Isotope variations of dissolved Zn in the Rio Grande watershed, USA: The role of adsorption on Zn isotope composition

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Abstract

In order to better understand the factors influencing zinc (Zn) isotope composition in hydrological systems, we analyzed the $\delta^{66}\text{Zn}$ of dissolved Zn in the streams and groundwater of the Upper and Middle Rio Grande watershed in Colorado and New Mexico, United States. The stream water samples have a wider variation of $\delta^{66}\text{Zn}$ (-0.57 to +0.41 ‰ relative to the JMC 3-0749-Lyon standard) than groundwater samples (-0.13 to +0.12 ‰) and than samples from streams that are in close proximity to abandoned mining sites (+0.24 to +0.40 ‰). Regional changes of bedrock geology, from primarily igneous rocks to primarily sedimentary rocks, have no resolvable effect on the $\delta^{66}\text{Zn}$ of aqueous samples. Instead, an increase in water pH from 7.5 to 8.5 corresponds to a considerable decrease in the $\delta^{66}\text{Zn}$ of dissolved Zn ($R^2 = -0.37$, $p = 0.003$, $n = 22$). Consequently, we link the observed Zn isotope variations to the process of adsorption of Zn onto suspended sediment and bedrock minerals (average $\Delta^{66}\text{Zn}_{\text{adsorbed-dissolved}} = +0.31\text{‰}$). Our results are in good agreement with previous experimental and empirical studies suggesting that Zn adsorption leads to a residual dissolved pool enriched in light Zn isotopes. Given that anthropogenic Zn sources can also be responsible for lowering of $\delta^{66}\text{Zn}$, and may overlap with the pH/adsorption effect on $\delta^{66}\text{Zn}$, the latter needs to be carefully considered in future studies to differentiate between natural and anthropogenic factors influencing Zn isotopes in this and other aquatic systems.

1. Introduction

Zinc (Zn) is an important metal pollutant in many hydrological systems. Common sources of anthropogenic Zn are tire wear (Councell et al., 2004; Thapalia et al., 2010), gasoline combustion and smelting (Cloquet et al., 2006; Gioia et al., 2008; Mattielli et al., 2009; Borrok et al., 2010), corrosion of galvanized steel (John et al., 2007), and waste water and urban runoff (Chen et al., 2009). Additionally, elevated Zn loads are associated with the low-pH weathering of natural sulfide minerals, which is often accelerated by active and historical mining (Borrok et al., 2008a, 2009).

The stable isotopic composition of Zn ($\delta^{66}\text{Zn}$) has been used to trace the sources of metal pollution in aqueous systems (e.g., Wiederhold 2015). Generally, anthropogenic Zn is isotopically lighter than natural Zn sources (e.g., Thapalia et al., 2015). The $\delta^{66}\text{Zn}$ of most anthropogenic Zn ranges from -1.0 to +0.15‰ (Cloquet et al., 2006; Gioia et al., 2008; Sonke et al., 2008; Chen et al., 2009; Mattielli et al., 2009; Thapalia et al., 2010, 2015). In contrast, the $\delta^{66}\text{Zn}$ of geologic sources ranges from +0.2 to +1.3‰, but averages around +0.35‰ (Marèchal et al., 1999, 2000; Luck et al., 1999; Wilkinson et al., 2005; Cloquet et al., 2006, 2007; Chen et al., 2008, 2009; Juillot et al., 2011; Bigalke et al., 2012; Dong et al., 2013; Matthies et al., 2014a; Little et al. 2014a; Thapalia et al., 2015).

Natural processes such as biological uptake, ligand exchange in aqueous solutions, and adsorption on organic and inorganic surfaces can also influence the isotope composition of dissolved Zn in aqueous environments (e.g., Pichat et al., 2003; Stenberg et al., 2004; Weiss et al., 2005; Pokrovsky et al., 2005; Bermin et al., 2006; Gèlabert et al., 2006; Balistrieri et al., 2008; Peel et al., 2009; Fujii et al., 2011; Little et al., 2014b; Kafantaris et al., 2014; Matthies et al., 2014b; Dekov et al., 2014; Coutaud et al., 2014; Zhao et al., 2015; Bryan et al., 2015). The mobility of Zn in aqueous systems is significantly controlled by pH. An increase in pH typically leads to increased adsorption of Zn in natural systems (e.g., Balistrieri et al., 2008). The adsorption of Zn on sediment/mineral particles and plant roots generally lowers the $\delta^{66}\text{Zn}$ of dissolved Zn in solution because of the preferential incorporation of heavier Zn isotopes in adsorbed phases (e.g., Pokrovsky et al., 2005; Gèlabert et al., 2006; Viers et al., 2007; Balistrieri et al., 2008; Juillot et al., 2008; Houben et al., 2014; Kafantaris et al., 2014; Bryan et al., 2015). The magnitude of $\Delta^{66}\text{Zn}_{\text{adsorbed-dissolved}}$ for adsorption onto mineral/sediment surfaces, ranges from ~0.1 to 0.7‰ (Pokrovsky et al., 2005; Juillot et al., 2008; Balistrieri et al., 2008; Bryan et al., 2015), depending on the mineral and solution conditions. Therefore, both anthropogenic and natural processes can lead to a decrease in $\delta^{66}\text{Zn}$ in hydrological systems (e.g., Chen et al., 2008, 2009). Other complicating factors controlling the isotopic compositions of dissolved Zn in hydrologic systems include complexation with dissolved organic constituents (e.g., Jouvin et al., 2009; Coutaud et al., 2014; Fujii et al., 2014) and metabolic uptake by plants and microorganisms (e.g., Pichat et al., 2003; Gèlabert et al., 2006; Borrok et al., 2008b; John et al., 2007; Peel et al., 2009; Anderson et al., 2011; Wanty et al., 2013; Zhao et al., 2014). These processes can potentially lead to an increase in the $\delta^{66}\text{Zn}$ of dissolved Zn. The relative importance of the source of Zn relative to its biogeochemical cycling in controlling its isotopic signature in hydrologic systems remains unclear.

