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Dissolved Organic Carbon and Dissolved Metal Pulses During Snowmelt Runoff in the Upper Provo River Watershed, Utah, USA

Hannah Nicole Checketts

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Master of Science

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ABSTRACT

Dissolved Organic Carbon and Dissolved Metal Pulses During Snowmelt Runoff in the Upper Provo River Watershed, Utah, USA

Hannah Nicole Checketts
Department of Geological Sciences, BYU
Master of Science

Snowmelt river systems exhibit seasonal fluxes in water chemistry, potentially affecting the water supply of one-sixth of the world's population. In this study, we examined water chemistry of the upper Provo River, northern Utah, which supplies water to over two million people along the urban Wasatch Front. Seasonal changes in water chemistry were characterized by analyzing discharge and dissolved organic carbon (DOC with dissolved trace metal and cation concentrations (La, Pb, Cu, Al, Be, Sr and K over three consecutive water years 2014—2016, with intensive sampling during snowmelt runoff. To better understand links between metal movement and DOC, we sampled the river in three locations (Soapstone, Woodland, and Hailstone, snowpack, and ephemeral snowmelt channels. Concentrations of La, Pb, Cu, Al, and Be increased with discharge/snowmelt during the 2014, 2015 and 2016 water years. Over 90% of La, Pb, Cu, Al, Be and between 70-90% Sr and K loads occurred during the snowmelt season (April-June. In relation to discharge, concentrations of each element varied between the river sampling sites. At Soapstone, DOC, La, Pb, Cu, Al and Be increased slightly with discharge, but Sr and K remained chemostatic. At Woodland and Hailstone, DOC, La, Pb, Cu, Al and Be had sharp increases with discharge, and Sr and K were diluted. Hysteresis patterns showed that concentrations of DOC, La, Pb, Cu, Al, Be, Sr and K all peaked on the rising limb of the hydrograph at the higher elevation Soapstone site but patterns were variable at the lower elevation Woodland and Hailstone sites. Concentrations for ephemeral channels were significantly higher than river and snow concentrations in La, Pb, Cu and Al, suggesting soil water was a significant source of flushed metals and DOC to the upper Provo River. DOC was highly correlated with La ($R^2 = 0.94$, $P = < .0001$, Pb ($R^2 = 0.76$, $P = < .0023$, Cu ($R^2 = 0.83$, $P = < .0001$, Al ($R^2 = 0.94$, $P = < .0001$ and Be ($R^2 = 0.93$, $P = < .0005$, and likely facilitating metal transport. More work is needed to determine the mechanisms of DOC and metal transport, and potential metal complexation. This study has implications for understanding water quality impacts from metal flushing during snowmelt in mountain watersheds.

Keywords: metals, dissolved organic carbon (DOC, concentration-discharge, snowmelt

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To the department of geological sciences at Brigham Young University, including all professors and secretaries, thank you for helping make my experience wonderful. I cannot express how truly grateful I am for my time spent in the geology department.

Finally, I would like to thank my parents, Lannie and Sandy Checketts for their love, encouragement and support. I could not have done this without the two of you.

TABLE OF CONTENTS

LIST OF FIGURES

1. Introduction

Snowmelt-fed river systems exhibit seasonal fluxes in water chemistry, with increased fluxes of dissolved organic carbon (DOC) and trace metals during spring runoff (Carling et al., 2015; Ogendi et al., 2007; Rember and Tefrey, 2004; Shafer et al., 1997). The seasonal changes in water chemistry of snow dominated watersheds may be detrimental to water supplies impacting up to one-sixth of the world's population (Barnett et al., 2008). Environmental factors can influence dissolved metal and cation water chemistry in alpine to sub-alpine regions during runoff. One factor is dissolved organic carbon (DOC). DOC is often found in the upper soil horizon (Brooks et al., 1999) by biodegradation of plant material, and flushed during snowmelt (Boyer et al., 1997; Hornberger et al., 1994; Rember and Tefrey, 2004). During transport, DOC can form complexes with metals and aid their transport (Rember and Tefrey, 2004). Metal sources in alpine watersheds include atmospheric deposition, which alters snow and soil composition (Carling et al., 2012; Munroe, 2014; Reynolds et al., 2014; Reynolds et al., 2010). Further research is needed to describe relationships between trace element concentrations measured in snow, soil water, and rivers.

Relationships between element concentration and stream discharge can describe material availability and sources within a watershed (Evans and Davies, 1998; Godsey et al., 2009; Lloyd et al., 2016; Williams, 1989). Concentration-discharge graphs may show cyclic patterns referred to as hysteresis. Hysteresis occurs when concentrations on the rising limb of the hydrograph are different than concentrations on the falling limb of the hydrograph (Evans et al., 1999). If the slope of the hysteresis loop is positive, concentrations are being flushed. If the slope of the hysteresis loop is negative, concentrations are being diluted (Long et al., 2017). If there is little or no slope the relationship between concentration-discharge is chemostatic (Godsey et al., 2009;

Long et al., 2017). The direction of hysteresis also provides information about the watershed. When the hysteresis cycle is clockwise the concentration peak occurs prior to discharge peak. When the hysteresis cycle is counter-clockwise, the concentration peak occurs after the discharge peak (Williams, 1989). Clockwise concentration-discharge hysteresis has been suggested to indicate the concentration source is autochthonous, whereas, a counter-clockwise rotation suggest concentrations are allochthonous (Creed et al., 2015). Examples of non-traditional sources of dissolved materials into a river could include varying flow paths at high discharge and soil water.

Considering potential adverse effects to the ecosystem and water quality of the Provo River during snowmelt runoff, the purpose of this study is to evaluate seasonal changes in dissolved metal and cation chemistry in relationship with DOC. Specific objectives are to: 1) compare changes of metal and cation chemistry from baseflow to snowmelt runoff; 2) evaluate concentration-discharge relationships to characterize elements that show chemostatic or non-chemostatic behavior and hysteresis; 3) evaluate relationships between DOC concentrations and metal/cation concentrations; and 4) identify trace element sources to the upper Provo River watershed.

2. Methods

2.1 Upper Provo River watershed study area

The upper Provo River watershed is located in the Uinta Mountain range in northeastern Utah and is primarily fed by high elevation snowmelt (~3000 m above sea level (Figure 1)). The entire Provo River spans ~110 km before discharging at Utah Lake (~1370 m above sea level), totaling >1600 m in relief through both rural and urban areas. The upper Provo River watershed is primarily rural, starting in the high Uintas and ending at Jordanelle Reservoir, dropping 1170 m from headwaters (accounting for almost 60% of elevation decline on the Provo River). Because the upper Provo River watershed has little urban impact, much of the water chemistry is determined by the local geology, biology, and atmospheric deposition.

