

GEOLOGIC MISFORTUNE: THE SOURCING, FATE, AND TRANSPORT OF RARE EARTH
ELEMENTS IN THE SNAKE RIVER WATERSHED, MONTEZUMA, COLORADO.

by

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Geologic Misfortune: The Source, Fate, and Transport of Rare Earth Elements in the Snake River Watershed, Montezuma, Colorado.

Thesis directed by Professor Diane M. McKnight

The environmental impacts of acid rock drainage (ARD) and acid mine drainage (AMD) are a problem facing many waterways across the Rocky Mountains and throughout the world, particularly in areas of historic mining. Here we examine ARD/AMD enriched in rare earth elements (REE) in the Snake River watershed, located near the former mining boomtown of Montezuma, Colorado. Long-term data sets of precipitation, temperature, river discharge at many sites throughout the region show decreasing trends in summer flows from 1980 to 2010 which correlate to a snowpack melting occurring 2-3 weeks earlier. A 30-year water chemistry data set from the Upper Snake River further shows that metal concentrations are 100 to 400% higher than baseline concentrations during low-flow months. In addition, a low water table and decreased snow cover have increased the area of exposed sulfide minerals and the production of ARD, enhancing dissolution of metals from the disseminate pyrite present in the country rock and other secondary minerals present. The concentration of REEs present in tributaries of ARD-impacted Upper Snake and AMD-effected Peru Creek are three orders-of-magnitude higher than rivers worldwide and offer the unique opportunity to contrast their behavior against other dominant aspects of water chemistry. Iron is the predominant metal present both in the Upper Snake River and Peru Creek. In these headwaters, acidic water with pH 3.3 to 3.8 maintains a significant fraction of iron and aluminum dissolved, but mixing with shallow groundwater and pristine, circumneutral surface inflows downstream facilitate oxide precipitation. Of additional influence are diurnal changes in the valence state of dissolved iron coupled with the re-

dissolution of precipitates owing to competing microbial and photochemical reactions. This study hypothesizes that headwaters loading of REEs are historically increasing at rates observed with other conservative solutes such as zinc. Similarly suggested and also related to alterations of hydrologic regime, are the enhanced enrichment of REEs by periods of extreme flow. In support, investigations for this thesis present data collected over the last 3 years regarding the sourcing, fate, and transport of rare earth elements as well as in relation to other solutes in the Snake River Watershed.

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OVERVIEW

The Snake River has been long studied as a critically impacted watershed due to a long history of mining activities combined with its location in the Colorado Mineral Belt. The two major sources of metals and acids to its streams are the upper Snake River, located on the western slope of the Continental Divide, and Peru Creek, an adjacent valley dotted by long abandoned mine workings, collapsed tunnels, and excavated tailings left in large, exposed piles in proximity of the mill at the Pennsylvania Mine site. Similar geochemical weathering processes affect both regions, although the mechanisms for mineral dissolution and acid generation are relative to their site characteristics. The upper Snake River, while not heavily mined, has pyrite disseminated among the country rock and is oxidized by season precipitation and percolation of waters through fractured, mineralized zones. In contrast, Peru Creek is most affected by the direct outflows from the Penn Mine. Seasonal snowmelt infiltrates the mine upper workings, eventually draining out the bottom adits on the valley floor, and in the processes promoting oxidative weathering and enhanced mineral dissolution.

These respective contributions of solutes and acid conditions to the Snake River by acid rock drainage (ARD) and acid mine drainage (AMD) furthermore appear to be increasing (Crouch 2011), in relation to observed changes climate and the hydrologic regime (Rood 2008; Clow 2010). This advancement of peak spring snowmelt, increased drought frequency, warmer summer air temperature, and reduced groundwater recharge are cumulatively resulting in lower flows coupled to rising concentrations of metals (Manning et al. 2013). The increasing generation of acids from these reactions are likewise responsible for the dissolution of secondary and accessory mineral stocks such a monazite, noted in large surface deposits in early geologic surveys of the area (Loverling 1935; Loverling and Goddard 1950). Contained within these ores

are an abundance of rare earth elements (REE), which are dissolved and mobilized by these low pH waters (Rue 2012, Duren 2013).

