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Article

Enhanced Rare Earth Element Mobilization in a Mountain Watershed of the Colorado Mineral Belt with Concomitant Detection in Aquatic Biota: Increasing Climate Change-Driven Degradation to Water Quality

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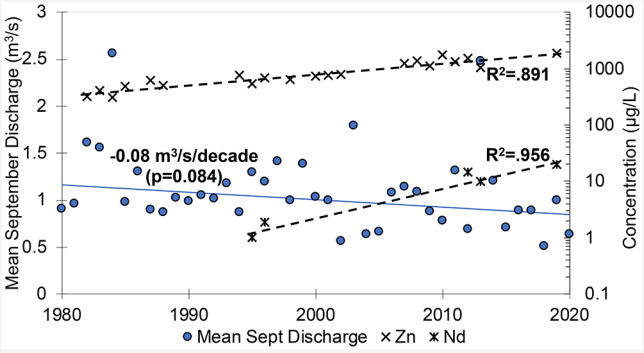
ABSTRACT: In the western USA, one legacy of historic mining is drainage of acidic, metal-rich water generated by exposure to oxygen of sulfide minerals in mine workings, referred to as acid mine drainage (AMD). Streams receiving AMD and natural acid rock drainage (ARD) have a low pH, high dissolved metal concentrations, and extensive streambed oxide deposits. Recently, enhanced ARD generation in the Snake River watershed in the Rocky Mountains has been shown to be associated with warmer summer air temperatures, which has been attributed to expanding weathering fronts that promote oxidation due to earlier drying of shallow soils. In mountain watersheds where complex orogeny disseminated minerals throughout the landscape, weathering processes may also mobilize rare earth elements (REEs). We report that in the Snake River REEs are currently distributed in streams at concentrations ranging from 1 to 100 μg/L. Further, analysis of archived sample indicates that REE increases over time are also associated with increased summer air temperatures. In downstream reaches where the Snake River discharges into a water supply reservoir, colloidal and particulate metal oxides are abundant and sorptive processes may influence REE speciation. We also show that REEs accumulate in benthic invertebrates at concentrations comparable to toxic metals associated with ARD.



KEYWORDS: *Acid Mine Drainage, Acid Rock Drainage, Rare Earth Elements, Water Quality, Climate Change, Ecotoxicity*

INTRODUCTION

In the mountainous regions of the western United States, one legacy of historic mining has been the drainage of acidic, metal-rich water generated by exposure to oxygen of sulfide minerals in mine workings and tailings. Recently, it has been demonstrated that this long-standing water quality challenge of acid mine drainage (AMD) is now potentially compounded by climate-change driven acceleration of natural acid rock drainage (ARD) in high elevation watersheds containing hydrothermally altered, pyritized bedrock where little or no mining has occurred.[1] This acceleration of natural ARD is an important consideration in the establishment of environmental baselines related to cleanup efforts at nearby mine sites, which can involve bulkheading and/or direct treatment of drainage from adits of abandoned mines.[2−4] Streams receiving AMD/ARD typically have a low pH, high dissolved metal concentrations, and extensive deposition of hydrous iron and aluminum oxides on the streambed. These stream conditions greatly impact aquatic ecosystem health, typically preventing the establishment of sustainable fish populations.[6] In addition to impacts on receiving streams, this AMD/ARD can constrain the potential use as a potable water supply and for commercial snowmaking.[6]

The observed increasing concentrations of natural ARD solutes, primarily SO_4 and Zn, occurred in the summer and have been shown to be associated with warmer summer temperatures independent of decreasing summer stream flows.[1,4] Because natural ARD production and transport are influenced by subsurface flow of oxygen and water, this observation has led to the interpretation that more extensive summertime drying of tailings piles, shallow soils, and talus fields has lowered the water table. This expansion of the vadose zone has exposed a fresh weathering front that generates elevated concentrations of sulfate and metals in these high elevation watersheds.[7] Shifts in climate affecting the hydro-

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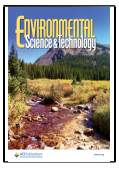

