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Timothy Holman Goodsell
Brigham Young University

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Trace Element Inputs from Natural and Anthropogenic Sources in an Agricultural Watershed, Middle Provo River, Utah

Timothy Holman Goodsell

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

Master of Science

Gregory T. Carling, Chair
Stephen T. Nelson
Zachary T. Aanderud

Department of Geological Sciences
Brigham Young University
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ABSTRACT

Trace Element Inputs from Natural and Anthropogenic Sources in an Agricultural Watershed, Middle Provo River, Utah

Timothy Holman Goodsell
Department of Geological Sciences, BYU
Master of Science

Water chemistry in rivers is impacted by a variety of natural and anthropogenic processes including agricultural runoff, urban runoff, storm runoff, groundwater inputs, and the built environment. In this study we used trace element concentrations (including As, B, Ce, Co, Cu, Li, Mn, Rb, Sb, Sr, Tl, V, and Zn) and continuous measurements of flow rates and specific conductance to investigate dynamic processes affecting water quality in a rapidly urbanizing agricultural area typical of the western U.S.

The middle Provo River, located in northern Utah, USA, was selected as the study area because it is well instrumented with water quality stations and streamflow gauges. We sampled 6 sites on the middle Provo River and 15 sites on tributaries in the watershed a minimum of 5 times between April 2014 and March 2015 to evaluate potential contributions from surface water and groundwater inputs to the Provo River. Additional water samples were collected at 13 cold, thermal, and mixed cold/thermal springs in Heber Valley during summer 2014 to evaluate regional groundwater chemistry. Samples were also collected during two storm events including high frequency sampling in a tributary and road-puddle samples to characterize potential storm runoff chemistry. Specific conductance data loggers were deployed in tributaries to monitor effects of precipitation and other runoff on the middle Provo River at 15-min intervals. See Table 1 for a summary of sampling events.

Middle Provo River water chemistry is impacted by natural groundwater inputs as well as surface water tributaries. Li, B, Sr, As concentrations increased dramatically (3-10 fold) downstream of the confluence with a major tributary, Snake Creek. Snake Creek had average As concentrations of ~15 µg/L above the confluence with Provo River and accounted for roughly 20% of the flow to the middle Provo River, but increased the As concentration in Provo River ~4 fold. Thermal springs had ~20 and ~80 times higher concentrations of As and Li, respectively, relative to cold springs and was found to be a major contributor of trace elements to Snake Creek and the middle Provo River. Cl mixing calculations indicated that groundwater contributions increased downstream with up to 15% of the flow to the middle Provo River being contributed within the most downstream reach. Tributaries were found to impact the Provo River based on specific conductance fluxes in tributaries corresponding to fluxes in the river. Notably, Spring Creek, a dominantly agricultural tributary, accounts for >40% of the annual V load and >18% of the annual U, Mn, Pb, Ba, La, and Ce loads to the middle Provo River. The trace elements B, Li, As, and Sr which are found in high concentrations in groundwater, were strongly correlated with Provo River specific conductance and may indicate a potential method of predicting select trace element concentrations in the middle Provo River based on specific conductance data. Filtered puddle samples collected during a storm event had higher concentrations of Co, Cu, V, and Zn, but lower concentrations of major and select trace elements including As, Li, and Sr, relative to the middle Provo River. This study has implications for understanding water quality in complex coupled human-natural systems.

Keywords: trace elements, groundwater, agricultural runoff, urban runoff, storm runoff

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1. Introduction

Water chemistry in rivers is impacted by a variety of natural and anthropogenic processes including built environment, agricultural runoff, urban runoff, storm runoff, and groundwater inputs. Water quality is typically evaluated using a variety of measurements specific to each watershed or resource type. For example, in agricultural areas water quality is typically characterized by measuring nutrient and organic matter concentrations (Cerro et al., 2014; Graeber et al., 2012; Ouyang et al., 2015). In urban areas, water quality is evaluated by measuring trace metal concentrations, especially during storm runoff events (Joshi and Balasubramanian, 2010; Mayer et al., 2011; Tiefenthaler et al., 2008; Yang et al., 2016), and nutrients from wastewater (Bhatt et al., 2014; Shtereva et al., 2015). Groundwater quality is determined by measuring major solutes, total dissolved solids or specific conductance, and water hardness (Monjerezi and Ngongondo, 2012) as well as naturally occurring metals including As (Munoz et al., 2015; Stuben et al., 2003). In this study we use trace element concentrations and continuous measurements of flow rates and specific conductance to investigate dynamic processes affecting water quality in a rapidly urbanizing agricultural area typical of the western U.S.

Land use changes in a watershed lead to varying amounts of runoff from agricultural and urban areas and alter groundwater flow paths. Agricultural and impermeable surfaces potentially pose the most challenges to aquatic systems, so land use/land cover changes can result in very important changes in water chemistry (Li et al., 2011; Teixeira et al., 2014). For example, agricultural runoff contributes fertilizers, animal waste, pesticides, salts and dissolved organic matter (Graeber et al., 2012; Vidal-Dorsch et al., 2012), and urban runoff contributes salts, metals, and fertilizers (Kabir et al., 2014). As agricultural lands across the western U.S. are converted to urban areas, the relative amounts of each input (agriculture, urban, storm runoff, and groundwater) change accordingly.

Urban development can alter water quality by increasing impervious surfaces and introducing new contaminant sources. Increased development raises potential runoff that can promote non-point source pollution from urban runoff making any necessary remediation more difficult (Vidal-Dorsch et al., 2012). Urban top soil and dust are common sources of trace metals (Akhter and Madany, 1993). Trace elements can be filtered naturally as water percolates through soils, allowing some metals to bind to sediments, removing them from the water. However, as urbanization increases, so does impermeable surface cover, thus creating a lack of natural filtration through soils. Flushing of legacy solutes, including nutrients, in newly urbanized landscapes can affect water quality for more than 5 years after development (Barron et al., 2013).

Groundwater can heavily influence rivers and streams depending on the hydrology, topography and geomorphology of the system (Findlay, 1995; Kasahara and Wondzell, 2003; Wondzell, 2011). Gaining rivers are most affected by groundwater chemistry and can alter the chemistry and ecology of the river significantly (Kasahara and Wondzell, 2003). Groundwater-surface water interactions in the hyporheic zone, the area close to the sediment-water interface, have been found to be very influential in controlling solutes, metals and nutrients in rivers (Fuller and Harvey, 2000; Triska et al., 1989; Wondzell, 2011).

Storm runoff can affect river chemistry depending on land cover and built infrastructure. Storm water runoff contributes solutes from soil erosion and surface runoff as well as chemicals and pollutants from atmospheric deposition (Ahiablame et al., 2012; Akhter and Madany, 1993). An increase in urbanization can cause an increase in the frequency of flood events, which can negatively impact water quality (Chu et al., 2013). Peak metal concentrations tend to occur before peak runoff and early season storms tend to have higher concentrations of metals in runoff (Tiefenthaler et al., 2008). Increased suspended solid concentrations during storm runoff may lead to increased trace element concentrations (Benoit et al., 2010). Metals and ions contributed from storm water runoff typically include Al, Zn, Cu, Pb, Cd, Ca, Na, Mg, NH_4, HCO_3, SO_4, NO_3, and PO_4 (Kabir et al., 2014). Storm events can change the chemistry of receiving streams and potentially cause an increase in specific conductance depending on flow rates, precipitation amounts, and vegetation cover (Reale et al., 2015; Sherson et al., 2015).

The purpose of this study is to investigate trace element contributions from storm events and urban, agricultural, and groundwater inputs to the middle Provo River, Utah, which is located in a watershed that is undergoing rapid agriculture to urban land use changes. Previous work investigating trace element chemistry across the entire length of the Provo River showed that some of the most important changes in water quality occurred in the middle Provo River, but did not investigate the chemistry of tributaries and groundwater inputs (Carling et al., 2015). This study builds on previous work by investigating trace element contributions from groundwater and surface water tributaries to better understand processes affecting water quality in the middle Provo River. Specific objectives include: 1) evaluate longitudinal trends in chemistry in the middle Provo River and tributaries; 2) quantify groundwater contributions and impacts on water chemistry; and 3) evaluate potential impacts of storm events on water quality. This study is part of the iUTAH project (innovative Urban Transitions and Aridregion Hydro-sustainability; http://iutahepscor.org/) funded by the U.S. National Science Foundation with the goal of better understanding water quality, quantity and sustainability in arid regions.

2. Methods

2.1 Hydrogeologic setting

The Provo River, located in northern Utah, supplies drinking water to over half of Utah's population (G. Yates, CUWCD, personal communication) and is important for recreational uses. The middle Provo River in Heber Valley (Fig. 1) is an ideal location to study water quality impacts from agriculture return flow, urban runoff, groundwater inputs, and storm events. Agriculture dominates land use in the watershed and is rapidly transitioning to urban land use. The population of Heber Valley is 15,000 and growing steadily (www.census.gov). For this study, the middle Provo River is defined as the stretch of river from Jordanelle Reservoir to the outlet of Deer Creek Reservoir. Flow is controlled by the Jordanelle Dam, with additional inputs from groundwater and surface water tributaries, including Spring Creek, Center Creek, Wastewater Creek, Snake Creek, Daniels Creek, and Main Creek.

The middle Provo River watershed is well instrumented with water quality stations and streamflow gauges. Water quality parameters including water temperature, conductivity, pH, and dissolved oxygen are measured at 15 min intervals at three locations in the middle Provo River as part of the iUTAH project (Fig. 1). Streamflow is measured by the U.S. Geological Survey (USGS) at Provo River sites P2 and P4, Daniels Creek (D), and Snake Creek site S4 (http://waterdata.usgs.gov/nwis), sites P1 and P3 on Provo River and Spring Creek (S), from the Central Utah Water Conservancy District (CUWCD) (http://www.cuwcd.com), and Provo River site P6 from the Provo River Water Users Association (PRWUA) (http://www.prwua.org/) for April 2014-2015.

The geology of Heber Valley consists of Mississippian to Jurassic sedimentary rocks, Tertiary volcanic and intrusive rocks, and Quaternary alluvial sand and gravel (Hintze 1993, Willis and Willis 2000). Thermal springs and associated tufa deposits overlie or inter-finger with basin-fill sediments on the west side of Heber Valley (Carreon-Diazconti et al., 2003; Mayo et al., 2013). Basin-fill alluvial sediments are estimated to be between 150 and 245 m thick (Carreon-Diazconti et al., 2003).

Snake Creek is an important contributor of solutes to the Provo River because of prevalent thermal groundwater in watershed (Carling et al., 2015; Mayo et al., 2013). Upwelling thermal groundwater mixes with cold shallow groundwater on the western side of Heber Valley before entering the Provo River (Carreon-Diazconti et al., 2003; Mayo et al., 2013). Previous investigations of thermal springs (Carreon-Diazconti et al., 2003; Mayo et al., 2013) on the west side of Heber Valley found that high solute bearing thermal groundwater upwells and discharges into shallow aquifer systems, which in turn contribute solutes to the Provo River. Three groundwater components have been identified in Heber Valley: an unconfined aquifer within the upper tufa layer, a deeper bedrock aquifer below the valley fill, and upwelling thermal groundwater, which mix to some extent before entering the Provo River (Mayo et al., 2013).

2.1.1 Sample site descriptions

To investigate water chemistry in the middle Provo River, we sampled 6 sites (labeled P1-P6) from the outlet of Jordanelle Reservoir to the outlet of Deer Creek Reservoir a minimum of 5 times between April 2014 and March 2015 (Fig. 1). On each of the sampling dates, water samples were also collected at 15 sites to evaluate potential contributions from surface tributaries. These sites included transects on Wastewater Creek (W1-W2), Center Creek (C1-C3), Snake Creek (S1-S4), and Main Creek (M1-M3), with additional samples at Spring Creek (S), Heber Underflow (H), Sagebrush & Spring Creek Canal (SS), and Daniels Creek (D) (Fig. 1). Additional water samples were collected at 13 springs in Heber Valley during summer 2014 to determine regional groundwater chemistry. The springs included 4 cold springs (<13°C), 7 thermal springs (>21°C), and 2 springs that represent mixed cold/thermal groundwater in Heber Valley (Carreon-Diazconti et al., 2003).

Provo River site 1 (P1) is considered a relatively pristine site because there are minimal agricultural or urban activities upstream, whereas sites P2-P5 receive increasing amounts of inflow from agricultural/urban-impacted waters (Fig. 1). There are no surface water tributaries between sites P1-P3 but there is a major diversion below site P1 that supplies water for agricultural uses. Spring Creek and Center Creek enter the Provo River between sites P3 and P4, and Snake Creek enters the river between sites P4 and P5. Site P6 below Deer Creek Reservoir represents a mixture of all tributaries and groundwater inputs to the middle Provo River, including any effects from reservoir storage.

