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Dynamics of Dissolved and Particulate Trace Metals in a Snowmelt-Dominated Stream, Provo River, Utah, USA

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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

Dynamics of Dissolved and Particulate Trace Metals in a Snowmelt-Dominated Stream, Provo River, Utah, USA

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Master of Science

Trace element concentrations vary substantially during snowmelt runoff, with changes in the dissolved versus particulate fractions potentially impacting their movement at the catchment scale. To investigate trace element behavior in a snowmelt dominated stream, we measured concentrations in different size fractions in the Provo River (northern Utah, USA). We sampled the river at three locations during water years 2016-2018 and 2021-2023 for trace metal and major ion concentrations. During the final year, we collected three fractions (unfiltered, <0.45 µm filtered, and <0.22 µm filtered) for trace metal chemistry and calculated the particulate concentration as the difference between the unfiltered and 0.45 µm fraction. Stream measurements included pH, discharge, turbidity, and fluorescent dissolved organic matter (fDOM). We also sampled water sources (soil water, ephemeral streams, and snowpack) to compare trace metal concentrations across the watershed with the stream. Trace metal (Al, Be, Fe, Pb) and rare earth element (REE +Y) concentrations had the highest particulate and dissolved concentrations during snowmelt runoff. In contrast, major cations were primarily found in the dissolved fraction with lowest concentrations during snowmelt runoff. Major cation and particulate metal concentrations increased from upstream to downstream. The increased trace metal and REE + Y concentrations during snowmelt relative to baseflow may be explained by increased discharge and associated increased turbidity and fDOM. A comparison with water sources suggests that dissolved and particulate trace metals in the stream are sourced from flushed soil water, as trace metal transport through the watershed is facilitated by suspended sediment and dissolved organic matter. For most of the trace metals and REE +Y, concentrations were similar in the <0.45 µm and <0.22 µm fractions. Yet Al tended to have higher concentrations in the <0.45 µm fraction, suggesting a colloidal form of Al between 0.22 µm and 0.45 µm may exist. Differences from upstream to downstream may be related to changes in pH, from ~7 at the upper site to ~8 at the lower sites, which would change sorption capacity, saturation indices, or speciation. Our study demonstrates that trace metal concentrations are variable during snowmelt as the metals interact with suspended particles or dissolved organic matter and are influenced by changing water chemistry, with implications for understanding water quality impairments in snowmelt-dominated streams.

Key words: dissolved trace metals, particulate trace metals, water sources, trace metal transport, snowmelt

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1. Introduction

Trace metals are transported through watersheds in dissolved form or associated with suspended sediment and colloids, with variability during periods of snowmelt runoff. The amount of particulate and dissolved trace metals in a river is important for water quality, as some metals may contribute to impairments for drinking water or aquatic life. Water quality standards rely on "dissolved" concentrations, defined as the concentration that passes through a 0.45 µm filter (USEPA 1996), yet a large fraction of the element mass is often associated with particles >0.45 µm in size. Even in the "dissolved" form, metals may be associated with colloids or dissolved organic matter (DOM) (Shafer 1997;Trostle et al. 2016). For example, Al, Ti, and Fe were associated with colloids (<0.45 µm) in different stream systems (Trostle et al. 2016;Olshansky et al. 2018;Olshansky et al. 2018). Suspended sediment/turbidity facilitates trace metal transport, especially during high flow events. Other factors, such as water pH, may affect the behavior of particulate and dissolved trace metals in different aquatic systems (Martin 1993;Dai 1995). Although progress has been made to understand trace metal transport in rivers, there remains a lack of studies focused on trace metal behavior in snowmelt-dominated streams.

Concentration-discharge (C-Q) relationships are useful to demonstrate solute behavior with changing streamflow conditions. Some elements such as Cl can show a chemostatic relationship with discharge, while other trace metals show a flushing or dilution trend (Godsey et al. 2009;Creed et al. 2015;Li et al. 2017). The residence time in a catchment may affect dissolved and particulate fluxes in a system (Godsey et al. 2009;Maher 2011). Dissolved concentrations behave differently with discharge as the flowpath connectivity and expansion of channels in a catchment changes (Rose et al. 2018). The relationship between dissolved and particulate loads in streams may help with investigating the transport of trace metals and other anthropogenic pollutants (Rember et al. 2004;Moatar et al. 2020;Lucic et al. 2022) .

Different water sources such as soil water, snowmelt, and groundwater may contribute different types of solutes to streams (Bazzano et al. 2017). Metal concentrations in a stream reflect changing sources in a watershed, such as contributions from snowmelt or stormwater (Galfi et al. 2017). Groundwater sources may have long flow paths that carry trace metals through the watershed and transfer them to the river system (McIntosh et al. 2024). With climate change having a large effect on the high discharge events, snow-fed and high precipitation systems may become more relevant as the environment of these areas is changing (Burger et al. 2021).

The purpose of our study was to investigate trace metal transport in dissolved and particulate forms in a snowmelt dominated stream. Specific objectives were to characterize particulate and dissolved trace metal concentrations; evaluate changes from upstream to downstream in relation to water chemistry and discharge; compare trace metal concentrations in the stream with different water sources (snow, ephemeral stream, and soil water); and relate trace metal concentrations with fluorescent dissolved organic matter (fDOM) and turbidity. This study was conducted in the upper Provo River watershed, a snowmelt dominated stream in northeastern Utah that is an important water supply for over a million people in the Wasatch Front (PRWUA 2022). Our previous work demonstrated positive C-Q relationships with trace metals in the river during snowmelt due to soil water flushing and suggested that metals are sourced from dust deposition (Checketts et al. 2020;Hale et al. 2022). The previous studies showed an increase in trace metal concentrations in the <0.45 μm fraction but did not measure the particulate fraction

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2. Methods

2.1 Study area

The Provo River watershed (northeastern Utah) is primarily fed by snowmelt in the Uinta Mountains. Three different monitoring stations were located from upstream to downstream at Soapstone, Woodland, and Hailstone (Fig 1). The Soapstone subwatershed includes interbedded siliciclastic rock with minor amounts of carbonate rocks, with additional carbonate rocks plus volcanic rocks in the Woodland and Hailstone subwatersheds (Fig 1). Due to groundwater inputs from carbonate rocks, the river pH typically increases from 7 to 8 between Soapstone and Woodland. The river feeds two reservoirs, Jordanelle and Deer Creek, before flowing down Provo Canyon and into Utah Lake. Water quality is generally good in the upper Provo River watershed, except that aluminum exceeds water quality criteria across the entire upper watershed (DWQ 2022). Additionally, copper, zinc, and pH do not meet water quality criteria in parts of the upper watershed (DWQ 2022).

The US Geological Survey (USGS) maintains gauging stations at Woodland (USGS 10154200) and Hailstone (USGS 10155000). Discharge at Soapstone was estimated using 15-min water level measurements input into a rating curve equation (Dastrup 2017). Snowpack and precipitation were monitored by the US Department of Agriculture with a snow telemetry (SNOTEL) site at Trial Lake (https://wcc.sc.egov.usda.gov/nwcc/view) .