In this study, we measured the dissolved Zn isotope compositions and concentrations of several tributaries and the main river stem within the Rio Grande watershed in southern Colorado and New Mexico, USA. Heterogeneous bedrock geology, comprised of volcanic, metamorphic and sedimentary rocks, and some areas of intensive sulfide mineralization, allow for assessing the role of bedrock

mineralogy (sources) as well as water pH (a primary driver of geochemical processes) on $\delta^{66}\text{Zn}$ in the aquatic environment. The studied area hosts smaller population centers than those characterized in previous studies that were undertaken in more urban/industrial regions (e.g., Chen et al., 2008, 2009; Bigalke et al., 2010; Thapalia et al., 2010, 2015). Therefore, our results are likely to better address the natural dynamics of Zn isotope systematics in hydrological systems, particularly those where Zn concentrations are controlled primarily by weathering and adsorption reactions.

2. Geological and environmental setting

The Rio Grande watershed (Fig. 1) comprises of a series of alluvial-fill basins formed by half grabens that developed during the formation of the Rio Grande rift ~30 Ma ago due to an episode of widespread extension of the western United States (Keller and Baldrige, 1999). These basins are filled with alluvial, fluvial, playa, and lacustrine sediments derived from erosion of adjacent Precambrian crystalline, Paleozoic/Mesozoic sedimentary, and Tertiary volcanic bedrock highlands and range in depth from less than 30 m to 4,000 m. The major river system draining the watershed is the Rio Grande, with its headwater region in the San Juan Mountains of southern Colorado. In New Mexico, the Rio Grande flows from north to south and becomes a semi-arid river in the central and southern portions of this state.

The majority of groundwater recharge in the Rio Grande valley occurs during the spring from snowmelt in the headwaters region of the San Juan Mountains, Colorado, and in the high mountain areas of northern New Mexico. Recharge also occurs from runoff in mountain catchments, inflow from adjacent aquifers, and infiltration of water from both the Rio Grande and its adjacent irrigation network (Ellis et al., 1993). The irrigation network of interconnected canals and drains is a distinctive hydrological feature, particularly in central and southern New Mexico. Average annual precipitation delivered to the Rio Grande is less than 254 mm and decreases southward, reaching less than 203 mm in El Paso, Texas (e.g., Ellis et al., 1993).

Our water sampling concentrated on areas of the Rio Grande watershed with different bedrock (Fig. 1). For example, the Rio Grande headwaters in southern Colorado (Locations 1 through 11 on Fig. 1) are dominated by sulfide-rich, Tertiary volcanic and volcanoclastic sedimentary rocks of the 28 Ma old San Juan Caldera (Lipman et al., 1976; Bove et al., 2000). Mineralization in this area is characterized by widespread hydrothermal pyritization and fault/vein controlled ore bodies consisting of Cu, Fe, Zn, and Pb sulfides. In northern New Mexico (between Locations 12 and 16), the Rio Grande flows through the Late Cenozoic Taos Volcanic Field with 35 central-vent volcanic shields and cones which range in composition from basalt to silicic rhyolite. Additionally, some of the Rio Grande tributaries in this area, such as the Red River (Locations 13 through 16), drain bedrock comprised of the Late-Oligocene Latir volcanic field with the adjacent Questa caldera, emplaced between 28 and 25 Ma years ago (Lipman et

al., 1986). The major rocks of the Red River valley are hydrothermally altered volcanic and intrusive rocks with variable amounts of pyrite which weathers to produce alteration scars and natural acid rock drainage (Campbell and Lueth, 2008). Further downstream (Locations 19 through 25), the Rio Grande receives additional recharge from the Santa Fe Mountains, which are primarily composed of the Precambrian basement rocks with limited exposures of Paleozoic rocks. Precambrian rocks are predominantly granitic, with subordinate schist, gneiss and amphibolite (e.g., Grauch et al., 2009).

In contrast, the semi-arid portion of the Rio Grande watershed in central and southern New Mexico has more Paleozoic and Mesozoic sedimentary formations in the bedrock. In Locations 17, 18, and 28, the bedrock is mainly composed of Permian through Tertiary age continental and marine sandstones, shales, coals, mudstones, and carbonate rocks. These strata are generally horizontal, often faulted, and eroded into broad valleys flanked by mesas and mountains. Further south (Locations 26-27 and 29-34), the bedrock is comprised of various Precambrian (e.g., granite, metamorphosed sedimentary and volcanic rocks) and Paleozoic sedimentary rocks. The Late Cambrian to Permian sediments are usually composed of sandstone, limestone, dolomite, shale, and in some locations also gypsum and anhydrite (New Mexico Geological Society, 2005).

In this study, we did not analyze bedrock samples for Zn isotopes because of the complex geology in various parts of the Rio Grande watershed and the relatively large area spanned by the studied stretch (~1000 km) of the Rio Grande. Generally, linking the changes of stream Zn isotope composition to each bedrock unit would be impossible on a regional scale. Nevertheless, we assumed that if bedrock composition was a primary factor controlling the $\delta^{66}\text{Zn}$ of the studied streams, this influence would be distinctive when comparing $\delta^{66}\text{Zn}$ between the upstream and downstream Rio Grande with volcanic/crystalline-rich and sedimentary-rich bedrock, respectively.

3. Methods

3.1. Field sampling

In August 2009, ten surface water samples were collected from several streams (Locations 1 to 10 on Fig. 1) draining the Silverton mining district of the San Juan Mountains in southern Colorado. This area is adjacent to the Rio Grande headwaters (although on the opposite side of the continental divide) and representative of elevated Zn loads from natural and anthropogenically-derived weathering of the Tertiary sulfide-rich mineralization (Bove et al., 2007; Borrok et al., 2009). For comparison, in April and August of 2010 we also collected eight surface water samples along the Red River (Locations 13 to 16), one of the Rio Grande tributaries draining the Questa mining district and the natural alteration scars of the Sangre de Cristo Mountains in northern New Mexico.