Spring Creek gains significant flow from drainage of flood-irrigated fields in the northern part of Heber Valley (Fig. 1). Sagebrush and Spring Creek Canal receives diverted water from numerous springs and canals and storm runoff from Heber City before draining into Daniels Creek. Daniels Creek captures water from the southern end of Heber Valley, including canals and ditches containing spring water, and irrigation return flow. Center Creek is channelized on the southern end of Heber Valley and receives inputs from ditches before draining into the Provo River. Snake Creek gains significant inflow from groundwater and spring discharge on the west side of Heber Valley before entering the Provo River. Main Creek is a mountain stream that flows through the agricultural community of Wallsburg and is fed by multiple springs and agricultural return flow before entering Deer Creek Reservoir.

2.2 Field methods

To investigate agricultural and urban impacts on trace element and major ion chemistry in the middle Provo River and watershed, samples were collected a minimum of 5 times over a one year period beginning April 2014 (April 4, 2014, May 12, 2014, July 14, 2014, October 31, 2014, March 10, 2015) at 22 sites described above in Heber Valley, Utah (Fig. 1). Samples were collected in varying containers for different analyses including a pre-rinsed 1 L LDPE bottle for major anions and bicarbonate, a 60 mL acid-washed amber glass bottle for dissolved organic carbon (DOC) and total nitrogen (TN), and a 125 mL acid-leached LDPE bottle for trace elements and major cations. Samples were collected using EPA "clean hands, dirty hands" technique (USEPA, 1996). Bottles were triple rinsed with sample water before sample was taken. Field blanks were collected during each sampling day by pouring Milli-Q water into a 125 mL acid-leached LDPE bottle to test for background contamination during sampling, analysis or handling. Samples were stored in a cooler with ice until returning to the lab. Field parameters were measured at each sample location using a calibrated YSI Quatro multiparameter probe.

To examine potential influence of thermal groundwater on Provo River chemistry, 13 springs on the western side of Heber Valley (described above) were sampled using acid-leached (10% v/v HCl) tubing and a Geotech Geopump peristaltic pump. Trace element and DOC/TN samples were filtered directly in the field into acid-washed, pre-acidified bottles.

To investigate potential impacts of storm events on water quality in the middle Provo River, high frequency storm samples were collected in a tributary, Center Creek (C3), every 20 minutes for two hours, immediately following a storm event. Puddle samples were collected during a separate storm event as a possible end member for trace metal concentrations that could potentially impact the river. Acid-leached tubing and a geotech geopump peristaltic pump were used to collect samples from puddles on roadways. Puddle samples were filtered in the field into acid-leached, pre-acidified, 30 mL LDPE bottles.

To compare with iUTAH water quality data and investigate storm event dynamics and impacts on tributaries and the middle Provo River, pressure transducers and conductivity loggers were installed to collect continuous data. Three HOBO U20-001 series water level loggers or pressure transducers were deployed, two in tributaries (Main Creek and Center Creek) to calculate continuous flow rates and one in the air for barometric correction. Four HOBO U24-001 series conductivity loggers were deployed at M3, C3, S, and S4 (Fig. 1). Loggers recorded pressure, conductivity and temperature at 15 min intervals from July 2014 to June 2015. Loggers were placed in lengths of 3-inch diameter ABS pipe with holes drilled to allow flow through the pipe. ABS pipes were secured to T-posts in the channel to maintain constant pipe elevation and loggers were submerged in the water and attached to eyelet screws to maintain a constant depth. Raw data were corrected for barometric pressure using HOBOware software. Flow rates were measured, using a flow meter and tape measure, on multiple occasions in the tributaries with water level loggers to create a rating curve for each tributary were flow was not already available. See Table 1 for a summary of sampling events.

2.3 Laboratory methods

To measure trace element concentrations, 15-30 mL of sample from the 125 mL LDPE bottle were filtered into acid-leached LDPE bottles using acid-leached polypropylene syringes and 0.45-micron PES syringe filters within 8 hours of sample collection. All equipment used for trace elements sampling or analysis was acid-leached with 10% HCl and triple rinsed with Milli-Q water to prevent any pre-contamination of samples. Both filtered and unfiltered fractions were acidified to 2.4% v/v trace metal grade HNO_3. Filtering was done in a Class 100 laminar flow hood upon returning from sampling. Filtered and unfiltered samples were stored in a cold dark refrigerator until analysis. Trace elements were analyzed using an Agilent 7500ce quadrupole inductively coupled plasma mass spectrometer (ICP-MS) at the University of Utah. Concentrations were measured for a suite of 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).

Analysis for major cations, including Ca, Mg, K, and Na, by an alternate method was performed using a Perkin-Elmer 5100 PC atomic absorption spectrophotometer (AAS) to aid in charge balances. 50 mL of sample were filtered from the pre-rinsed 1 L LDPE bottle for major cation analysis using a clean plastic vacuum filter with a 0.45-micron hydrophilic mixed cellulose ester membrane filter. Filtered samples were acidified with HNO_3 to a $pH < 2$ and stored in a cold, dark refrigerator until analysis.

To measure major anions, including Cl, F, HPO_4, NO_3, and SO_4, 50 mL of sample were filtered from the pre-rinsed 1 L LDPE bottle using a clean plastic vacuum filter with a 0.45-micron hydrophilic mixed cellulose ester membrane filter. Filtered samples were stored in a refrigerator until analysis using a Dionex ICS-90 ion chromatograph.

Alkalinity was measured as bicarbonate using a Mettler Toledo DL50 titrator on 50 mL of unfiltered sample from the pre-rinsed 1 L LDPE bottle. Bicarbonate concentrations were used in charge balancing samples.

Amber glass bottle samples for nutrient analyses (TN and DOC) were filtered using glass microfiber filters into clean amber glass bottles and acidified to 2% v/v HCl. DOC samples were analyzed on a Shimadzu TOC-L Total Organic Carbon analyzer by combustion catalytic oxidation method. TN samples were analyzed on a Shimadzu TNM-L Total Nitrogen Unit by catalytic thermal decomposition method.

Quality control of data was evaluated using analysis of field blanks for trace elements which showed concentrations below detection limit for most elements in almost every sample set analysis. Values below detection limit were set as ½ detection limit. Trace elements with concentrations below detection limit for most samples were not used as part of the dataset for statistical analysis. Charge balances were calculated for each sample using cation (Ca, Mg, K, and Na) concentrations from the ICP-MS, anions (Cl, F, HPO_4, NO_3, and SO_4) concentrations from the IC, and bicarbonate (HCO_3) concentrations from titrations. Cations from ICP-MS were corrected using known concentrations of standards with their measurement error and applying a simple correction factor to all sample measurements for each of the four elements. Most samples were within the acceptable range of + or – 5%, but for those outside this range, cations were rerun using the AAS, yielding acceptable charge balance on all but a few. Cation concentrations from ICP-MS and AAS that yielded the better charge balances were used for analysis and interpretation.

2.4 Multivariate statistics

Nonmetric multidimensional scaling (NMS) was used to explore the relationships between Provo River sites, tributaries and springs in Heber Valley. NMS uses visual representations to analyze and explain relationships and trends within a group and does not make assumptions about linearity or normality of datasets. Variables included in the ordination analysis were elemental concentrations and conductivity. We used PC-ORD for NMS ordination following methods described in Carling et al. (2013) and Carling et al. (2015). Data were log generalized 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 plot samples in ordination space. Two hundred fifty (250) iterations were used to analyze the real data which were compared to 250 iterations of randomized data in Monte Carlo simulations. Stability of the model solution and a goodness of fit measure is indicated by model stress, low being best. Calculations of variability described by each axis were performed after model analyses. A 2-D graph displays the model results with data from each site or grouping bounded by "convex hulls" (polygons containing each sample point in a group).

3. Results

3.1 Water chemistry in the middle Provo River and tributaries

3.1.1 Major ions and field parameters

Major ion concentrations increased gradually downstream in the Provo River from Provo River site P1 to P4, but increased sharply after the confluence of Snake Creek at site P5 (Fig. 3). Snake Creek is clearly a major contributor of solutes to Provo River, accounting for ~50-90% increase in solute concentrations (Fig. 3). This is consistent with Carling et al. (2015) who found comparable increases after Snake Creek. After mixing in Deer Creek Reservoir concentrations remained relatively constant as in Na and Ca, but some including Cl, SO_4, and HCO_3 decreased slightly. Cl concentrations in Deer Creek Reservoir decrease slightly indicating a potential dilution of solutes from groundwater or small streams directly feeding the reservoir.

3.1.2 Trace element chemistry

Similar to major ions, a majority of trace elements showed increasing concentrations from upstream to downstream in the middle Provo River. In particular, Li, B, Sr, and As increased slightly between Provo River sites P1 to P4 and then increased dramatically (3-10 fold) at site P5 below the confluence with Snake Creek (Fig. 4). This demonstrates the importance of Snake Creek on Provo River chemistry for these elements. Likewise, Spring Creek provides important contributions of V likely from urban or agricultural sources. Seasonal variability for Li, B, Sr, As was typically small (except B October 2014; Fig. 4). In contrast, V concentrations were variable from month to month but with similar increasing trends along the river transect.

A subset of trace elements showed decreasing concentrations from upstream to downstream in the middle Provo River, including Sb, Ce, and Tl (Fig. 4). Sb and Tl showed significant decreases in concentration below the confluences of Spring Creek and Center Creek. Sb concentrations decrease further below the confluence with Snake Creek, but Tl concentrations increased back to comparable concentrations as Provo River site P1 (Fig. 4). Ce displayed decreasing trends in concentration during July 2014, but concentrations were low during other sampling months, reflecting seasonal differences such as releases from the Jordanelle dam.

To investigate the source of solutes in Snake Creek, we collected samples along a transect of 4 sites from the mountain front to above the confluence with the Provo River. Concentrations increased for the trace elements Li, B, Sr, and As, from upstream to downstream in Snake Creek (Fig. 5), the most significant of which occurred between Snake Creek sites S1 and S2. Mean specific conductance increased from 307 to 1073 μS/cm in that stretch. As presented below, upwelling thermal waters are highly concentrated in these elements and this stretch of stream transects the area of thermal springs, suggesting that upwelling of thermal groundwater in this area (Carreon-Diazconti et al., 2003; Mayo et al., 2013) contributes to flow. Normal faults in the area (Fig. 1) may act as conduits for upwelling thermal water. Concentrations at each site were similar throughout the sampling period suggesting limited seasonal variability in groundwater inputs to Snake Creek. From sites S1 to S2 Li increased by a factor of ~50 to 100, B concentrations increased by a factor of ~20 to 600, Sr concentrations increased by a factor of ~10 to 20, and As concentrations increased by a factor of ~2 to 14.

3.1.3 NMS results

The NMS results showed a 2-D model best represented the dataset (Fig. 2). Axis 1 captured 70.6% of the variance in the dataset and axis 2 described an additional 19.4% for a total of 90.0% of variance in the data set being captured by the model. The final stress of the model was 14.241. Parameters were excluded from the model if a significant number of analyses yielded values at or below detection, thus unnecessarily biasing the results. As, Li, F, Sr, Ba, Ce, V, and Tl were the principle parameters controlling the variation in axis 1 so horizontal distances between sample sites could be attributed to differences in these parameters. Axis 2 was described by Ce, As, F, Li and two redox sensitive elements, Mn and Fe. Parameters such as, Ce, As, Li and F, influence both axes and can be seen as important in distinguishing differences between sample sites (Fig. 2).

The NMS model shows that the Provo River sampling sites vary systematically downstream and that other contributing waters overlap with the Provo River or group separately (Fig. 2). The top panel in Figure 2 shows individual samples from each site grouped in convex hulls. Cold groundwater and thermal groundwater represent end members along axis 1 defined by high concentrations of Ba, Mo, and U in cold groundwater and high concentrations of Li, As, and Sr in thermal groundwater. Axis 2 further differentiated the sites on the basis of parameters As, Li, F, and NO_3 on the positive end and parameters Ce, Mn, and Fe on the negative end.

The NMS plot shows the strong influence of thermal groundwater on Snake Creek and the Provo River. Snake Creek plotted closest to the thermal groundwater convex hull than any other site. Snake Creek has been shown to be influenced by thermal groundwater on the western end of Heber Valley (Carreon-Diazconti et al., 2003; Mayo et al., 2013). Provo River sites P1-P2, P3-P4, and P5 are progressively pulled toward Snake Creek and thermal groundwater in NMS space with increasing groundwater inputs along the stretch of river in Heber City. Provo River site P6, which is below Deer Creek Reservoir, did not follow the trend toward Snake Creek, but plotted closer to the cold groundwater, suggesting important contributions from non-thermal groundwater and other tributaries like Main Creek. Interestingly, Provo River sites P1-P5 were encompassed by the Provo River tributaries indicating that the tributaries are influenced by similar chemical processes as the Provo River.