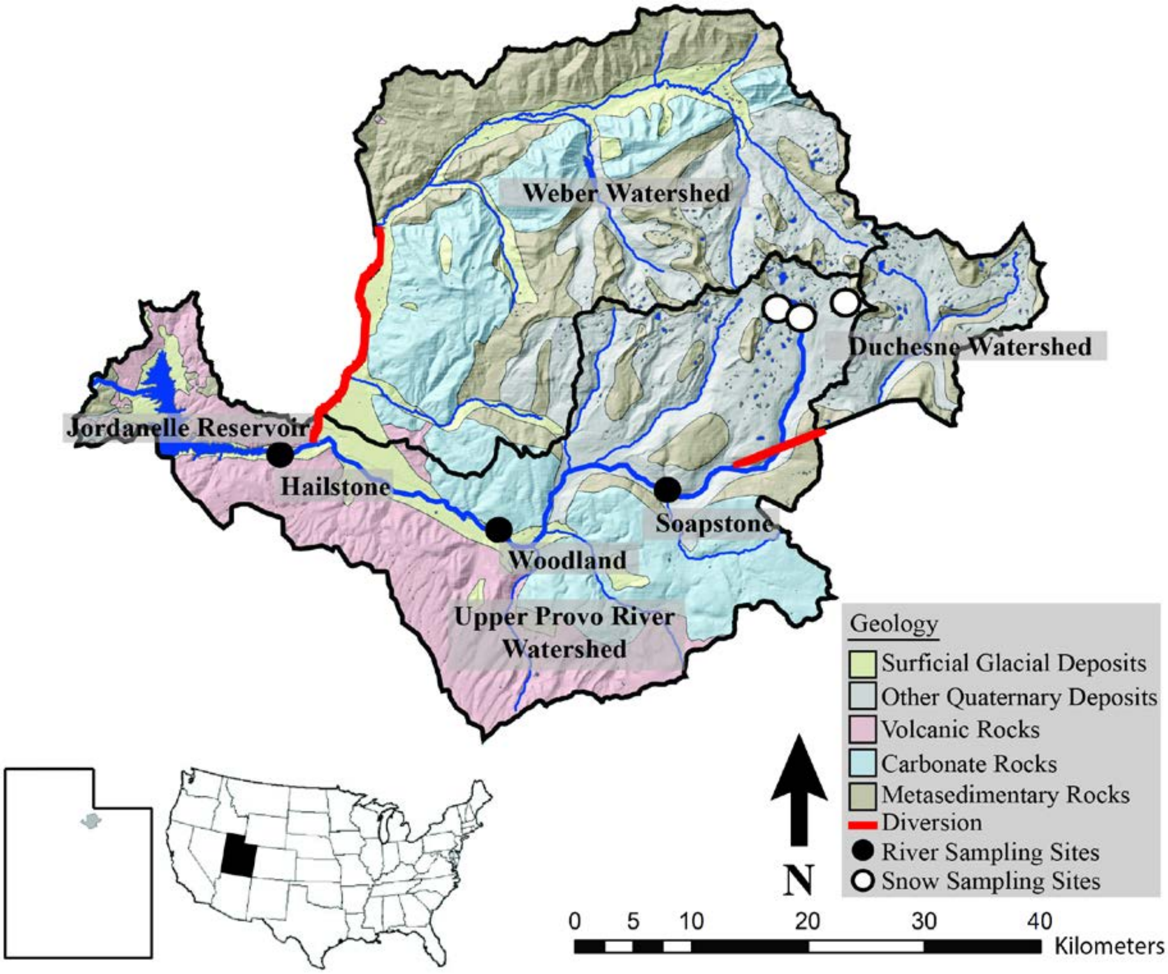

Figure 1 . Map of the upper Provo River watershed in northern Utah, USA. River sample sites are shown with black circles and site names. Snow sample sites are shown with white circles. Water from the Duchesne River is diverted into the Provo River above the Soapstone sampling site and water from the Weber River is diverted above the Hailstone sampling site. Near the headwaters of the Provo River the geology is composed of the silica-bound sandstones with interbedded shales, overlain by glacial till and Quaternary deposits (Figure 1). Further downstream, Paleozoic carbonate rocks and Tertiary volcanic rocks create a more complex water-rock interaction.

The hydrology of the upper Provo River, can be summarized simply as a snowmelt-dominated system. Primary precipitation occurs during the fall, winter and spring months, mostly in the form of snow. On average, the high Uintas gets about ~56 cm of precipitation per year. Peak runoff generally occurs in late May or early June when snowmelt increases with rising temperatures. The Provo River receives water diverted from the Duchesne and Weber Rivers (Figure 1).

The upper Provo River watershed is part of an ongoing NSF project that monitors additional parameters. The NSF EPSCoR funded research is a $20 million project called Innovative Urban Transitions and Aridregion Hydro-sustainability or “iUTAH” and supplies monitoring equipment along the Provo River. Specifically, three climate monitoring stations and one aquatic monitoring station are installed in the upper Provo River watershed. The climate stations include measurements of snowpack characteristics, soil moisture and meteorological parameters. The aquatic station delivers measurements of turbidity, conductivity, fluorescent dissolved organic carbon (fDOM), pH, streamflow, and water temperature. The iUTAH aquatic monitoring station is located at Soapstone and USGS streamflow gauges are located at Woodland and Hailstone (Figure 1).

The Provo River is a primary water source for over two million people along the Wasatch Front. In the montane portion of the reach, elevated levels of aluminum appear during peak flow surpassing secondary water quality regulations (EPA: Secondary Standards). Despite regional concerns, the Provo River system can be an analogue to other semi-arid regions where a large population depends on runoff.

2.2 Field sampling of river, snow and ephemeral samples

Over a 130 samples (river, ephemeral, and snow) were taken in the upper Provo River watershed for this study at Soapstone, Woodland, and Hailstone (Figure 1). More than 100 samples were routine river samples collected during the 2014, 2015 and 2016 water years, including 11 in 2014, 13 in 2015, and 85 in 2016. Routine river sampling for the 2016 water year favored frequent weekly sampling during runoff (April-June), bi-monthly sampling in the months prior to and post runoff (March, July) and monthly sampling at baseflow (August-February). Of those samples in 2014 and 2015, 16 were taken at Soapstone, 1 at Woodland and 7 at Hailstone. Equal sampling occurred at all three sites in 2016. During 2016, a total of 8 ephemeral channel samples were taken in the upper Provo River watershed, above the Soapstone sampling site. Ephemeral samples were gathered opportunistically off of seasonal snowmelt channels, in which the water has likely interacted with shallow groundwater and soils. All ephemeral samples were gathered in May 2016, just prior to peak snowmelt.

Water samples were gathered in the field by implementing the EPA "clean hands, dirty hands" methods, and each sample was triple rinsed with sample water. All water samples (river and ephemeral) were collected in assorted bottles specific to sampling type; low-density polyethylene (LDPE) for metals and cations, amber glasses for $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$ and DOC, and 1 liter plastic bottles, which were later broken into samples for major anion and bicarbonate analysis. Before sampling, the 125 mL-LDPE bottles used for metal and cation analysis were acid washed with 10% v/v HCL, triple rinsed with Milli-Q water and dried under a laminar flow hood. After drying, the bottles were removed and placed in clean Ziploc bags. Amber vials used to sample DOC were lightly washed with 10% v/v HCL, triple rinsed with Milli-Q water, dried in the oven for 3 hours at 450 degrees C and covered with aluminum foil.

Some filtering was done in the field for DOC samples using a 0.45 micron fiberglass disk filter and a peristaltic pump (which is cleaned by running 10% HCL through tubing for one minute, before rinsing with two pore volumes of Milli-Q water. Field blanks were taken at each site by pouring Milli-Q water into sample bottles or if necessary, pumping it through the peristaltic pump. Field blanks were gathered using the same procedures as samples. All water samples were stored at 4 degrees c following collection.

We collected snow samples to measure metal loading due to atmospheric deposition, including dust, in the winter months. A total of 20 snow samples were collected in the upper Provo River watershed, above the Soapstone sampling site in the 2016 water year. These samples were gathered in the month of April on two different days (18th and 29th), prior to major snowmelt. Three sites were chosen and three pits were excavated at each site. On April 18th, 2016, each snow pit was excavated to the ground and a complete snow column was taken from behind the snow pit face using a clean acrylic core. Snow was transferred from the core to a clean 2 L fluorinated high density polyethylene (FLPE) bottle. Clean sampling methods were used in all cases. Persons removing snow wore Tyvek jackets and vinyl gloves during sample collection. On April 29th, the same procedures were used, but pits dug to the latest dust storm event only. Field blanks were collected at each site by pouring Milli-Q water through the acrylic tube into a sample bottle. Field blanks were processed using the same procedures as samples. All snow samples were stored frozen until further processing.

2.3 Laboratory analysis of river, snow and ephemeral samples

In the laboratory, water samples (river, ephemeral channels, and melted snow) were analyzed for dissolved organic carbon, metals and major cations, major anions, and $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$. Dissolved organic carbon had been filtered in the field, and was acidified in the lab with 10% v/v HCl until 3.5-4 pH. A filtered and acidified (2.4% v/v HNO_3) sample was collected for trace elements in an acid-washed LDPE bottle using a 0.45 micron PES syringe filter and polypropylene syringe. The syringe and filter were acid-washed (10% v/v HCl) and triple- rinsed in Milli-Q water prior to processing the sample. To avoid sample contamination, all work was done in a laminar flow hood. The $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$ samples remained unfiltered and unacidified. The major anion samples were filtered through a .45 micron film and left unacidified.

Trace element and major cation concentrations were measured using an Agilent 7500ce quadrupole inductively coupled plasma mass spectrometer (ICP-MS). Concentrations were measured for the following elements: Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Sb, Se, Sm, Sr, Tb, Th, Ti, Tl, U, V, Y, Yb and Zn. DOC was measured using a Shidadzu TOC analyzer. $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$ were measured on unfiltered samples 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 0.4‰ and 1.0‰ for $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$, respectively. Major anions (Cl^-, NO_3^- , and SO_4^{2-}) were analyzed on filtered samples using a Dionex ICS-90 ion chromatograph.

2.4 Data management and presentation

We focused on specific metals to understand the water chemistry of the upper Provo River. La, Pb, Cu, Al, Be, Sr and K were chosen due to interesting relationships with discharge and DOC. La was chosen because it was representative of trends demonstrated by other rare earth elements. Pb and Cu were selected in response to work done in the Uinta Mountains on atmospheric deposition (Reynolds et al., 2010) and because of potential health hazards. Al was chosen because of high concentrations previously measured by the Utah Division of Water Quality. Be was chosen because of potential health hazards and interesting trends. Sr was selected because of its potential to be used as an isotope tracer to identify trace metal sources. Finally, K was chosen because it is a major cation with contrasting behavior to trace metals in the river during snowmelt.

A few analyses needed data control. For elements Pb and Be, river concentrations measured on the ICP-MS returned some values below detection limit. These values were recorded as half the detection limit for concentrations represented on line graphs. The same is also true for snow concentrations. However, for linear regression analysis, outputs below detection limit were eliminated in order to prevent improperly reported p-values. Linear regression between DOC and La, Pb, Cu, Al, Be, Sr and K was reported only for the Woodland site, due to interesting concentration-discharge trends. Outliers of linear regression were identified and eliminated using *Studentized Residuals*, via JMP. Value points that were clearly a result of sampling or analysis error were also eliminated. Another form of data checking was the use of a charge balance. In 2016, 10/85 water samples had incorrect charge balances, where a difference of + or - 5% was acceptable. However, of those 10, 7 were + or -2% away from the 5% mark.