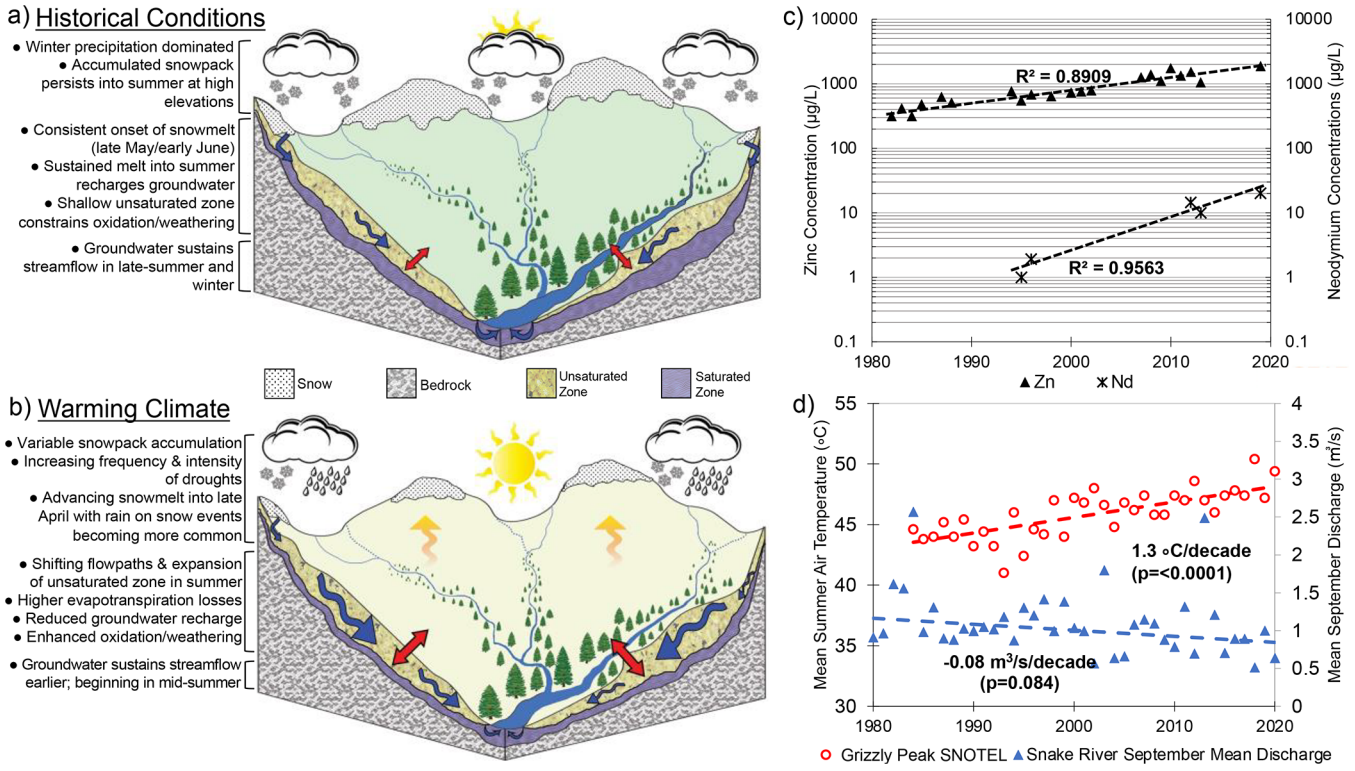

Figure 1. Conceptual diagram of the (a) historical conditions in the Snake River Watershed and transition toward a (b) warming climate. Key processes and rates are identified as well as arrows representing important fluxes of water, energy, and gases that influence weathering rates; infiltration and downslope water movement (blue), oxygen exchange between the atmosphere and unsaturated zone (red), and drying of the landscape via evapotranspiration (orange). Supporting observations at site SN-2 in September during baseflow of (c) Zn and Nd concentrations between 1984 and 2019 with a fitted exponential regression line, and (d) statistically significant trends from a Mann-Kendall Test showing an increasing mean summer air temperatures at nearby Grizzly Peak SNOTEL site and decreasing means flows in September measured at the Keystone USGS gauge.

logical regime in the Rocky Mountains in particular have exacerbated this problem,[8] as the earlier onset of snowmelt and more frequent summer drought conditions are prolonging the period of baseflow when pH conditions are lowest and solute concentrations are correspondingly at their highest.[9] These trends can be difficult to resolve at a regional scale because of limited monitoring of such sites, shifting seasonal flow paths, and extensive remediation efforts that have undetermined influences on water quality.[10]

The primary focus on the water quality challenges of AMD/ARD has been on trace metals that are known toxicants for stream and terrestrial ecosystems and may limit domestic usages, such as Zn, Cd, and Pb.[11−13] However, in watersheds where complex orogeny has disseminated minerals and ore bodies throughout the landscape, the acidity and low pH conditions from sulfide weathering may additionally disassociate other trace elements present in the country rock. As such, rare earth elements (REEs) are another class of mobilized solutes that may be associated with primary weathering of sulfidic minerals.[14,15] Given that the concentrations of REEs are expected to be lower in concentration due to their more diffuse geological presence and REE concentrations in major rivers are largely in the ng/L range of concentration,[16] it is not surprising that the dominant processes controlling the environmental fate and transport of REEs have received much less study than those for trace metals. In addition, REEs are not typically included in water quality monitoring programs and toxicity standards do not exist. However, the expanding use of REEs in modern industry and technologies is raising awareness of the potential risks of greater anthropogenic inputs of REEs into surface waters.[17,18] In this context, evaluation of the relative aqueous distribution of this series of 17 elements can be used to diagnose the geochemical signatures imparted by different sources and processes occurring along subsurface flow paths at synoptic scales. These geochemical signatures may reflect changing redox conditions, competitive interactions, and fractionation anomalies of insoluble species.[19−21] Furthermore, there is potentially an opportunity to apply the large body of knowledge on the biogeochemistry of the more commonly studied trace metals to the study of processes controlling the environmental mobility of REEs. For example, photochemical processes involving iron oxides have been found to be drivers not only for diel changes in dissolved iron concentrations but also for solutes that are sorbed onto oxide surfaces, such as copper, phosphate, and dissolved organic matter (DOM).[22−24]

The study presented here examines the distribution of REEs in a high elevation mineralized watershed in the Rocky Mountains, the Snake River watershed in Summit County CO, USA. This watershed is where climate-driven acceleration of ARD has been documented in a 30-year data set of streamwater chemistry,[1] and significant trends have continued in summer warming as well as in decreasing September mean flows (Figure 1d). These changes are potentially concerning, because this watershed flows into a reservoir that is a major water supply to the Denver metropolitan area. The conceptual diagram of Figure 1 highlights how the transition in the Snake River from (a) historical conditions to the (b) warming climate