3.2 Groundwater contributions to the middle Provo River

3.2.1 Groundwater chemistry

Groundwater samples from Heber Valley showed variable chemistry in cold, thermal, and mixed springs. Average concentrations of Li, B, As, and Sr for each type of spring are shown in Fig. 6. Cold springs had the lowest average concentration of most elements, while thermal springs had the highest concentrations. Thermal springs had 17 and 82 times higher concentrations of As and Li, respectively, relative to cold springs. Average As concentrations exceed EPA limits (>10 μg/L) in all thermal and mixed springs. Mixed spring concentrations were used as groundwater concentrations in groundwater discharge calculations described below.

3.2.2 Groundwater fluxes

Groundwater contributes an important flux of water and solutes to the middle Provo River that is variable throughout the year. Discharge measurements at USGS and CUWCD gauging stations at Provo River sites P1 (Jordanelle Release), P2 (Upper Midway) and P3

(Lower Midway) show decreasing discharge from upstream to downstream due to flow diversions. Thus gain-loss measurements are not useful for estimating groundwater fluxes to the Provo River for this reach. In contrast, USGS discharge data show consistently increasing discharge rates between Provo River sites P3 (Lower Midway) and P4 (Charleston) due to the contributions from tributaries and groundwater. Measured discharge on surface tributaries between Provo River sites P3 and P4, including Spring Creek and Center Creek, do not account for the difference in river discharge suggesting that groundwater inputs are important along this reach. Based off of discharge contributions from tributaries, groundwater contributes <1 – 11% of discharge to the river between P3 and P4.

3.3 Water quality during storm events

3.3.1 Continuous specific conductivity and temperature measurements

15-min specific conductance data collected at Provo River sites P1, P3, and P4, and tributaries Spring Creek and Center Creek yield insight to the daily changes in water chemistry. Specific conductance increases by about 40 µS/cm from site P1 to P3 and by about 25 µS/cm between sites P3 and P4. Site P1 does not exhibit large or sudden changes in specific conductance because discharge is controlled by Jordanelle Dam, whereas sites P3 and P4 exhibit diurnal cycles and changes >15 µS/cm (Fig. 7, Fig. 8, and Fig. 9).

Spring Creek and Center Creek were more susceptible to changes due to runoff relative to the Provo River and thus had greater fluctuations in specific conductance. On average, Spring Creek and Center Creek had 1.5-2 times greater specific conductance than the Provo River at site P3 (Fig. 7). Spring Creek had a significant effect on Provo River because increases in specific conductance on December 23, 2014 and January 14, 2015 are seen in Provo River site P4, but not site P3 (Fig. 8). Conversely, specific conductance fluctuations in Center Creek from May 13 to May 23, 2015 and a significant decrease on September 27, 2014 are not seen in Provo River site P4 (Fig. 9). In contrast to Spring Creek, Center Creek had little effect on the Provo River because it is so small.

Increases in specific conductance from storm runoff events were observed in the tributaries with corresponding changes downstream in the Provo River at site P4 (Fig. 7). Surprisingly, runoff during storm events tended to increase specific conductance in both tributaries. For example, on December 21, 2014, specific conductance increased by 70 µS/cm or ~18% in Spring Creek and 85 µS/cm or ~22% in Center Creek due to a 1.12 cm precipitation event (Fig. 7 and Fig. 8). However, in some cases specific conductance decreased or did not change more than 20 µS/cm during storm events as on July 29, 2014 in both Spring Creek and Center Creek (Fig. 7). During the largest precipitation event of 3.38 cm measured on September 27, 2014, specific conductance decreased in Center Creek. This appears to be an anomaly because specific conductance at Provo River site P4 increased during this event indicating that there was some water source with elevated specific conductance contributing to the middle Provo River. This is perhaps due to groundwater inputs during the storm event.

15-min water temperature data indicate an increase in temperature going downriver from Jordanelle Dam during spring and summer months. This trend is reversed during fall and winter months where the temperature decreases going downriver. Similarly, tributary temperatures are at or above Provo River temperatures during spring and summer, but are at or below during fall and winter (Fig. 10).

3.3.2 Discrete storm event sampling

To understand the potential runoff contributions of trace elements during a storm event, storm puddles were sampled for trace elements in filtered samples. Major elements had higher concentrations in the river than in puddles along with some trace elements including As, Li, and Sr (Fig. 11). These element concentrations could thus be diluted in Provo River with the addition of runoff. Other trace elements had higher concentrations in storm puddles including Co, Cu, V, and Zn (Fig. 11), indicating the potential for increased concentrations of these elements in Provo River during storm events. Pb concentrations in the middle Provo River ranged from below detection limit to 0.05 µg/L and were highly variable so were not investigated further.

High frequency sampling of Center Creek during a two-hour period of a storm event on July 29, 2014 showed increasing concentrations of most elements and nutrients. Dissolved N and DOC concentrations steadily increased during the two-hour period. Rb concentrations increased as well, while Mn, a redox sensitive element, concentrations decreased. Nearly all elements analyzed had higher concentrations during the storm event compared to concentrations measured previously on a clear day on July 14, 2014 indicating that the full concentration curve was not captured in the two-hour period.

4. Discussion

4.1 Groundwater inputs

Groundwater inputs are an important natural source of trace elements to the middle Provo River, especially thermal groundwater in the Snake Creek watershed. The NMS plot highlights the unique chemistry of thermal groundwater compared to other sites in Heber Valley and its closeness to Snake Creek (Fig. 2). NMS shows the middle Provo River sites trending toward Snake Creek and thermal groundwater emphasizing the influence of thermal groundwater on the

Provo River. Notably, thermal groundwater has high concentrations of total dissolved solids and specific trace elements, including Li, B, Sr, and As. These elements are typical of thermal groundwater (Bonte et al., 2013; Bundschuh et al., 2013; Munoz et al., 2015; Stuben et al., 2003). High Li and B concentrations are commonly a result of thermal dissolution of feldspars and aluminosilicate minerals and concentrations may vary depending on residence times (Edmunds and Smedley, 2000). A possible source of As could be reductive dissolution of Fe- and Mn-oxides/oxyhydroxides in the deeper aquifers. This is supported by high Fe and Mn concentrations as well as low dissolved oxygen concentrations measured in the thermal springs that suggest reducing conditions in the deeper aquifers. As concentrations exceed the EPA limit of 10 µg/L in all sampled thermal springs, with concentrations as high as ~90 µg/L (Fig. 6). More work is needed to investigate the source of As in the thermal springs.

Thermal groundwater mixes with cold shallow groundwater before entering Snake Creek (Carreon-Diazconti et al., 2003), decreasing total concentrations of most trace elements. Snake Creek has average As concentrations of ~15 µg/L above the confluence with Provo River. Snake Creek accounts for roughly 20% of the flow to the middle Provo River, but increases the As concentration in Provo River ~4 fold. This significant As load to the middle Provo River can be greatly attributed to the natural upwelling thermal groundwater in Heber Valley. Flow between Snake Creek sites S1 and S2 increased ~10 fold and at site S2 flow was comprised of ~80 to 90% groundwater. To estimate thermal groundwater fluxes to Snake Creek, we used a simple two end-member mixing model, with specific conductance as the mixing element, in six separate iterations between the warmest thermal spring (3038 µS/cm) as one end-member and each sampling of Snake Creek site S1 (293 – 319 µS/cm) and the uppermost cold spring (374 µS/cm) as the other end member. Calculations indicate that Snake Creek is comprised of 23 to 31% thermal groundwater.

In addition to inputs from Snake Creek to the Provo River, mixed thermal/cold groundwater contributes trace elements and other solutes to the middle Provo River via direct groundwater discharge. Elevated concentrations of As, Li, B, and Sr in groundwater (Fig. 6) relative to the Provo River (Fig. 4) suggest that increased concentrations of these elements between Provo River sites P2 and P3 and between sites P4 and P5 are due to groundwater inputs to the river. To estimate groundwater fluxes to the middle Provo River, we used a simple end-member mixing model to quantify possible groundwater inputs between each sample site from sites P1 to P2, P2 to P3, and P3 to P4 (Table 2). For groundwater discharge calculations, groundwater chemistry was assumed to be a mix of thermal groundwater and cold groundwater as described in Carreon-Diazconti et al. (2003) and Mayo et al. (2013). Both studies found groundwater in the area to be a mix of 15 to 30% thermal groundwater and 70 to 85% cold groundwater. Because of this we used the chemistry of a shallow mixed spring for mixing calculations.

For our mixing calculations, we used Cl concentrations as the tracer and measured stream discharge at each site. These calculations showed that groundwater contributes 0 to 5% of the flow between sites P1 and P2, 0 to 10% between sites P2 and P3, and 5 to 15% between sites P3 and P4 (Table 2). Assuming that this groundwater contribution is comprised of a similar ratio of thermal groundwater as found in Snake Creek, then thermal groundwater comprises 0 to 1% of the flow between sites P1 and P2, 0 to 3% between sites P2 and P3, and 1 to 4% between sites P3 and P4.These values are much lower than estimated by Carreon-Diazconti et al. (2003) who indicated gains as high as 50% from groundwater during winter months between sites P3 and P4.

The lower calculated values relative to Carreon-Diazconti et al. (2003) may be due to neglected tributary contributions, changes in irrigation patterns causing changes in groundwater flows, or time of year for groundwater calculations. The Provo River Restoration Project which took place between 1999 and 2008 altered the flow paths of the river and may have changed groundwater inputs (http://www.mitigationcommission.gov/prrp/prrp.html, February 2016). For more details on groundwater calculations see appendix.

To check mixing calculations using Cl, we also performed mixing calculations using Li, B, Sr, and As for the reach between Provo River sites P2 and P3. These calculations indicate that groundwater contributes 2 to 10% of the flow between Provo River sites P2 and P3. The lower calculated groundwater inflows were similar to those calculated using Cl. This suggests that higher concentrations of trace elements in groundwater, and more specifically thermal groundwater may have one of the greatest impacts on middle Provo River chemistry.

Hyporheic exchange is another possible control on trace metal concentrations to the middle Provo River. Under losing conditions, hyporheic interaction allows for trace metals in river water to bind with Fe and Mn-oxides in sediments close to the river bed or precipitate out in mineral form, thus removing them from the surface water (Fuller and Harvey, 2000). The reverse is also true in gaining conditions in that trace metals can be remobilized as reduced groundwater flows toward the river, causing reductive dissolution of bound metals. This can take place on variable scales (centimeters to 10's of meters) depending on the geomorphology and hydrogeology of the river system (Kasahara and Wondzell, 2003). The middle Provo River has pool and riffle sequences that promote hyporheic exchange through gaining and losing conditions, but the extent to which this interaction controls water chemistry in the river is unknown.

Changes in conductivity in the middle Provo River are possibly due to groundwater inputs because groundwater has direct interactions with the river through the hyporheic zone and the diurnal variability is seen in both Provo River sites P3 and P4. Additionally, Spring Creek and Center Creek do not display a consistently strong diurnal variation sufficient to cause the change we see. Hayashi et al. (2012) found that biological and physiochemical processes effecting carbonate chemistry could produce the diurnal cycles of specific conductance of rivers. Daytime carbonate precipitation and nighttime carbonate dissolution, respectively decreasing and increasing Provo River specific conductance is a possible cause of observed diurnal variation. Further work is needed to determine which is most important. Daily fluctuations in conductivity of 20 µS/cm are less than those observed in Hayashi et al. (2012) and Viswanathan et al. (2015) possibly because of the homogenized water being released from Jordanelle reservoir to the middle Provo River.

4.2 Agricultural versus urban influences on stream chemistry: implications for future urbanization

In addition to groundwater inputs, the Provo River is impacted by a variety of anthropogenic processes as it flows through Heber Valley and receives inflows from agricultural, urban, and storm runoff. Agricultural sources are another potential for river chemistry impacts and contamination. Heber Valley has about 70% agricultural land use, which includes irrigated grain/hay fields, livestock grazing, dairies, and hobby farms. Spring Creek is a major recipient of agricultural return flow from both flood and pressure irrigated fields. Spring Creek exhibits season flow changes with the highest flows occurring during the summer irrigation months when it contributes about 12% of the flow and lowest during the winter when it accounts for only 6% of the flow. Notably, Spring Creek accounts for >40% of the annual V load and >18% of the annual U, Mn, Pb, Ba, La, and Ce loads to the middle Provo River. This suggests that agricultural land use is an important source of these elements, especially during the summer months.

