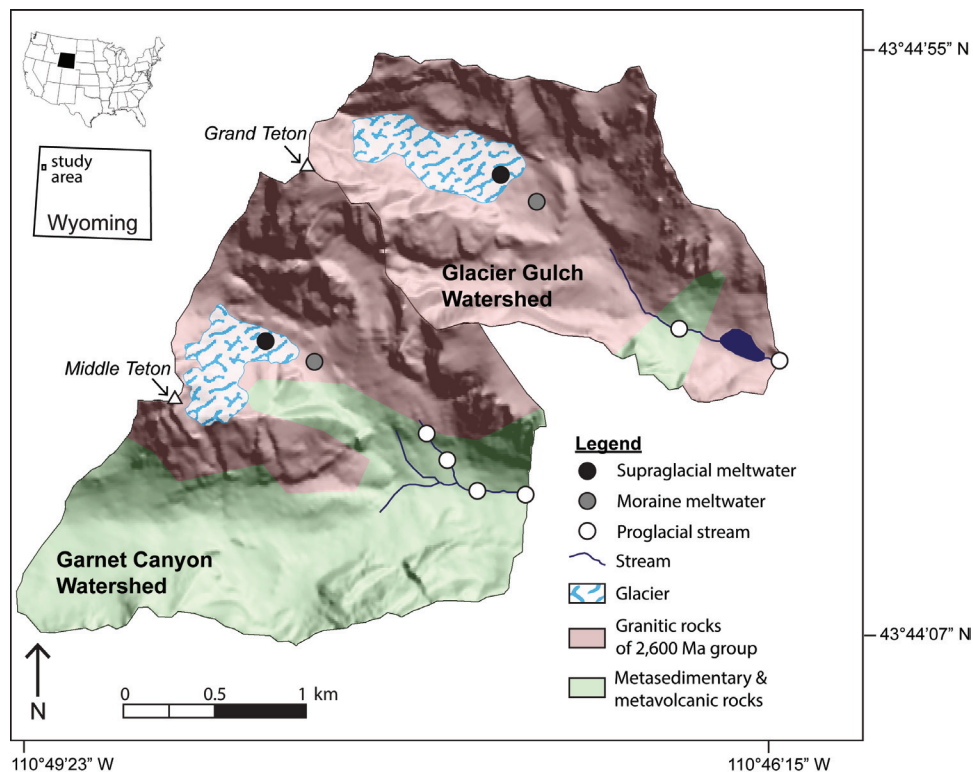


FIGURE 1. Simplified geologic map of the Garnet Canyon and Glacier Gulch watersheds in Grand Teton National Park, Wyoming, U.S.A. Sample sites are shown as shaded circles representing supraglacial meltwater (black), moraine meltwater (gray), and proglacial streams (white). The Middle Teton Glacier (0.14 km²) and Teton Glacier (0.24 km²) are located in the Garnet Canyon watershed (4.4 km²) and Glacier Gulch watershed (2.9 km²), respectively. Geologic map obtained from <http://www.wsgs.wyo.gov> on 9 September 2015.

comparison of atmospheric deposition versus weathering for controlling water chemistry.

STUDY SITE

Glaciers in the Teton Range have retreated rapidly over the past four decades, with the Teton, Middle Teton, and Teepe glaciers losing $17 \pm 3\%$, $25 \pm 4\%$ and $60 \pm 3\%$ of their surface area, respectively, between 1967 and 2006 (Edmunds et al., 2012). Currently the Middle Teton Glacier and Teton Glacier are approximately 0.14 km^2 and 0.24 km^2 in area and range in elevation from 3300 to 3700 m a.s.l. and 3100 to 3500 m a.s.l., respectively. Because the glaciers are relatively small and not heavily crevassed, surface runoff is more important than subglacial drainage during the summer melt sea-

son. Watershed areas above the lowest sampling point in this study for Garnet Canyon and Glacier Gulch are 4.4 km^2 and 2.9 km^2 , respectively. The bedrock in Garnet Canyon and Glacier Gulch is primarily composed of Archaean granite and metasedimentary/metavolcanic rocks (Fig. 1). Whole rock chemical analyses for these rocks are provided in Frost et al. (2006) and Barker et al. (1979).

Water samples were collected from Garnet Canyon (Middle Teton Glacier) and Glacier Gulch (Teton Glacier) (Fig. 1) during the summer of 2013 in July, when the glaciers were snow-covered, and August, when glacier ice was exposed at the surface (Fig. 2). Because of a lack of rainfall before and during the sampling period, snow and ice melt dominated the hydrology of the system. Snowpack depth measurements from the nearby Grand Targhee snow telemetry (SNOTEL) site (located $\sim 12 \text{ km}$ NW of the sampling area at an elevation of 2850 m a.s.l.) showed maximum snow water equivalent (SWE) of 106 cm on 3 May 2013 with no remaining snow cover by 24 June, slightly below the median SWE value of 118 cm (<http://wcc.sc.egov.usda.gov/nwcc/site?sitenum=1082>). Weather patterns were stable before each of the sampling events, with minimal precipitation recorded in the preceding days at nearby weather stations and above-freezing air temperatures throughout the study period at the Middle Teton glacier weather station at an elevation of 3540 m a.s.l. (Fig. 3). Precipitation in the region was approximately 70–90% and 50–70% of normal, and mean temperature was 1–3 °F (-17.2 to -16.1 °C) and 3–5 °F (-16.1 to -15 °C) warmer than normal in July and August 2013, respectively (<http://www.prism.oregonstate.edu/comparisons/anomalies.php>).