139 In November 2009 and April 2010, surface water samples were collected from the Rio Grande in
140 southern Colorado (Locations 11 and 12) and in central and southern New Mexico (Location 29 and
141 Locations 30 to 34, respectively). Additionally, we sampled two agricultural drains in El Paso, west Texas
142 (Locations 35-36). The Zn concentrations were below the detection limit of our instrumentation in
143 Locations 30 through 36 in these two sampling seasons ($<6 \mu\text{g/L}$). Therefore, for these locations we
144 report Zn isotope compositions from sampling seasons in July-August 2010 when Zn concentrations were
145 sufficiently high (0.010 to 0.131 mg/L) to perform Zn isotope analysis. For comparison with the Rio
146 Grande, in November 2011 and April 2012 we also collected three surface water samples from the Rio
147 Chama (Locations 17-18) and Rio Puerco (Location 28), two semi-arid tributaries to the Rio Grande.

148 In addition to surface water samples, in November 2009 we sampled seven groundwater samples
149 from the Espanola basin (Locations 19 to 25) and two groundwater samples from the Albuquerque basin
150 (Locations 26 to 27). Two N-P-K fertilizer samples with elevated Zn concentrations and two leachates
151 from the leaves of Pecan trees in southern New Mexico were also analyzed. The Pecan farms are
152 seasonally sprayed with Zn-rich fertilizers and may thus contribute considerable Zn loads into agricultural
153 drains and the Rio Grande. The pH was measured in situ in the stream for surface water and in the well
154 for groundwater samples using an Orion portable meter (Thermo Scientific 3 Star Multimeter).

155 In all locations, we collected two types of water samples in separate 125 mL pre-washed sample
156 bottles: 1) unfiltered grab (“raw”) water samples that contained water and suspended sediment, and 2)
157 dissolved water samples filtered with $0.45\mu\text{m}$ nylon syringe filters. Both samples were acidified with 16
158 drops of high-purity (ultra-pure metal grade) concentrated HNO_3 . Prior to analysis by ICP-OES and pre-
159 concentration for isotope determination (described below), the raw unfiltered, acidified water samples
160 were allowed to sit for several months while suspended sediment fully settled to the bottom of the sample
161 bottle. Water was pipetted from above the sediment and used in the analysis of Zn concentrations and
162 isotopic values described below. Because the raw samples were acidified, releasing any adsorbed Zn into
163 solution, we assume that Zn from these samples contained a combination of dissolved Zn and Zn that had
164 been adsorbed to the suspended sediments. Suspended sediments were not additionally processed or
165 analyzed. Further, the dissolved fraction of Zn in our study refers to all Zn that passed through the
166 $0.45\mu\text{m}$ filter, which could include some colloidal Zn.

168 3.2. Zn concentration analysis

169 The concentrations of Zn in all water samples were measured using a Perkin Elmer 5300 DV
170 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) at the University of Texas at El
171 Paso. Samples were analyzed using multi-element atomic adsorption standards (diluted from 10.00 mg/L
172 stock solutions) and U.S. Geological Survey standard reference water samples were used as external

checks of precision and accuracy. Uncertainty was less than $\pm 5\%$ and detection limits for Zn were around 6 $\mu\text{g/L}$.

3.3. Zn isotope analysis

Both the raw (unfiltered and acidified) and filtered samples were prepared for Zn isotope analysis according to the anion-exchange chromatographic method described in Borrok et al. (2007). Briefly, an aliquot of the sample was pre-concentrated to provide about 2 micrograms of Zn dissolved in 1 mL of 10M ultra-pure HCl. The acidified sample was then loaded onto a plastic pipette-style column with about 1 mL of pre-cleaned 100-200 mesh AG MP-1 resin (Bio-Rad™). An additional 2 mL of 10M HCl followed by 4 mL of 5M HCl then 3 mL of 1M HCl were added to the column to elute matrix elements while Zn remained on the column as an anionic Zn-chloride complex. The separation procedure was completed by adding 4 mL of ultra-pure water to elute the Zn fraction. This fraction was evaporated to dryness and re-dissolved in a volume of 2% HNO_3 to reach a concentration of $\sim 100 \mu\text{g/L}$. Column blanks contained 10 ng of Zn on average, which was less than 1% of the total mass of Zn. Some of the prepared samples were analyzed by ICP-OES. These samples demonstrated full Zn recovery (within analytical uncertainties) and a lack of any detectable potentially interfering elements. The $\delta^{66}\text{Zn}$ was determined using a Nu Instruments multicollector MC-ICP-MS at the Department of Geological Sciences at the University of Texas at El Paso. Samples were introduced into the Argon plasma using a desolvating nebulizer system (Nu DSN 100). Masses of four Zn isotopes (^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn) were simultaneously monitored and the standard sample bracketing method was used to correct for mass bias correction (e.g., Albarede and Beard, 2004; Borrok et al., 2007, 2009, 2010; Thapalia et al., 2010, 2015). The stability of the mass bias did not allow for improvement of the measurements through the use of an external dopant. The ratios of $^{66}\text{Zn}/^{64}\text{Zn}$ are reported in parts per thousand relative to the Johnson Matthey Zinc (JMC) standard solution 3-0749-Lyon. The $\delta^{66}\text{Zn}$ of the IRMM 3702 standard has been measured relative to the JMC standard previously in our laboratory by Borrok et al. (2010; $+0.27 \pm 0.04$ 1 σ ; n=24) and Aranda et al. (2012; $+0.31\text{‰} \pm 0.05\text{‰}$ 1 σ ; n=12) but was not done again in this investigation. The majority of samples were duplicated twice or more times over a period of three years and the average 1 σ uncertainty was 0.05 ‰. This average includes uncertainties associated with duplicating the column chromatography method. Blanks were evaluated for each group of column separates by comparing relative total voltage intensity of masses 64, 66, 67, and 68 to those of the samples. In all cases, the voltage intensity of the blanks was less than 0.1% of the samples, indicating that they had no measurable effect on the results. Mass dependency plots of the raw isotope data confirmed that the correct mass dependent relationships were obtained, verifying that spectral interferences were not present (Supplementary Fig. 1).