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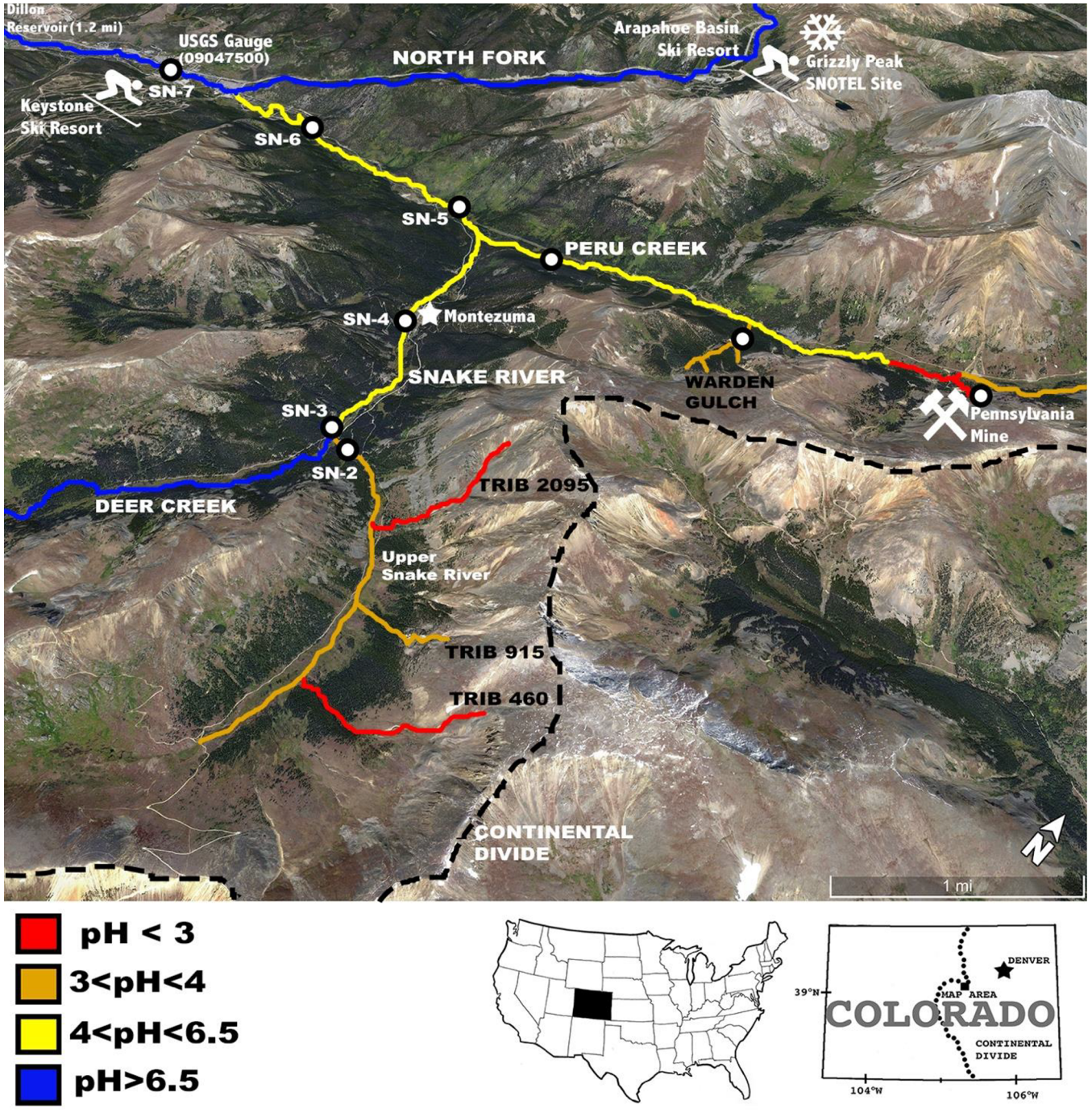

Figure 2. Map of the Snake River Watershed highlighting color-coded baseflow pH conditions, major tributaries contributing REEs, study sites, and other locations of interest. Sources: U.S. Geological Survey The National Map & National Hydrography Data set (NHD).

might be responsible for these observed trends. Further, given regional changes in climate (Figure S1) and their implicit influence on hydrology and key weathering processes, we hypothesize that the scenarios that are drivers for the observed pattern of exponentially increasing Zn concentrations during baseflow conditions (Figure 1b,c) may also be driving changes in REE concentrations. One objective of the study presented here was to evaluate REE concentrations and loadings in this watershed; we documented a concentration range of 1−100 μg/L, several orders of magnitude higher than typical for surface waters, with the highest concentrations in the headwaters and areas receiving drainage from abandoned mine workings. A second objective was to evaluate the coupling of long-term changes in REE concentrations to rising mean annual summer temperatures (MAST) (Figure 1d). Two additional objectives were to determine the downstream changes in the distribution of REEs among particulate, colloidal, and dissolved phases and the uptake of REEs by benthic macroinvertebrates (Table 1b), the toxicological effects of which are unknown.[25−27]

SITE DESCRIPTION

The Snake River watershed, located at an elevation between 2748 and 3689 m in Summit County, CO, USA is composed

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of a series of nested basins and drainages adjacent to the western boundary of the Continental Divide (Figure 2). Within the Colorado Mineral Belt, portions of the watershed were mined from 1860 through the 1940s, although this activity was largely confined to the Montezuma Mining District.[28] Comprehensive geological surveys noted both disseminated and vein deposits throughout the area, underlain by hydrothermally altered crystalline bedrock and abundant in sulfide minerals.[28,29] As such, the regional mineralogy supports mining and generates AMD and natural ARD, which contribute to the acidic conditions observed through the Snake River Watershed (Figure 2) The hydrology of the watershed is largely snowpack-driven because the surrounding high alpine slopes accumulate significant winter precipitation, which melts in the spring to produce peaks flows supplied by surficial runoff.[30] Groundwater recharge occurs through infiltrating shallow soils and percolating through bedrock fracture zones, which sustains baseflow.[31,32] As first noted by Theobald,[33] the oxidation of disseminated pyrite and weathering of schists and gneisses contribute both acidity and dissolved metals to the upper Snake River as ARD. While there are no abandoned mines in upper Snake River, there are a few mines at high elevation in the neighboring Deer Creek, a stream of equal flow.[34,35] The Deer Creek basin is underlain by basic, carbonate-bearing rocks, which generates alkaline waters and buffers acidity.[31,36]

Below the confluence with Deer Creek, the stream chemistry changes dramatically.[22] The pH increases from ∼3−4 to ∼5.5, and extensive hydrous iron and aluminum oxide precipitates cover the streambed, such that the stream biota are quite sparse.[37] The next major tributary to the Snake River is Peru Creek, where several notable abandoned mines are important sources of AMD to the stream.[38] Hydrous iron or aluminum oxides are abundant on the streambed and adjacent wetlands in several reaches of Peru Creek, especially below the inflows from the Shoe Basin, Pennsylvania and Jumbo Mines and Warden Gulch.[39] Below the confluence with Peru Creek, a deposit of hydrous aluminum oxide is commonly observed on the streambed of the Snake River.[40] Further downstream, the North Fork of the Snake River is a pristine inflow that dilutes these acidic conditions. However, loadings of metals such as zinc from these AMD/ARD sources remain in the Snake River at high concentration, presenting a continuing downstream water quality impairment that has proven acutely toxic to fish populations.[5] Below the Keystone Ski Resort where a USGS gauging station is co-located (09047500), the Snake River flows into the eastern end of Dillon Reservoir, which serves as a major storage reservoir and water supply for the metropolitan Denver area.