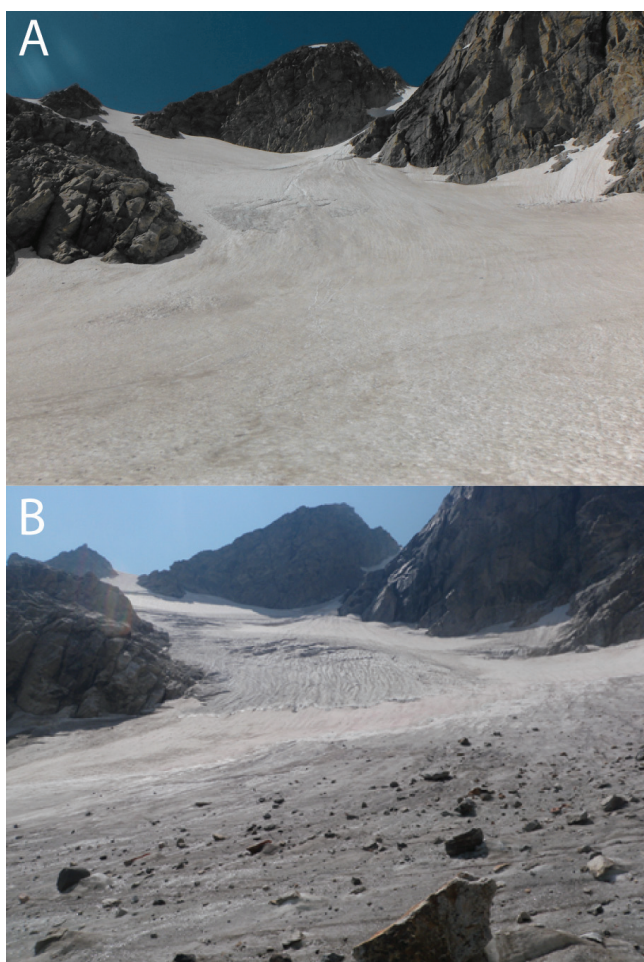


FIGURE 2. Photographs of the Middle Teton Glacier taken during sample collection on (A) 2 July 2013 and (B) 14 August 2013. The glacier was snow-covered during July, but glacier ice was exposed during August. The Teton Glacier (not shown) had similar changes between the two sampling dates.

MATERIALS AND METHODS

Water Sample Collection

To investigate solute and isotopic chemistry of supraglacial meltwater and proglacial streams in Grand Teton National Park, we collected water samples across longitudinal transects in Garnet Canyon (Middle Teton Glacier) and Glacier Gulch (Teton Glacier) on 2/5 July 2013 and 14/16 August 2013, respectively (Fig. 1). Sample sites ranged in elevation from 2750 to 3300 m a.s.l. During July the glaciers were covered with snowpack from the previous winter, whereas during August glacier ice was exposed at the surface (Fig. 2). Thus, the field sampling design allowed for evaluation of water chemistry under snowmelt-dominated conditions in July and icemelt-dominated conditions in August. Longitudinal sampling along transects allows for distinction of ele-

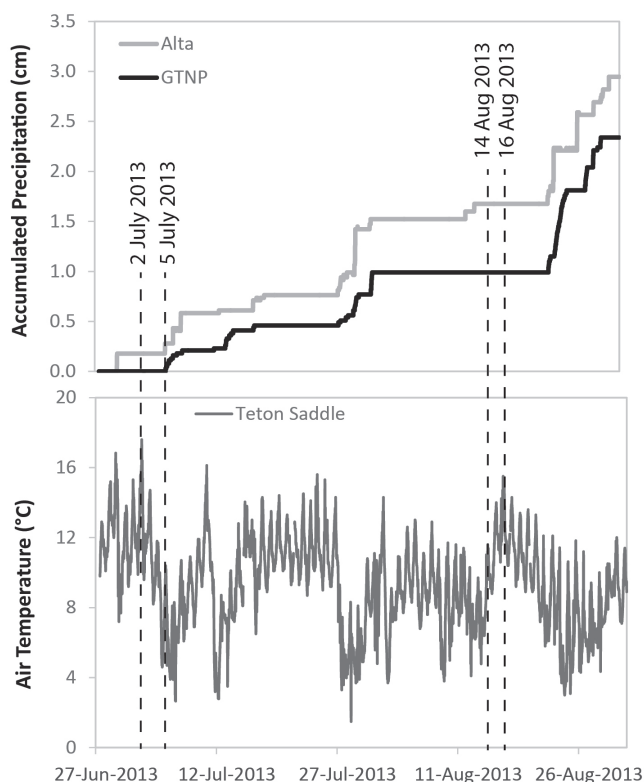


FIGURE 3. Accumulated precipitation and air temperature data for summer 2013 with sampling dates represented with vertical dashed lines. Precipitation data are from the nearest weather stations—Alta (Alta, Wyoming) and GTNP (Grand Teton National Park), located <20 km to the west and east, respectively, of the sampling area—both at an elevation approximately 1200 m below the glaciers. Air temperature data are from the Teton Saddle weather station adjacent to the Middle Teton Glacier at the saddle between the Middle Teton and Grand Teton peaks at an elevation of 3540 m a.s.l. (see Fig. 1). Data acquired from <http://mesowest.utah.edu/> on 18 September 2015.

ments that are contributed by atmospheric deposition to the glacier surface versus weathering of minerals in local bedrock.

The water samples included supraglacial meltwater (meltwater streams on the glaciers), moraine meltwater (meltwater streams in the terminal moraines of the glaciers), and proglacial streams. The Garnet Canyon transect included 11 sample sites each month: 4 samples of supraglacial meltwater on the Middle Teton glacier in July and 6 samples in August, 3 samples of moraine meltwater in July and 1 sample in August, and 4 samples of the proglacial stream during both months (Fig. 1). The Glacier Gulch transect included 8 sample sites each month: 4 samples of supraglacial meltwater on the Teton Glacier, 2 samples of moraine meltwater, and 2 samples of the proglacial stream (Fig. 1).

At each site, water was sampled with an acid-leached 125 mL low-density polyethylene (LDPE) bottle for trace elements and major cations and a triple-rinsed 250 mL fluorinated polyethylene (FLPE) bottle for Hg. To cover all the sampling sites along each transect in a single day, we divided into two teams of two people each to collect the samples. Each team followed “clean hands, dirty hands” protocols (USEPA, 1996). Upon returning to the field station at the end of the sampling day, aliquots of each sample were filtered into clean LDPE bottles (trace elements and major cations) and FLPE bottles (Hg) using an acid-washed polypropylene syringe and 0.45 μm polyethersulfone (PES) syringe filter. The filtered and unfiltered fractions were amended to 2.4% HNO_3 (trace element/major cation samples) and 1% v/v HCl (Hg samples). To address potential contamination during sample collection and transport, field blanks ($n = 8$) were collected by each team each sampling day by pouring Milli-Q water into clean 125 mL LDPE and 250 mL FLPE bottles and processed in a similar manner as actual samples.