2.2 River, snowpack, ephemeral stream, and soil water sampling

Water samples were collected regularly in three locations in the upper Provo River Watershed at Soapstone, Woodland, and Hailstone (Fig. 1). Samples were collected weekly to bi-weekly during snowmelt runoff (April-June) and approximately once per month throughout the remainder of the year. During the 2021 and 2022 water years, samples were collected at each location using a 0.45 µm filter to evaluate the dissolved metal concentrations. We collected 22 samples from each site during 2021 and 27 samples from each site during 2022. During the 2023 water year, we collected 24 samples from each site, including samples for three different size fractions: an unfiltered sample, a sample filtered with a 0.45 µm filter, and a sample filtered with a 0.22 µm filter. We calculated the particulate concentrations as the difference between the unfiltered sample and the 0.45 µm filtered sample. Over the three-year period, we collected a total of 73 samples at each river location.

Water samples were collected in acid washed (10% HCl) LDPE bottles or polypropylene centrifuge tubes for trace metal and major cation analysis. The samples were filtered with 0.45 µm PES filters (Foxx) attached to acid-washed polypropylene syringe. During 2023, additional samples were collected using 0.22 µm PES filters (Avantor). Unfiltered samples were collected by dipping an acid washed bottle directly into the stream. All trace metal samples were carefully collected using "clean hands, dirty hands" protocols (USEPA 1996). To assess potential contamination during sample collection and transport, field blank samples were collected most days by passing Milli-Q water through clean filters into new bottles. All samples were acidified to 2.4% v/v trace metal grade HNO_3 and stored in the refrigerator until analysis.

Additional parameters and samples were collected to supplement the trace metal data. Field parameters (temperature, pH, conductivity, dissolved oxygen, and turbidity) were measured at each site using a handheld YSI DSS multiparameter probe. Suspended sediment samples (n = 8) were collected before peak runoff, during peak runoff, and after peak runoff to analyze for minerals. Based on the amount of suspended that was needed for mineralogical analysis, we used one sample from Soapstone, three from Woodland, and four from Hailstone. Continuous turbidity and fDOM values were measured at 15-min intervals during spring and summer each year at Soapstone and Woodland locations using YSI EXO2 sondes.

To compare snowpack chemistry with river chemistry, we collected three snow samples from the higher part of the watershed above Soapstone. The samples were collected at peak snowpack on May 1, 2023. These samples were collected by digging three snow pits from a single area to the bottom of the ground surface. A snow profile was recorded from one of the pits by noting snow height, dust layers, and ice layers. Snow temperatures were also recorded for this pit at 10 cm intervals. Samples were collected from each of the three pits by scraping the snow into a tube from the surface to the bottom of the pit and transferred into clean 2 L FLPE bottles. To avoid potential contamination from soils, we did not sample the bottom ~10 cm from each pit. The three snow samples were thawed and subsampled for trace metal analysis with in the unfiltered, <0.45 µm, and the <0.22 µm fractions. A field blank was collected by pouring Milli-Q water through clean sampling tubes into a 2 L FLPE bottle while standing in one of the snow pits.

Soil water and ephemeral stream samples were collected in the upper watershed during the late snowmelt period (May-June) of 2023. Samples were collected from locations where water was flowing from the melting snowpack and percolating into soil. Soil was collected by digging shallow holes that were saturated with water, and soil water was extracted by centrifugation in the lab. Nine ephemeral stream samples and soil water samples were collected from paired locations.

2.3 Laboratory analysis

Water samples were analyzed at the University of Utah using an Agilent 7500ce quadrupole inductively coupled plasma mass spectrometer (ICP-MS). We measured concentrations of 44 different elements: 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, Sc, Se, Sm, Sr, Tb, Th, Tl, U, V, Y, Yb, Zn. The detection limit (DL) of each element was calculated as the standard deviation of the blanks analyzed in the run. For continuing calibration, a NIST standard reference material (SRM 1643f) was analyzed in each run multiple times with the other samples. The results from the SRM showed that the values were accurate within 10%.

Mineralogy of suspended sediment samples was analyzed by X-ray diffraction (XRD) using a Rigaku XRD Miniflex 600. The resulting patterns were interpreted using PDXL2 to provide mineral abundances.

2.4 Data analysis and quality control

Raw data from the ICP-MS was cleaned to remove elements with detection limit issues. In all samples, Sc, Se, Mo, Cd, Tl, and Th were excluded because nearly all samples had concentrations <DL. Some elements had few occurrences of samples with concentrations <DL, but most samples had measurable values. For these samples we had the <DL calculated as ½ DL. For the particulate concentrations (calculated as unfiltered - 0.45 μm) some elements had slightly negative particulate values in some of the samples, showing that these elements were mostly dissolved. For these samples, the negative values were replaces with a zero for the particulate concentration. Field blanks for river and snow samples showed generally low concentrations for all elements.

Particulate concentrations (calculated as unfiltered- 0.45 μm) were used in box plots of water sources and log-log plots of concentrations and discharge (C-Q), concentration and turbidity, and concentration and fDOM to compare particulate values to dissolved values (0.45 μm filtered samples). For plots that were created with particulate and dissolved concentrations, values were used from Woodland as they showed the most consistent and accurate measurements of discharge, turbidity, and fDOM. A best fit line was calculated for each of these plots. For the Ca C-Q plots, the r^2 was calculated using a log fit, while Al-Q, Al-turbidity, and Al-fDOM plots used a linear fit to calculate the r^2 values.

Water chemistry from selected samples was input into the Geochemists Workbench (GWB) software to evaluate metal speciation, mineral saturation indices, and mineral stability. Two samples were chosen before, during, and after peak runoff at each river location for a total of 18 water samples. Using the Spec8 app in GWB, speciation and saturation indices were calculated with the Minteq thermodynamic database. Using the Act2 app, a stability diagram was created for Al versus pH.

3. Results

3.1 Annual discharge and snow water equivalent

Stream discharge rates were variable during the three water years, with the highest discharge during May through June each year and increasing discharge from upstream to downstream (Fig. 2). The lowest peak discharge occurred in 2021, with each location having <35 m^3/sec during peak runoff. The 2022 water had higher maximum discharge rates up to ~70 m^3/sec. The Soapstone location had relatively higher runoff during 2022, but the values may be related to an error in the rating curve calculation. The 2023 peak discharge rates were comparable to the 2022 water year, but with a much longer duration of snowmelt runoff with a larger total amount of runoff. Compared with the 73-year record at Hailstone, annual flow was 44% of the mean during 2021, 82% of the mean during 2022, and 166% of the mean during 2023.

The high total discharge during 2023 was related to an exceptionally high snowpack that winter. The snow water equivalent (SWE) at Trial Lake reached 76.2 cm at its peak during April 2023, which was 216% of normal SWE. In contrast, SWE during 2021 and 2022 were only 75% and 89% of normal. Annual precipitation was 136% of normal in 2023, compared with 65% in 2021 and 96% in 2022 (NRCS 2021;NRCS 2022;NRCS 2023).

