Evaluating natural and anthropogenic trace element inputs along an alpine to urban gradient in the Provo River, Utah, USA

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Keywords

trace elements, strontium isotopes, urban runoff, snowmelt, nonmetric multidimensional scaling

Abstract

Numerous natural and anthropogenic processes in a watershed produce the geochemical composition of a river, which can be altered over time by snowmelt and rainfall events and by built infrastructure (i.e., dams and diversions). Trace element concentrations coupled with isotopic ratios offer valuable insights to disentangle the effects of these processes on water quality. In this study, we measured a suite of 40+ trace and major elements (including As, Cd, Ce, Cr, Cs, Fe, La, Li, Mo, Pb, Rb, Sb, Se, Sr, Ti, Tl, U, and Zn), Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$), and stable isotopes of H and O (δD and $\delta^{18}\text{O}$) to investigate natural and anthropogenic processes impacting the Provo River in northern Utah, USA. The river starts as a pristine

mountain stream and passes through agricultural and urban areas, with two major reservoirs and several major diversions to and from the river. We sampled the entire 120 km length of the Provo River at 13 locations from the Uinta Mountains to Utah Valley, as well as two important tributaries, across the range of hydrologic conditions from low flow to snowmelt runoff during the 2013 water year. We also sampled the furthest downstream site in the Utah Valley urban area during a major flood event. Trace element concentrations indicate that a variety of factors potentially influence Provo River chemistry, including inputs from weathering of carbonate/siliciclastic rocks (Sr) and black shales (Se and U), geothermal groundwater (As, Cs, Li, and Rb), soil erosion during snowmelt runoff (Ce, Cr, Fe, La, Pb, and Ti), legacy mining operations (Mo, Sb, and Tl), and urban runoff (Cr, Pb, and Zn). Although specific elements overlap between different groups, the combination of different elements together with isotopic measurements and streamflow observations may act as diagnostic tools to identify sources. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicate a strong influence of siliciclastic bedrock in the headwaters with values exceeding 0.714 and carbonate bedrock in the lower reaches of the river with values approaching 0.709. δD and $\delta^{18}\text{O}$ changed little throughout the year in the Provo River, suggesting that the river is primarily fed by snowmelt during spring runoff and snowmelt-fed groundwater during baseflow. Based on nonmetric multidimensional scaling (NMS) water chemistry was unique across the upper, middle, and lower portions of the river, with high temporal variability above the first reservoir but minimal temporal variability below the reservoir. Thus, the results show that dams alter water chemistry by allowing for settling of particle-associated elements and also by homogenizing inflows throughout the year to minimize dilution during snowmelt runoff. Taken together, trace element concentrations and isotopic measurements can be used to evaluate the complex geochemical patterns of rivers and their variability in space and time. These measurements are critical for identifying natural and anthropogenic impacts on river systems.

1. Introduction

The geochemical composition of a river is a complex function of natural and anthropogenic processes acting in the watershed. Degraded water quality in rivers is often assumed to be the result of human impacts associated with urban and agricultural land use, mining, and built infrastructure (i.e., dams and diversions), but natural processes such as weathering, soil erosion, and groundwater inputs also have the potential to impact water quality (Fortner et al., 2011; Huang et al., 2009; Mora et al., 2010). Flood events from snowmelt or rainfall often mask the typical geochemical composition of a river (Campbell et al., 1995; Mouri et al., 2014; Simpson et al., 2013). Therefore, to disentangle the origin and contribution of solutes influencing water chemistry it is essential to understand the relative contributions of various processes occurring in the natural and built environment. Trace element concentrations coupled with isotopic ratios offer the unique opportunity to “fingerprint” water, but these tools are rarely used to capture variability in water chemistry along a river reach through space and time.

Trace element concentrations (e.g., As, Cr, Mo, Pb, Sb, Se, Sr, Tl, and U) combined with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios provide powerful discriminatory leverage for distinguishing among the variety of natural and anthropogenic solute sources to a river, including inputs from weathering, soil erosion, groundwater, mining, agriculture, and urban runoff (Barats et al., 2014; Christofaro and Leao, 2009; Fitzpatrick et al., 2007; Le Pape et al., 2012, 2013; Luo et al., 2014; Ollivier et al., 2011; Potot et al., 2012; Xu and Han, 2009). For example, Sr is an important trace element for evaluating natural weathering processes in a watershed, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be used to distinguish between silicate and carbonate weathering (Bickle et al., 2005; Brennan et al., 2014; Chetelat et al., 2008; Jacobson et al., 2002; Voss et al., 2014; Wei et al., 2013). Furthermore, weathering of specific types of bedrock such as black shales may contribute other elements, including Se and U (Bates, 1957; Galindo et al., 2007; Lavergren et al., 2009a; Rawat et al., 2010; Stillings and Amacher, 2010; Tuttle et al., 2014a, 2014b; Wen and Carignan, 2011). Trace elements can be grouped based on similar behaviors to determine specific inputs to a river system (Ollivier et al., 2006, 2011). Toxic metals such as Cd, Cr, Pb, and Zn are particularly useful for identifying

anthropogenic impacts to a river including urban runoff and mining inputs (Elbaz-Poulichet et al., 2006; Fitzpatrick et al., 2007; Le Pape et al., 2012). Mo, Sb, and Tl also may reflect mining inputs to a stream (Carling et al., 2013a; Drahota et al., 2012; Druzbecka and Craw, 2013; Filella et al., 2009; Fu et al., 2010; Ollivier et al., 2006; Ritchie et al., 2013; Tatsi and Turner, 2014). Other elements, including As, may indicate either anthropogenic (Barringer et al., 2008) or natural (Barats et al., 2014; Grassi et al., 2014) inputs to river systems. Whereas individual elements are not always indicative of a specific source, element groupings combined with other observations may improve diagnostics associated with source determination.

Trace element concentrations coupled with isotopic composition of H and O (δD and $\delta^{18}O$) can provide insights into the hydrology of a river system, including temporal variability due to snowmelt, rain events, and other processes. δD and $\delta^{18}O$ are frequently used to identify water sources and inputs during snowmelt and rainfall events (Jin et al., 2012; Klaus and McDonnell, 2013; Liu et al., 2004; Mast et al., 1995). Similarly, specific trace elements may show unique systematic processes during flood events and across seasons (Elbaz-Poulichet et al., 2006; Ollivier et al., 2006; Roussiez et al., 2013; Wen et al., 2013). For example, dissolved Fe, Mn, Pb, and Zn concentrations were significantly higher in the Lena River (Russia) during the spring freshet relative to the rest of the year (Holemann et al., 2005). Furthermore, trace element concentrations coupled with δD and $\delta^{18}O$ reflect impacts from the built environment, including water sources and chemistry influenced by dams and diversions (Wen et al., 2013).

In this study, we use trace element concentrations (including As, Cd, Ce, Cr, Cs, Fe, La, Li, Mo, Pb, Rb, Sb, Se, Sr, Ti, Tl, U, and Zn), Sr isotopes ($^{87}Sr/^{86}Sr$), and H and O isotopes (δD and $\delta^{18}O$) to evaluate the relative contributions of solutes from natural and anthropogenic sources in the Provo River watershed in northern Utah, USA, which is an important water source for over two million people who live along the Wasatch Front (Fig. 1). The river provides an important context to study multiple impacts on water

chemistry because it begins as a pristine mountain stream and passes through areas affected by mining,
agriculture, and urban development. The watershed is seasonally snow covered and snowmelt runoff is
heavily controlled with built infrastructure, including dams and complex water delivery systems. Specific
objectives of this study are to: 1) quantify concentrations and loads of trace elements and major solutes;
2) evaluate seasonal variability in water chemistry; and 3) relate isotopic ratios to trace element sources,
including natural and anthropogenic phenomena. Our findings offer important transferrable information
to watersheds across the western U.S. that are experiencing urbanization and provide baseline
information for an expansive water quality effort in Utah. The Provo River is one of three watersheds
that are undergoing enhanced water quality monitoring as part of the iUTAH project (innovative Urban
Transitions and Arid region Hydro-sustainability; <http://iutahepscor.org/>) sponsored by the U.S. National
Science Foundation.