In addition to trace element sampling, each site was sampled using a pre-rinsed 1 L LDPE bottle for major anions, alkalinity, δD , and $\delta^{18}\text{O}$. The 1 L LDPE samples were stored in the dark in a refrigerator at 4 °C until analysis for alkalinity, δD , and $\delta^{18}\text{O}$. An aliquot of the 1 L LDPE samples was filtered for anion measurements using a 0.45 μm acetate filter in a serially rinsed plastic vacuum filtration device.

Field parameters (conductivity, pH, temperature, and dissolved oxygen) were measured in situ at each site using a YSI Quatro multiparameter probe, which was calibrated prior to each sampling day. We used a 100.0 $\mu\text{S}/\text{cm}$ conductivity standard to calibrate for low conductivity waters in the sampling area. We did not use low ionic strength buffers to calibrate for pH, which may have resulted in some error in the pH measurements. However, we assume that inaccuracies in pH were not significant enough to affect interpretations of our data set.

Sample Analyses

Trace element and major cation concentrations were measured on filtered and unfiltered sample aliquots using an Agilent 7500ce quadrupole inductively coupled plasma mass spectrometer (ICP-MS) with a collision cell, a double-pass spray chamber with perfluoroalkoxy (PFA) nebulizer (0.1 mL/min), a quartz torch, and platinum cones. Concentrations were measured for the following 40 elements: Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Fe, Gd, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Rb, Sb, Se, Sm, Sr, Tb, Ti, Tl, U, V, Y and Zn. A calibration solution containing all the elements

reported was prepared gravimetrically using 1000 mg/L single-element standards (Inorganic Ventures, Inc.). This solution was used to prepare a calibration curve with 6 points plus a blank. Al, Ca, Cr, Fe, K, Mn, Na, Sc and V were determined using 4 mL He/min in the collision cell; As and Se were determined using 4 mL He/min plus 2.5 mL H₂/min; and the other 29 elements were determined using Ar as the carrier gas. Detection limit (DL) was determined as three times the standard deviation of all blanks analyzed throughout each run. A U.S. Geological Survey (USGS) standard reference sample (T-205) and National Institute of Standards and Technology (NIST) standard reference material (SRM 1643e) were analyzed multiple times in each run together with the samples as a continuing calibration verification, with results accurate within $\pm 10\%$ for most elements in each sample run (Appendix data, Table A1, available online only at <http://geology.byu.edu/Home/sites/default/files/AAAR-49-3-06%20Appendix.xlsx>).

Hg concentrations were measured on filtered and unfiltered sample aliquots using a Brooks Rand MERX cold vapor atomic fluorescence spectrometer (CVAFS) after BrCl oxidation following Environmental Protection Agency (EPA) Method 1631e (USEPA, 2002). At a minimum, matrix spike recoveries and replicates were analyzed for every 10 samples. For the sample run to be accepted, matrix spike recoveries had to fall within 75–125% of the original sample run and replicate analyses had to fall within $\pm 10\%$. Method blanks were analyzed at the beginning of each run to calculate the DL, which typically fell below 0.2 ng/L. To check accuracy, each year our laboratory participates in the Brooks Rand Labs Interlaboratory Comparison Study (Creswell et al., 2015) with results consistently within $\pm 10\%$ of the most probable values.

Unfiltered water samples were analyzed for δD and $\delta^{18}O$ using a Los Gatos Research Liquid Water Isotope Analyzer (LWIA-24d). All measurements were made relative to Vienna Standard Mean Ocean Water (VSMOW), with a precision of 1.0‰ and 0.4‰ for δD and $\delta^{18}O$, respectively. Major anions (Cl⁻, NO₃⁻, and SO₄²⁻) were analyzed on filtered aliquots using a Dionex ICS-90 ion chromatograph, and alkalinity (assumed to be HCO₃⁻) was measured on unfiltered aliquots using a Mettler Toledo DL50 titrator with dilute HCl following EPA Method 310.1 (USEPA, 1978).

Data Quality Control

Field blanks showed low background concentrations for all measured elements, with concentrations <DL in nearly all cases (Appendix data, Table A1). Some elements had measureable values in the field blanks, including Al, Ba, Mo, Pb, and Sb, but the concentrations

measured in the field blanks were negligible relative to concentrations measured in actual samples. One exception was Ca, which showed small but significant concentrations in the four field blanks collected during July (mean = 0.13 ± 0.04 mg/L), indicating some source of contamination during sample collection or processing. Field blank Ca concentrations were similar to supraglacial meltwater but much lower than moraine meltwater or proglacial streams, and thus the Ca concentrations were considered valid for the purposes of this study. Another set of 7 elements had concentrations <DL in the field blanks and in a majority of filtered samples, including Ag, B, Be, Cr, Cu, Lu, and Ni, and thus were removed from the data set for statistical analyses. For other elements, any values <DL were set as 1/2 DL.

Charge balances calculated using cation (K⁺, Na⁺, Ca²⁺, Mg²⁺) concentrations from the ICP-MS, anion (Cl⁻, NO₃⁻, SO₄²⁻) concentrations from the IC, and HCO₃⁻ concentrations from titration were within an acceptable range of $\pm 5\%$ for 13 out of 38 samples. The remaining 25 samples were charge balanced by adjusting HCO₃⁻ concentrations. Given the low solute concentrations in all samples, HCO₃⁻ was adjusted by no more than ± 1 mg/L in most samples to achieve charge balance.

Data Ordination (NMS)

We used nonmetric multidimensional scaling (NMS) to explore water chemistry relationships of supraglacial meltwater, moraine meltwater, and proglacial streams in Garnet Canyon and Glacier Gulch during July and August 2013. NMS is an ordination technique that generates visual analyses to explain relationships of assemblages and communities (McCune and Grace, 2002). It is particularly appropriate for our analyses because it avoids the assumption of normal distributions and linear relationships among variables (Peck, 2010). Data included in the ordination were conductivity and filtered concentrations of 38 trace and major elements measured on 37 water samples. We used PC-ORD (McCune and Mefford, 1999) for NMS ordination following methods described in Carling et al. (2013, 2015). Briefly, data were log generalized prior to conducting NMS using the equation $b = \log(x + x_{\min}) - \log(x_{\min})$, where x_{\min} is the minimum value for each element. Euclidean distance measures were used to assign the samples in ordination space. The analyses were run 250 times with real data, and the results were compared with 250 randomized data in Monte Carlo simulations. The final model had a stable solution and provided the greatest reduction in the amount of stress, which is a goodness of fit measure for the model. We performed a post hoc analysis of the coefficient of determi-

nation between ordination distances and distances in the original n -dimensional space to estimate the amount of variability in the data described by each axis. The model results are provided as a 2-D graph with data from each site contained by convex hulls (i.e., the outer points for each sample site are connected by a closed polygon). Details defining labels and raw data associated with each sample shown in NMS plots are provided in the Appendix data Table A2, available online only at <http://geology.byu.edu/Home/sites/default/files/AAAR-49-3-06%20Appendix.xlsx>.