3.2 Trace metal and major cation concentration changes over time and XRD minerals

Time-series trends for the major ions displayed variability across the three water years (2021 through 2023) (Supplementary Figure). At Soapstone, Ca concentrations were consistent during 2021 and 2022 and showed a sharp increase during peak runoff. At Woodland and Hailstone, Ca concentrations were similar each year with a decrease during snowmelt runoff. Other cations such as K, showed lower concentrations during snowmelt at all sites, including Soapstone, during 2023. Although not shown in the figure, Mg behaved like Ca and Na behaved like K. Major cations had similar concentrations in the unfiltered, <0.45 µm, and <0.22 µm fractions, and behaved like this throughout the entire year.

Trace metals (Al, Be, Fe, Pb) and rare earth elements plus Y (REEs + Y) increased in concentrations every year during peak runoff (Fig. 3). The same trend happened in the 2023 year, but there was a difference in concentration between the different size fractions during peak runoff. Some trace metals had little difference between the <0.45 µm, and <0.22 µm fractions, while Al had differences in concentration between these size fractions (Fig. 4). Other trace metals such as Fe had small differences in these size fractions as well. The figure (Fig. 3) represents dissolved and particulate concentrations of Al, which other trace elements (Be, Fe, Pb, and Y) behaved similar. At Soapstone, the particulate and dissolved concentrations were close to the same amount. Woodland and Hailstone had larger concentrations of particulate Al, with the biggest difference between the dissolved and particulate occurring during peak runoff. Hailstone had the greatest amount of particulate Al, and Soapstone had the greatest amount of dissolved Al.

3.3 Modeled saturation indices and mineral stability

The minerals identified as oversaturated using GWB were: boehmite (γ-AlO(OH)), bromellite (BeO), corundum (Al_2O_3), diaspore (AlO(OH)), gibbsite ($Al(OH)_3$), and calcite ($CaCO_3$), with most of these containing Al. The stability diagram created in Act2 showed that most of the samples were stable around $Al(OH)^-_4$ (Fig. 4) . A few of the Soapstone samples that were collected earlier in the year were closer to the mineral kaolinite. Samples gradually became lower in Al activity later in the year at Woodland and Hailstone.

The oversaturated minerals that were plotted on the series plot with pH showed different results. Most of the Al bearing minerals showed a lower saturation index with increasing pH values. Calcite and Bromellite showed an increase in their saturation index with higher pH values. Corundum was oversaturated with the lower pH values, and then became undersaturated ~8.2 pH. The samples of corundum that were undersaturated were take in Hailstone and Woodland. Calcite was mostly undersaturated with low pH values, and then became oversaturated ~8.2 pH. The few samples that were oversaturated with calcite were from Woodland and Hailstone.

The other Al elements, such as Aluminite ($Al(OH)^-_4$), did not show much of a linear trend with its species activity and with its pH. There were higher activity values within the middle of the pH values, and lower activity values with lower pH values and higher pH values. $Al(OH)_3$

showed similar results, but were not quite as high. $Al(OH)_2^+$ had low activity values throughout, and were the lowest among these different phases.

3.4 Concentration-discharge relationships of trace elements and major cations

There were clear C-Q relationships with particulate and dissolved concentrations of some of the different cations and trace metals at Woodland (Fig. 5). Only dissolved (<0.45 µm) concentrations are represented in Fig 5 for Ca, since there were small differences between the unfiltered and filtered values. Calcium showed a slightly negative slope in this plot ($r^2 = 0.92$). Trace metals and REEs, such as Al showed a correlation between concentration and discharge between the dissolved and particulate content (Fig. 5). There was a positive correlation with the dissolved Al ($r^2= 0.72$), and with the particulate concentrations ($r^2= 0.79$). Overall, the amount that was in the particulate Al fraction was higher than the dissolved fraction, and the difference between the dissolved and particulate becomes greater with higher amounts of discharge. Other trace metals such as Fe and Y showed positive slopes and correlations as well, which showed that these metals were flushed with higher discharge events.

3.5 Trace element and major cation concentrations in snow, ephemeral streams, and soil waters

There were different results in the water sources between the cations and the metals in the box plots of these sources, with the soil water typically having the highest concentrations compared to the snow samples and the ephemeral stream samples (Fig. 6). There are high amounts of Ca in the soil water, and it is mostly dissolved, showing little to no difference in the amount between the filtered and unfiltered samples. The ephemeral stream samples also have mostly dissolved amounts of Ca, but these amounts are in much lower quantities than the samples in the soil water. Although not shown in the figure, other major cations were similar to

Ca. The amount of Na in the ephemeral streams is mostly dissolved, showing little variation between the amount in the filtered samples and the unfiltered samples. The same is true for Na in the soil water samples, with having overall higher concentrations of Na in the samples. Mg also shows higher amounts of dissolved Mg in the samples in both the soil water and the ephemeral streams. Five of the soil water samples showed high concentrations of Mg, over 5x the amount in the ephemeral streams.

Metals showed variable results in the water sources. The concentrations overall were highest among the dissolved and particulate values in the soil water samples. Snow samples were similar between particulate and dissolved, with the concentrations being so low making them comparable to each other. The Be concentrations were slightly higher in the particulate among some of the ephemeral stream and soil water samples, but the mean of the dissolved concentrations were higher. The concentrations between the different fractions were comparable to each other in the different water sources with Al, with the soil water particulate content being slightly higher than the dissolved content. The Fe had almost equal amounts dissolved and particulate concentrations in the soil water, while the ephemeral streams had higher amounts of particulate Fe.

3.6 Trace element concentrations with turbidity

Concentration values of trace elements had some correlation with measured turbidity values (Fig. 7). Dissolved Al concentrations showed a positive slope, with some values that were lower in the middle section of the turbidity values (r^2= 0.61). The particulate concentrations had a larger slope, with higher values than the dissolved Al (r^2= 0.98). The differences between the particulate and dissolved concentrations also became greater during higher amounts of turbidity. Other trace metals had similar results, where there was correlation between the particulate and the dissolved concentrations and turbidity.

3.7 Trace element concentrations with fDOM

There were some correlations between the trace element concentrations and fDOM values (Fig. 8). There were positive slopes with dissolved (r^2= 0.95), and particulate Al (r^2= 0.55) with the higher concentrations in the particulate Al. The differences between the dissolved and particulate Al, were not as large with the C-Q plots and the concentrations and turbidity plots. Similar correlations occurred in other trace metals (Fe and Y) where there were positive slopes between fDOM and concentration.

4. Discussion

4.1 Differences in trace element and major cation concentrations across water years

Dissolved trace elements from during water years 2021-2023 showed a clear C-Q relationship, similar to observations from water years 2016-2018 (Checketts et al. 2020). The year 2023 showed this same relationship amongst most of the metals (Al, Be, Fe, Pb), with the other size fractions showing a similar trend. Overall, the concentration values were comparable in between the three different water years, even with the different discharge rates. The concentrations were also comparable to concentrations seen in the 2016-2018 water years (Checketts et al. 2020). Dilution for Ca is about the same throughout the years in Woodland and Hailstone, with slight steeper dips in 2023. This could be due to more water from the high amounts of precipitation in 2023 contributing more to the dilution of it, but for the most part was comparable for each year. Ca showed an increase in concentration in Soapstone in the 2023 water year, which is a different result compared to other years. An increase of Ca could be a result of the larger water year seen in 2023, which would have fed more water from a carbonate spring into Soapstone. There could have also been a different road salt that contains Ca in it with roads nearby. Some of these metals that are having higher amounts from the 2023 year could be coming from different sources than just the dust, such as more elements being flushed from the soil water. The largest differences between the elements from year to year are occurring at the Soapstone location. Some elements (Fe) show not as consistent trends during the 2021 and 2022 water years, with more sporadic peaks, but still have the main spikes during peak runoff. Other metals, such as Pb, had more dissolved amounts in all the locations in the 2021 water year than the other years, even with the higher amounts of water flushing in the 2023 water year. This could be due to potential anthropogenic contamination in 2021 that did not contribute as much as the other years. This could also be due to not having as much a Pb content in the soil waters, so most of the lead comes from the dust sources that deposit on the snow surface at the top of the watershed. There were also higher concentrations of trace elements towards the end of the water year (September and October samples) during precipitation events, which may have a faster effect on flushing out soil water than snowmelt (Burger et al. 2021).