3 Results

3.1 Stream discharge responds to snowmelt

Peak discharge in the upper Provo River varied between water years 2014-2016 and between the Soapstone, Woodland and Hailstone sampling locations (Figure 2). The highest discharge was recorded in the 2014 water year at peak runoff in May approaching 90 m^3/sec at Hailstone and 67 m^3/sec at Woodland (discharge was not measured at Soapstone during the 2014 runoff season). In contrast, 2015 had the lowest runoff, with maximum discharge in June reaching 53

m^3/sec at Hailstone, 34 m^3/sec at Woodland, and 28 m^3/sec at Soapstone. The 2016 water year had moderate discharge with maximums of 76 m^3/sec at Hailstone, at 55 m^3/sec Woodland and 52 m^3/sec at Soapstone. Notably, the relative increase in discharge between Woodland and Hailstone was much greater during the low runoff year in 2015 (56% increase) relative to the higher runoff years in 2014 and 2016 (34% and 38% increase, respectively). During baseflow, discharge typically increased from ~0.3 m^3/sec to ~0.9 m^3/sec from Soapstone to Woodland and from ~0.9 m^3/sec to ~2 m^3/sec from Woodland to Hailstone. Notably, a summer storm in September 2014 caused a significant increase in discharge at the three sites, with maximum discharge of 24 m^3/sec at Hailstone.

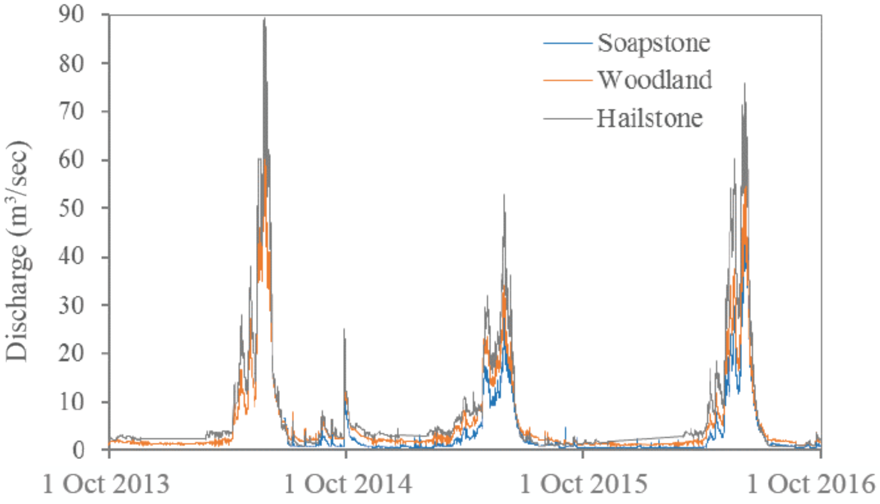

Figure 2 . Discharge at three sampling sites (Soapstone, Woodland and Hailstone) in the Upper Provo River watershed. Runoff discharge is observable in each water year (2014, 2015 and 2016), where peak discharge occurs in late May, early June, with an additional storm runoff in October, 2014.

3.2 DOC and element concentrations show seasonal variability

Elemental concentrations in the upper Provo River showed varying response to runoff over the three years of study (Figure 3). DOC, La, Pb, Cu, Al, and Be increased each year in response to spring runoff at the Soapstone site, whereas Sr and K showed little change during runoff. For

La, Cu, Be, the maximum concentrations were similar each year in spite of differences in total discharge. In contrast, Pb and Al showed differences in maximum concentration each year. Pb had the highest maximum concentration (0.12 µg/l) during 2015 when the discharge was lowest and the lowest maximum concentration (0.06 µg/L) when discharge was highest during 2014. Al also had the highest maximum concentration (183 µg/l) during 2015. The lowest peak concentration for Al (121 µg/l) occurred during 2016 with intermediate discharge, marking a 35% difference from 2015.

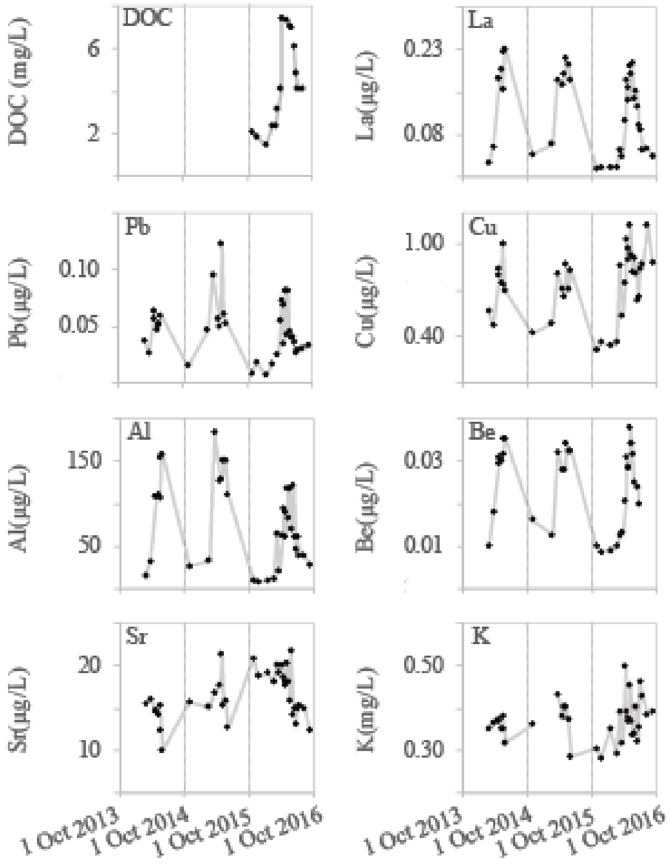

Figure 3 . Concentrations of soluble DOC and selected elements (La, Pb, Cu, Al, Be, Sr and K) from the 2014, 2015 and 2016 water years. DOC, La, Pb, Cu, Al and Be increased with high discharge during each water year.

Elemental concentrations in the upper Provo River showed different trends from upstream to downstream during the 2016 water year (Figure 4). DOC concentrations were similar at

Soapstone, Woodland, and Hailstone, peaking prior to maximum runoff (average max ~9 mg/L). La and Cu concentrations were highest at Soapstone and Woodland with lowest concentrations at Hailstone. Pb, Al and Be concentrations were highest at Soapstone, with decreasing concentrations downstream at Woodland and Hailstone. Concentrations tended to peak earlier during the runoff season at Soapstone relative to downstream sites.

Maximum element concentrations occurred at different times and locations for different elements (Figure 4). La had a peak concentration (0.21 µg/l) at Woodland (June 2016). Pb had a peak concentration (0.08 µg/l) at Soapstone (May 2016). Cu had a peak concentration (1.13 µg/l) at Woodland (May 2016). Al had a peak concentration (121 µg/l) at Soapstone (June 2016). Interestingly, on the same sampling day, the peak concentration for Al was measured at Woodland (71.1 µg/l), which is a 40% decrease from Soapstone. Be had a peak concentration (0.037 µg/l) at Soapstone (May 2016). Sr and K concentrations were diluted at Woodland and Hailstone during spring runoff but remained similar throughout the year at Soapstone.

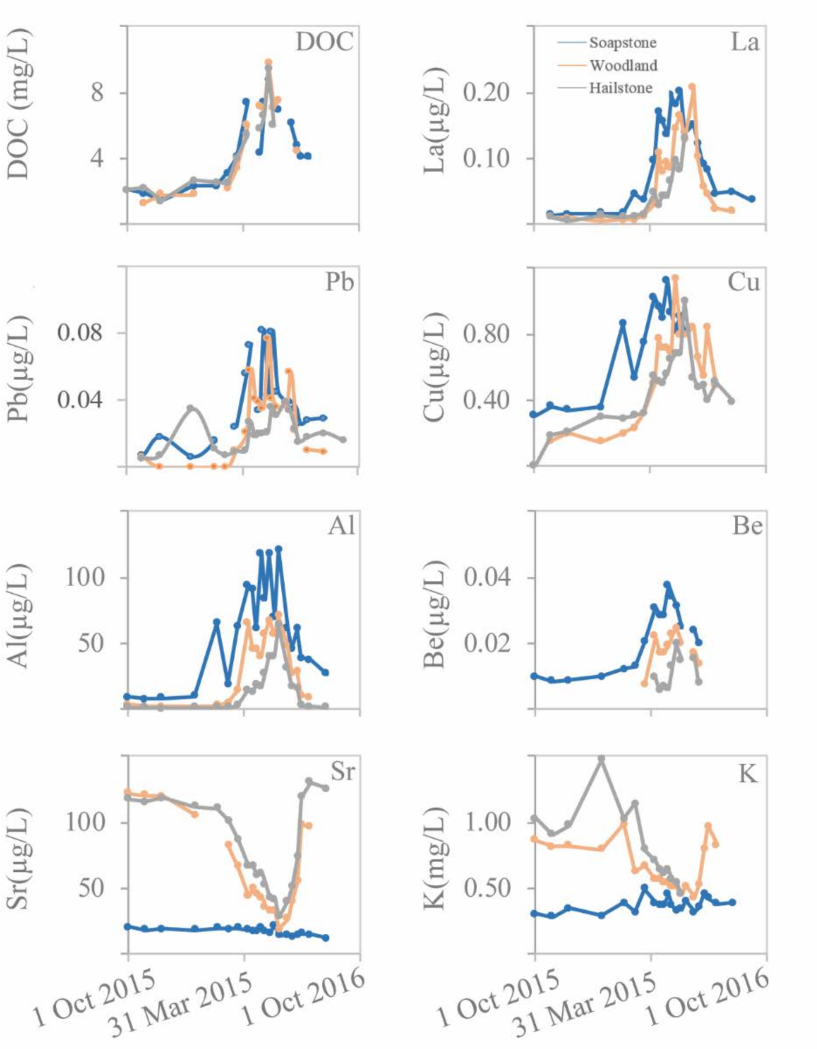

Figure 4 . Concentrations of DOC and selected elements (La, Pb, Cu, Al, Be, Sr and K shown from the 2016 water year at the Soapstone, Woodland and Hailstone sampling sites. DOC, La, Pb, Cu, Al and Be increase at Soapstone, Woodland and Hailstone during high discharge. La, Cu, Al and Be have a flush of high concentrations at Soapstone, prior to a flush of high concentrations experienced later at Woodland and Hailstone.