RESULTS

Stable Isotopes Show Differences between Early and Late Summer Meltwater

Stable isotopes of H (δD) and O ($\delta^{18}O$) show that the Garnet Canyon and Glacier Gulch watersheds are dominated by meltwater inputs because proglacial stream and moraine meltwater samples have similar isotopic ratios as supraglacial meltwater (Fig. 4). All water samples plotted on or near the global meteoric water line (GMWL), indicating little influence of evaporation from supraglacial meltwater to proglacial streams. Supraglacial meltwater isotope values were variable within each month, but overall were more enriched in August relative to July (with the exception of one supraglacial meltwater sample at Glacier Gulch in August). Proglacial stream and moraine meltwater samples were likewise more enriched in August when glacier contributions were greater relative to July, demonstrating that the

watersheds respond quickly to melt inputs. The stable isotope data show that the two sampling events successfully captured distinct hydrologic conditions affecting the glacierized catchments during the melt season: the early season snowmelt-dominated system and the late season icemelt-dominated system. These differences allow for a comparison of water chemistry from early to late in the melt season, with potential differences in trace and major element composition. Stable isotope data are provided in the Appendix data (Table A1).

Water Types Have Different Trace Element Concentrations

Figure 5 shows average concentrations of Sr, U, Mn, and Hg in filtered samples of supraglacial meltwater, moraine meltwater, and proglacial streams in Garnet Canyon (Fig. 5, part A) and Glacier Gulch (Fig. 5, part B). These elements represent the two opposing trends found among the elements in the data set with generally increasing concentrations (Sr and U) or decreasing concentrations (Mn and Hg), respectively, from upstream to downstream. Other elements that showed similar increasing trends as Sr and U include the major ions Na^+ , Cl^- , Mg^{2+} , K^+ , Ca^{2+} , HCO_3^- , and SO_4^{2-} and trace elements Mo, Ba, Li, Rb, and Ti. Other elements with similar decreasing trends as Hg and Mn include Zn, Cd, Co, and Pb. The remaining group of measured elements showed no differences in concentration between the supraglacial and proglacial samples, including NO_3^- , Al, V, Fe, As, Se, Y, Sb, Cs, Tl, and the rare earth elements (REEs) La, Ce, Nd, Sm, Gd, Tb, Dy, and Ho. Trace and major element concentrations (including data for both

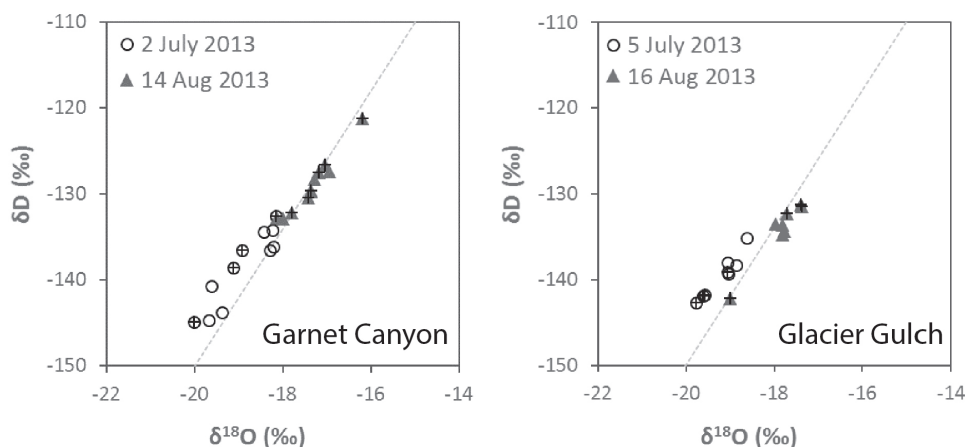


FIGURE 4. Stable isotopes of hydrogen and oxygen (δD and $\delta^{18}O$) for water samples collected in Garnet Canyon (left) and Glacier Gulch (right). Samples collected during July and August are shown with open circles and gray triangles, respectively. Supraglacial meltwater samples are indicated with a plus (+) sign. Values are expressed in ‰ notation relative to Vienna Standard Mean Ocean Water (VSMOW). The dashed line is the global meteoric water line (GMWL).