2. Materials and methods

2.1 Hydrologic setting of Provo River system

With abrupt gradients in land use from relatively undeveloped headwaters to heavily developed
urban/agricultural areas, the Provo River watershed is ideal for studying impacts from natural and
anthropogenic sources. In just over 100 km, the Provo River flows from the Uinta Mountains to Utah
Lake, which is the third largest freshwater lake by area in the western U.S., and passes through urban
and agricultural areas in Heber Valley and Utah Valley (Fig. 1). Specifically, the Provo River is divided into
three sections: the upper section is an undeveloped mountain catchment above Jordanelle Reservoir;
the middle section flows through Heber Valley, which is undergoing a rapid transition from agricultural
to urban land use, to Deer Creek Reservoir; and the lower section flows through Provo Canyon in the
Wasatch Mountains and the Utah Valley urban area to Utah Lake (Fig. 1). The middle and lower Provo
River and Jordanelle Reservoir are designated Blue Ribbon fisheries, underscoring the importance of the
river system for recreation and for the local economy

(<http://wildlife.utah.gov/hotspots/blueribbon.php>).Furthermore, the Provo River supplies over half of

120 Utah's population with drinking water as it is used by four different conservancy districts along the
Wasatch Front metropolitan area (R. Oberndorfer, CUWCD, personal communication).

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126 Flow in the Provo River is heavily controlled with dams and diversions as part of the Provo River Project
(http://www.usbr.gov/projects/Project.jsp?proj_Name=Provo%20River%20Project) and Central Utah
128 Project (<http://www.cupcao.gov/TheCUP/units.html#bonneville>). The Provo River starts at Trial Lake, a
small reservoir in the Uinta Mountains, and receives water diverted from the Duchesne and Weber River
130 watersheds before draining into Jordanelle Reservoir and then Deer Creek Reservoir (Fig. 1). The primary
purpose of the reservoirs, which together have the capacity to store over two years of Provo River flow,
132 is to store snowmelt runoff and distribute it throughout the year. Small diversions below Jordanelle
Reservoir distribute water to the Heber Valley urban/agricultural area. Below Deer Creek Reservoir, a
134 substantial fraction of the lower Provo River is diverted for municipal and other uses. Such diversions
and reservoirs have greatly altered natural flow patterns in the Provo River. Figure S1 (Supplementary
136 Material) shows stream gauge data from the 2013 water year taken at five sites along the Provo River
that are monitored by the U.S. Geological Survey and one site that is monitored by the Central Utah
138 Watershed Conservancy District (CUWCD). The upper Provo River showed the most natural flow regime,
with peak runoff in May because of snowmelt (hydrographs for sites 2 and 3). In contrast, the middle
140 Provo River showed relatively little variability throughout the year, with no pulse during the snowmelt
season (hydrographs for sites 5 and 7). The lower Provo River showed a small snowmelt peak discharge
142 of $\sim 15 \text{ m}^3/\text{sec}$ (hydrograph for site 11), which was less than half of peak discharge from snowmelt on the
upper Provo River.

144 Water quality is an important issue for the Provo River as the watershed transitions from agricultural to
urban land use. For example, recently a fish consumption advisory was issued for Jordanelle Reservoir to
146 limit consumption of brown trout and smallmouth bass due to elevated Hg concentrations
(<http://fishadvisories.utah.gov/index.htm>). A number of non-point sources potentially contribute trace
148 elements and nutrients to the river, including legacy mining zones in the Wasatch Mountains,
agricultural return flow in Heber Valley, and urban runoff in Utah Valley (population >500,000). In terms

of water quality, Snake Creek (Fig. 1) is one of the most important tributaries to the Provo River because it contributes water impacted by legacy mining, geothermal springs (Carreón-Díazconti et al., 2003), and agriculture. Main Creek (Fig. 1) is another important tributary that contributes water impacted by agricultural uses with the highest historical inputs of P and N to Deer Creek Reservoir (http://www.waterquality.utah.gov/TMDL/Deer_Creek_Reservoir_TMDL.pdf).

2.2 Sample collection

To investigate solute chemistry along the Provo River, we collected water samples at 13 sites (labeled 1–11, with additional samples collected at sites 1A and 1B on some of the sampling dates) and at two tributaries (Snake Creek and Main Creek) throughout the 2013 water year (Fig. 1). The sampling dates covered a wide range of hydrologic conditions, including low flow during fall and winter (sampled November 21, 2012 and February 18, 2013, respectively), early spring pre-runoff (sampled April 13, 2013), late spring peak runoff (sampled May 15, 2013), early summer post-runoff (sampled June 18, 2013), and low flow during late summer (sampled September 7, 2013) (Supplementary Material Fig. S1). At each site, we sampled the thalweg with an acid-leached 125 mL LDPE bottle (for trace elements, cations, and $^{87}\text{Sr}/^{86}\text{Sr}$) and a pre-rinsed 1 L LDPE bottle (for major anions, bicarbonate, δD , and $\delta^{18}\text{O}$). Field parameters (pH, temperature, dissolved oxygen, and conductivity) were measured in situ using a YSI Quatro multiparameter probe.

To address potential contamination during sample collection and transport, field blanks were collected each sampling day ($n=6$) by pouring 100 mL of Milli-Q water into an acid-leached 125 mL LDPE bottle. Trace element samples and field blanks were collected using “clean hands, dirty hands” protocols (USEPA, 1996). On each sampling day, sites were visited in random order to avoid potential temporal bias in sampling. In addition, on two different occasions, Provo River site 10 was sampled in the morning and afternoon to test for potential diel variability or differences due to holding time.

The majority of samples were collected on days with no significant precipitation. However, we

opportunistically sampled site 11 during an extreme storm event on September 7, 2013 that impacted the lower Provo River when nearly 2 cm of rain fell on Utah Valley in a 15-min period. The rain event caused major flooding in the urban area and in the Provo River, where streamflow at site 11 increased from ~0.5 m³/s to over 18 m³/s in 30 min. On this date, we collected samples in the morning before the storm (at 9:00), at peak runoff during the flood (at 17:15), and about 1 hr after peak runoff (at 18:20). Further, we measured field parameters during sample collection at 9:00, 17:15, and 18:20, and then left the probe in the stream to record field parameters at 5-min intervals until the following day.

2.3 Sample treatment and analysis

To measure trace element concentrations, cations, and ⁸⁷Sr/⁸⁶Sr, we filtered aliquots of the 125 mL LDPE samples in a Class 100 laminar flow hood immediately after returning from the field (maximum 8 hr holding time between sample collection and filtration). Approximately 15 – 50 mL of each sample was filtered into LDPE containers using a polypropylene syringe and 0.45 µm PES syringe filter. All materials that came in contact with the sample were acid-washed with 10% HCl and triple rinsed with Milli-Q water. The filtered and unfiltered fractions were amended to 2.4% v/v trace metal grade HNO₃.