The benthic macroinvertebrates in the ARD impacted stream reaches in the Snake River and Peru Creek are primarily stoneflies and chironomids.[37] The dominant stonefly, *Zapada haysi*, is in the shredder functional feeding group, consuming leaf litter entering the stream from the willows in valley bottoms. This stonefly is common in AMD/ARD impacted streams throughout the region.[41] In addition to the macroinvertebrates, the biota of the upper Snake River comprises a liverwort and diatoms in the periphyton which are characteristic of acidic, metal-contaminated streams.[37] The biota in Deer Creek are typical of a pristine mountain stream, including baetid mayflies.[37] The stream biota in Peru Creek are sparse, reflecting the extensive covering of the streambed by Fe and Al oxides.

MATERIALS AND METHODS

The collection of samples for data from 2012, 2014, 2017, and 2019[25,26,42,27,43] followed standards and methodologies for analyzing trace metals in surface waters as described in EPA Method 200.8.[44] Prior to collection, HDPE bottles were bathed in a reagent-grade 5% nitric acid bath, tripled rinsed with DI, and dried. Samples were filtered with 0.45 μm nylon Nuclepore filters, acidified with trace-metal-grade (TMG) nitric acid to a pH value near 1.5, and kept chilled. Samples were analyzed for trace element and REE concentration by the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado-Boulder by inductively coupled plasma mass spectrometry (ICP-MS) analysis on a Varian Model X.[45] To obtain historical data, selected archived water samples from prior studies of the Snake River that are stored at INSTAAR[1] were analyzed at LEGS. Samples from site SN-2 were chosen because they are among the oldest and this site was most frequently sampled during September baseflow conditions. Recent samples collected in 2019 from Warden Gulch,[43] site SN-2 and in Dillon Reservoir were analyzed by the University of Southern Mississippi Center for Trace Analysis (CETA) using high resolution inductively coupled plasma-mass spectrometer (HR-ICP-MS).

As shown in Table S5, 2012 was the lowest flow year on record. To calculate solute loadings from samples collected throughout the Snake River in 2014, discharge measurements were made at the time of sample collection with a model 6205 Pygmy Meter and the USGS Midsection method.[46] These data were used to calculate solute loadings, by multiplying concentration (μg/L) by volume per unit time (L/sec); these were then extrapolated (kg/day). Stream transects were chosen based upon morphology and location of previous measurements.[6,9,25,33,47] Supplemental streamflow data from the Snake River gauge at Keystone (#09047500) available via the USGS National Water Information System web interface were used to calculate loadings from a sampling at that site in early June. This sampling coincided with a major rain-on-snow event that rendered the third highest peak flow recorded over its 77-year record (Table S5).

For evaluating the influence of colloids in REE transport,[42] metal and REEs were measured in unfiltered samples and in 10 μm and 0.45 μm filtrate samples from each sampling site. An initial 250 mL sample was collected, and a 60 mL aliquot was used for analysis of total constituents. Then 190 mL was filtered through a paper 10 μm Whatman filter, and 60 mL of that filtrate was used to represent colloidal and dissolved phases. The remaining 130 mL was filtered through a 0.45 μm nuclepore filter and analyzed as the dissolved + fine colloid phase. The particulate phase was determined as the difference between the unfiltered samples and the 10 μm filtrate concentration. The coarse colloidal (0.45 μm < 10 μm) concentrations were determined as the difference between 10 μm filtrate concentration and the fine colloidal + dissolved concentration (<0.45 μm).[48] Field blanks were prepared using identical bottles and procedure to quantify any sources of contamination or error. For concentration of trace metal and REE present in biomass, benthic macroinvertebrates were collected using a Surber sampler at 13 sites on 2 dates.[27,49] Macroinvertebrates picked from the samples were placed in a zip-top bag, frozen immediately on dry ice, stored in a −10 °C freezer and then freeze-dried. The dried invertebrates were separated from any detritus and the dry mass of each sample

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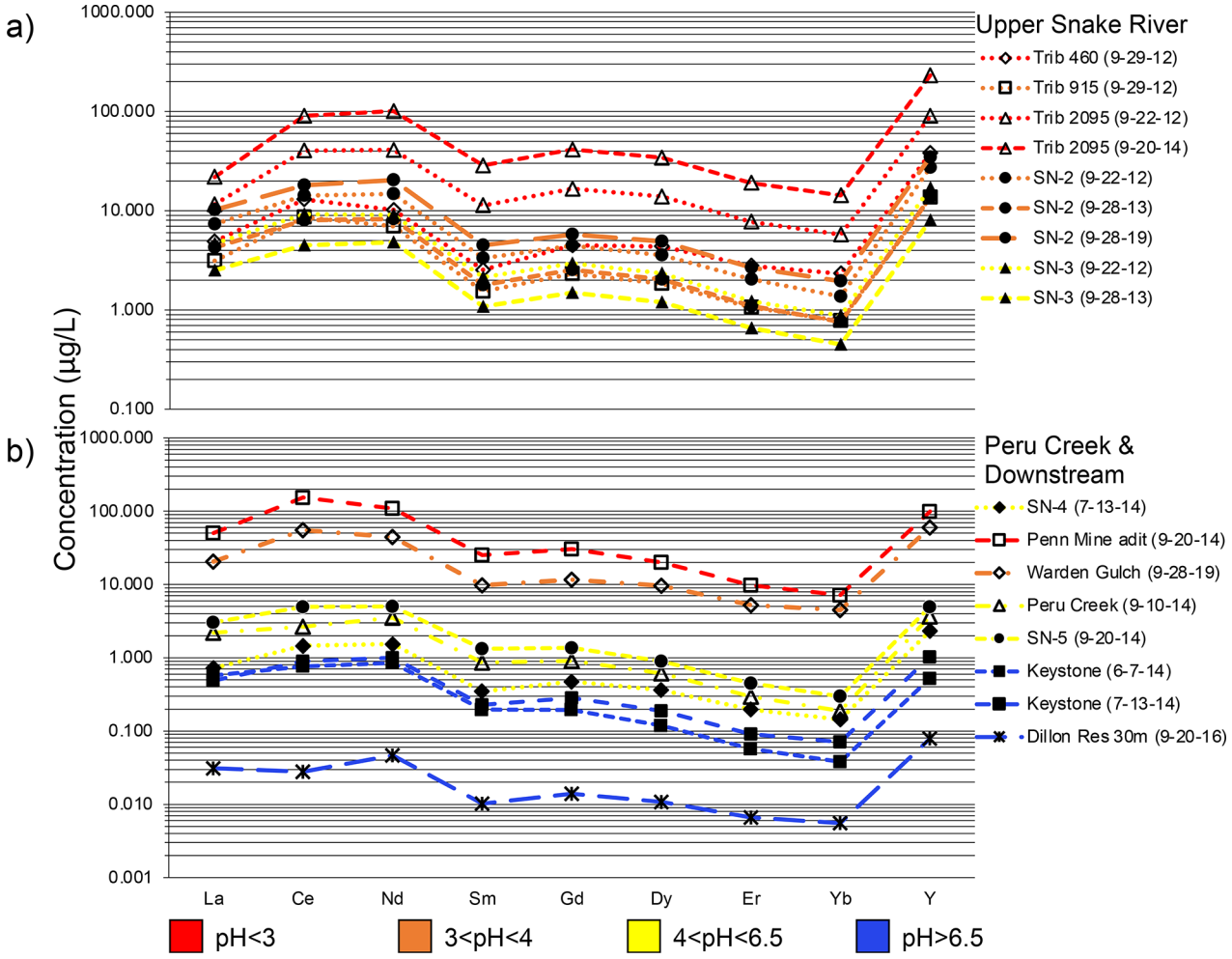