3.4. S isotope analysis

For comparison with Zn isotopes, we measured the $\delta^{34}\text{S}$ of dissolved sulfate (SO_4), which has been previously reported by Szyrkiewicz et al. (2015). These samples were collected in the same field campaigns as the samples collected for Zn isotope analysis. In the laboratory, the water samples were acidified with concentrated HCl and dissolved SO_4 was precipitated to BaSO_4 by adding 10 % BaCl_2 solution. The $\delta^{34}\text{S}$ of BaSO_4 was determined using an EA1110 elemental analyzer coupled to a Finnigan Mat 252 isotope ratio mass spectrometer via a ConFlo II split interface in the Stable Isotope Research Facility at Indiana University. Sulfur isotopic data are reported with respect to VCDT (Vienna Cañon Diablo Troilite). Analytical reproducibility was better than 0.3‰ (1 σ) based on sample duplicates. The $\delta^{34}\text{S}$ and bulk chemical analyses of surface water samples used in this study have been presented and summarized in a separate manuscript by Szyrkiewicz et al. (2015).

4. Results

In the studied portion of the Rio Grande watershed, the isotope composition of dissolved Zn varies from -0.57 to +0.41 ‰ (Supplementary Tab. 1). Generally the highest $\delta^{66}\text{Zn}$ (+0.24 to +0.40 ‰, average +0.31 ‰) and the highest Zn concentrations (0.23 to 70 mg/L, average 15 mg/L) are observed in streams draining the abandoned mining districts of the San Juan Mountains (Silverton area) in southern Colorado (Locations 1-10 on Fig. 1). The $\delta^{66}\text{Zn}$ is consistent with the previously measured stream $\delta^{66}\text{Zn}$ in this area of +0.1 to +0.5 ‰ (Borrok et al., 2008). Lower $\delta^{66}\text{Zn}$ (-0.24 to +0.41 ‰, average +0.09 ‰) and lower Zn concentrations (0.017 to 0.026 mg/L, average 0.024 mg/L) are observed in the Red River, a major stream draining the Questa mining district in northern New Mexico (Locations 13-16). Similar relationships are observed in upstream Rio Grande (Locations 11-12), that shows $\delta^{66}\text{Zn}$ of -0.07 to +0.25 ‰ (average +0.09 ‰) and Zn concentrations of 0.020 to 0.196 mg/L (average 0.076 mg/L). In contrast, the downstream Rio Grande and the Rio Chama have the lowest $\delta^{66}\text{Zn}$ (-0.57 to +0.15 ‰, average -0.24 ‰) with Zn concentrations of 0.012 to 0.043 mg/L (average 0.036 mg/L). Groundwater from the Española and Albuquerque basins (Locations 19-25 and 26-27, respectively) show a relatively narrow range of $\delta^{66}\text{Zn}$ (-0.13 to +0.12 ‰, average -0.04 ‰) but larger variation in Zn concentration (0.018 to 0.174 mg/L, average 0.107 mg/L) compared with the other sample areas. The $\delta^{66}\text{Zn}$ of two N-P-K-fertilizers that are extensively used in the downstream Rio Grande watershed has values of -0.06 to +0.21 ‰ (Supplementary Tab. 1). This is slightly lower (on average) compared to the previously reported $\delta^{66}\text{Zn}$ measurements of fertilizers used in France (+0.19 to +0.42 ‰; Chen et al., 2008). The $\delta^{66}\text{Zn}$ of the two samples collected from leachate of the leaves of Pecan trees in the Rio Grande valley are +0.33 and +0.35 ‰.

No significant correlation is observed between dissolved $\delta^{66}\text{Zn}$ and Zn concentration (Fig. 2). The concentration of dissolved $\delta^{66}\text{Zn}$, however, does decrease slightly with distance from the Rio Grande headwaters (Fig. 3). While there is no correlation of pH with dissolved $\delta^{66}\text{Zn}$ for water samples from the Silverton area, which generally all have lower pH values (3 to 7) and elevated Zn concentrations (0.23 to 70 mg/L), the dissolved $\delta^{66}\text{Zn}$ of the other samples generally decrease with increasing pH (Fig. 4). With the possible exception of the samples collected in the Silverton area, a comparison of the dissolved $\delta^{66}\text{Zn}$ with the $\delta^{34}\text{S}$ of sulfate in the same sample (Fig. 5) does not reveal any correlations.

5. Discussion

The studied stretch of the Rio Grande watershed spans a large area of ~1500 km where environmental conditions (e.g., wet versus dry climate, geology) and anthropogenic impacts (e.g., acid mine drainage, agriculture, urban centers) change significantly. Therefore, the wide range of dissolved $\delta^{66}\text{Zn}$ (-0.57 to +0.41‰) could be the result of a variety of factors, including differences in the isotopic composition of Zn in the primary bedrock, the fractionation of Zn during weathering reactions, the presence of anthropogenic Zn sources, and/or the biogeochemical cycling of Zn. Below we discuss each of these factors and their likely influence on the $\delta^{66}\text{Zn}$ in the Rio Grande watershed.