4.2 Dissolved and particulate concentrations with changes from upstream to downstream

The concentrations between the 0.22 μm and 0.45 μm filtered samples were small in some metals, but there were some differences in other metals like Al and Fe. There were some samples that higher amounts in the 0.45 μm fraction than the 0.22 μm fraction, which showed that some of this Al was in the small colloidal form. These differences were not as large compared to another study with Al in groundwater springs (Kim et al. 2017). This could be due to the environment of the Provo River watershed, where the river water is mostly snow melt fed (Thompson 2023). Major cations that showed dilution (Ca, K, Na, Mg), had little differences between the different size fractions, indicating that they were mostly dissolved. This is supports other findings that there was little to no colloidal influence on elements such Ca, K, Na and Mg (Trostle et al. 2016). These showed dilution from carbonate groundwater sources (Checketts et al. 2020).

The highest concentrations of dissolved trace elements (Al, Be, Fe, and Pb) during peak runoff were found at Soapstone and decreased in concentration down the watershed. These elements behave opposite with the unfiltered samples, showing that the highest concentrations occurred at Hailstone. During higher flow, the difference between the unfiltered and filtered samples were greater than the differences during low flow. Having more particulates like this in the water during periods of high flow could be a result of the pH increasing, as during peak runoff the pH was higher at each location. These metals were found to have some influence on colloids, which could explain the difference between how these metals behaved compared to the cations (Trostle et al. 2016). The amount of particulate content then increases from upstream to downstream, which could also be a result of increasing pH values. A similar study found that Al was more soluble at more neutral pH waters, which is typically what the water is like at Soapstone (Kim 2005). Metals like Al, Be, Fe, and Pb behaved very similar to each other with the trends of dissolved and particulate from upstream to downstream, similar to another study in Japan (Kim 2005).

The XRD results showed that there was quartz in all of the samples in all three of the locations (Table 1). Soapstone had mostly quartz (70%), with some micas in the sample. Woodland samples had variable amounts of quartz in, as low as ~ 5% and as high as ~ 73%. Most of the remaining minerals were in the form of micas, as well as calcite. Hailstone had on average ~47%, with the remaining minerals being micas, feldspar, and calcite. Aluminum probably picked up from volcanic wash, some could bind to quartz. Al has elevated concentrations above EPA standards in Upper Provo River (DWQ). More particulate material could have also been picked from the higher watershed to the lower watershed, showing this high amount of particulate material in the lower part of the watershed (Hailstone). This could also show that these metals are more associated in particle forms, similar to what was seen in other wetland conditions (Nimick et al. 2005;Carling et al. 2011).

The saturation indices that were calculated with GWB did not necessarily correlate with the trends that are seen in the time series data. The higher saturation values of Al occurred in the Soapstone location and the lower pH, while the Hailstone location had the higher amounts of particulate Al concentrations. This could be due to the GWB software requiring the dissolved concentrations for calculation, and Soapstone having the larger dissolved Al concentrations. The higher amounts of particulate concentrations in the lower watershed could be due to the stream picking up more material as it moves from upstream to downstream. The stability diagram showed that the form of Al is in aluminate, and aluminate had the highest activity with more neutral pH values. This shows that it is more soluble at these pH values, and less soluble with lower or higher pH values, which is similar to other results with Al (Kim et al. 2017).

4.3 Soil water contributes particulate and dissolved trace elements into the river

Snow, soil water, and ephemeral streams contribute to the discharge of the stream. Since the 2023 water showed very depleted isotopic results, we can conclude that most of the water that was fed into the river came from snowmelt. Other work in this watershed found that a large source of the trace metals in the river were from flushing of soil water (Hale et al. 2022). Trace metals concentrations in the water sources had some variable results with the different cations and trace metals compared to the concentrations to the river. Since Soapstone is the site that is most upstream, it has more of a direct input from the different water sources. The amount of dissolved and particulate concentrations in each water source were similar to what was found in the river, where major cations like Ca were mostly in the dissolved fraction, while trace elements such as Be, Al, Fe, Pb, and Y had both dissolved and particulate concentrations. The amount that were in the dissolved fraction and in the particulate fraction were variable between each sample of the water sources, but overall the snow had the lowest concentrations, and the soil water had the highest concentrations. The concentrations in soil water, especially among the trace elements were higher than concentrations found at Soapstone, but still comparable. Previous studies explain that these metals are transported into the river as the snow melts and flushes dissolved material out of the soil water (Checketts et al. 2020). Other work also showed that the humic and fulvic acid components of DOM in soil may contribute to transport of metals (Packer et al. 2020).This showed that the trace elements that are being flushed into the river from snowmelt and soil water are in both the dissolved and particulate form. The source of these particulate elements in these water sources could be dust that settled in the snowpack or dust that had been deposited in the soils from years before.

4.4 Controls on trace element transport in snowmelt-dominated streams

While there was some correlation between the fDOM and turbidity verses metal concentrations, there were some differences between how well these metals correlated with these measurements. The correlation with Ca concentrations was higher with the fDOM values than the turbidity values. This could be a result of Ca being more associated with DOM, than with particles or colloids (Trostle et al. 2016). Both the turbidity versus Ca concnetration and the fDOM versus Ca concentration had slightly negative slopes in their plots, with more of the Ca concentrations clustering more towards higher fDOM values. The Al particulate content had a stronger correlation with turbidity than fDOM, while the dissolved Al had a stronger correlation with fDOM. The differences between the dissolved and particulate Al became greater with higher amounts of turbidity but did not have that trend with the fDOM values. The dissolved concentrations of Fe did not have as strong of a correlation with turbidity and fDOM, though the correlation was slightly higher with fDOM. The particulate Fe concentrations had a stronger correlation with both the turbidity and fDOM values than the dissolved Fe, though the correlation was a stronger with turbidity. This could be because the Fe in this situation is more associated with particulate material since there is a much clearer correlation with particulate Fe than the dissolved Fe. The dissolved Y concentrations had stronger correlations with both turbidity and fDOM than the particulate Y, with the strongest correlation with fDOM. The particulate Y had a stronger correlation with turbidity than fDOM. Overall, the dissolved concentrations typically had a stronger correlation with fDOM, while the particulate concentrations had a stronger correlation with turbidity. This could suggest that DOM influences dissolved trace elements more than particles (or suspended sediment), while the particulate concentrations do not have as much of an influence with DOM. Although there were stronger relationships with the dissolved element concentrations, the DOM still had some influence on the particulate forms. These correlations of fDOM and concentration show that both dissolved and particulate metals are influenced by DOM, though the relationship may differ between each metal and what form they take (Martin 1993;Dai 1995). The DOM in a system can stimulate biogeochemical processes, mineral transformation, organic and inorganic nutrient and contaminant mobilization that can all contribute to the transport of dissolved trace metals in a stream system (Olshansky et al. 2018). Metal oxyhydroxides are often found as being the dominant adsorbent for DOM, which could explain the stronger relationship between certain metals such as Al with DOM (Chorover 2001;Vázquez-Ortega et al. 2014). Our results suggested that measured values of fDOM could help predict dissolved concentrations in trace elements such as Al and Y, while turbidity values could predict particulate concentrations in trace elements. These predictions can help predict water quality information in other snow-melt dominated streams. Where there are higher amounts of turbidity and fDOM measurements, there is potential for higher concentrations of dissolved and particulate trace elements that could be harmful for ecosystems and populations using the stream for drinking water.