Samples were analyzed for trace element and major cation concentrations using an Agilent 7500ce quadrupole inductively coupled plasma mass spectrometer (ICP-MS) with a collision cell, a double-pass spray chamber with perfluoroalkoxy (PFA) nebulizer (0.1 mL/min), a quartz torch, and platinum cones. Concentrations were measured for the following 40 elements: Ag, Al, As, 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, Sc, Se, Sm, Sr, Tb, Ti, Tl, U, V, Y, and Zn. A calibration solution containing all the reported elements was prepared gravimetrically using 1000 mg/L single-element standards (Inorganic Ventures, Inc.). This solution was used to prepare a calibration curve with 6 points plus a blank for each sample run. Al, Ca, Cr, Fe, K, Mn, Na, Sc, and V were

determined using 4 mL He/min in the collision cell, As and Se were determined using 4 mL He/min plus 2.5 mL H₂/min, and the other 29 elements were determined using Ar as the carrier gas. The detection limit (DL) was determined as three times the standard deviation of all blanks analyzed throughout each run. A USGS standard reference sample (T-205) and NIST standard reference material (SRM 1643e) were analyzed multiple times in each run together with the samples as a continuing calibration verification. The long-term reproducibility for T-205 and SRM 1643e show that our results are accurate within 10% for most elements.

A subset of filtered samples (n=27) were analyzed for ⁸⁷Sr/⁸⁶Sr ratios using a Thermo Scientific Neptunemulticollector ICP-MS. The samples were purified inline using a Sr-FAST ion chromatographic column packed with a crown ether resin (Mackey and Fernandez, 2011). During the analyses reported herein, we determined the ⁸⁷Sr/⁸⁶Sr ratio of the standard reference material SRM987 (n= 16) to be 0.71030±00001 (2σ standard error (SE)). Analytical precision (2σSE) of all samples ranged from ±00001 – 00003. The ⁸⁷Sr/⁸⁶Sr ratios were corrected for mass bias using an exponential law, normalizing to ⁸⁶Sr/⁸⁸Sr=0.1194 (Steiger and Jäger, 1977). Isobaric interferences on the ⁸⁷Sr/⁸⁶Sr ratios, such as from ⁸⁷Rb and ⁸⁶Kr, were corrected by simultaneous monitoring of ⁸⁵Rb and ⁸³Kr using the corresponding invariant ratios of ⁸⁷Rb/⁸⁵Rb=0.385706 and ⁸⁶Kr/⁸³Kr=1.502522 (Steiger and Jäger, 1977).

The 1 L LDPE samples for δD, δ¹⁸O, and major anion measurements were stored in the dark in a refrigerator at 4°C until further processing. δD and δ¹⁸O were measured on unfiltered aliquots using a Los Gatos Research Liquid Water Isotope Analyzer (LWIA-24d), with a precision of 1.0‰ and 0.4‰, respectively. A 50-mL aliquot was filtered for anion analyses (Cl⁻, F⁻, HPO₄⁻, NO₃⁻, and SO₄²⁻) using a serially rinsed plastic vacuum filter and a 0.45 μm acetate filter and analyzed using a Dionex ICS-90 ion chromatograph. Bicarbonate was measured on unfiltered aliquots using a Mettler Toledo DL50 titrator.

2.4 Data quality control

Field blanks showed low levels of contamination for all measured elements, with concentrations <DL in nearly all cases. Some elements had measureable values in the field blanks, including Al, Ce, Ni, Pb, and Zn, but the concentrations measured in the field blanks were negligible relative to concentrations measured in the river samples (Supplementary Material Table S1). Another set of 12 elements had concentrations <DL in the field blanks and in a majority of river samples, including Ag, Be, Cd, and Cu, and thus were removed from the dataset for statistical analyses. For other elements, values <DL were set as 1/2 DL.

Charge balances, calculated using cation (Ca^{2+} , K^+ , Mg^{2+} , Na^+) concentrations from the ICP-MS, anion (Cl^- , F^- , HPO_4^- , NO_3^- , SO_4^{2-}) concentrations from the IC, and bicarbonate (HCO_3^-) concentrations from titration, were within an acceptable range of $\pm 5\%$ for 44 out of 86 samples (Supplementary Material Table S2). The remaining 42 samples were just outside the acceptable range with charge balances falling between ± 5 and $\pm 10\%$. To improve the charge balance on these 42 samples, the major cations were reanalyzed by atomic adsorption spectroscopy (AAS), resulting in acceptable charge balances for all samples (Supplementary Material Table S2). Data from the cation analysis (ICP-MS or AAS) that provided the better charge balance were used in all further analysis and interpretation.

2.5 Data ordination (NMS)

We used nonmetric multidimensional scaling (NMS) to explore water chemistry relationships among montane, agricultural, and urban sites on Provo River, Snake Creek, and Main Creek over time. NMS is an ordination technique that generates visual analyses to explain relationships of assemblages and communities (McCune and Grace, 2002). It is particularly appropriate for our analyses because it avoids the assumption of normal distributions and linear relationships among variables (Peck, 2010). Data included in the ordination were conductivity, pH, and elemental concentrations (33 elements). We used PC-ORD (McCune and Mefford, 1999) for NMS ordination following methods described in Carling et al.

(2013b). Briefly, data were log generalized prior to conducting NMS using the equation $b = \log(x + x_{\min}) - \log(x_{\min})$, where $x_{\min}$ is the minimum value for each element. Euclidean distance measures were used to assign the samples in ordination space. The analyses were run 250 times with real data, and the results were compared with 250 randomized data in Monte Carlo simulations. The final model had a stable solution and provided the greatest reduction in the amount of stress, which is a goodness of fit measure for the model. We performed a post hoc analysis of the coefficient of determination between ordination distances and distances in the original n-dimensional space to estimate the amount of variability in the data described by each axis. The model results are provided as a 2-D graph with data from each site contained by convex hulls (i.e., the outer points for each sample site are connected by a closed polygon). Details defining labels and raw data associated with each sample shown in NMS plots are provided in the Supplementary Material (Table S3).

2.6 Loads

Annual trace and major element loads were calculated for sites with available streamflow data—Snake Creek and Provo River sites 2, 3, 4, 5, 6, 7, 8, and 11—using LOADEST software (Runkel, 2004). Streamflow data were obtained for Snake Creek and Provo River sites 2, 3, 5, 7, and 11 from the U.S. Geological Survey (<http://waterdata.usgs.gov/nwis>) (shown in Supplementary Material Figure S1), and streamflow data for Provo River sites 4, 6, and 8 were obtained from CUWCD (<http://www.cuwcd.com/>). Concentrations of a subset of representative trace elements (As, Cs, Li, Mo, Rb, Sb, Sr, and Tl) and major ions (Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} and HCO_3^-) were input to LOADEST along with average daily streamflow data for the 2013 water year, and loads were calculated using the adjusted maximum likelihood estimation regression model. Because we sampled only six times throughout the year and LOADEST requires a minimum of twelve data points, our calculated loads are considered first-order approximations. However, given the limited temporal variability in streamflow at most sites in the

middle and lower Provo River due to dam controls (Supplementary Material Fig. S1) additional samples

266 most likely would not have substantially improved the LOADEST models.

3. Results

268 3.1 Major ion and trace element chemistry of the Provo River

Trace elements in the Provo River were divided into four separate categories based on their association
270 with changing lithology in the watershed, seasonality, and inputs: 1) Sr behaved similarly to the major
solutes (Fig. 2); 2) Li, Cs, As, Rb, U, and Se showed distinct patterns based on specific inputs in the
272 middle and lower sections of the river (Fig. 3); 3) Mo, Sb, and Tl showed very large increases due to
inputs in Jordanelle Reservoir (Fig. 4); and 4) Ti, Fe, Pb, Cr, La, Ce, and other rare earth elements (REEs)
274 showed decreasing concentrations from upstream to downstream, with highest the
concentrations during snowmelt runoff (Fig. 5). These groupings are described in more detail below.