5.1. Bedrock and Zn isotopes

The majority of lithogenic samples measured to date exhibit relatively small Zn isotope variations, with the majority of $\delta^{66}\text{Zn}$ measurements ranging from +0.2 to +0.4 ‰ (e.g., Wilkinson et al., 2005; Thapalia et al., 2015). Nevertheless, larger variations in $\delta^{66}\text{Zn}$ have been observed locally. For example, carbonates and some shales are enriched in heavy Zn isotopes ($\delta^{66}\text{Zn}$ of +0.8 to +1.3 ‰; Pichat et al., 2003; Weiss et al., 2007; Chen et al., 2008) compared to granite and hydrothermal ore deposits, which show lower $\delta^{66}\text{Zn}$ of -0.6 to +0.3 ‰ (Dolgoplova et al., 2006). The larger variation in $\delta^{66}\text{Zn}$ of magmatic/hydrothermal systems is likely a function of kinetically controlled reactions that result in the incorporation of isotopically light Zn in ore minerals like sphalerite (ZnS , Wilkinson et al., 2005).

Although the bedrock geology does change over the Rio Grande watershed (see Section 2 for more details), these changes do not correspond with a significant change in the $\delta^{66}\text{Zn}$ of stream water. For example, the surface water samples in upstream locations rich in hydrothermal sulfide-rich mineralization, show only slightly higher $\delta^{66}\text{Zn}$ (-0.2 to +0.4 ‰) compared to downstream locations, with more marine and continental sedimentary rocks of Paleozoic/Mesozoic age (-0.6 to +0.2 ‰). Since Zn concentrations are always higher upstream (0.020 to 0.196) compared to downstream locations (<0.043 ppm), the hydrothermal deposits are likely a bigger Zn contributor into this particular aquatic system compared to a smaller input, if any, from sedimentary formations.

The bedrock of the Rio Chama (Locations 17-18) and southern Rio Grande (Locations 30-36) has more carbonate and shale units. However, in these locations the stream $\delta^{66}\text{Zn}$ shows distinctively lower $\delta^{66}\text{Zn}$ of -0.6 to +0.2 ‰ (Tab. 1) compared to the $\delta^{66}\text{Zn}$ of carbonate/shale bedrock reported in previous studies (+0.8 to +1.3 ‰; Weiss et al., 2007; Chen et al., 2008). The comparison of $\delta^{66}\text{Zn}$ with $\delta^{34}\text{S}$ of dissolved sulfate (SO_4) provides further evidence that bedrock is probably not a first order control on $\delta^{66}\text{Zn}$ (Fig. 5). In a previous study, Szyrkiewicz et al. (2015) showed that in the Rio Grande watershed the lower $\delta^{34}\text{S}$ values of riverine SO_4 are reflective of SO_4 contributions from oxidation of hydrothermal and sedimentary sulfides: -8.9 to +2.7 ‰ and -22.3 to -9.5 ‰, respectively (Nordstrom et al., 2007; Cambel and Lueth, 2008; Szyrkiewicz et al., 2015). In contrast, the dissolution of sulfate minerals present in sedimentary formations (+10.9 to +17.7 ‰) leads to considerable increases in riverine $\delta^{34}\text{S}$. Given that $\delta^{66}\text{Zn}$ does not correlate with $\delta^{34}\text{S}$, we infer that on the regional scale the change of bedrock composition from volcanic/hydrothermal- to sedimentary-rich is not a first order factor controlling Zn isotope variations in the Rio Grande system.

Nevertheless, a weak negative correlation ($R^2 = -0.32$; Fig. 5) is observed locally between $\delta^{34}\text{S}$ and $\delta^{66}\text{Zn}$ in the streams of the Silverton area, in southern Colorado (Locations 1 through 10, Fig. 1). This may reflect the initial variation of $\delta^{66}\text{Zn}$ in ore mineralization (e.g., sulfides) present in this area (e.g., Borrok et al., 2009). A similar relationship between $\delta^{34}\text{S}$ and $\delta^{66}\text{Zn}$ was previously observed for the hydrothermal sulfide deposits in Ireland (Wilkinson et al., 2005). Generally, early precipitating sulfide minerals incorporate lighter Zn isotopes leading to increases of $\delta^{66}\text{Zn}$ in hydrothermal fluids (John et al., 2008). Consequently, sulfides precipitating in later stages are characterized by higher $\delta^{66}\text{Zn}$. It should be noted that in our water samples from the Silverton area, the $\delta^{34}\text{S}$ of stream SO_4 is slightly higher (-2.5 to +6.0 ‰) compared to the local sulfide mineralization (-6.9 to +2.5 ‰), suggesting some contribution of SO_4 from dissolution of hydrothermal sulfate minerals (gypsum, anhydrite) with higher $\delta^{34}\text{S}$ of +14.6 to +18.0 ‰ (Nordstrom et al., 2007). Therefore, our results imply that, in addition to potential kinetic Zn isotope fractionations during sulfide ore formation, there might be another process involving preferential uptake of lighter Zn isotopes into sulfate minerals and heavier Zn isotopes into sulfides. Based on our results, however, these fractionations would be relatively small (within 0.2 ‰) and would require further focused investigations to properly quantify.

5.2. Isotopic fractionation of Zn isotopes during weathering

Previous laboratory studies of the oxidative weathering of Zn-rich sulfide minerals (specifically from the Silverton area) have demonstrated that there is no measurable fractionation of Zn isotopes between sulfide mineral phases and the coexisting fluid phase (Fernandez and Borrok, 2008). Although this is true for low pH weathering (e.g., acid rock drainage), it is more likely that at higher pH Zn isotopes will be

fractionated by secondary processes like adsorption (e.g., Matthies et al., 2014; Weiss et al., 2014). These studies suggest, however, that even at higher pH the Zn isotopic composition of the bedrock would generally be reflected in nearby streams. It seems that measured isotope fractionations between bedrock and aqueous Zn are insignificant once the system is in steady state, as opposed to kinetic effects that might occur in the earliest stages (e.g., first few hours) of weathering. This is also true for the water samples in our study. Except for a few samples with low $\delta^{66}\text{Zn}$ of -0.6 to -0.2 ‰ (Locations 15, 29, 30, 31, 36), the majority of the streams show $\delta^{66}\text{Zn}$ of -0.1 to +0.4 ‰, similar to the sulfide mineralization of the Rio Grande headwaters (+0.1 to +0.4 ‰; Borrok et al., 2008) that appeared to be the largest contributor of Zn (See section 5.1 for more details).