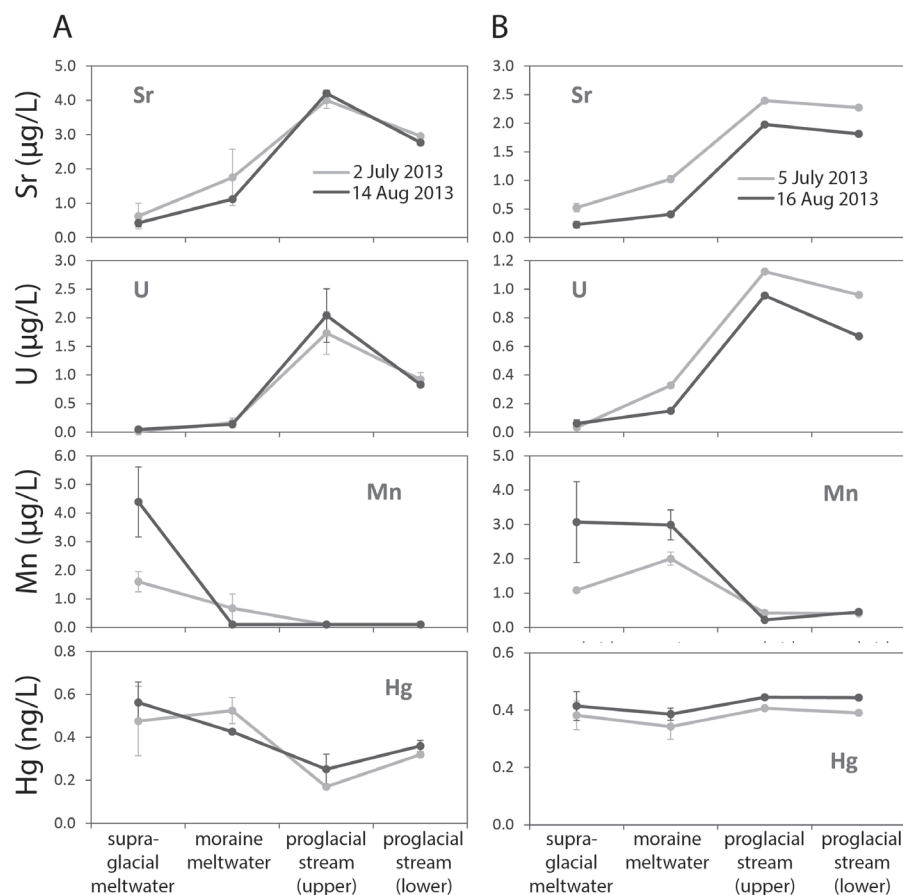


FIGURE 5. Concentrations of Sr, U, Mn, and Hg in (A) Garnet Canyon and (B) Glacier Gulch for filtered samples collected 2/5 July 2013 and 14/16 August 2013. The selected elements are representative of elements that generally showed increasing concentrations (Sr and U) and decreasing concentrations (Mn and Hg) from supraglacial meltwater to proglacial streams. All elements showed minimal differences in concentrations between July and August even though samples represented predominant snowmelt and glacier ice melt, respectively. Note different scales, with higher overall concentrations in Garnet Canyon relative to Glacier Gulch.

filtered and unfiltered samples) are provided in the Appendix data (Table A1).

Concentrations of Sr and U were low in the supraglacial meltwater and increased substantially downstream in both catchments from ~ 0.5 to >2 $\mu\text{g/L}$ and from ~ 0.05 to >1 $\mu\text{g/L}$, respectively, with higher concentrations in Garnet Canyon (Fig. 5, part A) relative to Glacier Gulch (Fig. 5, part B). In contrast to Sr and U, Mn concentrations were relatively high in supraglacial meltwater and decreased downstream in the proglacial streams from ~ 2 to ~ 0.2 $\mu\text{g/L}$ (Fig. 5). Hg concentrations followed a similar trend as Mn in the Garnet Canyon catchment (Fig. 5, part A), decreasing from upstream to downstream from ~ 0.5 to ~ 0.25 ng/L , but were similar in all sample types (~ 0.4 ng/L) in the Glacier Gulch catchment (Fig. 5, part B). Trace element concentrations were similar in samples collected during July and August, suggesting snowmelt and glacier melt contribute similar amounts of trace elements to stream systems in both catchments.

To further evaluate trace element trends, data from filtered samples for both catchments and both sampling periods were combined and averaged in box plots for supraglacial meltwater, moraine meltwater, and proglacial stream (Figs. 6–7). Figure 6 shows elements or other

parameters with increasing median concentrations from supraglacial meltwater to moraine meltwater and proglacial stream samples, including U, Mo, Sr, Rb, Ca, Na, HCO_3 and conductivity, with increases of over twenty-fold for U and threefold to tenfold for Mo, Sr, Rb, Ca, Na, and HCO_3 . Figure 7 shows elements with decreasing median concentrations from supraglacial meltwater to moraine meltwater and proglacial streams, including Hg, Cd, Zn, Co, Mn and Pb, with decreases of $\sim 30\%$ for Hg and Cd and 50–90% for Zn, Co, Mn, and Pb. It is notable that these trends emerge even when combining data from both catchments and both months.

Multivariate Statistics Show Distinct Geochemical Groupings by Sample Type

The NMS ordination results showed that supraglacial meltwater, moraine meltwater, and proglacial streams are geochemically distinct (Fig. 8). The NMS model that best described the dataset was a 2-D solution with a final stress of 6.685, where stress values <10 are typically considered interpretable and reliable (Peck, 2010). In the NMS model, axis 1 explains 83.7% of the variability in the data set, and axis 2 explains an additional 13.0%. The model is structured by showing samples with relatively

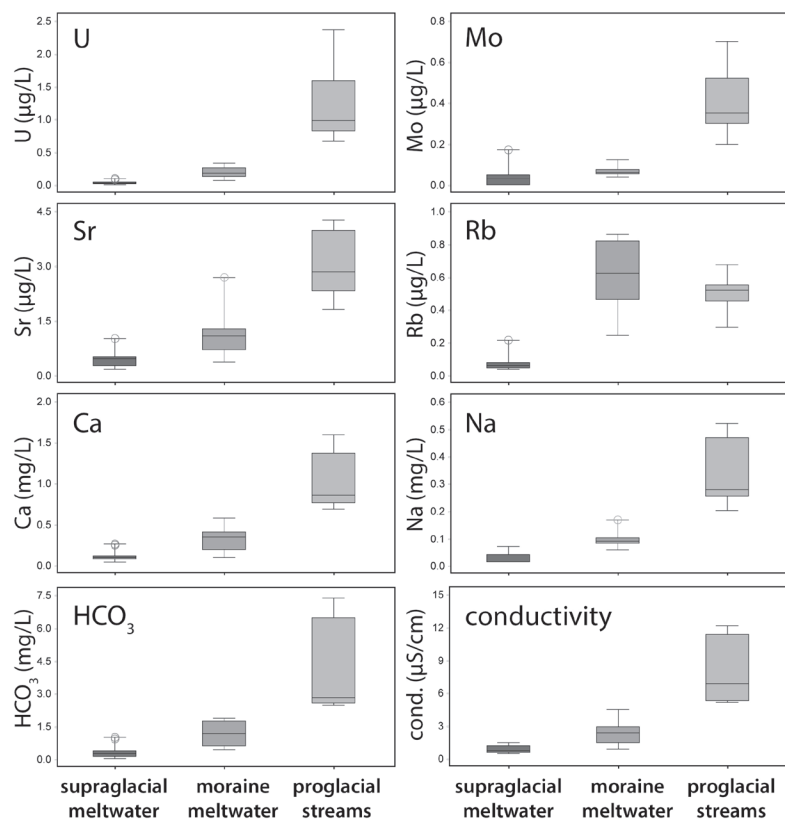


FIGURE 6. Box plots showing solute concentrations in supraglacial meltwater ($n = 17$), moraine meltwater ($n = 7$), and proglacial streams ($n = 13$) for all samples collected from the Garnet Canyon and Glacier Gulch sites during July and August 2013. Data shown are for filtered samples except HCO₃ and conductivity. Outliers are represented as circles over the whiskers. The elements or parameters shown here had increasing concentrations from supraglacial meltwater to moraine meltwater and proglacial streams.