Figure 3. Distribution of dissolved concentrations of nine Rare Earth Elements (La, Ce, Nd, Sm, Gd, Dy, Er, Yb, Y) in (a) Upper Snake River (b) Peru Creek and Downstream. Sites are color-coded by pH conditions, with open symbols representing tributaries and solid symbols the main stem of Snake River.

was recorded. Due to the low mass, some samples taken on different days from the same site were combined. Per EPA Method 3052,[50] combined samples were then digested in a PerkinElmer Multiwave 3000 microwave digestor with Fisher Scientific TMG nitric acid. The digested macroinvertebrate samples were analyzed for cations, metals and REEs using ICP-MS by the LEGS laboratory. On the basis of a duplicate analysis, the maximum percent error for the macroinvertebrate sample was 11.11% (lutetium), with an average error of 2.01%. Because the error values were consistently low, metal concentrations are reported without adjustments for error.

Trends in climate, hydrology, and geochemistry data were assessed using a nonparametric Mann-Kendall test and were statistically significant if p-values were <0.10 to support rejecting the null hypothesis of no trend (Table S6).[51] To assess the correlation of observed concentrations of Zn and Nd, as related constitutes to weathering processes, as well as to MAST in terms of driving reaction kinetics and weathering front area, Pearson Correlation tests were performed and deemed statistically significant if p-values were <0.05 (Table S6).[52−54]

RESULTS AND DISCUSSION

REEs in Snake River Watershed: Concentration and Distribution. The September synoptic sampling campaign in 2012 occurred during a drought which had the lowest flows on record. At that time, the highest concentrations of REEs in the upper Snake River, in the range of 6−40 μg/L, occurred in one of the acidic, headwater tributaries (Trib 2095), which is not impacted by historic mining activity (Figure 3a, Table S1). In the other acidic nonmine impacted tributaries (Tribs 460 and 915) and at the SN-2 site above the confluence with Deer Creek, the REE concentrations were about 2-fold lower and similar patterns in relative REE distribution were observed. Two years later, in the summer of 2014, the REE concentrations in Trib 2095 were about 2-fold higher than in 2012 (Figure 3a).

In the Peru Creek watershed, during the summer of 2014, the acidic drainage from the abandoned Pennsylvania Mine had REE concentrations that were the highest observed, with Nd concentrations at 108 μg/L for example. Furthermore, in 2014, the REE concentrations at the Peru Creek site near the confluence with the Snake River were in the range of 0.1 to 3.5 μg/L, slightly lower than those at the SN-2 site in 2012 (Figure 3b, Table S1). In 2019, the REE concentrations in the acidic Warden Gulch tributary to Peru Creek were comparable to those in Trib 2095 during the 2012 drought. There was also a shift in the distribution of certain REEs, showing a low depletion of cerium in areas associated with inflows from mine workings (Penn Mine, Warden Gulch) as well as acidic

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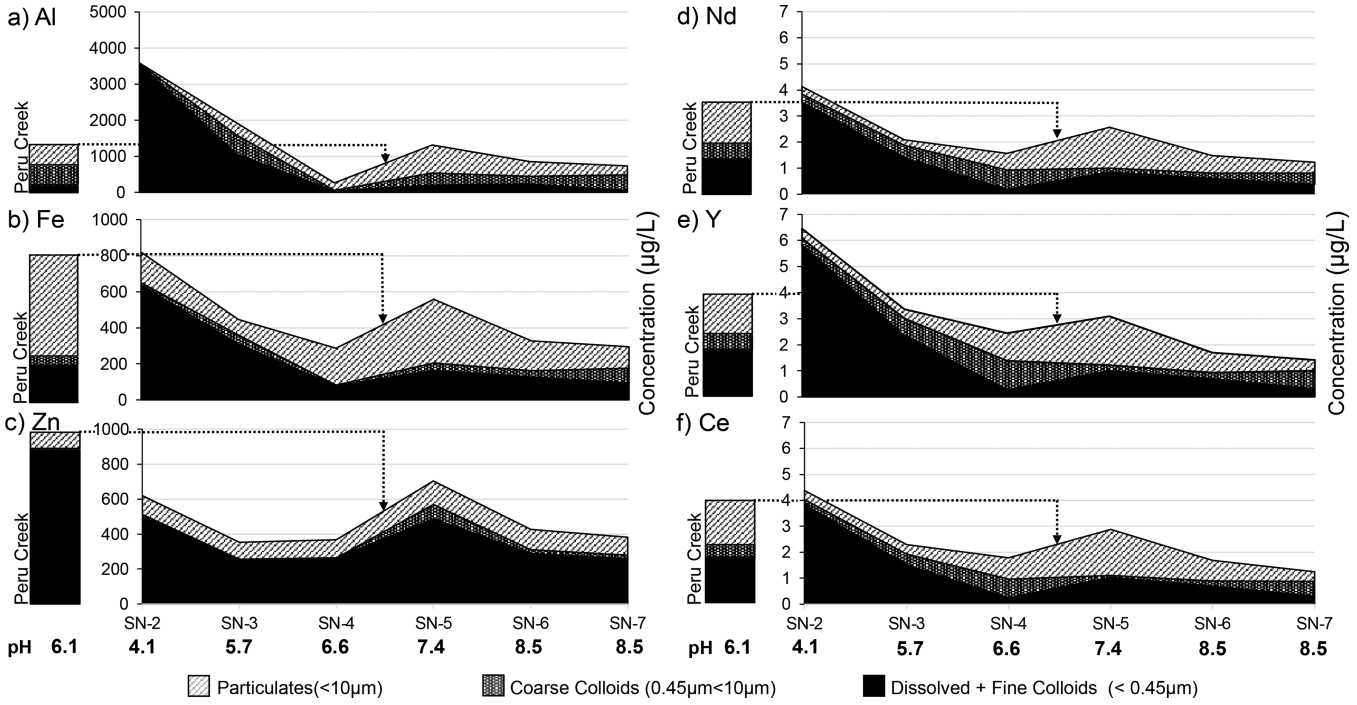