—◆— Nov 21, 2012 —□— Feb 18, 2013 —△— April 13, 2013 —×— May 15, 2013 —+— June 18, 2013 —○— Sep 7, 2013

Figure 2. Concentrations of selected major ions (Na^+ , SO_4^{2-} , Ca^{2+} , HCO_3^-) and strontium (Sr) measured on filtered water samples and conductivity (cond) measured in situ at the Provo River during the 2013 water year. Sample locations on the horizontal axis are scaled according to river distance from Provo River site 1 through 11. Units are mg/L for the major ions, $\mu\text{g/L}$ for Sr, and $\mu\text{S/cm}$ for conductivity. Dashed vertical lines show the location of Jordanelle and Deer Creek Reservoirs. Each of these parameters showed increasing concentrations from site 1 through 11, with the largest increase occurring between sites 7 and 8 due to mixing of Snake Creek with the Provo River in Deer Creek Reservoir.

—◇— Nov 21, 2012 —□— Feb 18, 2013 —△— April 13, 2013 —×— May 15, 2013 —+— June 18, 2013 —○— Sep 7, 2013

Figure 3. Lithium (Li), cesium (Cs), arsenic (As), rubidium (Rb), uranium (U), and selenium (Se) concentrations measured on filtered water samples collected from the Provo River during the 2013 water year. Sample locations on the horizontal axis are scaled according to river distance from Provo River site 1 through 11. Dashed vertical lines show the location of Jordanelle and Deer Creek Reservoirs. Li, Cs, As, and Rb showed very large increases between sites 7 and 8 because of mixing of Snake Creek with the Provo River in Deer Creek Reservoir, whereas U and Se showed the largest increases between sites 8 and 9, where the river passes through Provo Canyon (and the Wasatch Mountains).

Figure 4. Molybdenum (Mo), antimony (Sb), and thallium (Tl) concentrations measured on filtered water samples collected from the Provo River during the 2013 water year. Sample locations on the horizontal axis are scaled according to river distance from Provo River site 1 through 11. Dashed vertical lines show the location of Jordanelle and Deer Creek Reservoirs. This subset of elements showed very large increases between sites 3 and 4 due to inputs in Jordanelle Reservoir.

—◆— Nov 21, 2012 —□— Feb 18, 2013 —△— April 13, 2013 —×— May 15, 2013 —+— June 18, 2013 —○— Sep 7, 2013

Figure 5. Titanium (Ti), iron (Fe), lead (Pb), chromium (Cr), lanthanum (La), and cerium (Ce) concentrations measured on filtered water samples collected from the Provo River during the 2013 water year. Sample locations on the horizontal axis are scaled according to river distance from Provo River site 1 through 11. Dashed vertical lines show the location of Jordanelle and Deer Creek Reservoirs. This subset of trace elements showed relatively high concentrations above Jordanelle Reservoir and low concentrations downstream due to particle settling in the reservoir.

Major ion concentrations increased steadily from upstream to downstream along the Provo River, as demonstrated with representative elements Na^+ , SO_4^{2-} , Ca^{2+} , and HCO_3^- in Figure 2. As expected, field-measured conductivity was a reasonable proxy for the major ions (Fig. 2). Notably, Sr was the only trace element that tracked closely with the major ions and conductivity (Fig. 2). Major ion and Sr concentrations increased substantially between site 1 in the Uinta Mountains and sites 2 and 3 above Jordanelle Reservoir. Concentrations increased slightly in the middle Provo River below Jordanelle Reservoir between sites 4 through 7. The largest increase in major ion concentrations (50–100%) occurred between sites 7 and 8 due to mixing with Snake Creek in Deer Creek Reservoir. In the lower Provo River, Na^+ and SO_4^{2-} were diluted between sites 8 and 9 before increasing slightly at sites 10 and 11, whereas Ca^{2+} and HCO_3^- increased steadily from site 8 through 11.

Major ion concentrations were diluted during snowmelt runoff above Jordanelle Reservoir but showed little variability below (Fig. 2). Above Jordanelle Reservoir, Ca^{2+} , HCO_3^- , and SO_4^{2-} concentrations were ~75% lower during snowmelt runoff on May 15, 2013 relative to low flow conditions on September 7, 2013. At Provo River site 2, flow increased by a factor of 20 from the baseflow value of $\sim 1.5 \text{ m}^3/\text{sec}$ to a maximum of $32.5 \text{ m}^3/\text{sec}$ during snowmelt runoff, whereas conductivity values only decreased by a factor of ~ 4 from $250 \text{ }\mu\text{S}/\text{cm}$ to $60 \text{ }\mu\text{S}/\text{cm}$. Hydrograph separation indicated that snowmelt contributed nearly 80% of observed increase in streamflow at peak runoff assuming a simple two-component system of snowmelt (estimated conductivity of $10 \text{ }\mu\text{S}/\text{cm}$) and groundwater (estimated conductivity of $250 \text{ }\mu\text{S}/\text{cm}$ based on river measurements during groundwater-dominated pre-runoff conditions). In contrast, conductivity values stayed relatively constant year-round below Jordanelle Reservoir.

A subset of trace elements generally showed similar trends as the major ions but had notable differences reflecting additional sources of these elements. For example, the trace elements Li, Cs, As, and Rb showed two- to three-fold increases below the confluence of Snake Creek (between sites 7 and 8) (Fig.

306 3). Li, Cs, and Rb concentrations also increased substantially between sites 5 and 6 in the middle Provo River, whereas As concentrations showed no significant increase. U and Se showed the largest increase
308 between sites 8 and 9 in Provo Canyon where the river passes through the Wasatch Mountains (Fig. 3).

Mo, Sb, and Tl showed unique trends relative to all other measured parameters, with four- to ten-fold
310 increases in Jordanelle Reservoir (between sites 3 and 4) (Fig. 4). Whereas Mo concentrations continued to increase through the middle and lower Provo River similar to the major ions, Sb and Tl concentrations
312 actually decreased steadily downstream.

Another group of trace elements, including Ti, Fe, Pb, Cr, La, and Ce showed decreasing concentrations
314 from upstream to downstream on the upper Provo River, particularly during snowmelt runoff (i.e., samples collected on May 15, 2013) (Fig. 5). Al and Y, and the rare earth elements Sm, Gd, Dy, and Ho
316 also showed similar decreasing trends (Supplementary Material Fig. S2). These elements are distinguished by their affinity for suspended solids—with 40 – 80% of the total concentration in the
318 particulate fraction (calculated as the difference between unfiltered and filtered concentrations)—suggesting that the filtered fraction of these elements was likely associated with colloids <0.45 µm in
320 size (i.e., not truly dissolved) (Supplementary Material Table S1). Other studies have shown that REEs are mobilized with snowmelt-derived dissolved organic carbon in association with Fe and Al
322 (oxy)hydroxide particles (Vázquez-Ortega et al., 2015). In contrast, elements that were diluted during snowmelt, including those shown in Fig. 2, had only 5 – 30% of the total concentration in the particulate
324 fraction. Fe was unique among the particle-associated group of elements because it showed relatively high concentrations in the upper Provo River even during low flow conditions (Fig. 5). Further
326 downstream, Fe concentrations were low immediately below Jordanelle Reservoir (similar to other particle-associated elements) but increased in the middle Provo River (between sites 4 and 7) during
328 most sampling events.

