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

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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 ($^{87}Sr/^{86}Sr$), and stable isotopes of H and O (δD and $\delta^{18}O$) 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. $^{87}Sr/^{86}Sr$ 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 $\delta^{18}O$ 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,

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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 $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ 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; Druzbicka 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 (**i**nnovative **U**rban **T**ransitions and **A**rid region **H**ydro-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 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).

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 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 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, 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 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. Fig. S1 (Supplementary