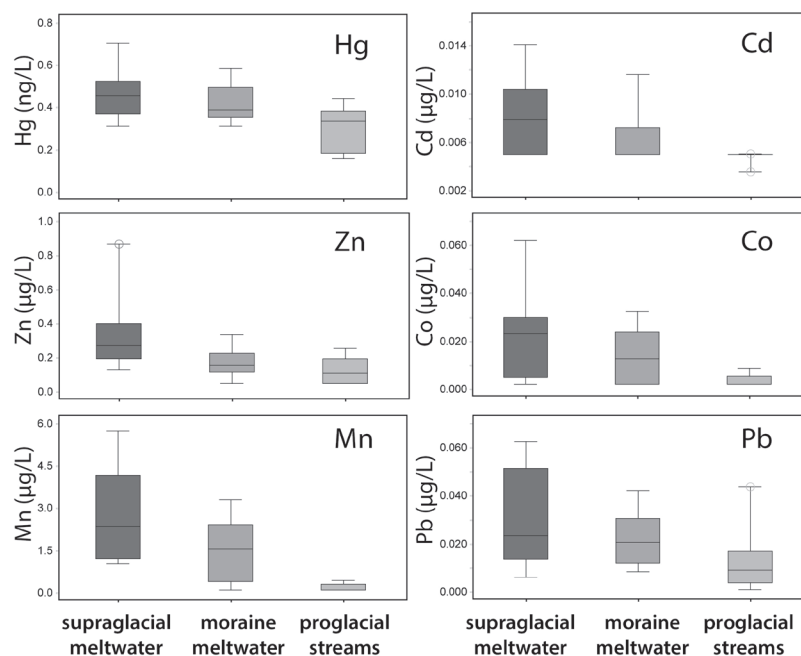


FIGURE 7. Box plots showing solute concentrations in supraglacial meltwater ($n = 17$), moraine meltwater ($n = 7$), and proglacial streams ($n = 13$) for all samples collected from the Garnet Canyon and Glacier Gulch sites during July and August 2013. All data shown are for filtered samples. Outliers are represented as circles over the whiskers. The elements shown here had decreasing concentrations from supraglacial meltwater to moraine meltwater and proglacial streams.

higher concentrations of Mn, Co, Zn, Pb, Cd, and Hg on the negative end of axis 1 (supraglacial meltwater) and samples with relatively higher conductivity and higher concentrations of the major ions Na⁺, Cl⁻, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻, HCO₃⁻, and trace elements U, Sr, Rb, Mo, Li, Ba, and Ti on the positive end of axis 1 (proglacial streams). The other elements included in the NMS

ordination (NO₃, Al, V, Fe, As, Se, Y, Sb, Cs, Tl, La, Ce, Nd, Sm, Gd, Tb, Dy, and Ho) had similar concentrations in all samples and thus explained little of the variability in the data set. In all instances sample type, not temporal differences (July versus August) or watershed (Garnet Canyon versus Glacier Gulch), structured differences among samples. This is highlighted by the unique groupings of

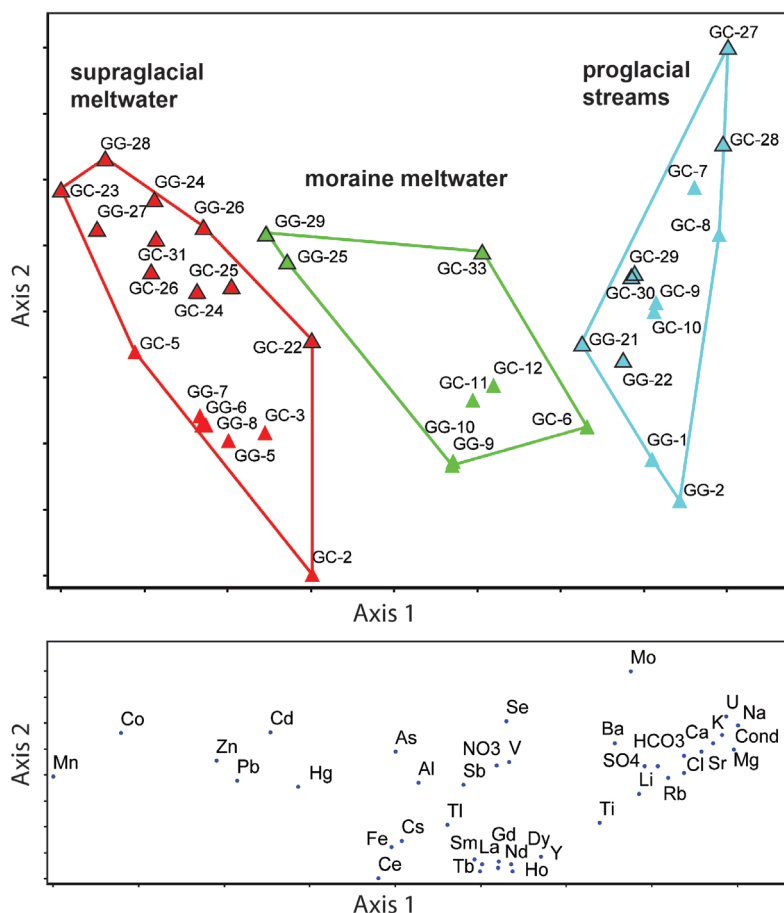


FIGURE 8. NMS (nonmetric dimensional scaling) results for supraglacial meltwater, moraine meltwater, and proglacial stream for filtered samples collected from Glacier Gulch (GG) and Garnet Canyon (GC) during July (colored symbols) and August (colored symbols with black outline). Axis 1 explains 83.7% of the variance in the data set, and axis 2 explains an additional 13.0%. Final stress for the two axis model = 6.685. Raw data for each sample are provided in the Appendix data (Table A2, available online only at <http://geology.byu.edu/Home/sites/default/files/AAAR-49-3-06%20Appendix.xlsx>).

samples in polygons referred to as “convex hulls,” which distinguish samples into three groups: supraglacial meltwater, moraine meltwater, and proglacial streams. Samples from Garnet Canyon and Glacier Gulch overlap within each group. The NMS plot shows the evolution of water chemistry from supraglacial meltwater, which has high concentrations of anthropogenic trace metals (Mn, Co, Zn, Pb, and Hg), to proglacial streams, which are characterized by higher concentrations of major ions. The supraglacial and moraine meltwater samples plot separately between July and August along axis 2, which explains only a small amount of the variability in the data set. Samples with higher Mo concentrations plot on the positive end of axis 2 (August meltwater), and samples with higher REEs, Y, Fe, Cs, and Ti concentrations plot on the negative end (July meltwater).