5. Conclusion

Dissolved and particulate trace element concentrations showed different behaviors with changing parameters in the stream. Dissolved trace element concentrations were typically highest at Soapstone, with decreasing concentrations downstream. This could be due to pH changes which could cause differences in sorption of certain elements. There could also have been dilution to the dissolved trace elements due to spring input, which could feed in more particles. The river had comparable amounts of particulate concentration with the same trace metals as the water sources, indicating that the soil water flushed out particulate trace metals as well as dissolved trace metals. Particulate trace elements were more correlated with turbidity, while dissolved trace elements were more correlated with fDOM, though dissolved trace elements were correlated well with both. This result showed that particulates are most likely associated with suspended sediment while dissolved trace elements are associated more with dissolved organic matter. Knowing the turbidity and fDOM measurements of an area could help predict particulate and dissolved trace element concentrations. These relationships can be used for other snowmelt dominated streams for understanding trace element behavior and predictions to provide solutions for water quality remediation.

`Trace elements in stream systems can have negative water quality impacts on different populations that use the water for various reasons. While there have been studies done on the transport and behaviors of different metals and cations, additional information is needed to better characterize their behavior in different environments and how they behave over time as conditions change. Our study showed that there were relationships between dissolved and particulate trace elements with changes in discharge, pH, turbidity, and fDOM. These relationships can be used to understand trace element behavior in other snow-melt dominated streams and make predictions about concentrations that could affect the water quality in these streams. Based on the result of our study, the amount of particulate and dissolved trace elements could be related to pH differences in the stream which could be true for other streams that are snowmelt dominated. The relationship between particulate concentrations and turbidity and the relationship between dissolved concentrations and fDOM also can provide insight in predicting concentrations in a stream, and what these elements are associated with. These relationships may have value in remediation of snowmelt dominated streams as turbidity and fDOM values may have variable results during baseflow and during snow melt. Understanding these behaviors could also help foster more discussion for solutions for elevated trace metal concentrations, whether they occur naturally or from anthropogenic sources. This study can be applied to other snow melt dominated streams to show how these metals are transported over time and to different environments, as snowmelt dominated streams are an important source of water for lots of areas around the world.

6. Tables

Table 1. Table of XRD results of suspended sediment samples. These results show the percentage of the minerals that were in the suspended sediment.

Location	**Date**	**Quartz (% weight)**	**Mica**	**Calcite**	**Anorthoclase**	**Other**
Soapstone	**5/16/23**	70	26			3.8
Hailstone	**5/16/23**	47	45	8.2		
Woodland	**5/26/23**	54.6	42	2.9		
Hailstone	**5/26/23**	50.1	41	8.8		
Woodland	**6/3/23**	73	22	4.5		
Hailstone	**6/3/23**	48	23	4.5	18	1
Woodland	**6/7/23**	5.58	94			
Hailstone	**6/7/23**	41.2			47.9	10.9

7. Figures

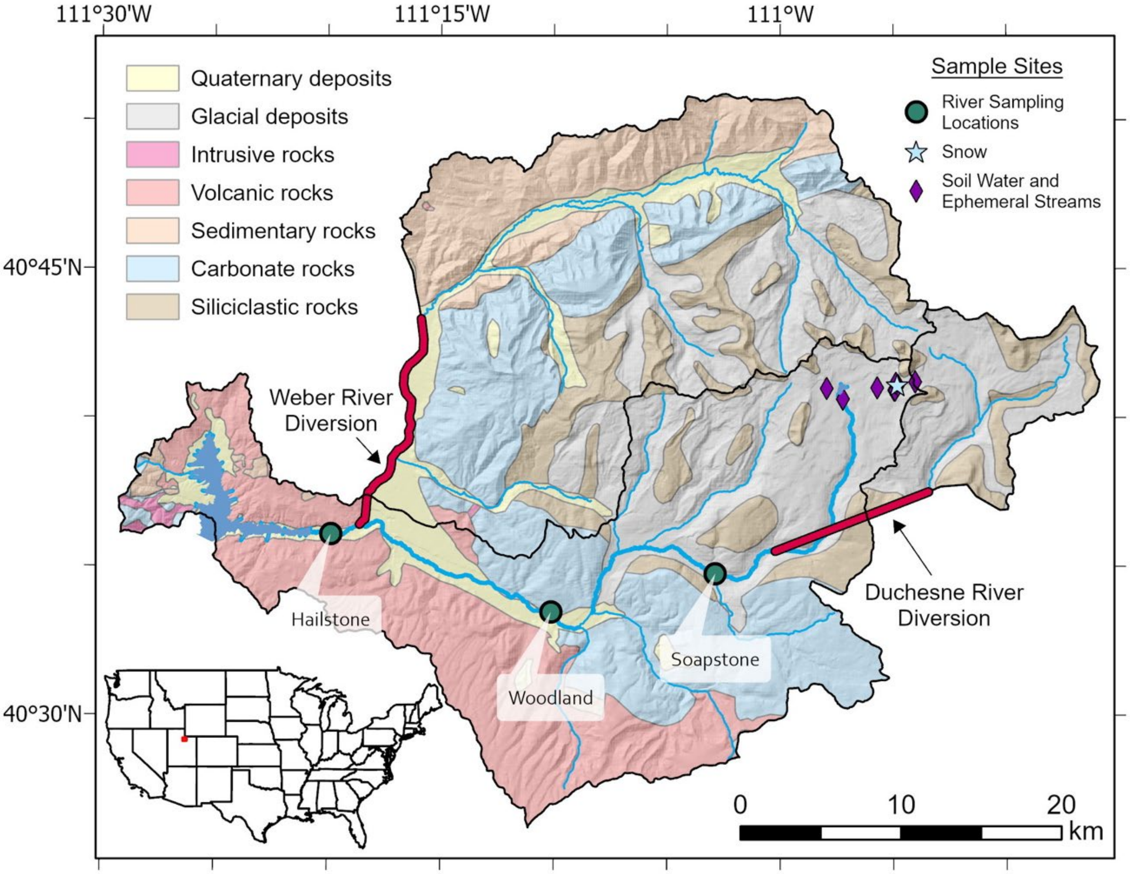

Figure 1. A map of the upper Provo River watershed. Different geology units are identified by type and age from the different colors. The three different river sampling locations, ephemeral stream and soil water locations, and the snow sampling sites are also included.