Another source of trace elements to the middle Provo River is runoff from urban land use. Heber Valley is ~30% urban land use including commercial developments, an airport, shopping centers, paved parking lots, and residential neighborhoods. Center Creek receives water from urban runoff, storm drain overflows, and agricultural runoff. Trace elements including Ba, Ce, V, Pb, Ti, and U are disproportionately contributed from Center Creek. Loads of these elements are all between 2 and 5% of the total loading to the middle Provo River with V contributing the most at 5%. V is an urban element that is sourced from mineral oils used for combustion and manufacturing (Herpin et al., 2004; Moreno et al., 2010). In contrast, other urban-sourced trace elements including Zn, Cu, Al, Ni, Co, and Cr (Kabir et al., 2014; Mayer et al., 2011; Tiefenthaler et al., 2008; Yang et al., 2016) contributed only between 1.1 and 1.8% of the total middle Provo River load. Since Center Creek contributes ~1.5% of the flow to the middle Provo River, loads from these common urban trace elements are not abnormally high. This may be because of the lack of industrial lands in Heber Valley, or because Center Creek receives a mix of water inputs from a variety of sources.

Although flow contributions from the tributaries Spring Creek to the middle Provo River are relatively small, it does have an impact on Provo River chemistry. Specific conductance increased from upstream to downstream for three locations in the middle Provo River (Fig. 7). The increase from Provo River site P1 to P3 is likely due to groundwater inputs since there are no major surface inflows along this river reach. The increase between sites P3 and P4 is mainly due to inputs from Spring Creek. Figure 8 shows the increases in specific conductance between sites P3 and P4 and the simultaneous increase in Spring Creek, thus highlighting the connectivity of these two water bodies. In contrast, Center Creek had minimal impact on specific conductance in the Provo River because it contributed minimal flow. Increases in specific conductance in Center Creek did not have an effect on the Provo River at site P4 (Fig. 9).

Correlations between trace elements and specific conductance indicate that specific conductance can be used as a proxy for certain trace elements in the middle Provo River. Major and some trace elements in the Provo River are strongly correlated with specific conductance having an $r^2 > 0.72$ including B, Mg, Li, As, Ca, Rb, Sr, Na, and K (Table 3). Two other trace elements, U and V, shared a moderate correlation with specific conductance, $r^2 > 0.54$. Interestingly, the trace elements B, Li, As, and Sr which are found in high concentrations in groundwater, were strongly correlated with Provo River specific conductance. This points to a close connection between groundwater and the middle Provo River. Additionally, these correlations indicate a potential method of predicting select trace element concentrations in the middle Provo River based on specific conductance data. For instance, plotting specific conductance (x) with As concentrations (y) for all sites on the middle Provo River yields a trend line with the equation $y = 0.0125x - 1.3778$ and an $r^2 = 0.78$. Thus As concentration in the middle Provo River could be estimated with only a specific conductance measurement. This relationship can be applied to multiple trace elements, and further work should be done to determine the effectiveness of predicting trace element concentrations from specific conductance and other common water quality measures.

4.3 Importance of storm events for controlling stream chemistry

Center Creek site C3 was opportunistically sampled at high frequency during a storm event in mid-summer 2014 (Fig. 12). During this event 1.14 cm of precipitation was accumulated and was the first major storm event of the summer making this a seasonal first flush event which would have washed off about 2 months of accumulated dust, salt, and other pollutants. First flush events are important controllers of water chemistry because they can introduce high concentrations of trace elements to a water body within a short period of time. Schiff and Tiefenthaler (2011) found that seasonal first flush events generated 3-10 times the event mean concentration of later storm events in the season. We were only able to sample during a two-hour period and thus did not capture the entire storm hydrographic flow profile that is required for mean event concentrations. However, concentrations of trace elements including Rb, B, and Fe, were >1.5 times greater and continuing to increase, while Mn were 2.2 times greater and continuing to decrease during the two-hour sampling period of the storm compared to a clear day two weeks previous. Total nitrogen and dissolved organic carbon concentrations were 2.3 and 2.5 times clear day concentrations, respectively, with increasing trends. This suggests that we may have still been pre-peak runoff for the storm and maybe did not capture the maximum concentrations for the storm.

Surprisingly, specific conductance did not change drastically in Center Creek during the storm. This may be due to the initial first flush that was high in dissolved solids counteracting the typical low specific conductance of rainwater. Despite this small change in specific conductance during some storm events, specific conductance is correlated with some trace elements. During the summer storm, K and Rb were strongly correlated with specific conductance with r^2 values of 0.79 and 0.85 respectively. Mn had a strong negative correlation with specific conductance during the storm with an r^2 of 0.88. This suggests that Mn concentrations decrease under oxidizing conditions during a storm event. Other elements including Ba, La, and Ce were moderately correlated with specific conductance during the storm event with $r^2 > 0.60$. This is important for monitoring schemes because specific conductance is a simple measurement that could provide insight into behavior of these elements, especially Ce, which can have negative health effects (Dahle and Arai, 2015).

Analysis of trace elements in storm puddles on roadways during a September 27, 2014 storm event showed that puddles had higher concentrations of Co, Cu, V, and Zn, but lower concentrations of Ca, As, Li, and Sr relative to the middle Provo River (Fig. 11). Even though some metals had higher concentrations in puddles, the concentrations were still below drinking water standards and thus should not affect drinking water quality on a frequent basis. However, trace elements can be stored in soils and build up over many years during drier years (Schiff and Tiefenthaler, 2011). During wetter years they can be released in larger storm events and create a larger than normal flux of trace elements to the middle Provo River. Interestingly, Cu and Zn have been found in highest quantities in industrial runoff (Tiefenthaler et al., 2008), but Heber Valley does not have significant industrial operations. Commercial land use is another common source of Cu and Zn and could be a potential source of these metals in Heber Valley.

Analysis of storm water samples in Center Creek (Fig. 12) indicated that trace element concentrations did not approach maximum contaminant levels for freshwater bodies or aquatic life. This may be because Heber Valley is still dominated by agricultural land use, however as this changes to urban dominated future work should be carried out to compare to our data. We did not analyze pesticides, fertilizers, or other substances common to agricultural runoff, which would be useful for analyzing total water quality in the future.

4.4 Comparison with historical data

Historical data from the National Water Quality Monitoring Council (http://waterqualitydata.us/portal/, February 2016) indicates that specific conductance decreased an average 135 μS/cm at Provo River site P4 after construction of Jordanelle Dam (Fig. 13). This may be caused by the retention and controlled release of water from the dam changing hydraulic gradients downriver which may have lowered the groundwater fluxes to the river. This change also coincides with the Provo River Restoration Project which changed the course of the river and may have altered groundwater and surface tributary contributions as a result. The lack of consistent historical data makes it difficult to recognize concrete changes in water quality and even more difficult to pinpoint causes such as land use change. However, further urban development may lead to increased concentrations of specific trace metals. Future work is needed to assess water quality at progressive stages of urbanization along the middle Provo River to determine if trace metal trends can be linked to various types of urbanization.

5. Conclusions

In this study we used trace element concentrations and continuous measurements of flow rates and specific conductance to investigate dynamic processes affecting water quality in a rapidly urbanizing agricultural area typical of the western U.S. The Provo River is an integral part of the lives of half of Utah's population because it serves as drinking water for much of the region. We found that both natural and anthropogenic sources influence solutes concentrations in the middle Provo River. Thermal groundwater is one of the most important contributors of trace elements including Li, B, As, and Sr. Tributaries were responsible for contributing the most V to the middle Provo River. Continuous specific conductance measurements were useful in understanding the relative importance of specific tributaries on Provo River chemistry. Storm events have the potential to change trace metal concentrations in receiving waters, but more work is needed to better understand the influence of first flush storm events on trace element chemistry in rivers and their tributaries.

Further work on thermal groundwater in the middle Provo River should investigate biological impacts and controls on water quality, including a bacterial survey to explore mobilization of arsenic and other trace metals. Further studies on groundwater influences on the middle Provo River should include hyporheic exchange as a possible moderator of river chemistry. Further work on storm runoff from the urban environment should continue along the middle Provo River as agricultural lands are urbanized and should be expanded to include sampling of organic materials including polycyclic aromatic hydrocarbons.

Table 1. Summary of sampling events.

Sample type	*Frequency*	*Dates*	*Analyses*
Surface Water (Provo River and tributaries)	≥ 5 times	February 26, 2014 April 4, 2014 May 12, 2014 July 14, 2014 October 31, 2014 February 20, 2015 March 10, 2015	Major anions Alkalinity Major cations Trace elements DOC TN
Springs (cold, thermal, mixed)	1 time	June 19-20, 2014	Same as Surface Water
Storm Event - High Frequency	1 time at 20 min intervals	July 29, 2014	Same as Surface Water
Storm Event - Puddles	1 time	September 27, 2014	Trace elements
Specific Conductance	Continuous at 15-minute intervals	June 2014 to June 2015	Specific Conductance
Water Temperature	Continuous at 15-minute intervals	June 2014 to June 2015	Water Temperature

Table 2. Calculated groundwater discharge to the middle Provo River.

	P1 to P2		P2 to P3		P3 to P4	
	ft^3/s	%	ft^3/s	%	ft^3/s	%
April 2014	0.0 - 7.40	0 - 5	0.0 - 6.70	0 - 5	12.77 - 19.15	10 – 15
May 2014	0.0 - 12.66	0 - 5	0.0 - 8.20	0 - 5	7.80 - 15.60	5 – 10
July 2014	0.0 - 14.06	0 - 5	0.0 - 9.30	0 - 5	18.13 - 27.20	10 – 15
October 2014	0.0 - 7.57	0 - 5	6.79 - 13.57	5 - 10	6.51 - 13.02	5 – 10
March 2015	0.0 - 7.38	0 - 5	0.0 - 6.77	0 - 5	6.91 - 13.82	5 - 10

Table 3. Regression coefficients (r^2) for specific conductance and various trace elements in the middle Provo River.

Element	r^2
U	0.54
V	0.59
B	0.72
Mg	0.75
Li	0.75
As	0.78
Ca	0.79
Rb	0.80
Sr	0.82
Na	0.86
K	0.87

Table 4. Calculated groundwater discharge between Provo River sites P2 and P3.

	Using Li concentration		*Using Sr concentration*	
	ft^3/s	%	ft^3/s	%
April 2014	3.35 - 6.70	3 - 5	1.96 - 3.93	2 - 3
May 2014	5.01 - 10.02	3 - 6	3.62 - 7.25	2 - 5
July 2014	6.64 - 13.28	4 - 7	9.36 - 18.72	5 - 10
October 2014	7.71 - 15.43	6 - 12	13.54 - 27.09	10 - 21
March 2015	7.38 - 14.75	5 - 11	6.60 - 13.21	5 - 10