5.3. Anthropogenic Zn

Previous studies have shown that the anthropogenic pollution of Zn can lead to decreases in $\delta^{66}\text{Zn}$ in river and lake systems that correspond with increases in Zn concentrations (Chen et al., 2008, 2009; Thapalia et al., 2010, 2015). While anthropogenic Zn associated with high-temperature combustion processes is usually enriched in light isotopes and can be transported substantial distances in the atmosphere, the heavier anthropogenic Zn residue from these and other processes can also enter the hydrologic system if they are in close proximity (e.g., Cloquet et al., 2006; Sonke et al., 2008; Borrok et al., 2010). Roof leaching (at least in some regions), vehicle emissions, and tire wear in urban areas are common sources of anthropogenic Zn with $\delta^{66}\text{Zn}$ values ranging from -0.11 to -0.02 ‰, -0.04 to +0.30 ‰, and -0.10 to +0.14 ‰, respectively (Cloquet et al., 2006; Chen et al., 2008, 2009; Thapalia et al., 2010). Because there is generally a lack of large urban centers in our study area, particularly in the headwaters region of the Rio Grande, where Zn concentrations are the highest (up to 0.196-70 mg/L), it is unlikely that Zn pollution (other than sulfide sources from abandoned mining sites) has a significant effect on the Zn isotopic composition over most of the region. Further downstream the density of population centers (e.g., cities, agricultural irrigation districts) in the Rio Grande Valley increases, with the highest concentrations in southern New Mexico (Loc. 31-36). However, the differences in $\delta^{66}\text{Zn}$ between downstream and upstream Rio Grande are relatively small and the $\delta^{66}\text{Zn}$ varies over a similar range, from -0.57 to +0.14 ‰ and from -0.51 to +0.27 ‰, respectively (Fig. 3). Also, Zn concentrations in downstream locations are very low (<0.045 mg/L) and in some investigated seasons the Zn was below the detection limit (<0.006 mg/L). This is substantially different from most polluted river systems in urban environments with elevated Zn concentrations (Chen et al., 2008, 2009).

In addition to growing urban centers in downstream locations, agriculture is an important user of the Rio Grande surface water for flood irrigation (e.g., Szykiewicz et al., 2015). Some fertilizers are enriched in Zn because Zn is needed for plant growth and development. Nevertheless, the studied

fertilizer samples and leachates from Pecan trees in southern New Mexico have higher $\delta^{66}\text{Zn}$ (-0.06 to +0.35 ‰) compared to the downstream Rio Grande (-0.57 to +0.14 ‰). Therefore, we infer that the agricultural sources likely have an insignificant effect on stream $\delta^{66}\text{Zn}$ in downstream locations.

5.4. Biogeochemical fractionation of Zn isotopes

The concentrations of dissolved Zn in the Rio Grande and other tested streams and groundwater do not correlate well with $\delta^{66}\text{Zn}$ either within individual sample locations or collectively (Fig. 2). However, the samples with the highest concentrations of Zn (up to 70 mg/L), attributable to acid rock drainage in the Silverton area of Colorado, show the smallest variation in $\delta^{66}\text{Zn}$ (+0.24 to +0.40 ‰). As concentrations of Zn decreased (<0.196 mg/L) there is a great deal more variability in $\delta^{66}\text{Zn}$ (-0.56 to +0.41 ‰), suggesting that in situ biogeochemical processes cause changes in Zn concentration. However, a clearer relationship is observed between dissolved $\delta^{66}\text{Zn}$ and pH over the range of ~7.0 to 8.5 (Fig. 4). In this pH range, $\delta^{66}\text{Zn}$ decreases markedly with increasing pH ($R^2 = -0.32$). This indicates that pH exerts an important control on dissolved $\delta^{66}\text{Zn}$ in the studied area.

We propose that the concentration of dissolved Zn decreases with increasing pH because of adsorption onto solid surfaces. The “adsorption edge”, where the extent of adsorption onto environmental surfaces changes most rapidly with pH, occurs for many minerals and solid organic matter (e.g., Pokrovsky et al., 2005; Gèlabert et al., 2006; Viers et al., 2007; Balistrieri et al., 2008; Julliot et al., 2008; Houben et al., 2014; Kafantaris et al., 2014; Bryan et al., 2015), including bacteria (e.g., Kafantaris and Borrok, 2014), over the pH range from ~7 to about 8.5. Except for some hydrous manganese and iron oxides, Zn adsorption on various mineral surfaces has been shown to leave the residual dissolved $\delta^{66}\text{Zn}$ pool depleted in Zn isotopes (by 0.10 to 0.73‰) due to incorporation of heavier Zn isotopes onto adsorbed phases (Pokrovsky et al., 2005; Balistrieri et al., 2008; Juillot et al., 2008). In some cases, however, these Zn isotope fractionations can reach ~3‰ when high ionic strength solutions (e.g., seawater) are present (Bryan et al., 2015). Because of arid climate and past deforestation/overgrazing of the Rio Grande watershed, the sediment loads into the streams are significant, particularly in downstream locations abundant in Paleozoic and Mesozoic sedimentary formations. Although we did not analyze the content and composition of the suspended sediments, the visual observations (i.e., muddy waters that rapidly plugged 0.45µm filters) were indicative of high sediment loads in the investigated seasons. Generally, the $\delta^{66}\text{Zn}$ of dissolved Zn measured for large river systems in North and South America, Europe, Asia and Africa has shown significantly higher values (-0.12 to +0.61 ‰, +0.07 to +0.88 ‰, +0.31 to +0.83 ‰, and +0.04 to +0.31, respectively; Chen et al., 2008; Little et al., 2014a) compared to the studied stretch of the Rio Grande (-0.57 to +0.26 ‰). We suggest that the extremely high sediment

loads into the Rio Grande might intensify the adsorption effect and lead to further decreases in dissolved $\delta^{66}\text{Zn}$.