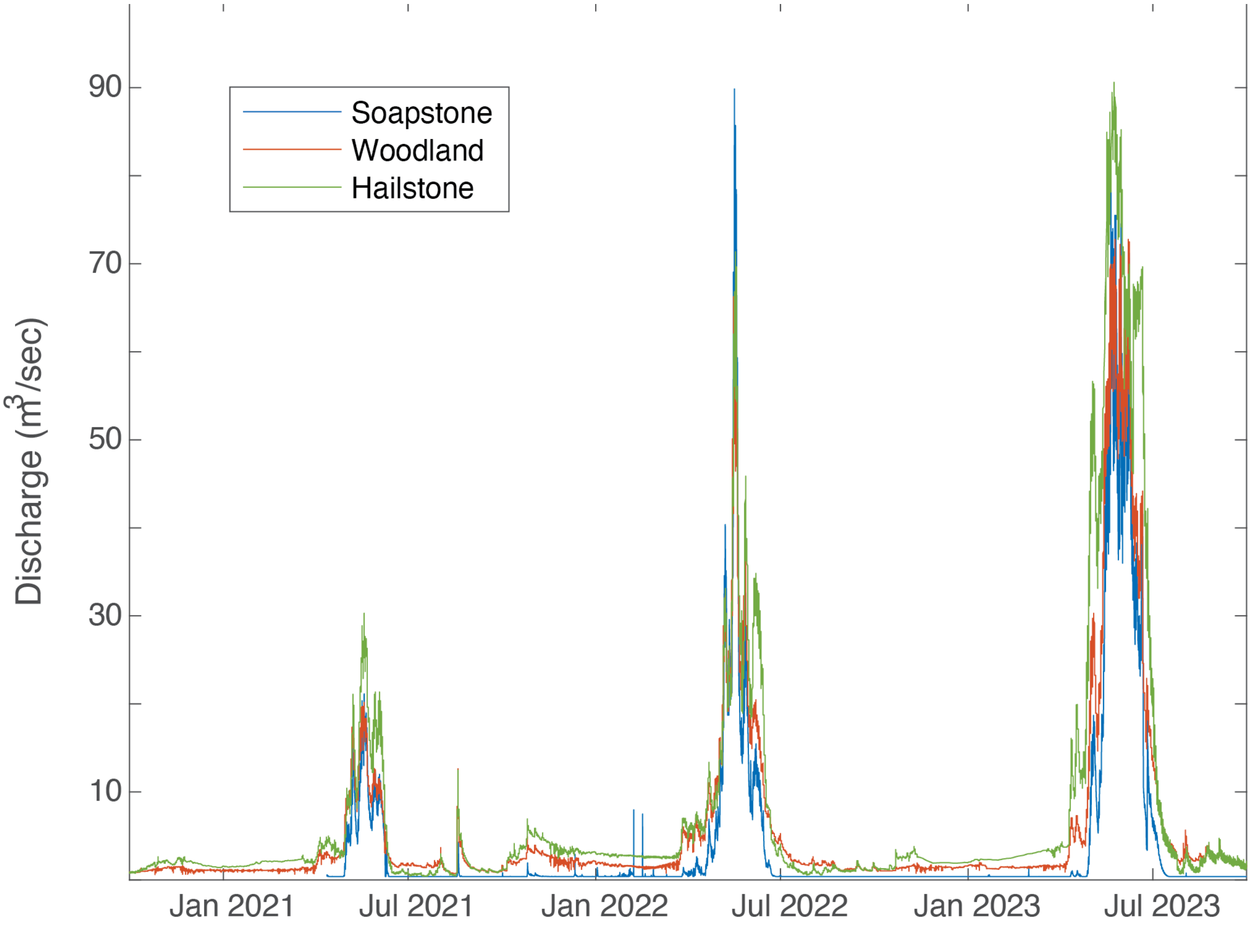

Figure 2. Discharge plot of the three different river sampling locations in the 2021-2023 water years. Extreme spikes in the Soapstone could be a result in error of discharge calculation using the rating curve. The 2021 year had much lower discharge values in all locations while the 2023 water year had the highest discharge values.

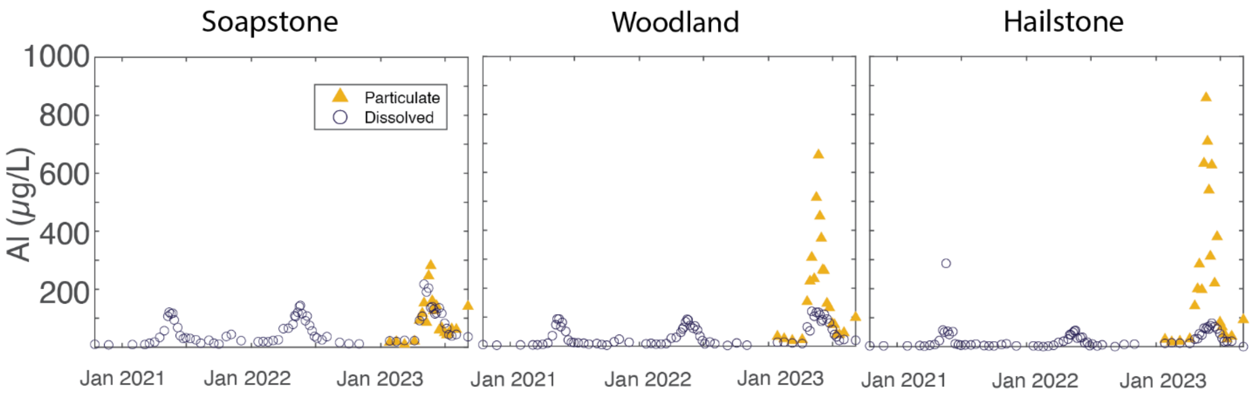

Figure 3. Time series of particulate and dissolved Al. Al was chosen to represent other trace elements, such as Fe, Pb, and Y, as these elements showed similar results. The amount of dissolved Al was highest at Soapstone, and the amount of particulate Al was highest at Hailstone.