3.2 NMS results for Provo River, Main Creek, and Snake Creek water samples

330 The NMS model that best described the dataset, influenced primarily by differences in La, Ce, Pb, Fe, Y,
Al, Cr, Tl and Cs concentrations, was a 2-D solution with a final stress of 9.964, where axis 1 described
332 86.9% of the variability in the dataset and axis 2 described an additional 9.1% (Fig. 6). In almost all
instances, site differences, not temporal differences, structured differences among samples. This is
334 highlighted by the unique, closely-clustered groupings of samples in polygons referred to as “convex
hulls,” which distinguish samples from individual sites regardless of time of sample collection. The
336 exception to this trend was site 11 on the lower Provo River during the September 7, 2013 flood event,
when the chemistry was unique relative to all other samples (Fig. 6). The raw data for all samples are
338 provided in the Supplementary Material (Table S3).

Figure 6. NMS results for Provo River sites 1 through 11, Snake Creek, and Main Creek. Axis 1 explains 86.9% of the variability in the dataset, and axis 2 explains an additional 9.1%. Final stress for the two axis model = 9.964.

Sites plotted in NMS space based on concentrations of specific elements, with Provo River sites 1–1A and Snake Creek defining end-of-spectrum chemistries (Fig. 6). Provo River sites 1 and 1A at the headwaters are defined by higher concentrations of rare earth and particle-associated elements (La, Ce, Pb, Fe, Y, Al, and Cr), whereas Snake Creek is defined by higher concentrations of Cs, Tl, Li, U, Mo, As, Rb, and Se. In between the end members of sites 1–1A and Snake Creek, the NMS plot shows the evolution of Provo River chemistry from the upper section (sites 2 and 3) to the middle (sites 4, 5, 6, and 7) and lower sections (sites 8, 9, 10, and 11), following a positive trajectory along axis 1. The NMS plot clearly shows the influence of the tributary Snake Creek on Provo River composition as samples from site 8 are pulled toward the Snake Creek samples in ordination space. Axis 2 describes a small amount of variability in the dataset due primarily to higher concentrations of Pb, Cs, La, Ce, and Cr toward the positive end of the axis. In particular, the Main Creek samples are differentiated along axis 2, with spring runoff samples from May 15, 2013 and June 18, 2013 plotting toward the positive end and the other samples plotting toward the negative end.

The NMS plot shows that some of the sites have overlapping convex hulls, including sites 1 and 1A, sites 2 and 3, sites 4 and 5, and sites 8 through 11 (Fig. 6). Therefore, to capture most of the variability in chemistry along the river, a simple monitoring scheme could be devised consisting of sites 1, 1B, 3, 5, 6, 7, and 11. This monitoring scheme would save money and sampling time while still providing a sufficient level of detail on the geochemical patterns of the river. The lack of major changes in water chemistry between sites 8 through 11 where the river traverses the urban area suggests that the river is merely a channelized canal without hydrologic connection with the surrounding watershed. However, water chemistry at site 11 (in the urban area) changed dramatically during the September 7, 2013 flood due to storm runoff (Fig. 6).

Seasonal variability was most important above Jordanelle Reservoir, as demonstrated by the larger convex hulls at the upstream sites (1 through 3) relative to the downstream sites (4 through 11) (Fig. 6). Sites 2 and 3 showed the most variability due to large fluctuations in streamflow throughout the year (Supplementary Material Figure S1), which led to higher concentrations of the particle-associated elements shown on the negative end of axis 1 (La, Ce, Pb, Fe, Y, Al, Cr). Because of this variability, sites 2 and 3 are more similar to 1B during snowmelt runoff, but more similar to sites 4 and 5 during the rest of the year. Notably, water chemistry of Main Creek is remarkably similar to Provo River site 7 (i.e., the sites have overlapping convex hulls) even though Main Creek watershed is much smaller and the water likely has less time to interact with the Paleozoic bedrock. Furthermore, the Main Creek watershed does not contain Tertiary volcanic rocks or Proterozoic metasedimentary rocks like are found in the upper Provo River watershed (Fig. 1). This suggests that weathering of Paleozoic carbonate rocks dominates water chemistry in both watersheds and that equilibration with the carbonate bedrock occurs rapidly. However, Main Creek did show greater temporal variability in water chemistry relative to Provo River site 7 (i.e., larger convex hull for the Main Creek samples) because it is an undammed stream.

3.3 Trace element loads

LOADEST-calculated annual loads of representative trace elements (Sr, As, Li, Rb, Cs, Mo, Sb, and Tl) for the 2013 water year are shown in Figure 7 and major ion loads are shown in Fig. S3 (Supplementary Material). Sr, As, Li, Rb, and major ion loads generally increased from upstream to downstream. The largest increase occurred between sites 7 and 8 due to loads from Snake Creek. Snake Creek is the most important single source of solutes in the Provo River system, contributing at least half of the element loading to the lower Provo River and a majority of the As, Li, Rb, and Cs. Of the elements shown in Figure 7, only Sb had negligible loads in Snake Creek relative to Provo River site 7. Loads decreased substantially between sites 8 and 11 primarily because streamflow is much lower at site 11 due to water

386 diversions (Supplementary Material Fig. S1). Thus, the water diversions result in less streamflow reaching
Utah Lake and correspondingly smaller loads of trace and major elements. Similarly, the decrease in
388 element loads between sites 4 and 5 is due to water diversions in Heber Valley.

Figure 7. Annual loads of selected trace elements (Sr, As, Li, Rb, Cs, Mo, Sb, and Tl) at Provo River sites 2, 3, 4, 5, 6, 7, 8, 11, and Snake Creek (SC). The tributary Snake Creek enters the Provo River below site 7. For conservative elements like Sr, the loads at site 8 are equal to the sum of the loads at site 7 and Snake Creek. For nonconservative elements like Cs and Tl the loads were much smaller at site 8.

The loading data indicate that not all elements behave conservatively in the Provo River system. For conservative elements, the sum of loads at Provo River site 7 and Snake Creek should equal the loads in site 8 below Deer Creek Reservoir. Loads at site 8 were within 80-120% of the combined loads at site 7 and Snake Creek for Mo (113%), Sb (98%), Sr (96%), Li (87%), Rb (82%), As (80%) and all of the major ions. Given uncertainties in sampling, laboratory analyses, and LOADEST calculations, these elements likely behaved conservatively in the reservoir. However, Tl and Cs loads at site 8 were only ~30% of the combined loads at site 7 and site 8, indicating substantial mass loss in the reservoir. The pathways of Tl and Cs loss in the reservoir were not considered in this study but may be caused by sorption, sedimentation, or biological processes. Notably, Cs concentrations increased between sites 7 and 8 (Fig. 3) even though such a large fraction was lost in the reservoir.

The loading data show that Sb, Tl, and Mo behaved conservatively in the middle Provo River with similar loads between sites 5 – 7 (Fig. 7) despite decreasing concentrations (Fig. 4). This suggests that the decrease in Sb, Tl, and Mo concentrations is simply a result of dilution rather than in-stream losses from biogeochemical or physical processes.