To a first approximation, the role of adsorption can be evaluated by comparing the measured $\delta^{66}\text{Zn}$ for filtered versus raw (unfiltered but acidified samples). The raw samples were acidified to pH ~ 1.0 with concentrated nitric acid after sampling, such that any Zn adsorbed to solid particles would desorb into solution prior to analysis. Therefore, the Zn concentrations and $\delta^{66}\text{Zn}$ of the raw samples include both dissolved and adsorbed Zn fractions. By comparison of these raw sample values with the measured dissolved Zn concentration and dissolved $\delta^{66}\text{Zn}$, the concentration and isotopic composition of the adsorbed phase can be calculated via mass balance constraints. The mass balance relationship is shown in Eq. 1 and is re-arranged to form Eq. 2:

$$\delta^{66}\text{Zn}_{\text{raw}} = X \cdot \delta^{66}\text{Zn}_{\text{dissolved}} + (1-X) \cdot \delta^{66}\text{Zn}_{\text{adsorbed}} \quad (1)$$

$$\delta^{66}\text{Zn}_{\text{adsorbed}} = (\delta^{66}\text{Zn}_{\text{raw}} - (X \cdot \delta^{66}\text{Zn}_{\text{dissolved}}))/(1-X) \quad (2)$$

where X is a fraction of Zn dissolved determined using Zn concentrations of the filtered and “raw” samples. Our calculations show that the $\Delta^{66}\text{Zn}_{\text{adsorbed-dissolved}}$ ($\delta^{66}\text{Zn}_{\text{adsorbed}} - \delta^{66}\text{Zn}_{\text{dissolved}}$) ranges from -0.15 to +1.04‰ and it does not show any distinctive relationship within the pH range of 7.5 to 9 (Fig. 6). The average $\Delta^{66}\text{Zn}_{\text{adsorbed-dissolved}}$ is +0.31‰ which is generally consistent with the extent of Zn isotope fractionation for adsorption onto many minerals and organic surfaces established in other experimental and empirical studies (e.g., Gélabert et al., 2006; Borrok et al., 2008; John et al., 2007; Wanty et al., 2013; Bryan et al., 2015). There are, however, a variety of complicating factors that could explain inconsistency between field data and previously published results on adsorption. For example, the experimental adsorption studies are based on pure mineral phases and are absent competing dissolved organic ligands. Dissolved metal-organic complexes are important in many natural waters and can be the dominant form of dissolved metals in some systems (e.g., Mantoura et al., 1978; Tipping et al., 2015). These dissolved metal complexes will compete with adsorbed solid-surface complexes for the heavier Zn isotopes (Jovin et al., 2009). Although surface adsorptive processes appear to be the major control for Zn isotope distributions in the Rio Grande system (Fig. 4), the presence of dissolved Zn-organic metal complexes could be the cause for much of the measured variability. Moreover, the mineralogy of the solid phases that comprise the suspended river sediment is likely to be heterogeneous and different Zn isotope effects may be associated with adsorption onto minerals (e.g., clays, iron/aluminum oxides) and solid organic particles such as bacteria. During adsorption some Zn may co-precipitate on the suspended particles, involving different isotope fractionations. Also, the acidification of the raw samples could have released

geologic Zn with higher $\delta^{66}\text{Zn}$ (+0.2 to +0.3‰) that was originally present in the suspended sediment (including Zn associated with the interlayers of clays).

For four samples of the Rio Grande and groundwater with higher pH >8.5, we do not observe a significant relationship between pH and $\delta^{66}\text{Zn}$ (Fig. 4). While at pH < ~8.5 most of the dissolved Zn is present as free Zn^{2+} , at higher pH the dissolved Zn will exhibit different aqueous speciation which usually includes dissolved hydroxide and carbonate species (e.g., $\text{Zn}(\text{OH})^+$, ZnHCO_3^+ , $\text{Zn}(\text{CO}_3)$, $\text{Zn}(\text{OH})_2$) and various organic ligands. These Zn hydroxide and carbonate species are less likely to adsorb onto mineral surfaces relative to Zn^{2+} because of their monovalent or neutral charge. Therefore, at high pH the observed $\delta^{66}\text{Zn}$ in solution and the calculated $\Delta^{66}\text{Zn}_{\text{adsorbed-dissolved}}$ would be affected by the degree of fractionation among coexisting aqueous Zn species.

Additionally, we expect that the higher salinity of the studied streams may be additional factor leading to greater variability of the measured $\delta^{66}\text{Zn}$ compared to some of the adsorption effects measured in laboratory studies (Pokrovsky et al, 2005; Juillot et al., 2008; Balistrieri et al., 2008). Solutions with elevated salinity have been shown to affect dissolved $\delta^{66}\text{Zn}$ (Juillot et al., 2008; Bryan, et al. 2015). For example, we do find relatively weak correlations between decreasing $\delta^{66}\text{Zn}$ and increasing SO_4 , Cl, HCO_3 concentrations for some samples (Fig. 7). This could suggest an isotopic impact due to the speciation of Zn in aqueous solution, as inferred by Bryan et al. (2015). However, our data imply that aqueous Zn speciation has rather minor effect on $\delta^{66}\text{Zn}$ (Fig. 7) compared to more evident pH effect in the studied area (Fig. 4).