DISCUSSION

Trace Element Contributions from Atmospheric Deposition and Weathering

Three groups of elements emerged from this analysis: (1) elements with relatively higher concentrations in su-

praglacial meltwater (Mn, Hg, Zn, Cd, Co, and Pb); (2) elements with relatively higher concentrations in proglacial streams (Sr, U, Mo, Ba, Li, Rb, Ti, Na, Cl, Mg, K, Ca, HCO₃, and SO₄); and (3) elements with similar concentrations in all sample types (NO₃, Al, V, Fe, As, Se, Y, Sb, Cs, Ti, La, Ce, Nd, Sm, Gd, Tb, Dy, and Ho). Moraine meltwater showed intermediate concentrations for the elements in groups 1 and 2. Notably, the three groups of elements emerged regardless of the method of interpretation, including graphs of raw data from each site and each season (Fig. 5), averaged data in box plots (Figs. 6–7), and multivariate statistics (Fig. 8).

Group 1 elements with relatively higher concentrations in supraglacial meltwater likely come from distal anthropogenic sources. Assuming that supraglacial meltwater samples are representative of atmospheric deposition, with limited water-rock interaction time in the glacial environment, the anthropogenic trace metals Mn, Hg, Zn, Cd, Co, and Pb in group 1 are likely deposited with aerosols, dust, or snowfall. There is no evidence for increasing concentrations for these elements downstream of the glaciers, suggesting that at a minimum there is no important weathering source or that addition by weathering is small compared with atmos-

pheric deposition. Whole-rock analyses show relatively low concentrations of MnO, Zn, and Co in the granite and gneiss bedrock in the sampling area (Barker et al., 1979; Frost et al., 2006) indicating minimal contributions from weathering. No data are available for Pb, Cd, or Hg, but these metals are likely not abundant nor easily weathered from the local bedrock.

Anthropogenic aerosols, wildfire ash, and mineral dust are important sources of nutrients and trace metals to otherwise pristine and protected alpine catchments in the Western United States (Earl and Blinn, 2003; Aarons et al., 2016). Dust contributes substantial loading of soluble salts, metals, and metalloids to snowpack (Turk et al., 2001; Clow et al., 2002; Ingersoll et al., 2008; Lawrence et al., 2010; Rhoades et al., 2010; Carling et al., 2012). Trace metal concentrations in dust (e.g., As, Cd, Cu, Mo, Pb, and Zn) are enriched relative to average upper continental crust, and dust-derived trace metals are more available and mobile relative to other sources (Lawrence and Neff, 2009; Lawrence et al., 2010, 2013). Dust sources impacting the Teton Range include the Snake River Plain agricultural area to the west and oil and gas extraction to the south and east (Spaulding et al., 2015). The Teton Range is also downwind from a number of known atmospheric Hg sources that impact southern Idaho (Abbott et al., 2008). Local, regional, and global sources of air pollution can contribute to Hg deposition in remote areas of the Western United States (Wright et al., 2014). Thus, the elevated concentrations of Group 1 elements are most likely the result of various anthropogenic sources of aerosols and dust.

In contrast, the higher concentrations of group 2 elements in proglacial streams are likely the result of weathering of local bedrock. Water-rock interactions likely control concentrations of the trace elements Sr, U, Mo, Ba, Li, Rb, and Ti, with more contact time in the larger Garnet Canyon watershed leading to overall higher concentrations (Fig. 5). The igneous and metamorphic bedrock in the catchments (Fig. 1) contains minerals that likely release these elements during weathering processes (Barker et al., 1979; Frost et al., 2006). Group 3 elements, with similar concentrations in all samples, likely represent background concentrations that could be from a combination of atmospheric deposition and weathering such that concentrations remain fairly constant during water transport from glaciers to proglacial streams and subsequent mixing with groundwater and other tributary streams.

The trend in group 1 elements, especially in light of the potential negative environmental impacts of these metals, is worth further discussion. In particular, it is possible that higher concentrations of Mn, Hg, Zn, Cd, Co, and Pb (group 1 elements) in supraglacial meltwater

relative to proglacial streams are related to total suspended solids (TSS) concentrations because these are generally considered particle-reactive elements. Although we did not measure TSS, the supraglacial and moraine meltwater samples were visibly more turbid than proglacial stream samples. Particulate concentrations (unfiltered-filtered concentrations) of these elements were much higher in supraglacial meltwater samples relative to proglacial streams (Appendix data, Table A3, available online only at <http://geology.byu.edu/Home/sites/default/files/AAAR-49-3-06%20Appendix.xlsx>). For example, particulate Mn concentrations averaged 27 $\mu\text{g/L}$ in supraglacial meltwater compared with 3 $\mu\text{g/L}$ in proglacial streams, and particulate Hg concentrations averaged 0.8 ng/L in supraglacial meltwater compared with 0.2 ng/L in proglacial streams. However, the same is true for all other elements measured in this study, including the group 2 and group 3 elements. For example, particulate Li concentrations averaged 2.9 $\mu\text{g/L}$ in supraglacial meltwater compared with 0.4 $\mu\text{g/L}$ in proglacial streams, and particulate Al concentrations averaged 1.13 mg/L in supraglacial meltwater compared with 0.13 mg/L in proglacial streams. Further, a majority of element mass (50–95%) of most group 1, 2, and 3 elements was found in the particulate fraction in supraglacial meltwater (Appendix data, Table A3). Therefore, it seems unlikely that the elevated dissolved concentrations of the group 1 subset of anthropogenic metals (Mn, Hg, Zn, Cd, Co, and Pb) in supraglacial meltwater are related to water turbidity because other elements should have also shown higher concentrations in supraglacial meltwater if it was due merely to partitioning between dissolved and particulate phases. Rather, this observation suggests that the anthropogenic metals behave differently from other particle-reactive elements in that they are either truly dissolved or that they are more likely to form small ($<0.45\ \mu\text{m}$) colloids that pass through a filter. The tendency of this group of anthropogenic metals to be found in the dissolved or colloidal form means that they are likely more bioavailable in supraglacial meltwater than other metals, with potential negative implications for downstream ecosystems.