Figure 4. Downstream longitudinal fractional transport of (a) aluminum (b) iron (c) zinc (d) neodymium (e) ytrium (f) cerium into dissolved and fine colloids, coarse colloids, particulate phases, and relative contributions by Peru Creek inflow as well as observed pH conditions during early-June 2015 peak flow conditions.

condition, and increasing cerium depletion appearing related to rising pH (Table S4). These concentrations at the stream and mine sites in the Snake River watershed were 2 to 3 orders of magnitude higher that the concentrations of REEs that were observed in a sample from Dillon Reservoir at a depth of 30 m near the inflow from the Snake River, which was also collected in late August.[52]

Changes in the relative distribution of REEs from their source to downstream sites can be indicative of processes controlling transport.[19,20] Contrary to the other lanthanides, which form trivalent (3+) ions, europium and cerium have additional valences (Eu^{2+}, Eu^{3+}, Ce^{3+}, Ce^{4+}). In the case of cerium, under oxidizing conditions Ce^{3+} becomes relatively insoluble and its depletion leads to a negative cerium anomaly. The development of these anomalies can provide information regarding redox conditions occurring along flow paths.[19] These anomalies can be promoted by sorption onto the freshly precipitated Al and Fe oxides as well as by complexation with colloids,[55,56] but these can also be influenced by pH conditions, high concentrations of iron, and dissolved organic matter (DOM).[57−59] For the Snake River, negative cerium anomalies occur at downstream sites at increasing distances from the sources in the tributaries of the upper Snake (0.575−0.7) River and in Peru Creek (Penn Mine: 0.822, Warden Gulch: 0.734) (Table S4), suggesting rising pH and metal speciation selectively remove Ce^{3+} from solution.[21] Given that the negative Ce anomaly in Dillon Reservoir (0.389) is much more pronounced than upstream Snake River sites (Table S4, Figure S2), this depletion could be attributed to both more complete Ce^{3+} oxidation during transit and further Ce^{4+} scavenging by iron, aluminum, and manganese oxides present in nearshore sediments and in those being deposited at the mouth of the Snake River.[58,59]

Long-Term Trends in Climate, Hydrology, Zn, and REEs in Snake River. In Figure 1c, the concentrations of Nd in archived and recent September samples collected in September from the SN-2 site are compared with the well-documented trend of increasing Zn concentrations at the same site, which was first reported by Todd et al.[1] The more recent data for Zn shows that this increasing trend has continued since the occurrence of a record drought in 2012 with a significant relationship between year and Zn concentration (320 μg/L per decade, $p < 0.0001$) (Table S6). While the data for the September Nd concentrations are sparse, the Nd concentrations have increased about an order of magnitude (Table S2) and the relationship between year and Nd concentration is also significant (7.8 μg/L per decade, p = 0.083) (Table S6). Furthermore, a ratio of Nd/Zn of 1:68 has persisted since the 1990s (r = 0.991, p = 0.0005). The long-term trend in Nd concentrations is matched by order of magnitude increases in Ce and Y as well (Table S2). It is important to note that the concentrations from September 1995 and 1996 for Nd, Y and Ce are in the same range of 1−4 μg/L as those in archived samples from other months of the year (Table S3). Furthermore, the relative concentrations of the REEs to Zn were similar in the 1990s as in the recent samples, consistent with the same dominant ARD sources.

Figure 1d presents significant trends in mean annual summer temperature (MAST) of 1.3 °C/decade ($p < 0.0001$) at the nearby Grizzly Peak SNOTEL station (Figure 1d), which also agreed with significant warming observed at other local SNOTEL sites (Figure S1).[1] There appears to be a concomitant decrease of 0.08 m^3/s (p = 0.084) in mean September streamflow per decade at the Keystone gauge near the outlet of the Snake River to Dillon Reservoir. This streamflow trend, which was reported as not significant in 2011[1] prior to the record 2012 drought, highlights the declining recharge of groundwater that sustains baseflow conditions. The Pearson correlation between Zn and Nd concentrations with MAST are both highly significant (r =

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Table 1. Daily Loading for Major ARD Trace Metals and Dry Biomass of Benthic Macroinvertebrates[a]

a) Daily Loadings (kg/day) Location/Flow/Date	Fe	Al	Zn	Nd	Pb	Cd	La	∑REE
SN-2 − 0.57 m^3/s - 7/13/14	49.9	226.0	27.9	0.25	0.03	0.09	0.13	1.28
SN-3 − 0.94 m^3/s - 7/13/14	48.8	138.5	25.0	0.22	0.16	0.11	0.11	1.11
Peru Creek - 2.69 m^3/s - 7/13/14	125.2	331.9	195.7	1.25	1.85	0.90	0.76	5.70
Keystone gauge - 4.92 m^3/s - 7/13/14	79.6	158.1	67.2	0.42	0.51	0.30	0.21	1.75
Keystone gauge - 15.17 m^3/s - 6/7/14	255.6	375.6	242.7	1.11	3.63	0.72	0.76	4.17

b) Benthic Macroinvertebrate Biomass (nmol/g) Location & Date	Zn	Pb	Cd	Nd	Y	Ce	La	∑REE
SN-3 - 7/14 and 7/24/17	4634	112	17.5	43.3	68.0	51.0	34.1	257.3
SN-4 - 7/17/2017	3656	97	10.5	33.2	56.1	31.2	14.2	185.8
Peru Creek -7/20/2017	6883	66	4.8	19.0	25.6	25.0	13.0	111.6