3.3 DOC and trace element loads

For DOC and the other selected elements, instantaneous loads increased during snowmelt in 2016, indicating a seasonal flush (Figure 5). Runoff loads account for >80% of DOC, La, Pb, Cu, Al, Be, Sr and K of annual loads at Soapstone, Woodland, and Hailstone. For the elements Sr and K, this seems contradictory because concentrations were diluted during snowmelt. Although concentrations of Sr and K decrease due to dilution, the overall load increases with the increasing stream discharge. The loads of Sr and K are two-fold higher at Hailstone relative to Woodland, likely due to contributions from the Weber River diversion.

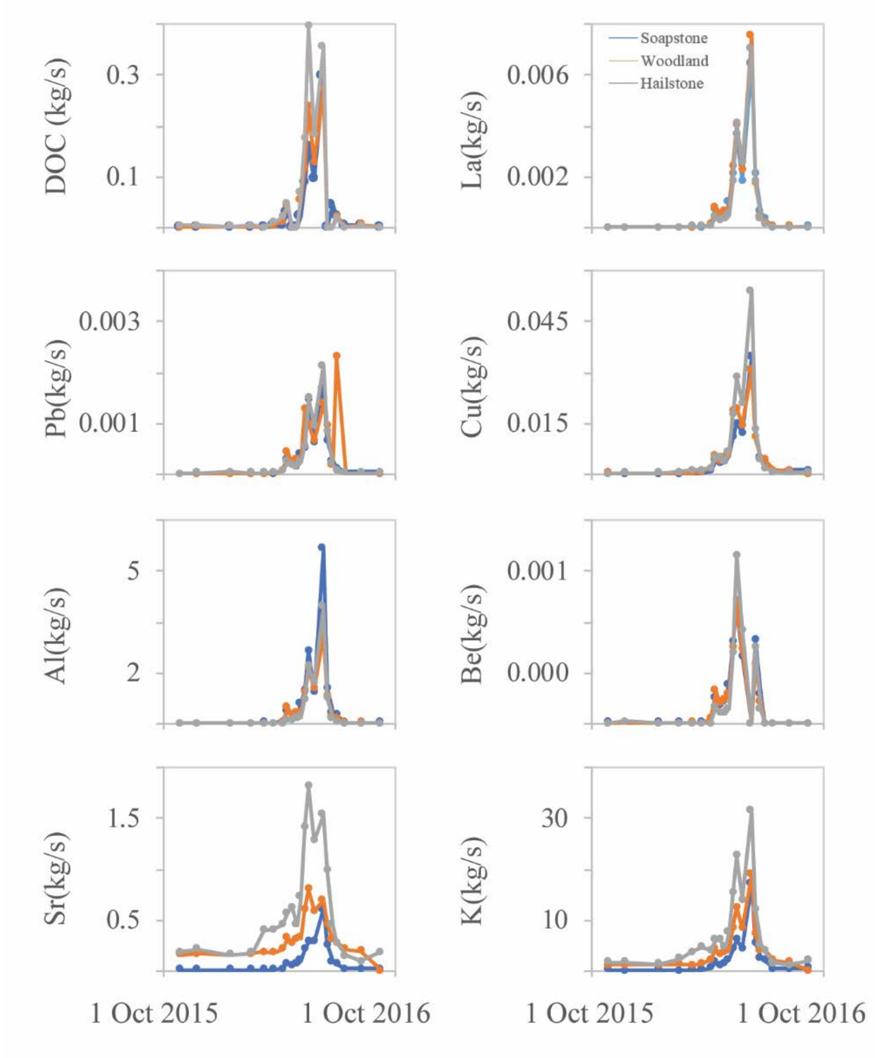

Figure 5 . Instantaneous loads for DOC and selected elements (La, Pb, Cu, Al, Be Sr and K) at Soapstone, Woodland and Hailstone during the 2016 water year. Note that loads of Sr and K increase, despite concentrations being diluted at high discharge. Also note that >90% of all element loads at Soapstone, Woodland and Hailstone occurred during runoff months (April-June), with the exception of Sr and K at Woodland and Hailstone where 70-90% of elemental loads occurred during runoff months (April-June).

3.4 DOC and element concentrations versus discharge shows chemostatic behavior, dilution, or inputs

Element concentrations displayed varying responses to discharge during the 2016 water year at Soapstone (Figure 6), Woodland (Figure 7), and Hailstone (Figure 8). In Figures 6-8, concentrations of DOC, La, Pb, Cu, Al, Be, Sr and K are plotted against discharge, both at a log scale. At Soapstone (Figure 6), DOC, La, Pb, Cu and Al increase slightly in response to increasing discharge, with especially large increases between a discharge of 0.2 to 1 m^3/sec. Sr and K showed chemostatic behavior, with no noticeable changes in concentration in response to discharge. At Woodland (Figure 7), DOC La, Pb, Cu, Al and Be increase in response to discharge, particularly at lower discharge between 1 -10 m^3/sec. Sr concentrations were diluted with increasing discharge, whereas K showed chemostatic behavior. At Hailstone (Figure 8), the concentrations for DOC, Pb, Cu, and Be slightly increased in response to discharge. La and Al concentrations increased sharply in response to discharge, similar to the response at Woodland. Sr and K showed slight dilution in response to increasing discharge.

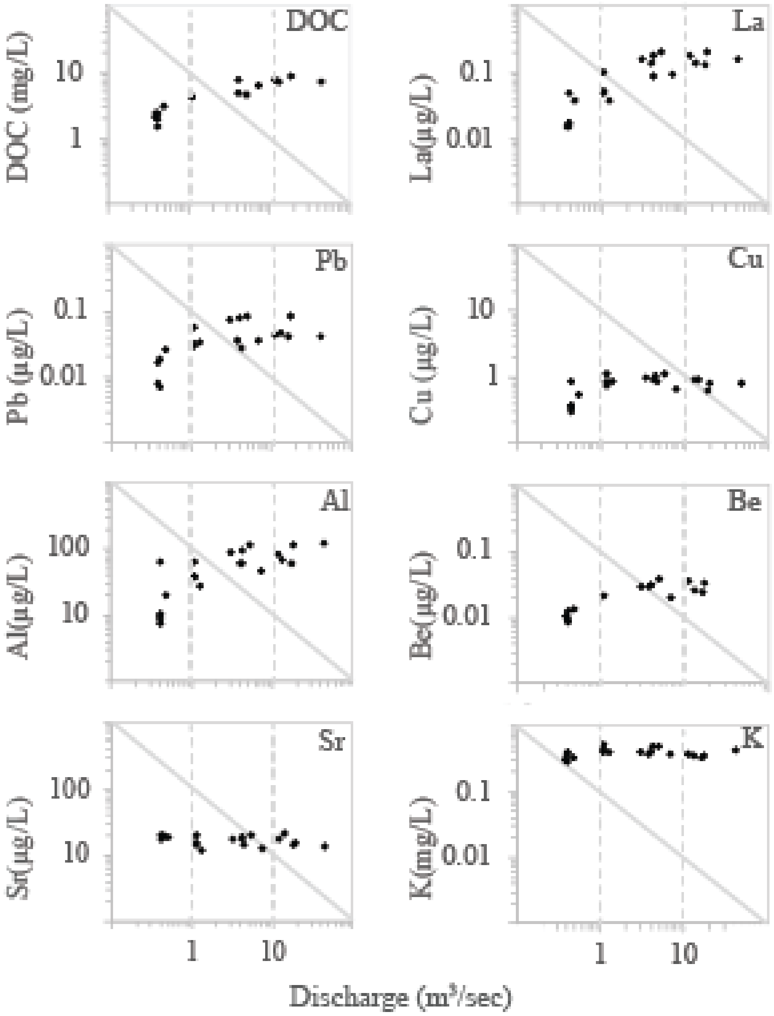

Figure 6 . Concentration vs. Discharge plots for DOC and selected elements (La, Pb, Cu, Al, Be, Sr and K), where concentrations were measured at Soapstone during the 2016 water year. Concentration vs. discharge plots are outlined similar to (Godsey et al., 2009) and gray diagonal lines represent dilution. DOC, La, Pb, Cu, Al and Be increase slightly with discharge at the log scale, whereas Sr and K are chemostatic.