The decreasing concentrations of Mn, Hg, Zn, Cd, Co, and Pb (group 1 elements) from supraglacial meltwater to proglacial streams could be a result of dilution by groundwater or removal by geochemical processes. For example, it is possible that these cation-forming metals are affected by sorption in response to increasing pH. On average, pH increases from ~ 5 to over 6 from supraglacial meltwater to proglacial streams (Appendix data, Table A1). These metals could begin to sorb to mineral surfaces in the streambed at circumneutral pH in dilute meltwater (Dzombak and Morel, 1990; Bar-

row and Whelan, 1998), leading to decreased concentrations from upstream to downstream. Regardless of the mechanism for decreasing concentrations of these metals from upstream to downstream, atmospheric deposition is the likely source of these metals with subsequent dilution or removal in proglacial streams.

Of the group 1 anthropogenic metals discussed above, Hg has potentially significant negative impacts on alpine ecosystems. Hg is a particularly toxic element that is deposited to mountain watersheds primarily by atmospheric deposition (Fitzgerald et al., 1998; Wright et al., 2014). The contributions of Hg in supraglacial meltwater suggest that atmospheric deposition contributes an important flux of Hg to the watershed with minimal contributions from water-rock interactions, confirming previous results from another location that melting glaciers serve as sources of Hg to downstream ecosystems (Huang et al., 2012). As the glaciers in GTNP continue to recede they will make reduced meltwater contributions to the watersheds in the study area. Nevertheless, even low Hg concentrations can be harmful if inorganic Hg is methylated, as methyl Hg can bioaccumulate up the food web to a point that is harmful to wildlife and ecosystems in remote areas such as national parks (Schwindt et al., 2008). Evaluating ecological impacts from Hg and other metals in glacial meltwater is beyond the scope of this paper but the issue deserves further study.

Chemistry of Snowmelt and Ice Melt on Glaciers

Differences in stable isotopic composition of water samples collected in July and August suggest differences in water sources from snowmelt-dominated early season conditions to a mixture of snow- and ice-melt during late season conditions (Fig. 4). The variability in stable isotopic composition within each month is likely a function of the hydrology of the glacier systems, which are a mixture of snowmelt and melting ice of different ages and from different elevations on the glacier. Glacier ice melt (dominant in August) was more enriched relative to snowmelt (dominant in July), possibly because the ice has undergone multiple freeze-thaw cycles, sublimation, and/or was formed in a different climate than snowpack from the previous season. Meltwater is typically more depleted in early season melt and becomes progressively more enriched throughout the melt season owing to fractionation effects (Stichler and Schotterer, 2000). Although stable isotopes show differences in water sources during July and August, trace element concentrations were similar during both months. This suggests that snowpack and glacial ice contain similar trace element concentrations as they are both impacted by the same

sources of atmospheric deposition. It is possible that fresh snowmelt earlier in the melt season contains higher metal concentrations during the initial ionic pulse (Bales et al., 1990; Williams and Melack, 1991; Hürkamp et al., 2017), but investigating meltwater elution was beyond the scope of this study. Regardless of melt timing, atmospheric deposition is probably the most important factor controlling the delivery of anthropogenic elements to stream water in these catchments.

Implications for Protecting National Park Resources

Continued monitoring of water quality is necessary to protect wildlife in snow- and glacier-melt-dominated catchments across GTNP under a warming climate. Changes in the timing and extent of snowmelt, shrinking glaciers and other factors could result in negative impacts on water quality of streams, lakes, and wetlands at GTNP. For example, as glaciers continue to recede, seasonal snowmelt will interact with bedrock and glacial till to a greater extent. Increased water-rock interactions could lead to higher concentrations of harmful weathering products such as U or Mo downstream of the glaciers. The presence of glaciers, especially of retreating glaciers like those at GTNP, greatly affect the solute content of melting waters. This may be because of, for instance, biogeochemical processes occurring in the subglacial environments (Wadham et al., 2010) or to a change in flow paths and residence time of meltwater (Cooper et al., 2002). Glaciers enhance weathering of local bedrock by producing geochemically reactive rock flour (Mitchell et al., 2001) and thus non-glacial catchments may be less impacted by solutes and suspended sediments derived from weathering products. Non-glacial catchments could also be impacted by decreasing snow cover that may lead to increased weathering rates and weathering products (Riebe et al., 2004). To address these issues, future work should compare water chemistry in glacial and non-glacial watersheds at GTNP and elsewhere. A long-term monitoring system at selected locations would allow GTNP scientists to compare glacial and non-glacial watersheds and evaluate the impacts of melting glaciers on water quality.

CONCLUSIONS

Melting glaciers may represent an important source of anthropogenic metals to glacier-dominated watersheds around the globe with continued warming. In this study, we examined trace and major element concentrations in supraglacial meltwater and proglacial streams

in two glaciated watersheds in Grand Teton National Park (Wyoming, U.S.A.) during early season snowmelt-dominated conditions and late-season snow- and ice-melt conditions. A majority of elements were found in higher concentrations in proglacial streams relative to supraglacial meltwater because of inputs from weathered bedrock and glacial flour. However, a subset of anthropogenic metals—Hg, Mn, Cd, Zn, Co and Pb—had relatively higher concentrations in supraglacial meltwater relative to proglacial streams. This suggests that atmospheric deposition of harmful trace metals is affecting remote and protected watersheds in the Teton Range. The metals are released during snow and ice melt and may have negative impacts on downstream ecosystems in the national park. Whereas other studies have shown human-induced atmospheric deposition of N and P to the Tetons and nearby mountain ranges, this is the first study to suggest inputs of anthropogenic trace metal inputs from atmospheric deposition. Similar work is underway to understand trace element chemistry of glacial and non-glacial watersheds in the Wind River Range (Wyoming) and the European Alps.

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