[a](a) Estimates of Snake River daily loading of iron (Fe), aluminum (Al), zinc (Zn), neodymium (Nd), lead (Pb), cadmium (Cd), and lanthanum (La), and REE sum total calculated from samples and flows measured during collection in cubic meters/second (m^3/s) at sites SN-2, SN-3, Peru Creek, and the USGS Streamgauge (09047500) data from Keystone during recession of high flow conditions (7/13/14) and a record spring rain-on-snow event (6/7/14); (b) Concentrations of zinc (Zn), lead (Pb), cadmium (Cd), REEs neodymium (cd), ytrium (Y), cerium (Ce), lanthanum (La), and ∑REE in nmol/g dry biomass of benthic macroinvertebrate present at sites SN-3, SN-4, and Peru Creek in July 2017.

0.632, p = 0.00004 for Zn and r = 0.841, p = 0.037 for Nd). Overall, this analysis supports the role of warmer summer temperatures driving a cascade of changes, e.g., drier soil conditions, lowering the water table and exposing sulfidic minerals to oxic conditions, that result in increasing concentrations of Zn and REEs. The comparison with the long-term trend in Zn, for which the historical data are more extensive, raises the prospect of continuing acceleration of fluxes of REEs in headwater streams in mineralized watersheds associated with warming summer conditions driven by climate change.

Fractionation of REEs Among Dissolved, Colloidal, and Particulate Phases. In studies of AMD and ARD, pH has been considered the master variable influencing the biogeochemistry of trace metals and natural organic material.[61,62] In the Snake River watershed, the pH values generally increase from as low as less than 3 at the SN-2 site and upstream tributaries to above neutral pH at the outlet to Dillon Reservoir (Figure 2). Associated with this pH increase is an increase in particulate and colloidal Fe and Al oxides and in streambed oxide deposits, which in turn could exert controls on the speciation and transport of REEs.[63] In Figure 4, the downstream patterns of distribution of these phases are examined for (a) aluminum, (b) iron, (c) zinc, (d) neodymium, (e) yttrium, and (f) cerium. The overall patterns found for both light (LREE: Ce, Nd) and heavy rare earth elements (HREE: Y) appeared similar.[42] These results clearly show that under the acidic conditions of the upper Snake River the dissolved + fine colloids phase of Al, Fe, and REEs were dominant. As pH value rose to 6.6 at the SN-4 site, Al concentrations greatly decreased and the remaining Al was present in the particulate phase. Similarly, at this site the Fe concentrations decreased with the particulate phase most abundant. In contrast, while both REE and Zn concentrations decreased at the SN-4 site, the coarse colloidal phase was more abundant than the particulate phase for REEs and the dissolved + fine colloid phase was most abundant for Zn. Similar to the SN-4 site, at the Peru Creek site with a pH of 6.1, both Al and Fe were present predominantly in the particulate and coarse colloidal phases, however the dissolved + fine colloids phase for Fe was a greater proportion than for Al. At this site, the dissolved + fine colloids phrase of REEs were more prevalent than at the SN-4 site, while Zn was predominantly in the dissolved + fine colloidal phase at a higher concentration than at the SN-2 site. With the increasing pH values of 7.4 to 8.5 at the downstream sites (SN-5 to SN-7) Al, Fe, and REEs fractionated more toward particulate and coarse colloidal phases, whereas Zn remained predominately in the dissolved + fine colloid phase and displayed relative intransigence to rising pH.

The similar relative distribution among phases for Fe and REEs at the downstream sites suggest that sorption to Fe oxides may influence the transport of the REEs in this stream system more so than sorption to Al oxides,[21,64] even though Al oxide-based minerals such as basaluminite have also been shown to effectively scavenge REEs.[65] The rising pH conditions at the downstream sites are associated with increased acid neutralizing capacity (ANC) from the inflow of the pristine North Fork.[31,66] Both competitive interactions with other complexing ligands such as carbonate and surface adsorption to oxides have the potential to fractionate REEs to be more enriched in heavy REEs (HREE).[20,21] Nonetheless, a pattern of HREE enrichment is not evident for the sample at the furthest downstream sites in the Snake River in the 2012 study or in the 2016 sample from Dillon Reservoir (Figure 3, Table S1). One explanation may be that there is ongoing dissolution and precipitation reactions controlling Fe oxides associated with photochemical processes, such as production of hydrogen peroxide from photolysis of DOM.[67] These processes could in turn maintain some portion of Fe and REEs in the dissolved phase and thus enhance transport, as well as potential bioavailability. Overall, the persistence of REE concentrations in the μg/L range at downstream reaches suggest some constraints on the role of sorption in driving removal of REEs from the stream system and that stabilizing ligands, such as carbonate DOM, and photochemical processes involving iron colloids may enhance REE transport.[20,26,42]

Calculated Loadings of REEs in the Snake River Watershed. The sampling campaign completed in July of 2014 occurred during the falling limb of the snowmelt pulse, when streamflow was measured concurrently with dissolved concentrations of trace metals and REEs. A single sample was also collected earlier on 6/7/14 from the Keystone gauge following recession of the third highest flow event on record (Table S5) from a major rain-on-snow event that subsequently washed out the road above the Snake River confluence with Peru Creek. The daily loadings calculated from these data are shown for the major ARD trace metals, Fe, Al and Zn, and for

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Nd, Pb, and Cd in Table 1a. These calculations show that at the upper Snake River site (SN-2), which is below the inflows from the acidic tributaries, the daily loading for Nd was only 2 orders of magnitude lower than the daily loading for Zn and also greater than daily loading for Pb and Cd. The daily loadings calculated from Nd concentrations are representative of those for the other REEs (Table S1). At the site immediately downstream (SN-3) of the confluence with Deer Creek, the daily loading of both Zn and Nd were essentially unchanged. In contrast to Nd and Zn, the daily loading for Al was greatly reduced, which reflects the precipitation of hydrous Al oxides in the confluence.[22] This stability of the daily loading through this confluence suggests that Nd may exhibit comparably conservative behavior similar to Zn under some acidic conditions, with limited sorption of Nd and other REEs onto Al oxides.[21,63]

At the Peru Creek site just above the confluence with the main stem of the Snake River, the daily loading for Nd is 5-fold higher than at the upper Snake River sites. Similarly, the Nd daily loading is 2 orders of magnitude lower than the daily loading for Zn and comparable to the daily loadings for Pb and Cd. However, further downstream at the Keystone gauge site, which is well below the inflow of the pristine North Fork, the daily loadings of the trace metals and the REEs were less than a third of the combined daily loadings from the upper Snake River and Peru Creek. This instream loss over the more extensive stream reach of the lower Snake River suggests potential removal at the higher pH values through sorption onto precipitating Fe and Al oxides on the streambed and those present in hyporheic zone sediments.[60] Comparatively, loadings at the Keystone gauge in early June, highlight how such extreme high flow conditions may contribute additional sources of these solutes to dramatically increase loadings over a short period.