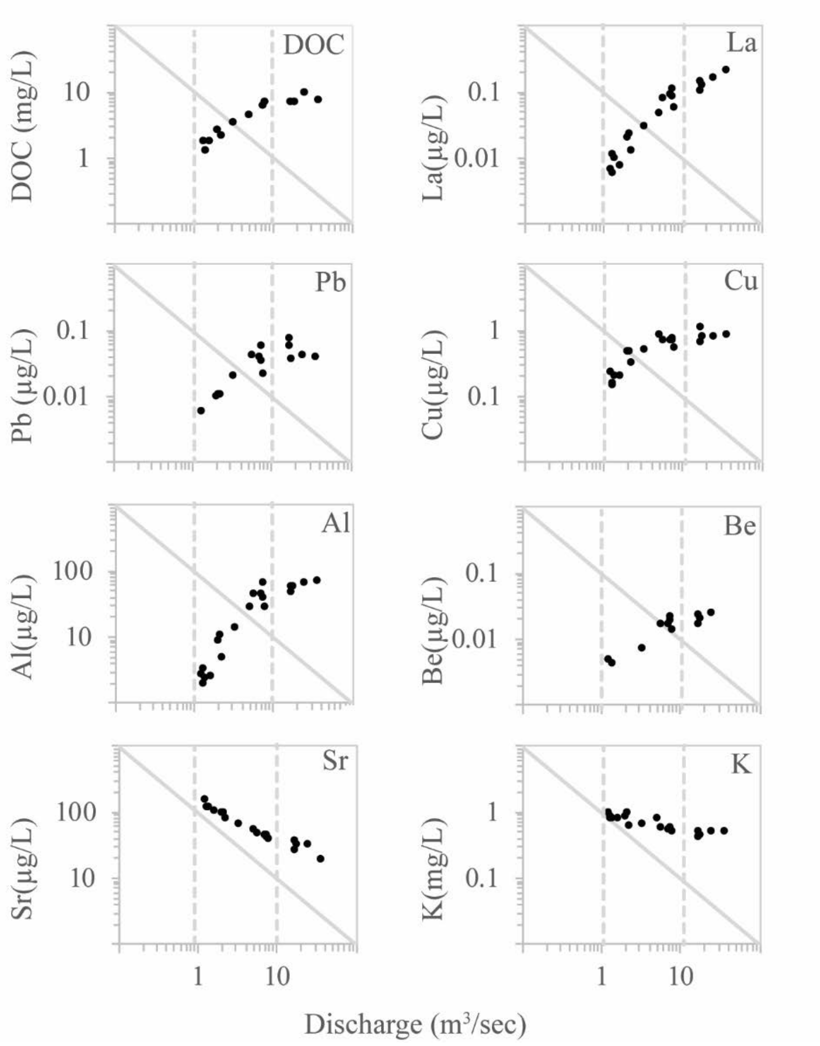

Figure 7 . Concentration vs. Discharge plots for DOC and selected elements (La, Pb, Cu, Al, Be, Sr and K), where concentrations were measured at Woodland in the 2016 water year. Concentration vs. discharge plots are outlined similar to (Godsey et al., 2009) and gray diagonal lines represent dilution. DOC, La, Pb, Cu, Al and Be increase significantly with discharge at the log scale, whereas Sr is diluted and K is chemostatic.

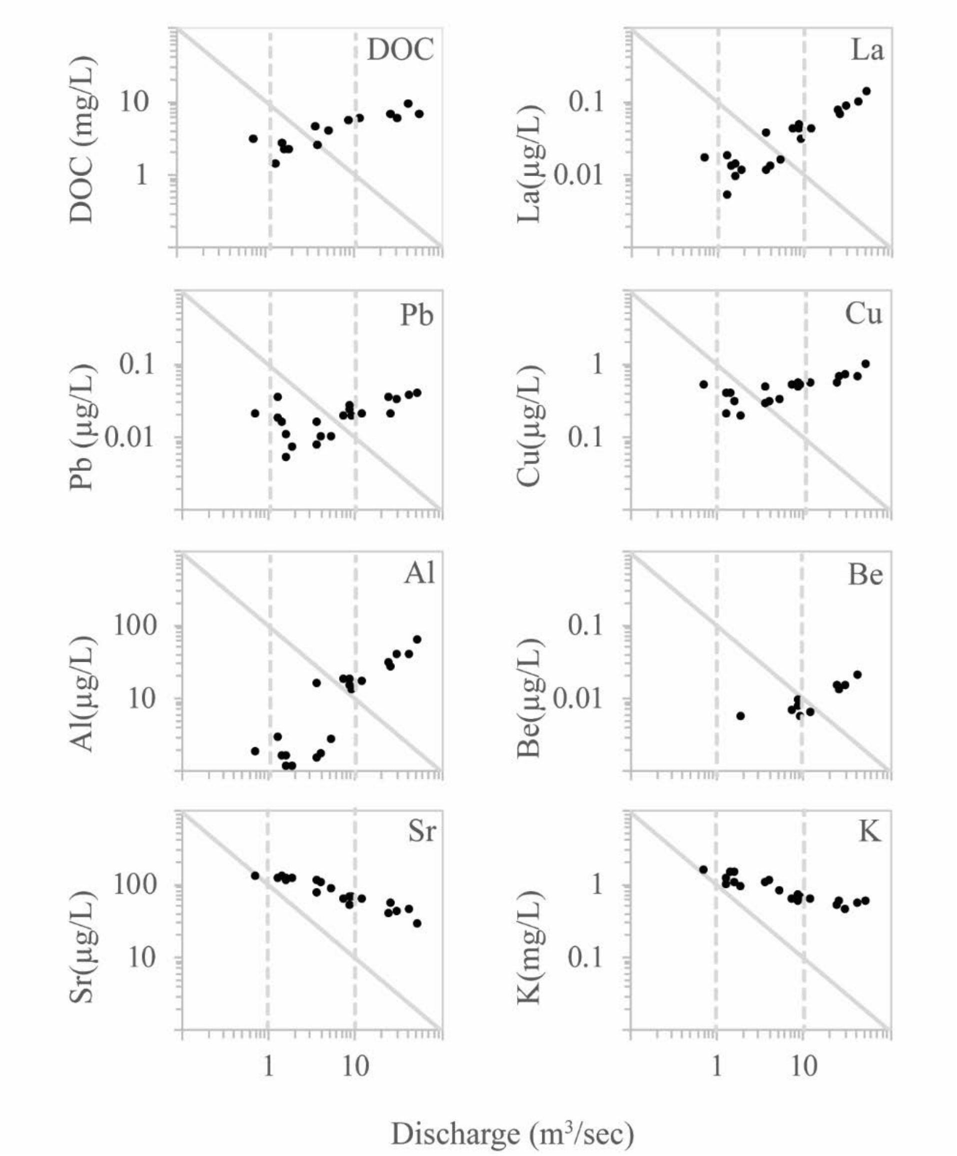

Figure 8 .Concentration vs. Discharge plots for DOC and selected elements (La, Pb, Cu, Al, Be, Sr and K), where concentrations were measured at Hailstone during the 2016 water year**.** Concentration vs. discharge plots are outlined similar to (Godsey et al., 2009) and gray diagonal lines represent dilution. DOC, La, Pb, Cu, Al and Be increase significantly with discharge at the log scale, whereas Sr and K are slightly diluted.

DOC, La, Pb, Cu, Al, Be, Sr and K showed different hysteresis patterns at each sampling location (Figure 9). DOC concentrations had a clockwise hysteresis at Soapstone, Woodland, and Hailstone. La concentrations had a clockwise hysteresis at Soapstone and Woodland, but a counter-clockwise hysteresis at Hailstone. Pb concentrations had a clock-wise hysteresis at Soapstone, a figure-eight hysteresis at Woodland and counter- clockwise hysteresis at Hailstone.

Cu concentrations had a clockwise hysteresis at all three sampling sites. Al concentrations had a clockwise hysteresis at Soapstone and Woodland, but a figure-eight hysteresis at Hailstone. Be concentrations had a clockwise hysteresis at Soapstone and Woodland, but a figure eight at Hailstone. Sr and K had clockwise hysteresis at Soapstone and Hailstone, but a figure eight hysteresis at Woodland. Notable is that at the onset of snowmelt, there is a knot of values plotted at the Woodland and Hailstone sites that tend to revolve in a circular motion (look for cluster of data on left hand side of plots). These revolving centers are not counted as figure-eight patterns because they follow the original direction, whereas figure-eight patterns change the direction from clockwise to counter-clockwise or vice versa.