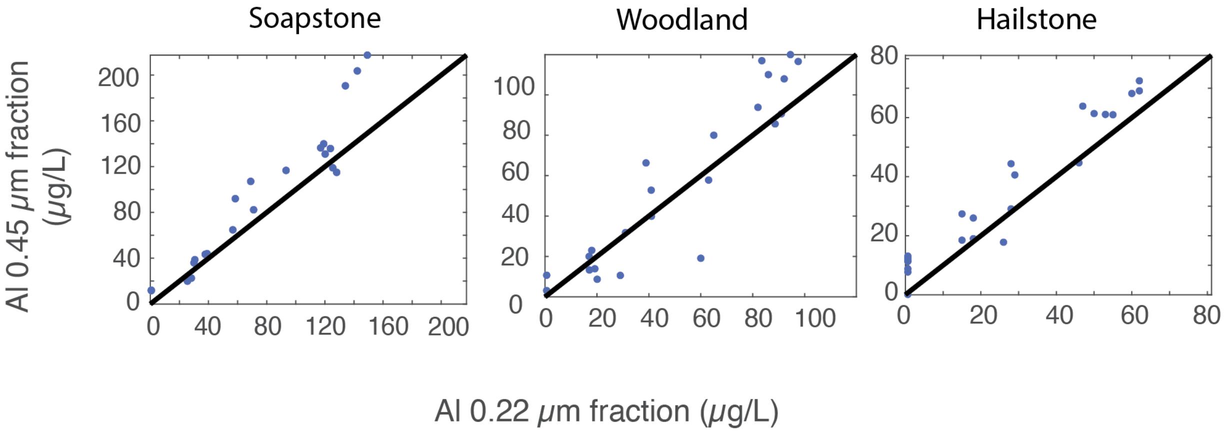

Figure 4. Plots showing correlation between concentrations measured with 0.22 µm and 0.45 µm filters. A 1:1 line was plotted to show if there were differences, data plotted to the left of the line had higher concentrations in the 0.45 µm fraction.

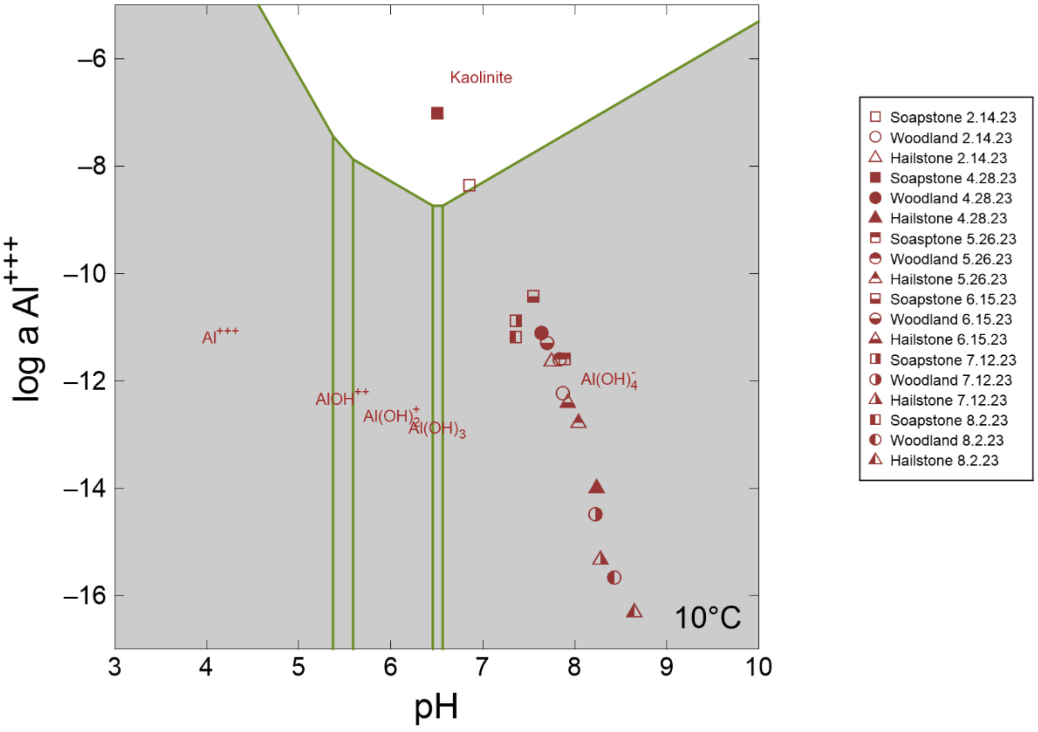

Figure 5. Al solubility diagram, plotting the solubility of Aluminum with the pH of the water sample and the activity of Al using Geochemist's Workbench. Samples from each of the three river sampling locations were used before peak runoff, during peak runoff, and after peak runoff. Most of the samples were stable in the form of aluminate.

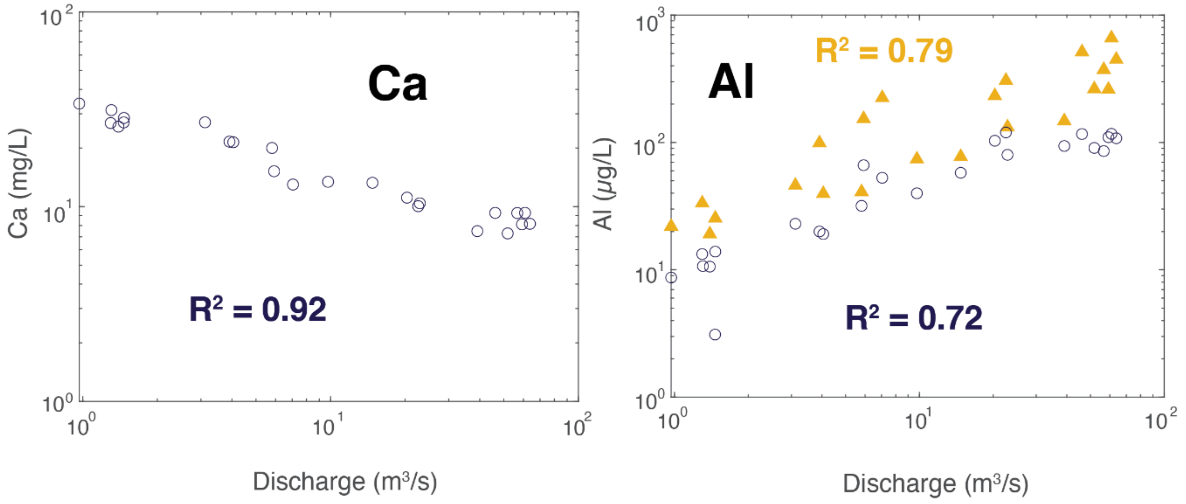

Figure 6. Concentration discharge plots for Ca and Al. Ca was used to represent the other major cations and Al was used to represent trace elements. Only dissolved Ca was used in this plot, as Ca was mostly dissolved in the samples.

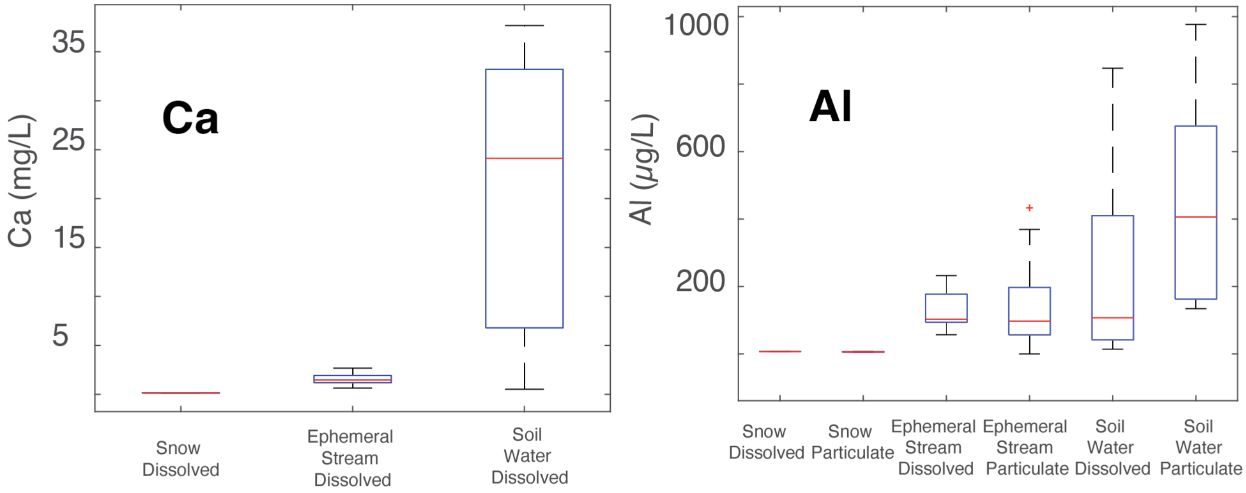

Figure 7. Box plots of dissolved and particulate concentrations in the different water sources in the Provo River watershed. The water sources include: snow, ephemeral streams, and soil water. Values range from the bottom of the box to the top of the box, with median values represented by the red line and outliers represented by red crosses.