5.5. Surface water versus groundwater

For the upstream Rio Grande (Locations 11, 12, 29) and the Red River (Locations 13 through 16) we observe higher $\delta^{66}\text{Zn}$ of +0.15 to +0.41 ‰ and lower pH of 7.78 to 7.91 during the snowmelt (April) compared to lower $\delta^{66}\text{Zn}$ of -0.24 to -0.02 ‰ and higher pH of 8.04 to 8.91 during base-flow conditions (July, August, November) (Fig. 3). Generally, the geochemistry of stream water during base flow conditions is strongly controlled by groundwater and, thus, reflects increased bedrock-water interaction. We suggest that these water-rock interactions might also cause lowering of $\delta^{66}\text{Zn}$ due to increases in pH and increased adsorption of Zn on bedrock mineral and/or organic surfaces. The $\delta^{66}\text{Zn}$ of groundwater in the northern portion of the Rio Grande watershed (Locations 19 through 27; Fig. 1) varies over a relatively narrow range of -0.13 to +0.12 ‰ and these values are comparable to the upstream Rio Grande (Location 11) and Red River (Locations 13-16) during base-flow conditions, -0.24 to -0.02 ‰ (Fig. 3). One exception is the Rio Grande at San Antonio (Location 29), with significantly lower $\delta^{66}\text{Zn}$ in April (-0.54 ‰) compared to November (+0.15 ‰). At San Antonio, during spring, the Rio Grande receives significant loads of suspended sediment from the Rio Puerco tributary, an ephemeral stream draining

semi-arid areas of central New Mexico. In other seasons, the Rio Puerco usually dries out. Therefore, the larger sediment loads from the Rio Puerco to the Rio Grande are particularly typical of April snowmelt compared to smaller loads in November when the stream flows are greatly reduced due to limited precipitation. Consequently, we infer that the lowest $\delta^{66}\text{Zn}$ of -0.56 ‰ observed at San Antonio in April 2010 might also reflect adsorptive processes on this high suspended load.

6. Conclusions

Generally, the Rio Grande is characterized by significantly lower $\delta^{66}\text{Zn}$ compared to previously studied large river systems in North and South America, Europe, Asia and Africa (Chen et al., 2008, 2009; Little et al., 2014). The results of this study show that major aqueous Zn sources are acidic drainage of hydrothermal deposits. Downstream changes in bedrock composition do not have a measurable effect on the dissolved $\delta^{66}\text{Zn}$ in the Rio Grande watershed. Likewise, there appears to be little influence from anthropogenic Zn throughout the study area. Instead, changes of pH appear to exert a significant control on dissolved $\delta^{66}\text{Zn}$. In this study, an increase in pH from ~7.0 to 8.5 correlates with a significant decrease in the dissolved $\delta^{66}\text{Zn}$. The average $\Delta^{66}\text{Zn}_{\text{adsorbed-dissolved}}$ is +0.31‰. We explain this relationship as the result of the preferential adsorption of heavy Zn isotopes on suspended sediments and/or organic matter carried by the studied streams and river. This is in good agreement with the elevated sediment loads in the studied streams, because of a dry climate and long-term deforestation/overgrazing. Additionally, we suggest that the seasonal enrichment of the studied streams in light Zn isotopes might result from groundwater recharge affected by higher Zn adsorption and removal of heavy Zn isotopes during water infiltration and interaction with the bedrock.

In addition to adsorption, other processes might lower the dissolved $\delta^{66}\text{Zn}$ in the studied streams. These include the aqueous speciation of Zn resulting from elevated water salinity and, possibly, coprecipitation of Zn onto the suspended sediments. Future field studies are needed to distinguish between these factors in natural waters and their effect on aqueous $\delta^{66}\text{Zn}$.

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Figure 1. Location map of water sampling points in the Rio Grande watershed.

Figure 2. Variation of dissolved $\delta^{66}\text{Zn}$ compared to Zn concentration. The error bars show 1σ uncertainties calculated from replicate analyses.

Figure 3. Variation of dissolved $\delta^{66}\text{Zn}$ compared to a distance from the Rio Grande headwaters in southern Colorado. Symbols are the same as in Figure 2. The error bars show 1σ uncertainties calculated from replicate analyses.

Figure 4. Variation of dissolved $\delta^{66}\text{Zn}$ compared to pH. The R^2 value of -0.37 ($p=0.003$, $n=22$) was calculated for water samples within the pH range of 7 to 8.5. For comparison, adsorbed $\delta^{66}\text{Zn}$ (calculated from mass balance constraints) versus pH is plotted for selected samples with adsorbed Zn > 25 % of total Zn. Because the uncertainty associated with concentration measurements ($\pm$ about 5%) as well as that for Zn isotope measurements of the dissolved phase is propagated when calculating the isotopic composition of the adsorbed phase, we only chose to look at samples with at least 25% adsorption where we would expect changes large enough to be quantified. Symbols are the same as in Figure 2. The error bars show 1σ uncertainties calculated from replicate analyses. For clarity, the error bars for the calculated adsorbed Zn endmembers are not shown.

Figure 5. Variation of dissolved $\delta^{66}\text{Zn}$ compared to variation of $\delta^{34}\text{S}$ of dissolved sulfate. Symbols are the same as in Figure 2. The error bars show 1σ uncertainties calculated from replicate analyses.

Figure 6. Variation of $\Delta^{66}\text{Zn}_{\text{Adsorbed-Dissolved}}$ compared to pH for samples with adsorbed Zn > 25 % of the total Zn. Symbols are the same as in Figure 2. Error bars are not shown for clarity.

Figure 7. Changes of dissolved $\delta^{66}\text{Zn}$ versus concentration of sulfate (A), chloride (B), and alkalinity (C). Because of high concentration of sulfate (400 to 1400 mg/L), on plot A we did not present the samples collected in Silverton area (Location 1-10) for better clarity. Symbols are the same as in Figure 2. The error bars show 1σ uncertainties calculated from replicate analyses.