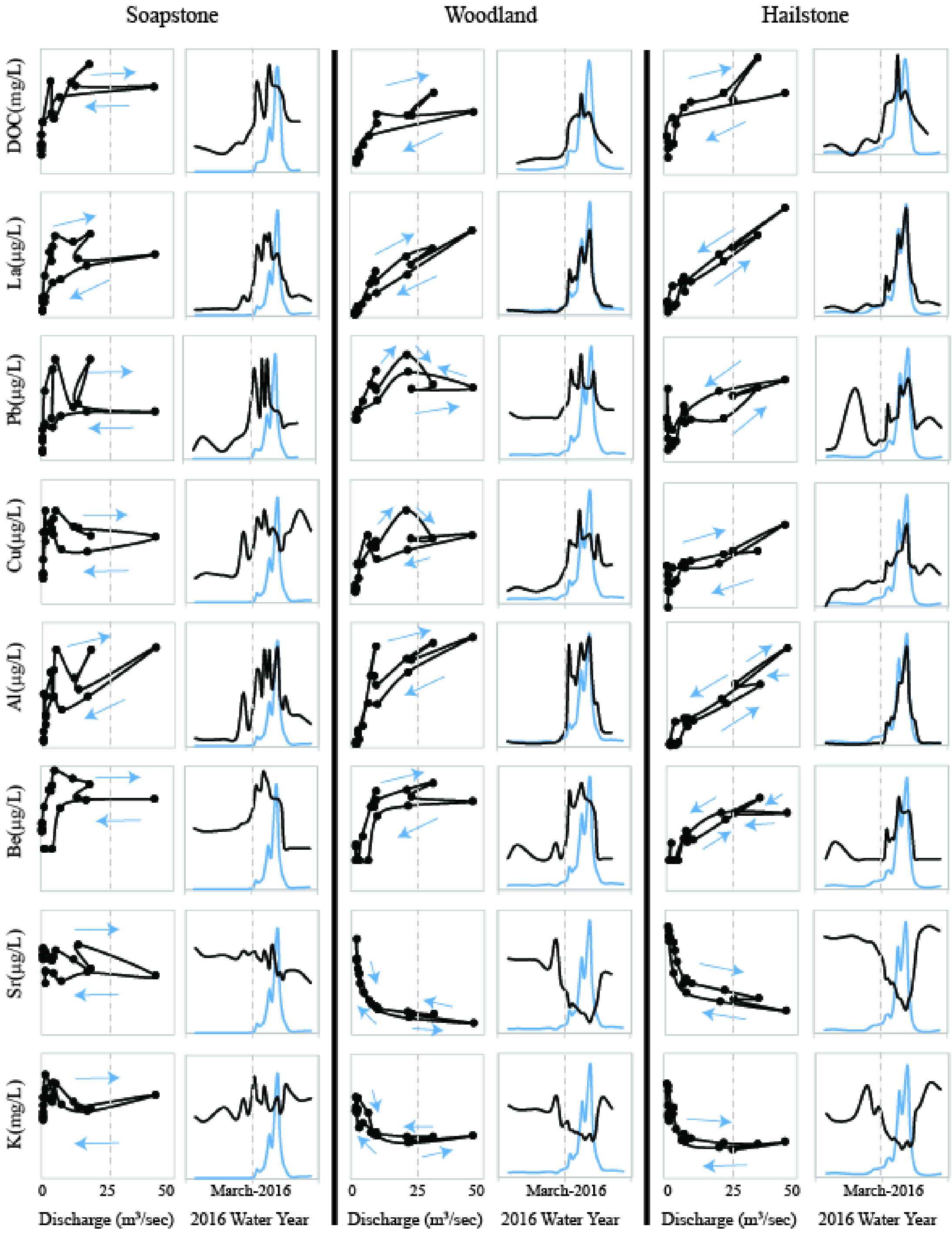

Figure 9 . Hysteresis patterns of DOC and selected elements from the 2016 water year. Clockwise hysteresis implies a flushing of local sources. Counter-clockwise hysteresis implies a delay in elemental concentration peaks (element peaks that align with or follow hydrograph peak) and a lag in elemental flushing. Figure-eight patterns suggest a mixing of both clockwise and counter-clockwise hysteresis. Note the knot where there is a crossover at the onset of snowmelt at the Woodland and Hailstone sites. Typically, concentrations revolve at this knot for a time.

3.5 Concentrations in snow, ephemeral channels, and river samples

DOC and element concentrations were typically lowest in snow samples, highest in ephemeral channels, with intermediate concentrations in snowmelt runoff at Soapstone (Figure 10). These relationships suggest that snow contributes minimally to observed water chemistry at Soapstone. Instead, soil water (represented by ephemeral channel samples) accounts for the majority of changes in river chemistry. During snowmelt, the soil zone is flushed by incoming meltwater that causes the release of DOC and metals to the river.

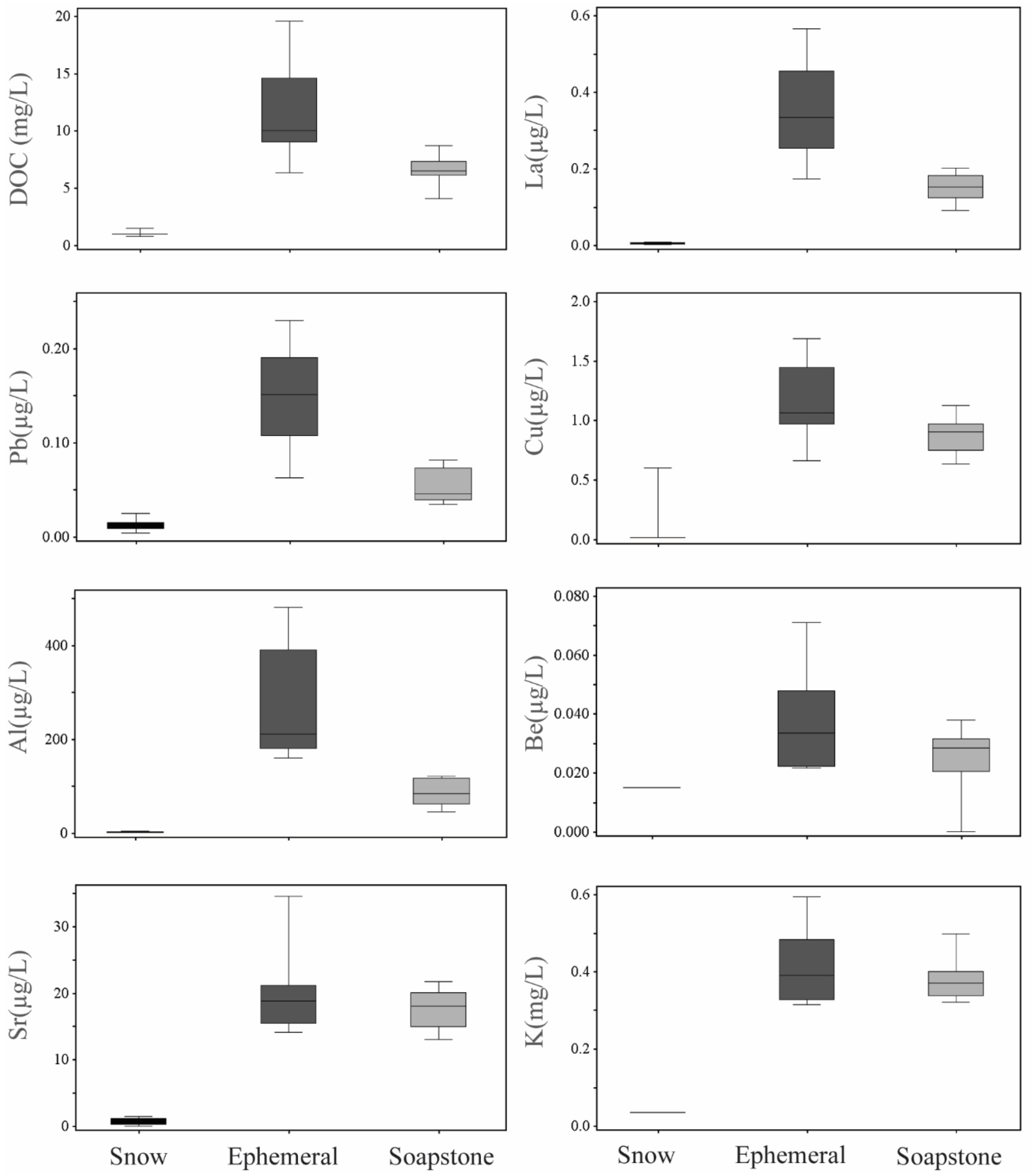

Figure 10 . DOC and selected element (La, Pb, Cu, Al, Be, Sr and K) concentrations in bulk snowpack, ephemeral channels, and runoff water (April – June) from the Soapstone site during spring 2016. Bulk snowmelt has the lowest concentrations in DOC, La, Ob, Cu, Al, Be, Sr and K, whereas ephemeral flow has the highest. However, there is significant overlap in ephemeral and Provo River (Soapstone) concentrations for Be, Sr and K.