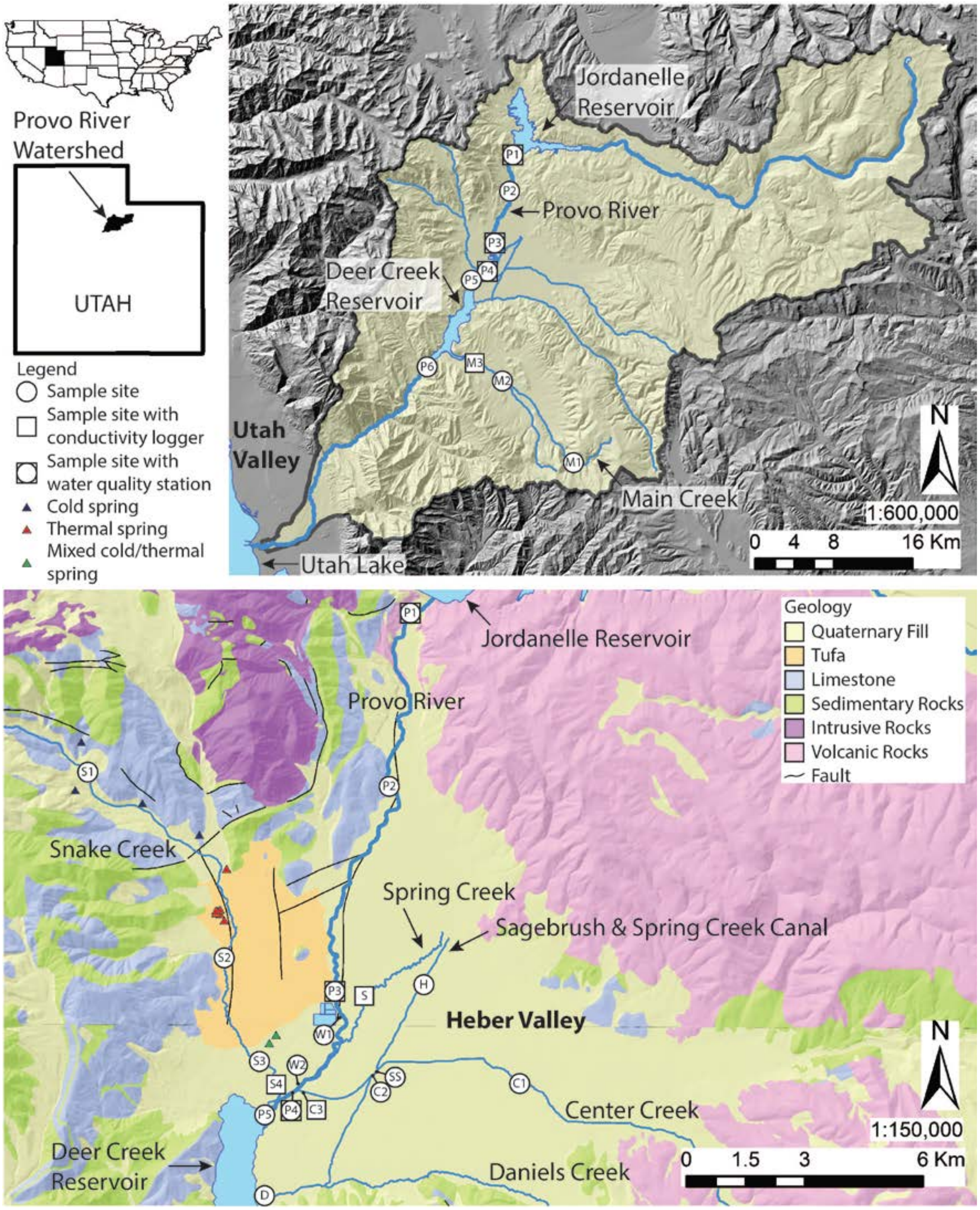

Figure 1. Map of Provo River watershed in northern Utah, USA. Sample sites are shown with numbers and letters in white circles or squares. This study was primarily undertaken in the middle Provo River (map below). Relative watershed location is shown in the index map of Utah. Provo River site P1 is used as the pristine mountain site, while sites P2-P5 are in the urbanizing environment, and site P6 is after mixing in Deer Creek Reservoir. Main Creek is a tributary to Deer Creek Reservoir. Below the watershed map is a close-up view of Heber Valley and some of the waterways that traverse the valley. Site abbreviations: Provo River – P1-P6, wetland stream – W1-W2, Spring Creek – S, Sagebrush and Spring Creek Canal – SS, Daniels Creek – D, Center Creek – C1-C3, Heber City underflow – H, Snake Creek – S1-S4.

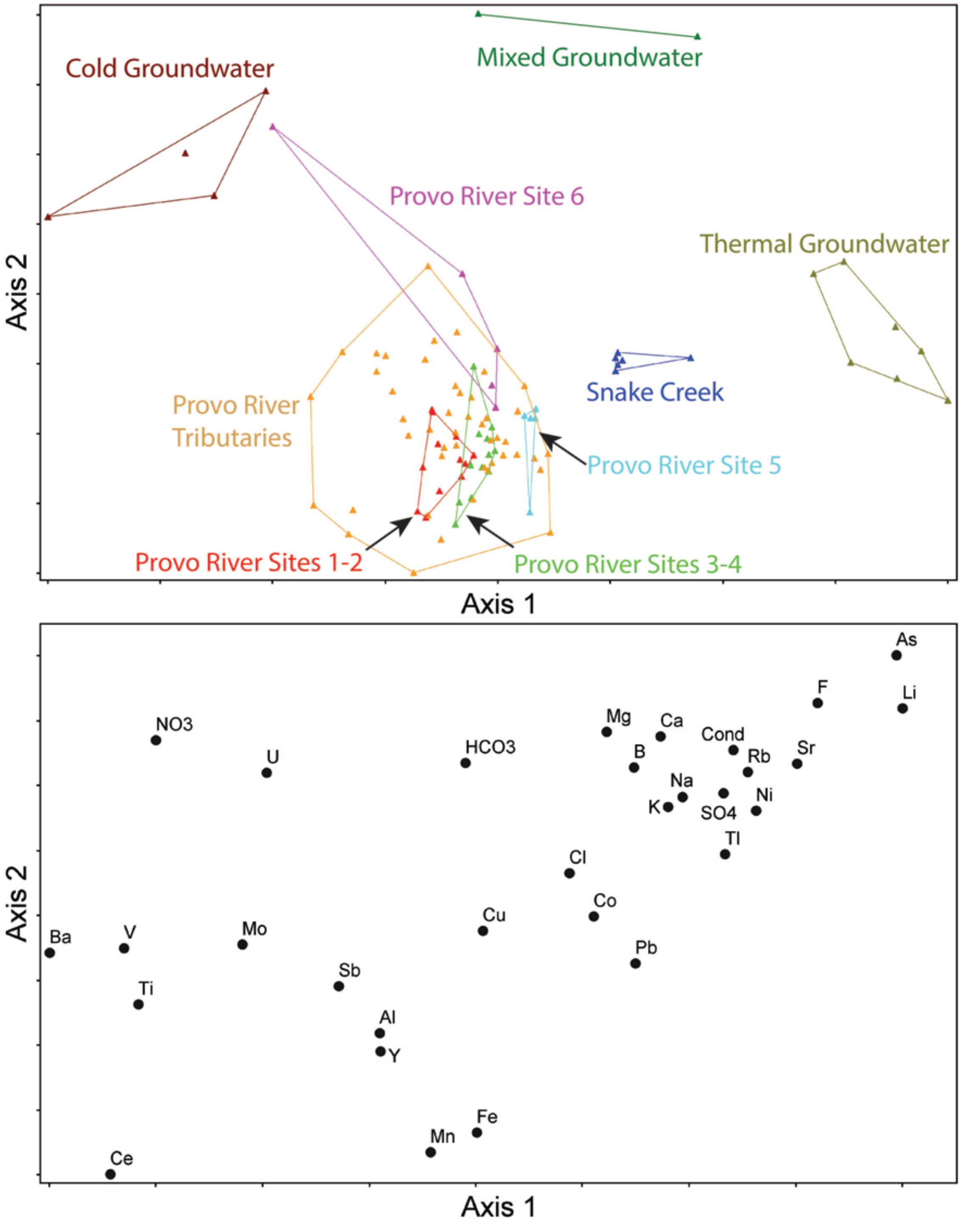

Figure 2. NMS results for sites in Heber Valley. Axis 1 explains 70.6% of the variability in the dataset while axis 2 explains 19.4% for a total of 90.0%. Final stress for the two axis model is 14.241. Provo River Tributaries include Spring Creek, Daniels Creek, Center Creek, wetland stream, Sagebrush and Spring Creek Canal, and Heber City underflow.

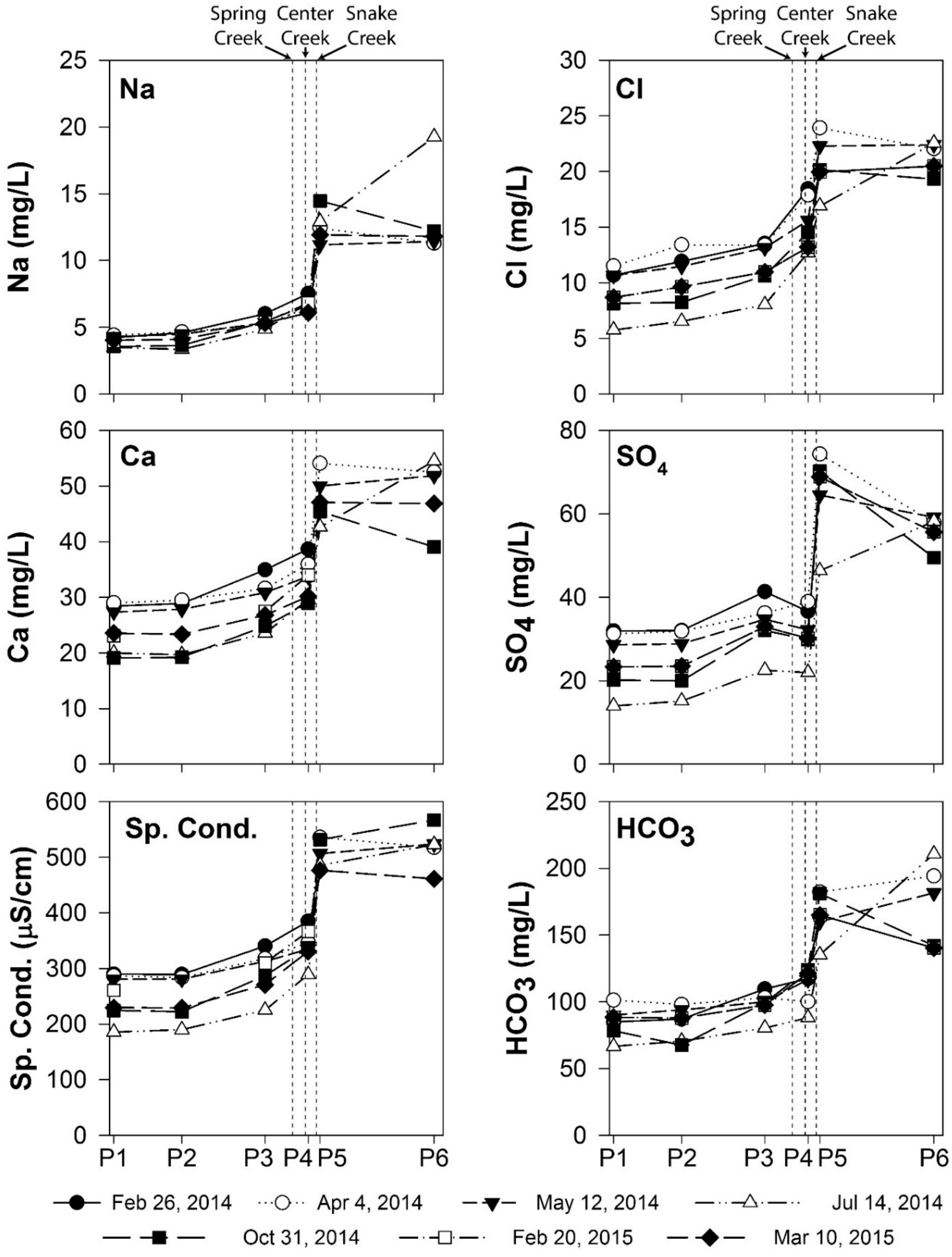

Figure 3. Line graphs of selected major ion (Na, Ca, Cl, SO$_4$, and HCO$_3$) concentrations measured on filtered water samples and specific conductance (Sp. Cond.) for sites P1-P6 on the middle Provo River, Utah. Samples locations are scaled according to river distance from Jordanelle Reservoir. Dashed vertical lines represent location of tributary confluences, including Spring Creek, Center Creek, and Snake Creek. Each of these parameters showed increasing concentrations from site P1 to P6, with some variability between sites P5 and P6.