Loads were not calculated for Main Creek due to lack of streamflow data, but calculated loads in Fig. 7 indicate that element loads in Main Creek were negligible. Main Creek contributes to Deer Creek Reservoir below Provo River site 7 and Snake Creek. However, calculated loads for conservative elements like Sr at site 8 (below Deer Creek Reservoir) were nearly equal to the sum of site 7 and Snake Creek (as described above) suggesting minimal additional loading from Main Creek or other tributaries to the reservoir. Main Creek had relatively high concentrations of specific trace and major elements, including Mg, Sc, V, Co, and U (see Supplementary Material Table S1), but discharge was too small to influence trace and major element chemistry in the Provo River. Historically, Main Creek has been a concern for P loading to Deer Creek Reservoir

(http://www.waterquality.utah.gov/TMDL/Deer_Creek_Reservoir_TMDL.pdf). Although we did not measure total P, our analyses showed nondetectable values (<0.1 mg/L) of HPO_4^{2-} , suggesting that Main Creek was not a major source of dissolved P during the 2013 water year. Particulate P may have been substantial but was not measured as part of this study.

3.4 Isotopic composition

3.4.1 H and O isotopes

Stable isotopes of H and O (δD and $\delta^{18}\text{O}$) show that the Provo River, Main Creek, and Snake Creek tributaries all have similar water sources, as the samples from these rivers overlap in isotopic space (Fig. 8; Supplementary Material Table S1). Most samples plot on or below the global meteoric water line (GMWL) with values between -14 and -17‰ for $\delta^{18}\text{O}$ and between -110 and -130‰ for δD . A subset of samples from Provo River sites 1 and 1A plot as a separate group from all other samples likely due to evaporation in Trial Lake. However, samples collected further downstream show minimal evidence for evaporation despite water storage in Jordanelle and Deer Creek Reservoirs. Notably, there were no major seasonal changes in stable isotope composition, even for sites 1 through 3 that had very large increases in flow during snowmelt runoff (Supplementary Material Fig. S1). The nearly constant stable isotope values with large changes in discharge suggests that snowmelt contributes the majority of recharge to groundwater that feeds the river throughout the year.

Figure 8 also shows isotope data from a full-depth snow sampling campaign in the Uinta Mountains (near Trial Lake) during April 2013 and two water samples collected during a flood event at Provo River site 11 on September 7, 2013. Provo River, Main Creek, and Snake Creek samples plot toward the isotopic composition of snowpack (Fig. 8). The rain-fed floodwaters were much more enriched relative to all other river samples, suggesting that summer rainfall is not an important contributor to river flow except

during storm events. Considering that snowpack becomes enriched during melt(e.g., Liu et al., 2004), the Provo River appears to be fed primarily by snowmelt. However, the enrichment in stable isotope values in river samples relative to snowpack could also be explained by mixing with summer rain. Further work is needed to understand streamflow generation processes in the watershed.

3.4.2 Strontium isotopes

Strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) ratios at Provo River sites 1, 1A, 1B, 2, 4, 8, 11, Snake Creek, and Main Creek are shown in Figure 9. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured for samples collected during low flow conditions (November 21, 2012 and September 7, 2013) and snowmelt runoff (May 15, 2013) and thus reflect the range in values possible throughout the year. At sites 1A and 1B, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured only on samples collected May 15, 2013 and September 7, 2013. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were also measured on storm runoff samples at Provo River site 11 on September 7, 2013. All $^{87}\text{Sr}/^{86}\text{Sr}$ results are provided in Table S1 (Supplementary Material).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios varied over a wide range in the Provo River from around 0.715 to 0.709 (Fig. 9A). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios decreased rapidly between site 1B (0.714) and site 2 (0.709) where the river gains water that has interacted with Paleozoic carbonate rocks on the periphery of the Uinta Mountains (Fig. 1). The sudden decline in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is facilitated by abundant Sr leached from carbonate rock. However, the sample collected at site 2 during snowmelt runoff on May 15, 2013 showed a relatively higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.712 and lower Sr concentrations, reflecting an influx of snowmelt water with a more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ composition perhaps due to enhanced contact time with Proterozoic siliciclastic bedrock in the Uinta Mountains or Sr contributions from aeolian dust in snowpack (Carling et al., 2012; Miller et al., 2014).

Snake Creek caused a significant increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the lower Provo River (Fig. 9B). As Sr
458 concentrations increased between sites 4 and 8 due to mixing with Snake Creek, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio
increased from near 0.709 to 0.7105. Further downstream at site 11, $^{87}\text{Sr}/^{86}\text{Sr}$ was slightly lower (0.710)
460 in two of three samples because the river gains water that has interacted with Paleozoic carbonate rocks
in the Wasatch Mountains (Fig. 1). However, the sample collected at site 11 during higher flows on May
462 15, 2013 had a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, similar to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at site 8 below Deer Creek Reservoir.

Figure 8. δD and $\delta^{18}O$ composition of Provo River, Snake Creek, and Main Creek samples collected during the 2013 water year and snowpack samples collected near Trial Lake at the headwaters of the Provo River during April 2013. Values are expressed in ‰ notation relative to Vienna Standard Mean Ocean Water (VSMOW). The Dotted line is the global meteoric water line (GMWL).

Figure 9. Plot of the inverse of Sr concentrations versus $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for (A) all data collected on the Provo River and (B) data from part A excluding sites 1, 1A, 1B, and site 2 during snowmelt runoff. The average seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is shown as a dashed horizontal line as reference. Part B shows the influence of Snake Creek on Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

3.5 Water chemistry during storm runoff in an urban environment

The water samples collected in the Utah Valley urban area at site 11 during a flash flood on September 7, 2013 provide an opportunity to explore trace element dynamics during extreme hydrologic events. During the flood, streamflow increased from $\sim 0.5 \text{ m}^3/\text{s}$ to over $18 \text{ m}^3/\text{s}$ in 30 min (Supplementary Material Fig. S4). Concomitant with the increase in streamflow, field-measured conductivity decreased from $\sim 600 \text{ }\mu\text{S}/\text{cm}$ to $\sim 200 \text{ }\mu\text{S}/\text{cm}$ (Supplementary Material Fig. S4). Within 4hr of peak runoff, streamflow decreased to $2 \text{ m}^3/\text{s}$ and conductivity increased to over $500 \text{ }\mu\text{S}/\text{cm}$. Whereas flow rate increased by a factor of ~ 40 and conductivity only decreased by a factor of 3 during the flood, increased flow from groundwater storage most likely modulated conductivity values. Simple two-component hydrograph separation indicated that groundwater (estimated conductivity of $600 \text{ }\mu\text{S}/\text{cm}$ based on pre-flood river measurements) and rainfall runoff (estimated conductivity of $10 \text{ }\mu\text{S}/\text{cm}$) contributed 30% and 70% of the flow during the storm, respectively. Therefore, groundwater flow likely contributed to the flood but the majority of floodwater was direct overland flow across impervious surfaces in the urban area.

Concentrations of specific trace elements varied dramatically before and after the onset of flooding (Fig. 10), although conclusions are tentative given the limited dataset (three samples on the day of the flood). For example, Sr, Ba, Li, and U concentrations decreased by a factor of 3 or more. In contrast, Zn concentrations increased fivefold, and Cr, Pb, and La concentrations increased tenfold. Trace element trends during the flood reflect dilution of the soluble elements and increase in the particle-associated elements, possibly due to increased soil erosion during the flood event. It is very likely that the increase in Zn, Cr, and Pb also reflects inputs from the urban area as these metals are commonly found in urban storm runoff (Burrows and Peters, 2012; Garnaud et al., 1999; Helmreich et al., 2010; Joshi and Balasubramanian, 2010). The increase in metal concentrations during the flood could also reflect

490 mobilization of legacy mining-associated sediment in the stream channel. Diel-driven variability (i.e.,
Carling et al., 2011; Gammons et al., 2005; Nimick et al., 2003; Shope et al., 2006) is likely not the cause
492 of observed increases in trace metal concentrations given the minimal changes in T_w and pH during the
flood (Supplementary Material Table S1).