REEs in Benthic Macroinvertebrate Biomass. Benthic macroinvertebrates have been identified as useful bioindicators of REE contamination.[68−70] Given that the dominant macroinvertebrate in these streams, *Zapada haysii*, is common at ARD streams throughout the Colorado Rocky Mountains,[41] this species is likely to be tolerant of low pH, trace metals and REEs. Even so, the Zn content in the macroinvertebrate biomass at the ARD impacted sites was in the range of that observed in macroinvertebrates exposed to low level metal contamination.[71] The Zn content was also generally much higher than the REE content, as well as the Pb and Cd content. As shown for Nd, Y, Ce, and La, the contents of individual REEs in the biomass of the macroinvertebrates were in the range of 10−70 nmol/g dry mass. These REE contents are generally an order of magnitude greater than values reported in the limited studies of pristine and human-impacted streams.[70,72] In addition, the Nd contents were about 5-fold higher than found in the tissue of a marine mussel experimentally exposed to 40 μg/L of Nd for a 4-week period.[73] Further, the REE contents were intermediate between the contents for Pb and Cd, both of which are recognized trace metal toxicants for aquatic biota.[74] These comparable contents of REEs and Pb and Cd are not surprising given that the REE concentrations are well within the continuous exposure toxicity thresholds of Pb and Cd which can cause ecological impairment at concentrations as low as 2.5 and 0.72 μg/L.[72] It is also notable that the total REE content of the invertebrate biomass was in the range of 250−100 nmol/g. These values are close to an order of magnitude higher than the mean value of 33 nmol/g reported for benthic invertebrates from the shore of a pristine subarctic lake,[68] although a wide range in total REE content was observed in that study.

Although the biological mechanisms for tolerance to REEs are not well-known, potential mechanisms are surface adsorption of the carapace of macroinvertebrates[68] and sequestering of REEs in metallothionein proteins.[71] In this context, for the headwater streams where natural ARD has been occurring for millennia, the potential impact of increasing REE concentrations may be limited for lower trophic levels. At higher trophic levels, the exclusion of trout populations has already occurred in the upper Snake River due to the increased Zn concentrations and decreased pH.[5] However, for downstream reaches with higher pH values and lower Zn concentrations, the contributions of REEs from natural ARD and AMD may be a concern for current trout populations or for reestablishment of trout populations.[75]

Including REEs in Water Quality and Aquatic Life Monitoring Programs. As REEs are now appearing in surface waters at increasing concentrations due to their usage in advanced technologies, REEs are becoming recognized as concerns for impairment to drinking water source waters. In Germany for example, lanthanides have been observed in tap water at concentrations to warrant designation as an "emerging contaminant".[76−78] Positive Gd anomalies have also appeared in the effluent of wastewater treatment plants, which can be measured well downstream of discharge points, proving an effective tracer for urban inputs to natural waters[79] and underlining the persistence and potential reactivity of REEs in aquatic environments for reuse.[80] There is also increasing evidence of the ecotoxicity of lanthanides to biota as well as their bioaccumulation in aquatic foodwebs.[70,72,81] Thus, the findings presented here that mountain watersheds experiencing the effects of climate change, such as the Snake River, are contributing to increasing concentrations of REEs represents an additional potential concern for both aquatic ecosystems and the water quality for drinking water sources. Yet no drinking water quality standards exist for REEs. One of the few studies focused on the human health-related impacts of REE consumption suggested an admissible drinking water concentration of 2 ppb for Sc, Y, La, Ce, Tb, and Yb.[82] Similarly, many questions remain regarding exposure threshold for impacts to aquatic life[83] and no standards have been developed.

Remediating ARD and AMD Via Recovery of REEs. By better understanding the fate and transport of REEs in natural systems as well the processes governing their mobility, we may consider applying this practical knowledge toward supporting the treatment of AMD and ARD through REE resource recovery.[84] As the demand of REEs for manufacturing of high technology products continues to outpace global supply chain constraints, the development of techniques for effectively harvesting these materials domestically from waste streams and other novel sources may become an attractive option.[85,86] It may prove possible to meet these needs while also addressing the water quality challenges of both ARD and AMD through the targeted treatment and recovery of valuable commodities, although this cannot occur without first investment and infrastructure. The cleanup of abandoned mines alone is estimated to cost upward of $54 billion in the western USA,[87] and the high continuing costs of maintaining on-site treatment facilities compounded by a complex regulatory policy frame-

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work have impeded pilot-scale testing of resource recovery.[88] The results of this study indicate that it may be timely to investigate such alternative strategies to address the problems associated with AMD and ARD, which are potentially poised to worsen in the near term due to climate change.

■ ASSOCIATED CONTENT

Supporting Information

Additional Data Quality Assurance Information acknowledging published data sets utilized to assess long-term changes in water chemistry, analytical methods and lab quality assurance; aqueous REE concentrations from previously unpublished sources; reanalyzed historical sample concentrations for Fe, Al, Zn, Nd, Ce, Y; calculated Ce anomaly values; annual peak streamflow value and date from 1943 to 2020 at USGS Keystone gauging station; results from statistical tests of Zn, Nd, and Grizzly Peak temperature data; observed mean summer air temperatures, Mann-Kendall trends and significance from Grizzly Peak, Loveland Pass, and Jackwacker Gulch SNOTEL sites; aqueous REE concentrations normalized by North American Shale Composition. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c02958.

(PDF)

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Notes

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