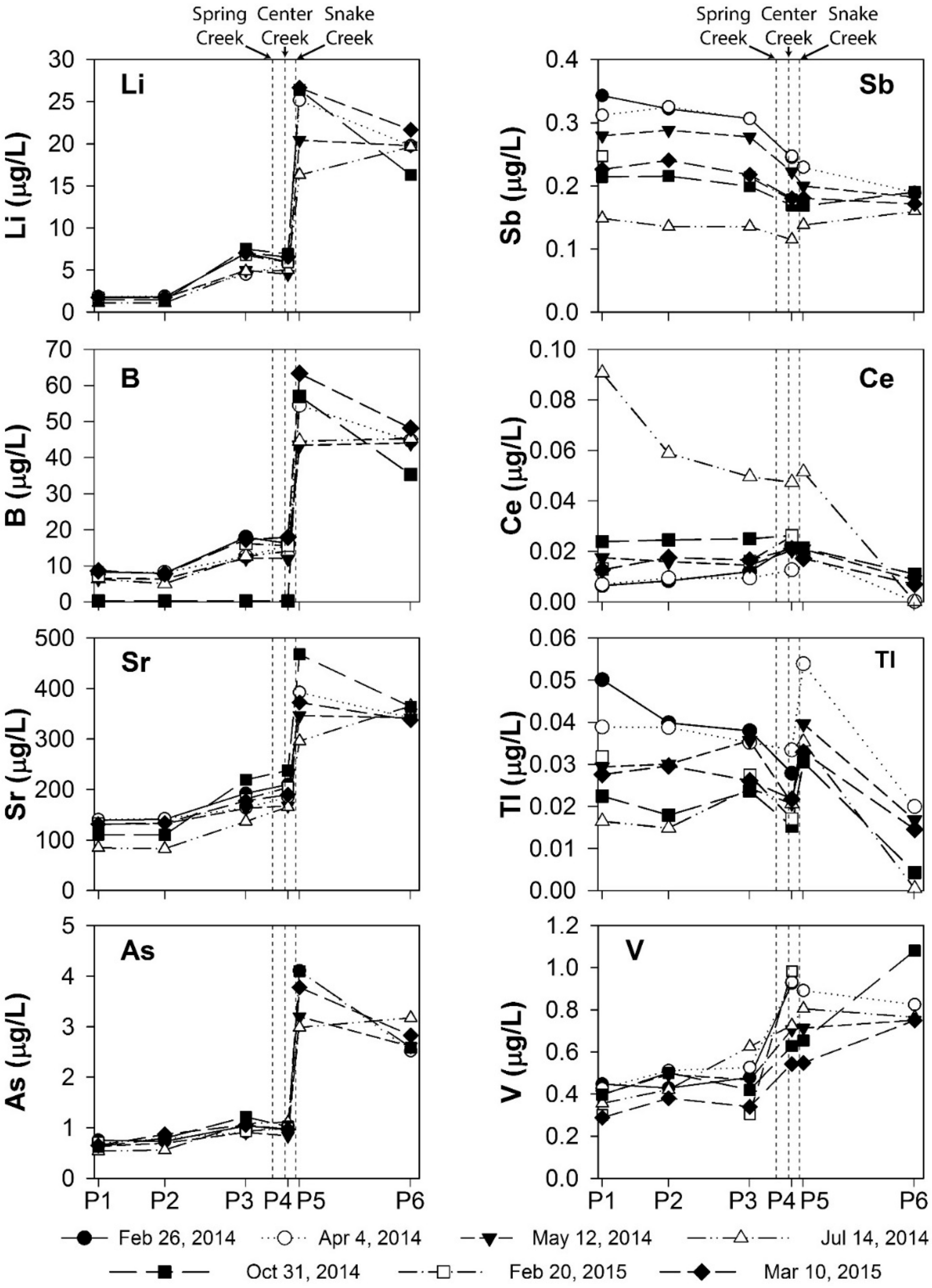

Figure 4. Line graphs of selected trace element concentrations measured on filtered water samples for sites P1-P6 on the middle Provo River, Utah. Samples locations are scaled according to river distance from Jordanelle Reservoir. Dashed vertical lines represent location of tributary confluences, including Spring Creek, Center Creek, and Snake Creek. Li, B, Sr, and As generally showed increasing concentrations downstream showing a slight increase between sites P2 and P3 and a large increase after the confluence of Snake Creek between sites P4 and P5. V generally increased downstream, but showed increased concentration after the confluences of Spring Creek and Center Creek rather than after Snake Creek. Sb, Ce, and Tl displayed generally decreasing concentrations downstream from Jordanelle Reservoir. Sb and Tl showed decreased concentrations after Spring Creek and Center Creek, but Tl concentrations spiked after the confluence of Snake Creek. Ce showed small increases after the tributary confluences.

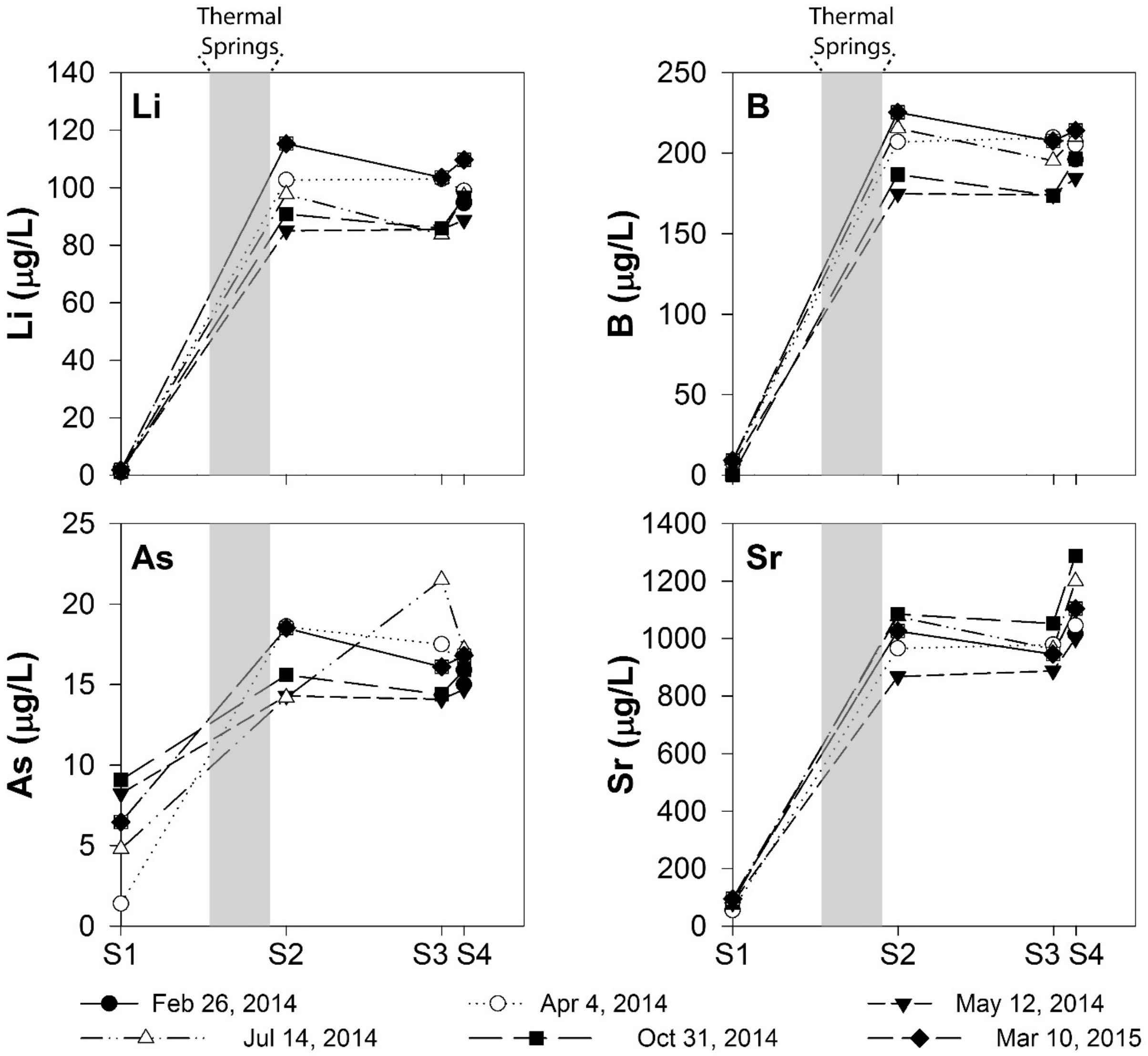

Figure 5. Line graphs of selected trace element concentrations measured on filtered water samples for sites S1-S4 on Snake Creek in Heber Valley, Utah. Snake Creek is a tributary to the middle Provo River. Li, B, Sr, and As showed increasing concentrations downstream after encountering upwelling thermal groundwater in Midway, Utah. Samples locations are scaled according to river distance from Snake Creek site S1. Shaded region represent location of thermal springs in Midway, Utah.

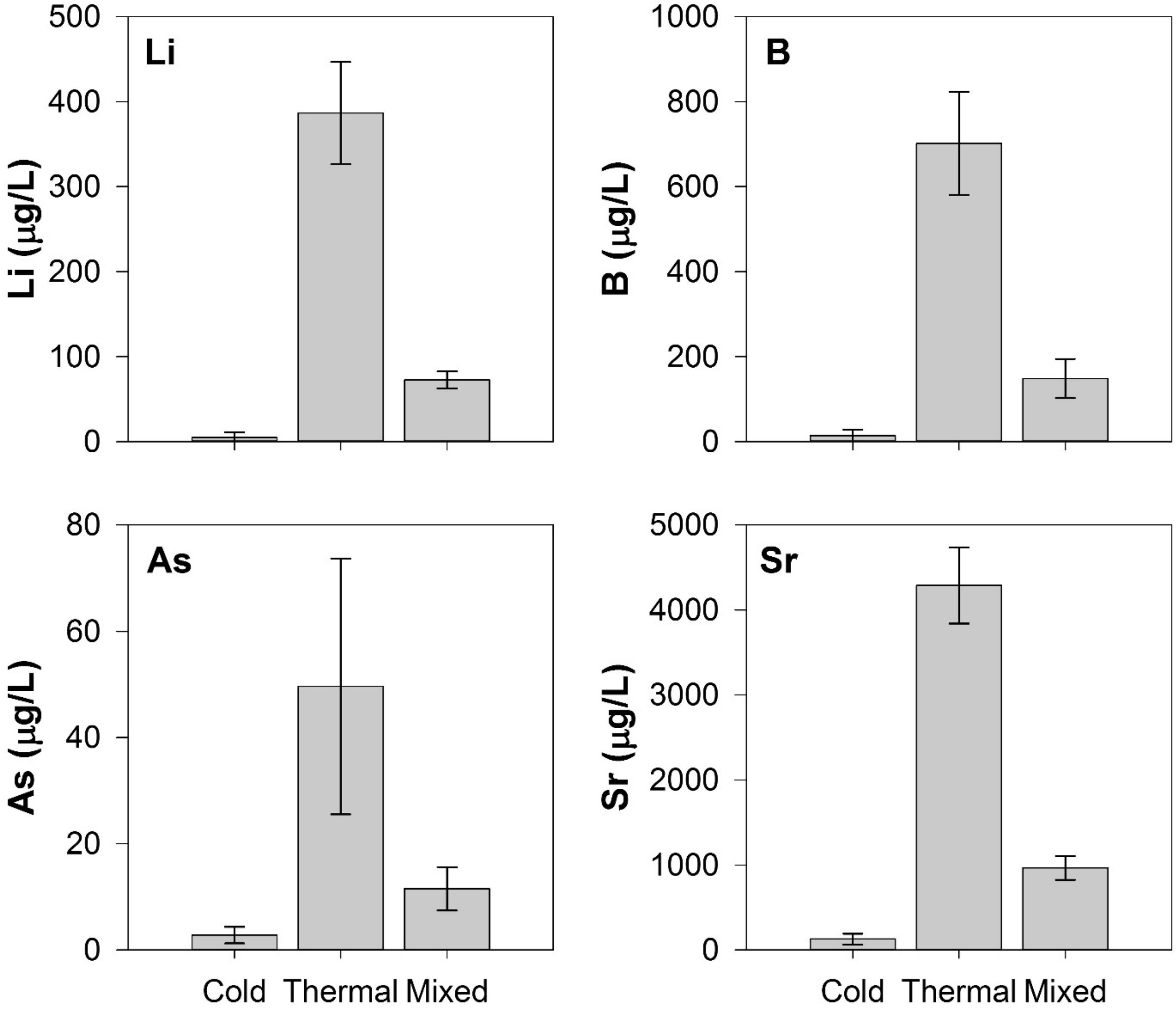

Figure 6. Average concentrations of Li, B, Sr, and As in springs on the west side of Heber Valley in the Snake Creek subwatershed. Cold springs (n=4) represent cold groundwater that has very little influence from upwelling thermal water, thermal springs (n=7) are the thermal groundwater found in tufa mounds throughout the city of Midway, and mixed springs (n=2) represent a mixture of cold and thermal groundwater.