4. Discussion

4.1 Interpretation of DOC and element responses during snowmelt

Numerous possibilities explain concentration differences from baseflow to snowmelt runoff in the Provo River. DOC concentrations increased prior to peak runoff at each sampling site during the 2016 water year, which is consistent with results found in watersheds of similar elevation (Boyer et al., 1997; Hornberger et al., 1994) and higher latitudes (Rember and Tefrey, 2004). Soil water is typically the main source of DOC in mountain watersheds (Hornberger et al., 1994; Rember and Tefrey, 2004). Similarly, the most likely source of stream DOC is from the upper soil horizon by degradation of plant material, where DOC is transported by soil water to the river system (Brooks et al., 1999). In this study, we found the highest DOC concentrations in ephemeral channels, which represents contributions from soil water (Figure 10). It is also possible that DOC is sourced from water-rock interactions or atmospheric deposition, but these seem less likely than soil water. Measurements of atmospheric deposition on snow, which is a seasonal dust trap, suggest low amounts of atmospheric DOC deposits (~<1.5 mg/L in 2016 Uinta snowpack). Water-rock interactions occurring below the surface might be a source of DOC in water. In the upper Provo River watershed, there is some exposure to the Red Pine Shale, where TOC measurements range between 0.32-5.9% (Dehler et al., 2006) and it has been previously suggested that dark shale (5-8% TOC) can be a source of higher DOC in surface water runoff (Ogendi et al., 2007). However, it is unlikely that that the Red Pine Shale is the sole or even primary source of DOC as TOC measurements range greatly and there is minimal exposure to the Red Pine Shale in the upper Provo River watershed.

Trace elements La, Pb, Cu, Al, Be, Sr and K had varying responses through time during spring runoff. La, Pb, Cu, Al and Be concentrations increased in the Provo River during high discharge (Figure 3) and at each sampling site (Figure 4), indicating that there are additional sources of these metals and cations in the watershed that are flushed during discharge. Soil water is the predicted key mechanism for La, Pb, Cu and Al to reach the river system, as measured ephemeral concentrations are significantly higher than concentrations in the Provo River (Figure 10). Concentrations of Be were not significantly greater in ephemeral flow in comparison to river water, but still considerably higher than river water, suggesting that soil water could also be a source of Be.

The elements Sr and K showed no obvious trends from year to year (Figure 3), but did decrease through time at each location in the 2016 water year (Figure 4). However, the decrease was more notable at Woodland and Hailstone and less at Soapstone. The decreases in concentration suggest that during discharge, there is not a significant contribution of additional Sr or K to keep the water from becoming chemostatic or diluted during snowmelt. This is further demonstrated by no significant difference between Sr and K concentrations in ephemeral and river samples (Figure 10).

4.2 Potential complexation of DOC with metals

DOC complexation is likely responsible for the transport of metals in the upper Provo River watershed. Both Al and La concentrations have the highest relationships with DOC concentrations out of the elements we have chosen to highlight ($R^2 = 0.94$, $P = < .0001$) and ($R^2 = 0.94$, $P = < .0001$), respectively (Figure 11). Be, Cu and Pb concentrations also had strong positive relationships with DOC concentrations ($R^2 = 0.93$, $P = < .0005$), ($R^2 = 0.83$, $P = < .0001$) ($R^2 = 0.76$, $P = < .0023$), respectively (Figure 11). Sr and K concentrations did not have positive relationships with DOC concentrations as they were diluted or chemostatic during snowmelt (Figure 11). Relationships between organic matter and metals are well documented

(Hölemann et al., 2005; Kerr et al., 2008; Rember and Tefrey, 2004; Reynolds et al., 2014). Fluorescent dissolved organic matter or fDOM measurements, solidify that organic material increases in the upper Provo Watershed during snowmelt (Figure 12) accompanying a flush of metal concentrations. However, it is unclear if this pattern is coincidental with the flushing of dissolved material found in soil water or if organic materials are truly facilitating metal transport. Further analysis of DOM (which is ~40-50% DOC), is needed to identify meaningful relationships between the complexation of metals with fulvic and humic acids. Similarly, research needs to be done on the amount of DOM complexing with metals, so it can be determined how much of DOC is complexing metals relative to the amount of DOC that is simply flushing from soils coincident with metals.

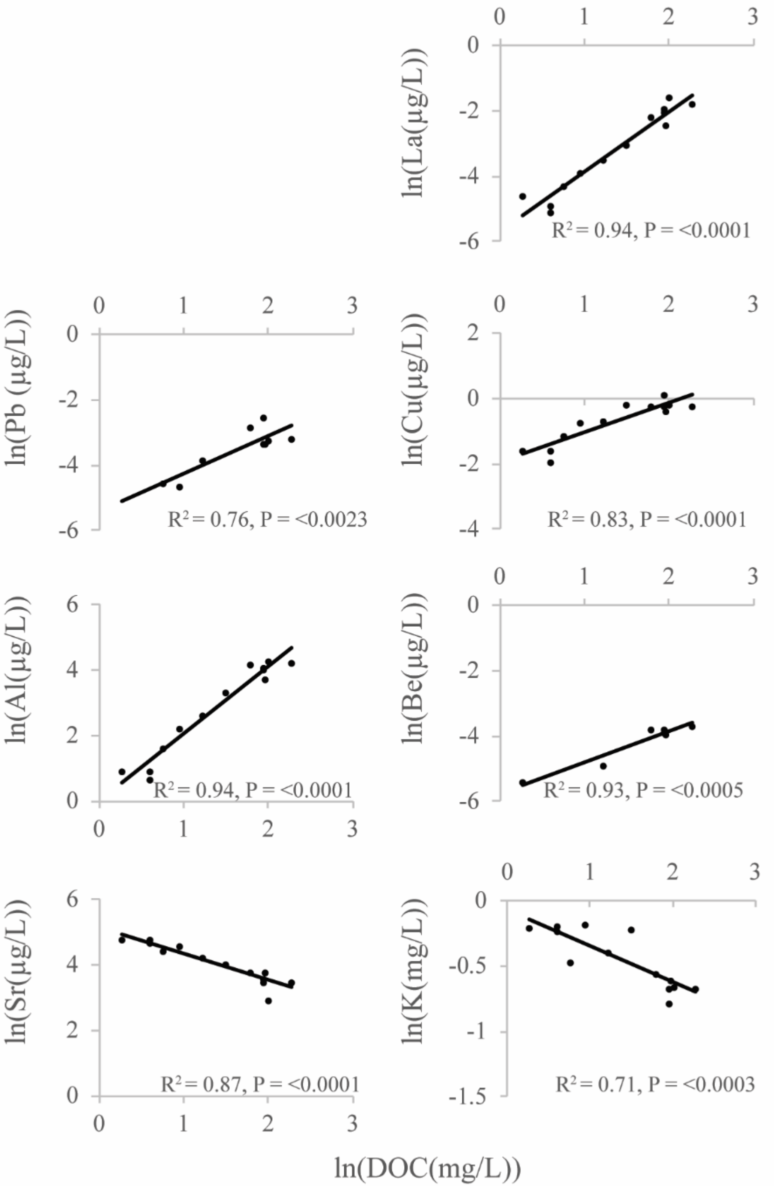

Figure 11 . Linear regression plots between DOC and the selected elements (La, Pb, Cu, Al, Be, Sr and K), where concentrations were measured at Woodland, 2016. Correlation is reported with R^2 values. La and Al had the strongest relationship with DOC ($R^2 = 0.94$, $R^2 = 0.94$, respectively), followed by Be, Cu, and Pb ($R^2 = 0.93$, $R^2 = 0.83$, $R^2 = 0.76$, respectively). Sr and K did not show a positive relationship with DOC.

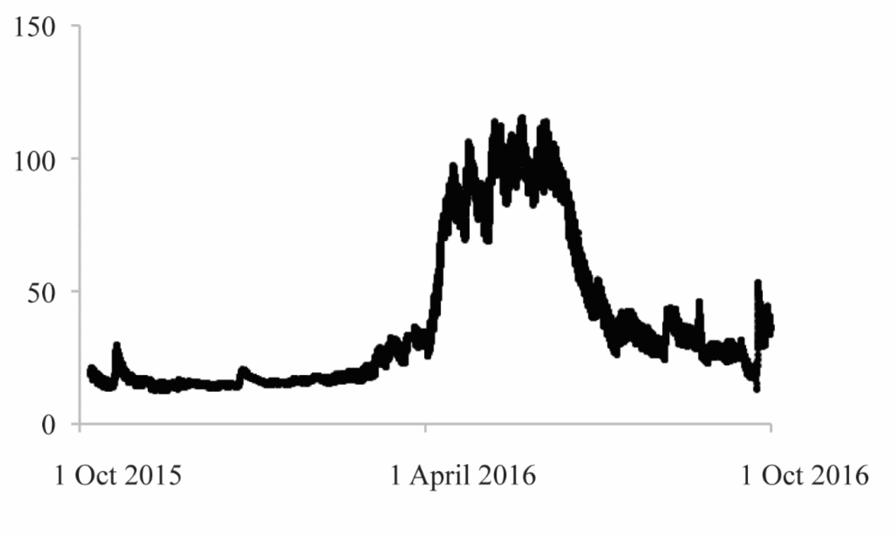

Figure 12 . Non-quality controlled fDOM data for Soapstone during the 2016 water year (iUTAH database). Fluoresced dissolved organic matter increases like DOC and selected elements (La, Pb, Cu, Al and Be) during high discharge.

The elevated metal concentrations prior to peak discharge at Soapstone could be related to colloid transport. Colloids have been known to sorb and facilitate metal transport, especially Pb (Citeau et al., 2003). When metals are sorbed, they can move more quickly through soil due to size exclusion, which might explain why a flux of metals precedes peak discharge and why metals in particular are being flushed, while other materials remain chemostatic (Grolimund et al., 1998).