494

Figure 10. Trace element concentrations measured on filtered samples collected September 7, 2013 at Provo River site 11 before the flood (9:00), at peak flooding (17:15), and during the flood recession (18:20). Sr, Ba, Li, and U concentrations decreased during the flood due to dilution. In contrast, Zn, Cr, Pb, and La concentrations increased during the flood. Note the log scale.

4. Discussion

4.1 Natural and anthropogenic sources of trace elements to the Provo River

The variety of trends observed in trace element concentrations along the Provo River reflect the dynamic processes occurring in the watershed and suggest a variety of inputs from natural and anthropogenic sources (Figs. 2–5). The most abrupt change in Provo River water chemistry occurred below the confluence of Snake Creek between sites 7 and 8 (Figs. 2–4). Although annual streamflow in Snake Creek during 2013 was only 20% of the flow at Provo River site 7 (Supplementary Material Fig. S1), Snake Creek was responsible for a substantial fraction of element loads to Deer Creek Reservoir (Fig. 7 and Supplementary Material Fig. S3), which is one of the main drinking water sources for the Wasatch Front metropolitan area. In particular, Snake Creek contributed nine-fold more Cs, three-fold more Li, and over twice as much As and Rb relative to the Provo River (Fig. 7). The influx of solutes from Snake Creek is mainly due to geothermal sources in the Snake Creek watershed (Carreón-Díazconti et al., 2003; Mayo et al., 2013). Streamflow on Snake Creek increases ten-fold as it passes through areas of fault-controlled tufa mounds, and the waters have high salt and metal concentrations. Thus, the natural geothermal waters in Snake Creek are one of the major “pollutant” sources in the Provo River system.

Another natural input of potentially toxic trace elements was observed in Provo Canyon, where the river passes through the Wasatch Mountains. Se and U concentrations doubled between sites 8 and 9 (Fig. 3), likely reflecting inputs of water that has interacted with the Manning Canyon shale in Provo Canyon. Indeed, springs in Provo Canyon that are located in or adjacent to Manning Canyon shale contain Se and U concentrations in excess of 1 µg/L (Supplementary Material Table S4 and Fig. S5). Black shales, rich in organic matter and sedimentary sulfides, are well-known reservoirs of toxic metals and metalloids (Brumsack, 2006; Tourtelot, 1979; Yu et al., 2014) and can serve as sources of toxic elements in the environment as shale units are oxidized and weathered (e.g., Falk et al., 2006; Lavergren et al., 2009a,

2009b). In a large survey of black shales in North America, Mapel (1956) noted that most samples contain <30 ppm U, although some samples contain as much as 100 ppm. U content is usually positively correlated with organic matter abundance (Fisher and Wignall, 2001; Mapel, 1956). Se is also known to be enriched in black shales (Mitchell et al., 2012; Park et al., 2010; Stillings and Amacher, 2010; Tuttle et al., 2014a, 2014b) including the Manning Canyon shale (Brimhall, 1963). Thus, this unit may serve as a natural source of Se and U to the Provo River, with enhanced releases coming from quarrying near the mouth of Provo Canyon (i.e., below site 8).

Snowmelt runoff also contributed naturally occurring metals to the Provo River. In the upper Provo River, concentrations of Ti, Al, Pb, Cr and the rare earth elements were highly enriched during peak runoff relative to the rest of the year (Fig. 5). This observation suggests that these elements were contributed to the river via enhanced soil erosion in the watershed during snowmelt runoff when the water was visibly turbid. Suspended solids settle out in Jordanelle Reservoir, resulting in lower concentrations of particle-associated elements in the middle and lower Provo River. The source of these elements in the Uinta Mountain soils may reflect weathering of interbedded shales within the metasedimentary rocks that contain relatively high concentrations of these metals (Condie et al., 2001) or may be a result of exogenous inputs of metal-enriched aeolian dust deposition to the Uinta Mountains (Carling et al., 2012; Munroe, 2014; Munroe et al., 2015; Reynolds et al., 2010). Atmospherically-deposited Pb is known to accumulate in mountain soils and can be released during high flow events (Jo and Park, 2010).

Variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Provo River reflect inputs from weathering of both silicate and carbonate rocks and other sources. More radiogenic values (ranging from 0.714 to 0.716) were found at Provo River sites 1, 1A, and 1B, reflecting Sr contributions from weathering of siliciclastic rocks in the Uinta Mountains (Fig. 1). These relatively radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are consistent with clastic sediment in the

western Uinta Mountains that is derived from both Archean and Proterozoic components (Ball and Farmer, 1998; Condie et al., 2001). Further downstream, lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reflect interactions with Paleozoic carbonate rocks. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios also showed changes in Sr sources during high flow events. On the upper Provo River, Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were lower at sites 1A and 1B during snowmelt relative to low flow conditions. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of sites 1A and 1B propagated downstream during snowmelt, causing diluted Sr concentrations but a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at site 2. Sr concentrations likewise decreased during the September 7, 2013 flood at site 11, but $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were unchanged (Fig. 9B). These findings suggest that Sr was simply diluted at site 11 during the rain event, but that the Sr sources changed in the upper Provo River during snowmelt (Fig. 9A). Similar to the metals discussed above, the Sr source to the upper Provo River during snowmelt may reflect contributions from weathering of interbedded shales or deposition of aeolian dust (Carling et al., 2012; Munroe, 2014; Munroe et al., 2015), which has a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio relative to the Uinta Mountain bedrock (Miller et al., 2014). Further work is needed to test these possibilities.

Anthropogenic sources of trace metals were also observed along the Provo River. The influx of Mo, Sb, and Tl in Jordanelle Reservoir (Fig. 4) likely reflects inputs from abandoned mines and mine tailings from the Park City mining district within the Provo River watershed above Deer Creek Reservoir. Previous work in streams within the Park City mining district showed elevated concentrations of these and other metals in water and soil (Giddings et al., 2001). These results suggest that further cleanup of the mine wastes may be necessary to improve water quality in the Provo River.

Whereas minimal changes in water quality were observed in the Provo River as it traversed the Utah Valley urban area under normal flow conditions, water quality was severely impacted during storm runoff (Fig. 10). These observations suggest that the river is hydrologically disconnected from the watershed where it is channelized through the urban area except during flood events when it receives

566 runoff from storm drains. The influx of anthropogenic trace metals such as Zn, Cr, and Pb during the storm event on September 7, 2013 contained high enough concentrations to be harmful to aquatic life.

568 Storm drains in the urban area empty directly into the Provo River without pretreatment, leading to enhanced runoff discharges to the river. Further work is needed to sample additional sites along the Provo River during storm events, particularly in the Heber Valley urban-agricultural area, to observe potential impacts from storm runoff.

572 Agriculture in Heber Valley surprisingly did not contribute appreciable amounts of trace elements or nutrients (NO_3^- or HPO_4^-) to the Provo River. Cs and Li loads increased substantially as the river crossed the agricultural area between sites 5 and 6 (Fig. 7), which could indicate underflow from the agricultural fields or groundwater flow from Snake Creek geothermal water. Although only small changes in water chemistry were observed through the agricultural area, higher-frequency temporal sampling may show large variability during storms and the summer irrigation season. Additional measurements such as $\delta^{15}\text{N}$, nitrite, ammonia, and total P are needed to identify potential nutrient contributions from the agricultural area.