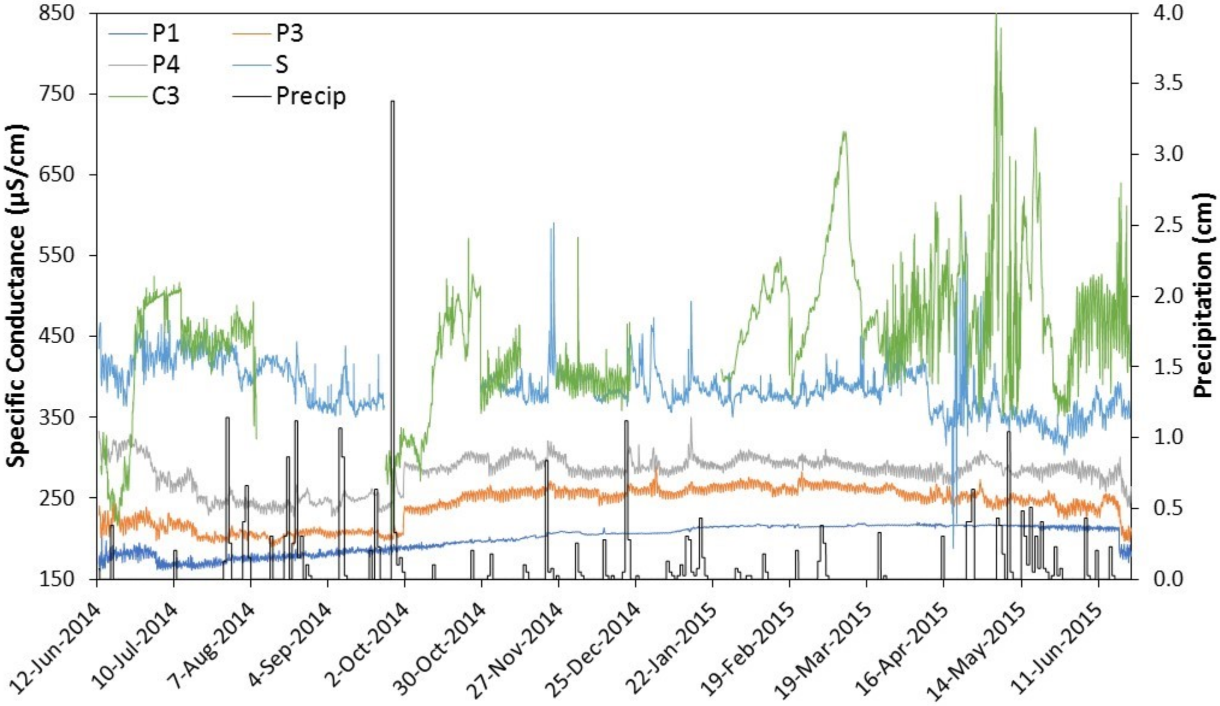

Figure 7. Fifteen minute specific conductance data for Spring Creek (S), Center Creek site C3 and three sites on Provo River (P1, P3, and P4) from June 2014-2015. Note the general increase in specific conductance from Provo River site P1 to site P3 and again from site P3 to site P4. There are no surface tributaries to the river between sites P1 and P3 suggesting groundwater may contribute to the increased specific conductance. Spring Creek and Center Creek enter the river between sites P3 and P4.

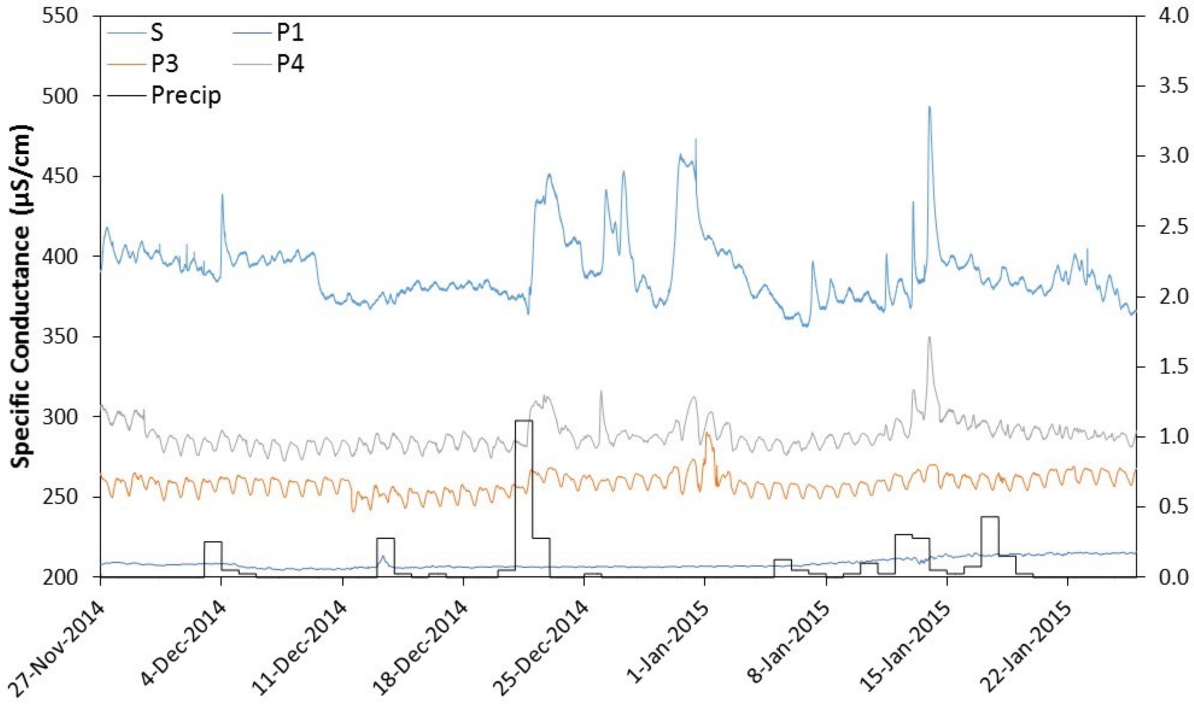

Figure 8. Fifteen minute specific conductance data for Spring Creek (S) and three Provo River sites (P1, P3, and P4). Spring Creek enters Provo River between sites P3 and P4. Note the increases in specific conductance at Provo River site P4 correspond with increases in Spring Creek.

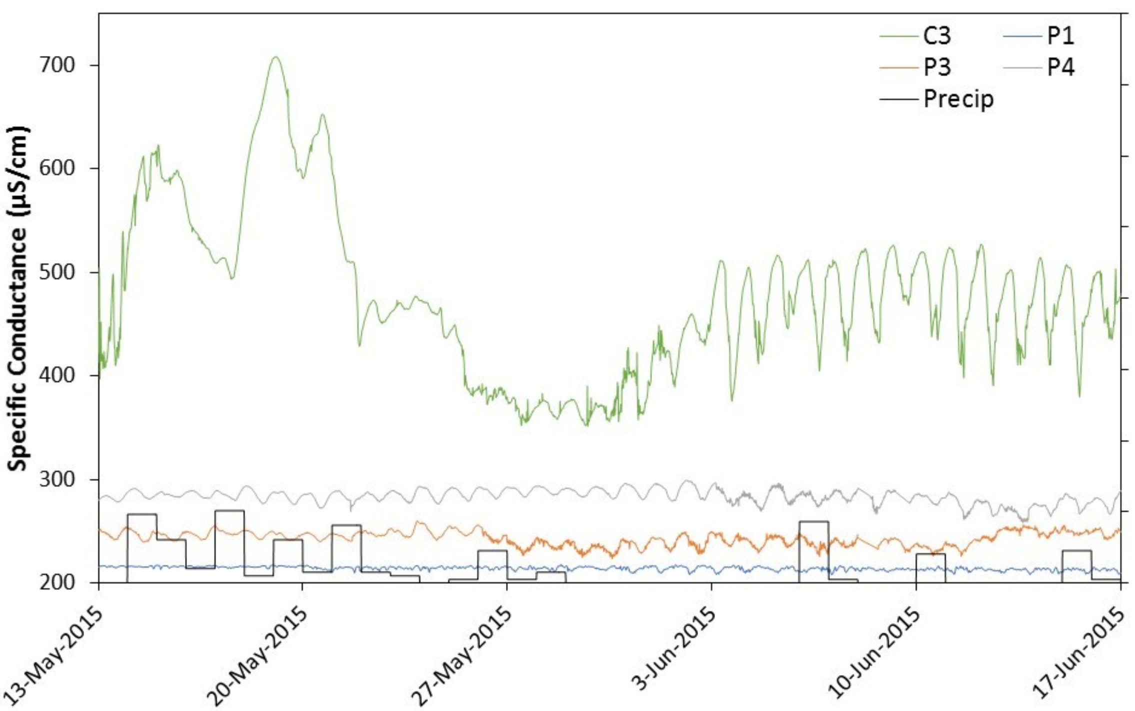

Figure 9. Fifteen minute specific conductance data for Center Creek site C3 and three Provo River sites (P1, P3, and P4). Center Creek enters Provo River between sites P3 and P4. Note the increases in specific conductance in Center Creek do not seem to have a significant impact on Provo River site P4 because of relatively small discharge rates compared to the Provo River.

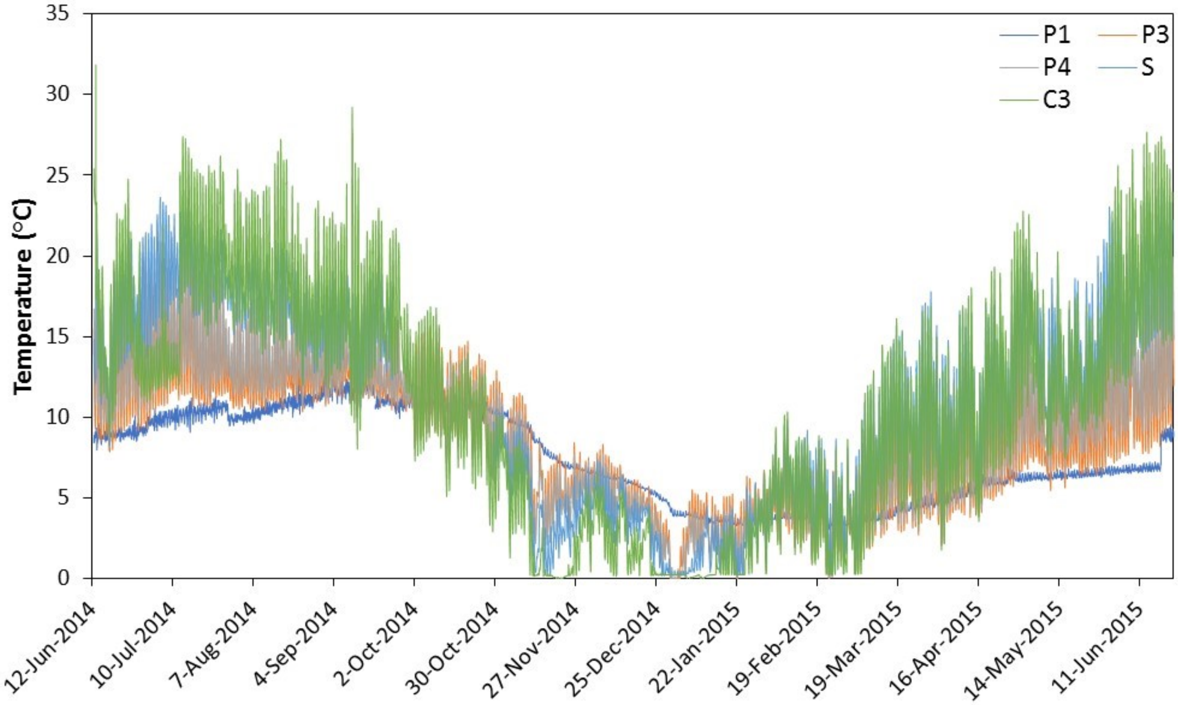

Figure 10. Fifteen minute water temperature data for Spring Creek (S), Center Creek site C3 and three sites on Provo River (P1, P3, and P4) from June 2014-2015. Note that during spring and summer the temperature in Provo River increases going down river, but during fall and winter temperature decreases going down river. There are no surface tributaries to the river between sites P1 and P3. Spring Creek and Center Creek enter the river between sites P3 and P4.