4.3 Interpretation of elements showing chemostatic, non-chemostatic and hysteresis patterns

The concentration-discharge patterns are dependent on concentration peaks of the discharge hydrograph (Williams, 1989) and the slope is the result of material availability (Long et al., 2017). The positive slope for DOC and elements La, Pb, Cu, Al and Be at all three sampling sites (in the exception of Soapstone, where Cu is not positively sloped), implies that these elements experience an initial flushing event at the onset of snowmelt. At Soapstone, Sr and K are chemostatic, indicating that Sr and K concentrations are independent of discharge. At Woodland and Hailstone, Sr and K are negatively sloped, suggesting that these elements are diluted with increasing discharge.

DOC, La, Pb, Cu, Al, Be, Sr and K concentrations at Soapstone have a clock-wise hysteresis with the concentrations peaking on the rising limb of the hydrograph (Williams, 1989). In other words, the movement of metals demonstrate a flushing of soil water and removal of material, until the flow paths are diluted and the concentrations in relation to discharge are chemostatic. Material availability for DOC, La, Pb, Cu, Al, Be, Sr and K at Soapstone were probably supplied from nearby sources (Creed et al., 2015), based on clockwise hysteresis patterns. The trends at Woodland and Hailstone were not as homogenous. At both locations, there was clockwise hysteresis, counter-clockwise hysteresis and figure-eight patterns. Also, at Woodland and Hailstone, the distance between peak concentrations and peak discharge is much smaller compared to Soapstone, which can be observed by their skinny hysteresis loops. At Soapstone, concentrations increased with the slightest change of discharge (0.2 to 1 m^3/sec), whereas significant changes to concentration occured at higher discharge (1 -10 m^3/sec) for Woodland and Hailstone. The quick flushing of elements imply that the Soapstone sampling site has a small threshold in comparison to Woodland and Hailstone. Likewise, the variable hysteresis directions at Woodland and Hailstone suggest that material was sourced from more than initial flushing (Creed et al., 2015) . The revolving center (or where the junction occurs near the month of April) in several elements (DOC, La, Pb, Cu, Al and Be) at the Woodland or Hailstone sites can be explained by the activation of new flow paths that are dormant during diluted baseflow and activated at the onset of snowmelt.

The theory of new flow paths being activated during high discharge and mixing with baseflow is supported by our $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$ measurements (Figure 13). In river samples (but not snow or ephemeral) $\delta^{18}O_{VSMOW}$ measurements are not correlated with $\delta^{2}H_{VSMOW}$ measurements. The variation could be a result $\delta^{18}O_{VSMOW}$ being less conservative than $\delta^{2}H_{VSMOW}$ and various interactions within the watershed. Interestingly, measurements taken at Soapstone, Woodland and Hailstone experience a directional change of slope during the onset of snowmelt (Figure 13), which coincides with transitions in figure-eight hysteresis patterns (Figure 9).

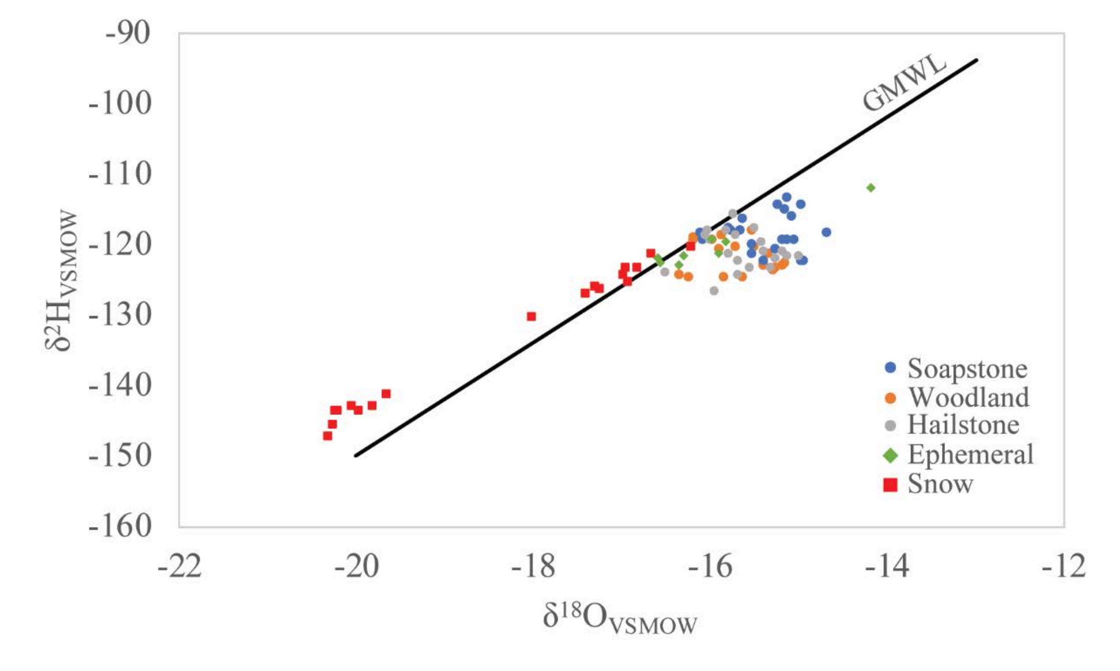

Figure 13 . $\delta^{18}O_{VSMOW}$ versus $\delta^{2}H_{VSMOW}$ for waters collected in the upper Provo River watershed, including the global meteoric water line (Craig, 1961). The variations in bulk snowpack are explained by two sampling days (18 and 29 April, 2016) where the latter followed a dust storm event. Both snow and ephemeral samples plot linearly, as $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$ are correlated. River samples, do not plot linearly and $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$ are not correlated. Soapstone samples are enriched compared to the Woodland and Hailstone samples. Bulk snowpack samples are depleted. Ephemeral samples are more enriched than snow and plot near river samples.

Also notable was the enrichment of $\delta^{18}O_{VSMOW}$ and $\delta^{2}H_{VSMOW}$ at Soapstone relative to Woodland and Hailstone. A likely explanation is that the higher elevation Soapstone received more convective summer moisture than lower elevation sites. Another possibility is snowpack, which becomes enriched through time, sits longer near Soapstone, due to lower temperatures at higher elevation. Thus, melt water is generally enriched.

4.4 Trace element sources during snowmelt runoff

The increase in dissolved metal and cation concentrations during snowmelt deserves further discussion given the limited source of these metals in local bedrock. The local bedrock geology above the Soapstone site is dominated by sedimentary/quartzite bedrock, interbedded shale and glacial till, which contain low concentrations of trace elements such as La, Pb, Cu, and Be (Munroe, 2014). It is possible that these elements are derived from atmospheric deposition, primarily in the form of aeolian dust. Previous research has demonstrated how dust derived metals, including Pb and Cu, increased dramatically in Uinta Mountain lake core sediments after the year 1870, implying dust derived material increased from anthropogenic activities (Reynolds et al., 2010). Similarly, others have found that dust contributes elevated metal concentrations to northern Utah snowpack (Carling et al., 2012; Reynolds et al., 2014). If dust deposits metals onto snowpack, it is also depositing metals onto nearby soil, thus contributing to relatively high concentrations in soil water (Figure 1).

The elements Al, Sr and K are probably sourced from water-rock interactions, but could also be impacted by dust deposition. Al can be sourced from water-rock interactions or weathered material from the Red Pine Shale, which consists of micas and plagioclase minerals (Myer, 2008). Al is also observed at ~2 fold higher concentrations at Soapstone than Woodland and Hailstone, indicating that the source could be localized at a higher elevation in the watershed.

Like Al, K can be sourced from the Red Pine Shale. However, it is notable that Al is more available in water than K (Figure 6, Figure 7, Figure 8) implying another Al source. Sr loads increase during runoff at each site. The loads are higher at the lower Woodland and Hailstone sites where there is a dissolution of Sr with $CaCO_3$ rocks (Figure 5). Sr concentrations change during runoff and become diluted at the lower sites, but remain consistent at Soapstone (Figure 4, Figure 5). It has been suggested that interbedded shales could be a source of Sr (Carling et al., 2015), but an additional source could be from aeolian dust as well (Carling et al., 2012). Whatever, the source, an additional input of Sr keeps the Soapstone site from becoming diluted.

5. Summary and Conclusion

DOC, La, Pb, Cu, Al and Be concentrations increased during snowmelt, while Sr and K remained chemostatic or became diluted in the upper Provo River watershed. Concentration responses were unique in terms of loads, timing, and discharge. The majority of annual loading of DOC and other elements occurred during snowmelt. However, concentrations of Sr and K decreased during runoff, while other elements experienced rising concentrations. All elements showed a clockwise hysteresis at Soapstone, demonstrating elements are limited in soil water, and flow paths taken during snowmelt become diluted. Other elements at different locations have varying concentration-discharge relationships, and imply that sources are from nearby and distant locations during different phases of runoff. Future work is required to understand the presence of elements such as La, Pb and Cu in the upper Provo River watershed and whether other elements such as Al, Sr and K have additional sources beyond source-rock interactions and weathering. Additional work is also needed to understand the process and likelihood of metals forming a complex with dissolved organic matter and undergoing transport in the upper Provo River Watershed.

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