580 *4.2 Contributions to streamflow from snowmelt and groundwater*

The similar stable isotope (δD and $\delta^{18}\text{O}$) composition of Provo River waters during low flow conditions and snowmelt runoff suggests that snowmelt and snowmelt-fed groundwater are critical to sustaining flow in the Provo River system. The shift toward more-enriched isotopes between snowpack and river water is likely due to loss of lighter isotopes to vaporization from the snowpack during the melt season (e.g., Clark and Fritz, 1997). However, the shift toward more-enriched isotopic values may also indicate that summer rainfall or lower elevation precipitation contribute some fraction of flow to the Provo River. Quantifying the relative contributions from snowpack and rainfall is an important issue considering the future projections of climate change. As precipitation in the Provo River watershed

transitions to a greater fraction of rainfall relative to snowfall, the implications on water resources are
590 unknown.

The decrease in solute concentrations during snowmelt without a change in stable isotopic composition
592 of stream water was also observed in a small watershed study at Cherry Creek, Wyoming (Jin et al.,
2012). The authors hypothesized that small headwater ponds homogenize the snowmelt water δD and
594 $\delta^{18}O$ composition while allowing for a dilution effect. The water reaching the stream, therefore, has a
constant stable isotopic signature but is diluted in solutes. In the Uinta Mountains, a similar process may
596 occur as headwater lakes and ponds homogenize the snowmelt runoff, effectively mixing the δD and
 $\delta^{18}O$ composition of the water while allowing for dilution.

598 *4.3 Correlations with field parameters and potential for high frequency proxy measurements*

As part of the iUTAH project sponsored by the U.S. National Science Foundation, four aquatic sensor
600 stations were installed along the Provo River during 2014 (after we completed sampling for this study),
including measurements of pH, water temperature, turbidity, and fluorescent dissolved organic matter
602 (fDOM) at 15-min intervals. Our present study provides the first opportunity to investigate relationships
between probe-measured parameters and trace elements in the Provo River. Although we did not
604 measure turbidity or fDOM as part of our routine sampling, we did find correlations of specific trace and
major elements with conductivity.

Field-measured conductivity is often used as a simple method for evaluating water quality. In the Provo
606 River, conductivity was strongly correlated with the major ions but less correlated with the trace
elements (Fig. 2). Correlation coefficients (r) between conductivity and the major ions Na^+ , K^+ , Ca^{2+} ,
608 Mg^{2+} , HCO_3^- , Cl^- , and SO_4^{2-} ranged from 0.91 to 0.98. Sr is the only trace element that was also strongly
correlated ($r=0.96$) with conductivity (Fig. 2). A subset of trace elements was moderately correlated
610

($0.7 < r < 0.9$) with conductivity, including Li, Cs, As, Rb, Se, U, and Mo (Figs. 3 and 4), but the majority of trace elements showed no significant correlation. This suggests that routine monitoring of conductivity or sampling for major ions without trace element chemistry does not fully characterize water chemistry or identify all potential contaminant sources. Field measurements of conductivity likely provide very good information regarding the major ion chemistry of a stream but very little information about trace element concentrations. More work is needed to test possible correlations of trace elements with other easily measured field parameters such as fDOM and turbidity in the Provo River and its tributaries.

4.4 Influence of built environment on water chemistry

Water chemistry was highly variable above Jordanelle Reservoir in the upper Provo River but showed little temporal changes below the dam, as demonstrated by NMS results for sites 1–3 relative to sites 4–11 (Fig. 6). Whereas major ion concentrations were diluted during spring runoff in the upper Provo River, concentrations were fairly constant year-round below Jordanelle Reservoir (Fig. 2). Furthermore, there was no inverse correlation between flow and conductivity below the reservoir like there was above the reservoir. Particle-associated elements showed much higher concentrations during spring runoff on the upper Provo River but were almost completely removed by settling in Jordanelle Reservoir. In the upper Provo River, trace element loads were dominated by spring runoff, but below Jordanelle Reservoir, loads were distributed throughout the year.

Historical data from the National Water Quality Monitoring Council Water Quality Portal (<http://www.waterqualitydata.us/>) show that concentrations of total suspended solids (TSS) decreased to near zero at Provo River site 4 after construction of Jordanelle Dam in 1995 (Supplementary Material Fig. S6). Likewise, concentrations of total dissolved solids (TDS) were highly variable before the construction of the dam but show little variability after the dam was completed. Although it is generally assumed that reservoirs improve water quality, the effect of the homogenization of water chemistry on

biota in the Provo River is unknown. One possible negative impact of the reservoir is that nutrients associated with the suspended solids are removed from the water column, potentially resulting in less productivity downstream of the dam. Further research is needed to evaluate impacts of Deer Creek and Jordanelle reservoirs on Provo River water quality.

Water diversions also have potential impacts on water quality and habitat. For example, diversions from the Provo River result in less flow and therefore less dilution of harmful trace elements in the middle and lower sections of the river. In contrast, diversions from the lower Provo River result in smaller loads of potentially harmful trace elements and salts to Utah Lake. Given the disproportionately large impact of Snake Creek on Provo River chemistry, diversion or pretreatment of Snake Creek waters would substantially improve water quality in Deer Creek Reservoir and the drinking water it supplies.

5. Conclusions

In this study, we used trace element concentrations coupled with $^{87}\text{Sr}/^{86}\text{Sr}$, δD , and $\delta^{18}\text{O}$ ratios to investigate natural and anthropogenic impacts on Provo River water chemistry. We found that a variety of natural solute sources impacted the river: weathering of both carbonate and silicate rocks contributed Sr, as indicated by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; geothermal groundwater contributed the majority of Li, Cs, As, and Rb; weathering of black shales contributed substantial Se and U; and soil erosion during snowmelt, and perhaps aeolian dust deposition on the Uinta Mountains, contributed the majority of Ti, Fe, Pb, Cr, La, and Ce. Furthermore, anthropogenic solute sources impacted the Provo River: runoff from legacy mine operations likely contributed Mo, Sb, and Tl and a flood event in the Utah Valley urban area contributed anthropogenic metals Zn, Cr, and Pb. These results suggest that changing landuse in the Provo River watershed, as agricultural lands are urbanized, may result in negative water quality impacts due to enhanced overland flow during storm events. The built water infrastructure also has an impact on the Provo River: dams altered water chemistry by allowing for particle settling and homogenizing water

chemistry to negate dilution during snowmelt runoff, and diversions decreased element loads on the
658 lower portion of the river. δD and $\delta^{18}O$ composition showed that the majority of water in the Provo
River and tributaries was sourced from snowmelt runoff, with potential negative impacts in the future as
660 a changing climate causes more precipitation to fall as rain rather than snow.

In conclusion, a variety of natural and anthropogenic processes work together to produce the
662 geochemical composition of a river. Trace element concentrations coupled with isotopic ratios are
necessary for disentangling these processes, especially in rivers that are undergoing rapid changes in
664 landuse or are heavily managed with dams and diversions. It is especially important to understand how
river geochemistry changes during snowmelt or rain events. This study shows how sampling across
666 seasons and during high flow events is necessary for characterizing natural and anthropogenic impacts
on a river system.

668 **Acknowledgements**

We appreciate the comments from two anonymous reviewers that greatly improved the manuscript.
670 This project was supported by the Department of Geological Sciences and College of Physical and
Mathematical Sciences at Brigham Young University. Additional support was provided by NSF EPSCoR
672 grant IIA 1208732 awarded to Utah State University, as part of the State of Utah EPSCoR Research
Infrastructure Improvement Award. Any opinions, findings, and conclusions or recommendations
674 expressed are those of the authors and do not necessarily reflect the views of the National Science
Foundation.

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