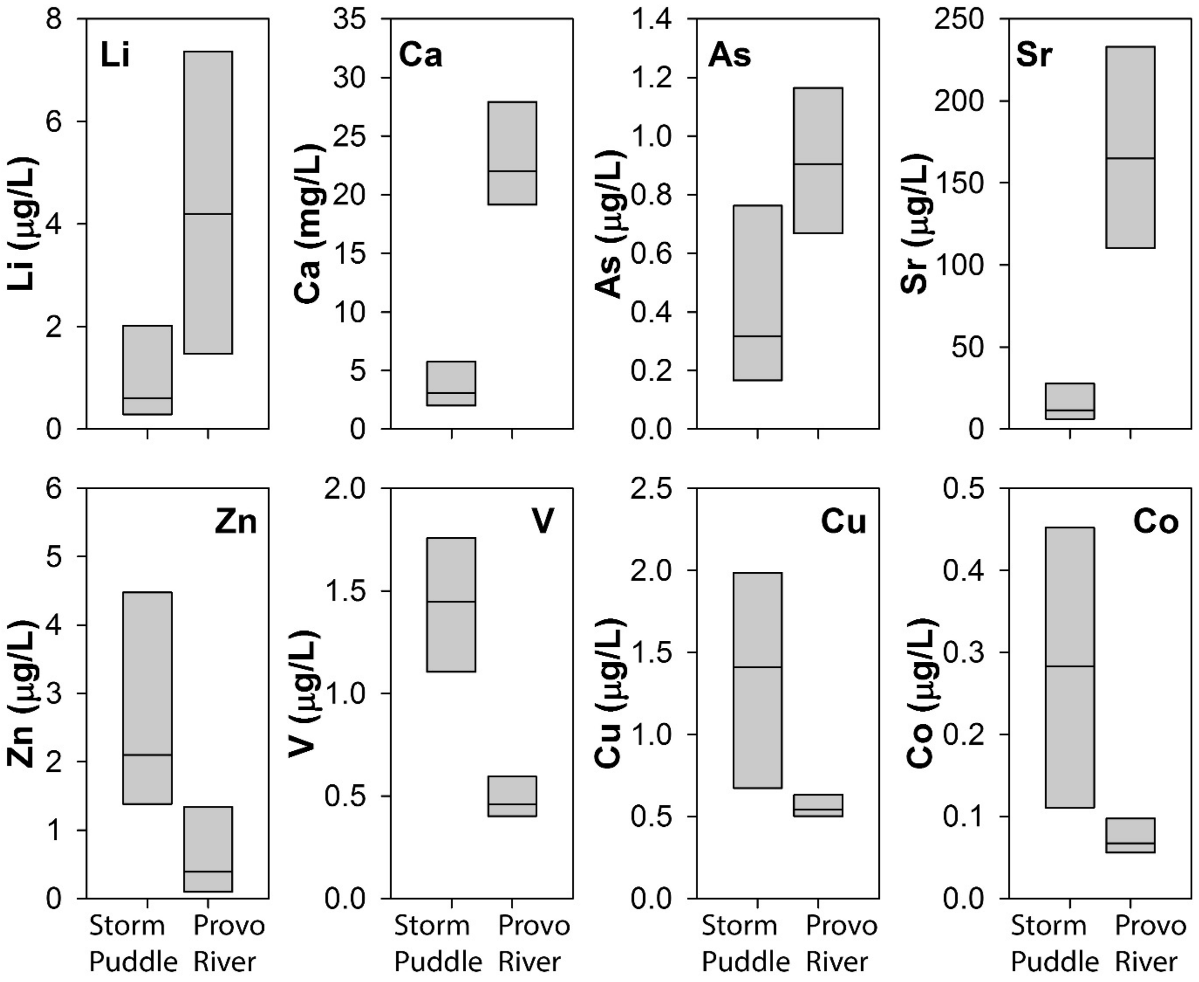

Figure 11. Concentrations of select trace elements in storm puddles sampled during a storm event September 27, 2014 in Heber Valley. Concentrations at Provo River sites P1-P4 from October 31, 2014 sampling are shown for comparison to potential storm water runoff from the urban environment. All concentrations were measured on filtered water samples. Note that Ca concentrations are in mg/L; all others are in µg/L.

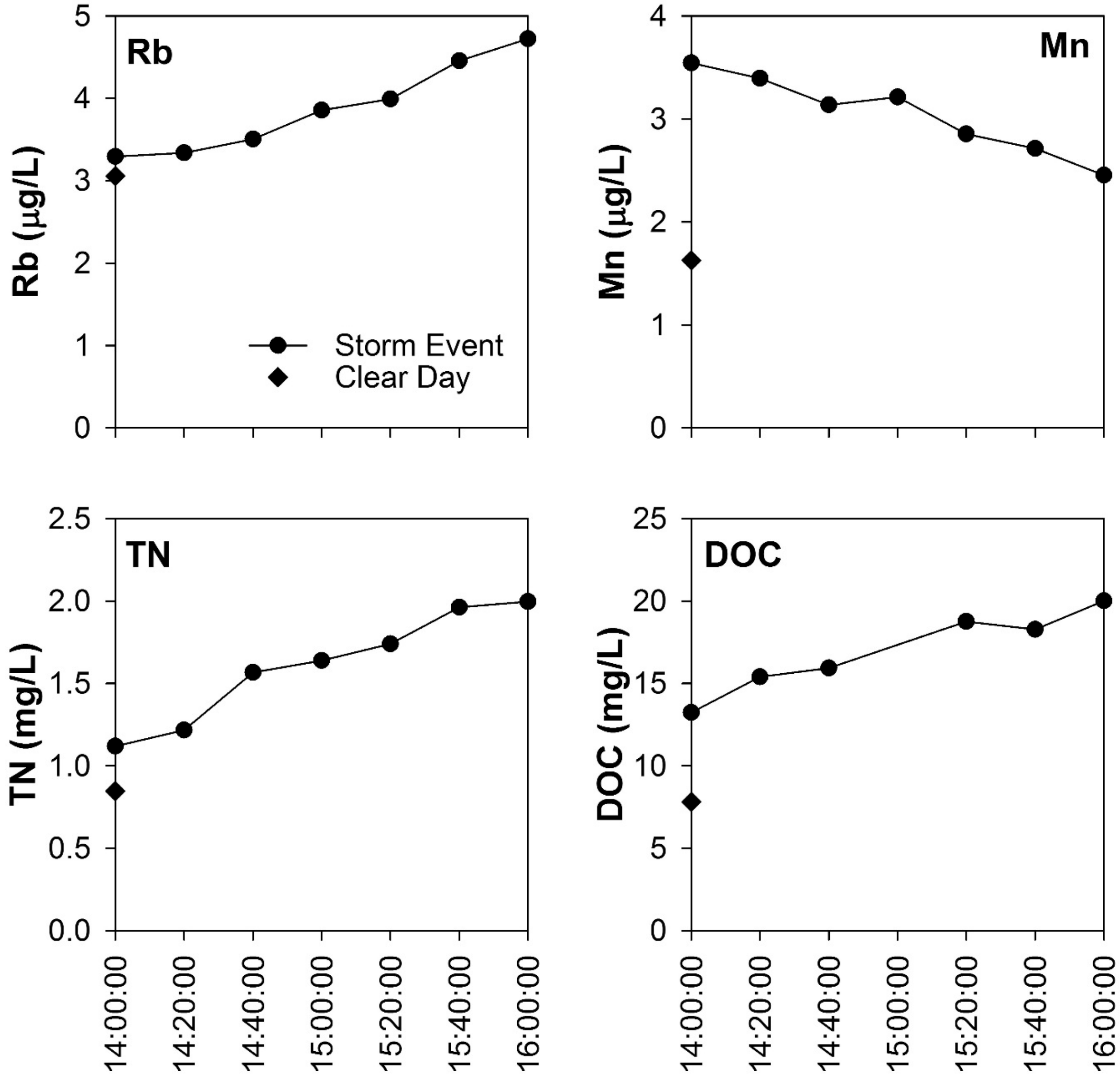

Figure 12. Concentrations of Rb, Mn, total nitrogen (TN), and dissolved organic carbon (DOC) on filtered water samples at site C3 in Center Creek during a storm event July 29, 2014. Concentration during a clear summer day on July 14, 2014 is shown for comparison to storm conditions. Note that DOC data for the 15:00 sample was an outlier and was omitted from the graph.

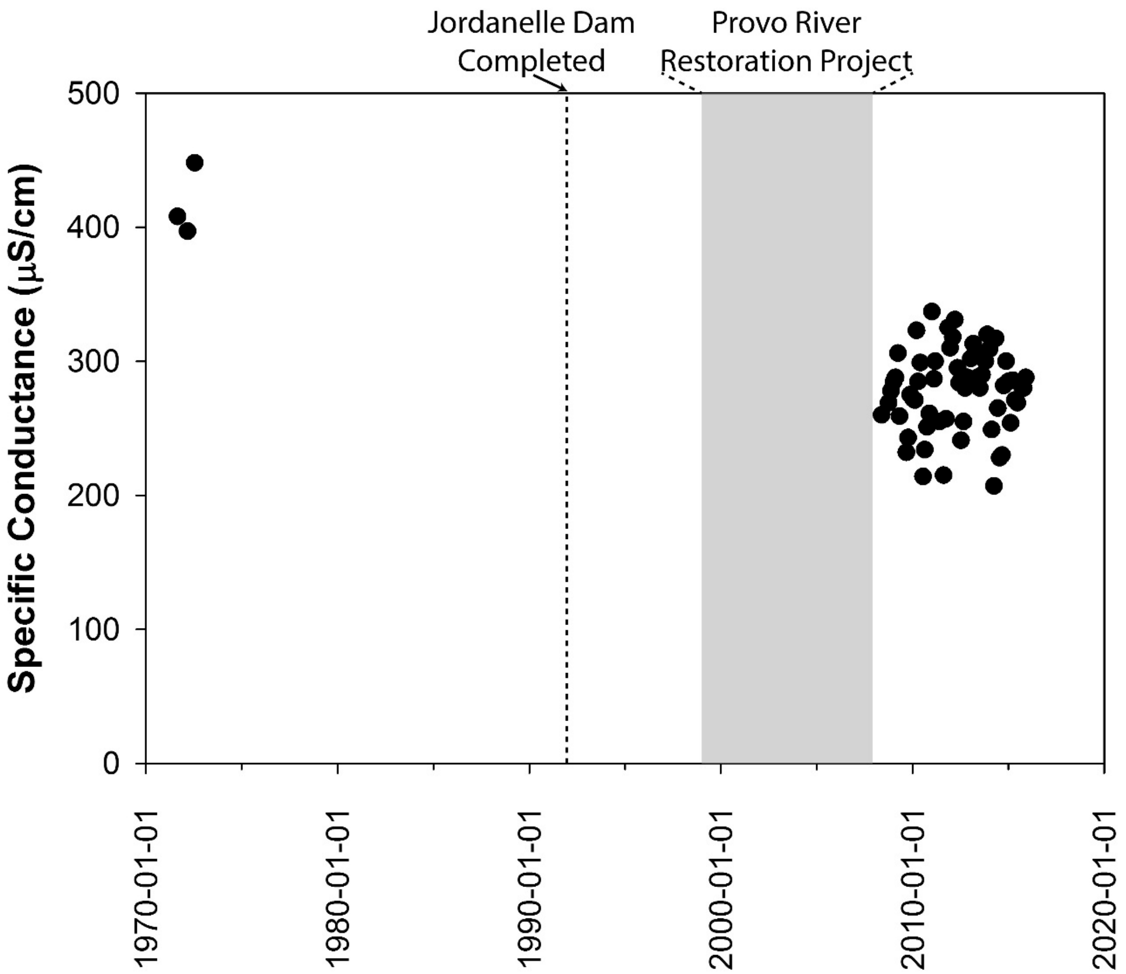

Figure 13. Historical specific conductance data for Provo River site P4. Shaded region represents a period of alteration to the Provo River during the Provo River Restoration Project. Dashed vertical line represents the completion of Jordanelle Dam. Data retrieved from the National Water Quality Monitoring Council (http://waterqualitydata.us/portal/, February 2016) and corresponds to USGS site number 10155500.

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APPENDIX

Groundwater Calculations

Increasing Cl concentrations between Provo River sites P1-P2 and P2-P3, yet lack of surface tributaries (Fig. 3), indicates that groundwater is the source of Cl. Because discharge decreases between these sites, thus not allowing for gain-loss measurements to calculate discharge, chloride mixing calculations were performed to estimate groundwater contributions along this reach.

Between sites P3 and P4, Spring Creek and Center Creek enter the middle Provo River allowing for more than two mixing members. Using only discharge data, we subtracted P3, S, and C3 discharge from P4 to get a value for groundwater discharge. This value was used in conjunction with Head Spring Cl concentration data as the groundwater component in the mixing equation: $\left[(Q_{P3} * C_{P3}) + (Q_{C3} * C_{C3}) + (Q_S * C_S) + (Q_g * C_g)\right]/Q_{P4} = C_{P4}$, where Q is discharge, C is concentration, subscript *P3, C3, S,* and *P4* are sample sites, and subscript g is groundwater, to validate the simple two end-member mixing model.

Due to the lack of surface inputs to the middle Provo River between sites P2 and P3, and the increase in trace element concentrations within this reach, we calculated potential ranges of groundwater inputs to the river based on Li and Sr concentrations using the following equation: $[(Q_d * C_d) - (Q_u * C_u)]/C_g = Q_g$, where Q is discharge, C is concentration of tracer, subscript d is downriver, subscript u is upriver, and subscript g is groundwater (Table 4). These calculated discharges were compared with discharges from previous Cl mixing calculations. Mixing calculations using the trace elements Sr and Li gave similar results as Cl (Table 4).