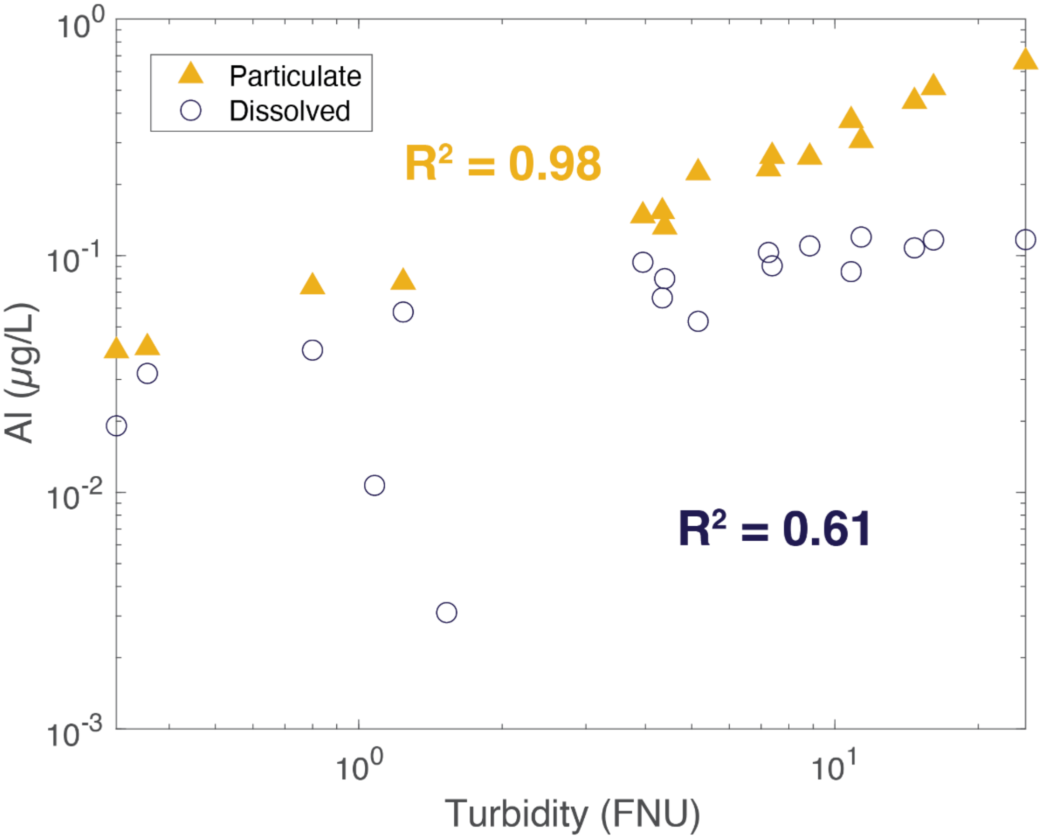

Figure 8. Concentration vs turbidity measurement plots using log-log scale for Al. The different sizes here were represented by particulate and dissolved content, where the particulate was calculated the unfiltered concentrations and subtracting it by the <0.45 μm concentrations.

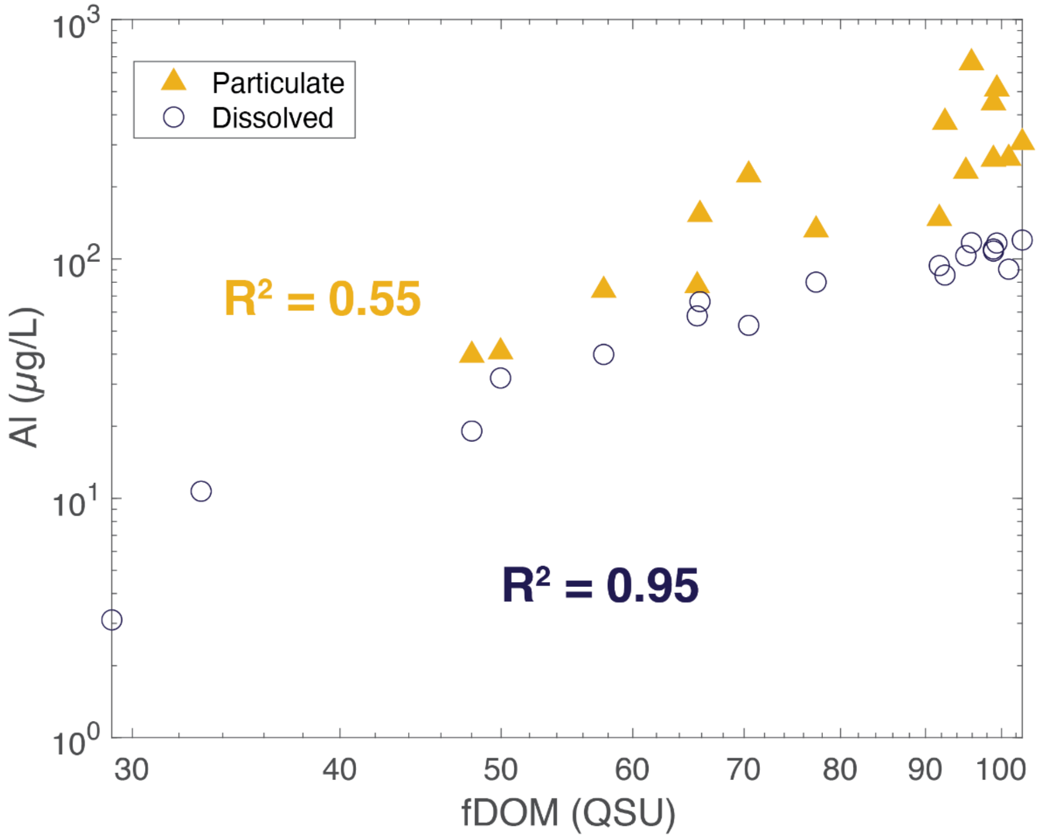

Figure 9. Concentration values vs fDOM measurement plot using log-log scale for Al. The different sizes here were represented by particulate and dissolved content, where the particulate was calculated the unfiltered concentrations and subtracting it by the <0.45 µm concentrations.

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