The amounts by which REEs are being introduced into the Snake River and the possible influence of enhanced weathering rates are the focus of this thesis. In Chapter 4, through the synoptic sampling of this watershed during varying flow conditions, and in comparing these data with historical samples re-analysed for REEs. This chapter additionally elucidates the influence of extreme flow conditions on transport of major solutes and REEs downstream. Chapter 5 seeks to quantify the influx of REEs at one of their major sources, Trib 2095, in the upper Snake River. Through a diel experiment, data was collected to trace the diurnal changes in REE in-stream concentrations against other solutes such as zinc, of which Trib 2095 was previously identified as responsible for upwards of 80% of total loadings (Crouch 2013). For Chapter 6, in order to explore this link in greater detail and understand the complex hydrology of this high alpine, first-order stream, a dual injection tracer experiment was performed to quantifying the contributions of surface and groundwaters here relative to solute concentrations. In reflection, Chapter 7 synthesizes the results from the 3 aforementioned focused investigations, including corollary observations to other research and overalls trends in the watershed behaviour of REEs.

The studied sourcing, fate, and transport of rare earth elements for this thesis has contributed to a much larger body of research on the Snake River (Theobald 1963; McKnight and Feder 1983, Runkel et al. 1988, McKnight et al. 1990, Boyer 1994, Sullivan et al. 1998, Boyer et al. 1999, Belanger 2002, Duren 2004, 2013, Todd 2005, Todd et al. 2005, 2006, 2012, Crouch 2011, Rue 2012, Crouch et al. 2013). Because of its confluence with Dillon Reservoir, decreasing water quality here has secondary implications; the City of Denver relies on this as a major source of drinking water. And although enhanced transport and enrichment of heavy

metals into this lake have potential to increase treatment costs for Denver, larger questions loom: are rare earth elements toxic, what are their effects on aquatic life, and at what concentrations are they a threat to human health?

Chapter 1: Introduction

1.1 History of the Snake River

Looming beyond the mining legacy that exists in Colorado is the drainage from long-abandoned mines and tailings piles, which represents a serious, continuing impairment on water quality. It is also estimated that upwards of 500,000 abandoned mines exist on federal lands in the United States. And in the American West, for example, acid rock (ARD) and mine drainage (AMD) impacts almost 40% of the major streams and rivers (Forhard 2003). One area of particular interest is the Snake River Watershed, located near the former mining boomtown of Montezuma, which faces a significant water quality challenge from both nearby abandoned mines discharging metal-laden waters and natural acid rock drainage forming from the iron-rich host rock of the area, much of which lies exposed in this high alpine location thus encouraging natural geochemical processes (Boyer et al, 1999). Some of the earliest research in the Snake River, dating back to the 1960s noting metal oxide deposition resultant from this weathering of pyrite (Theobald 1963), and countless studies since have continued to advance our understanding of the geochemical processes involved as well as their cumulative impacts on this watershed.



Photo 1: the mixing zone at the confluence of the upper Snake River and Deer Creek as described by Theobald in 1963 (G. Rue)

1.2 Relevant Research

These acidic, metal-rich inflows create an acutely harmful environment for fish and most aquatic organisms (McKnight and Feder 1984) for which the Snake River is currently listed as an EPA 303(d) Impaired Watershed. And despite dilution of dissolved metals by numerous pristine inflows downstream, previous study has proven throughout the reach these waters remain toxic to indigenous trout species (Todd et al. 2007). Of additional concern is that the Snake River flows into Dillon Reservoir, a major source of drinking water for Denver region. The sourcing of these high metal concentrations and the low pH conditions responsible for their rendering can be traced to high alpine areas at the headwaters of the catchment (Figure 1).

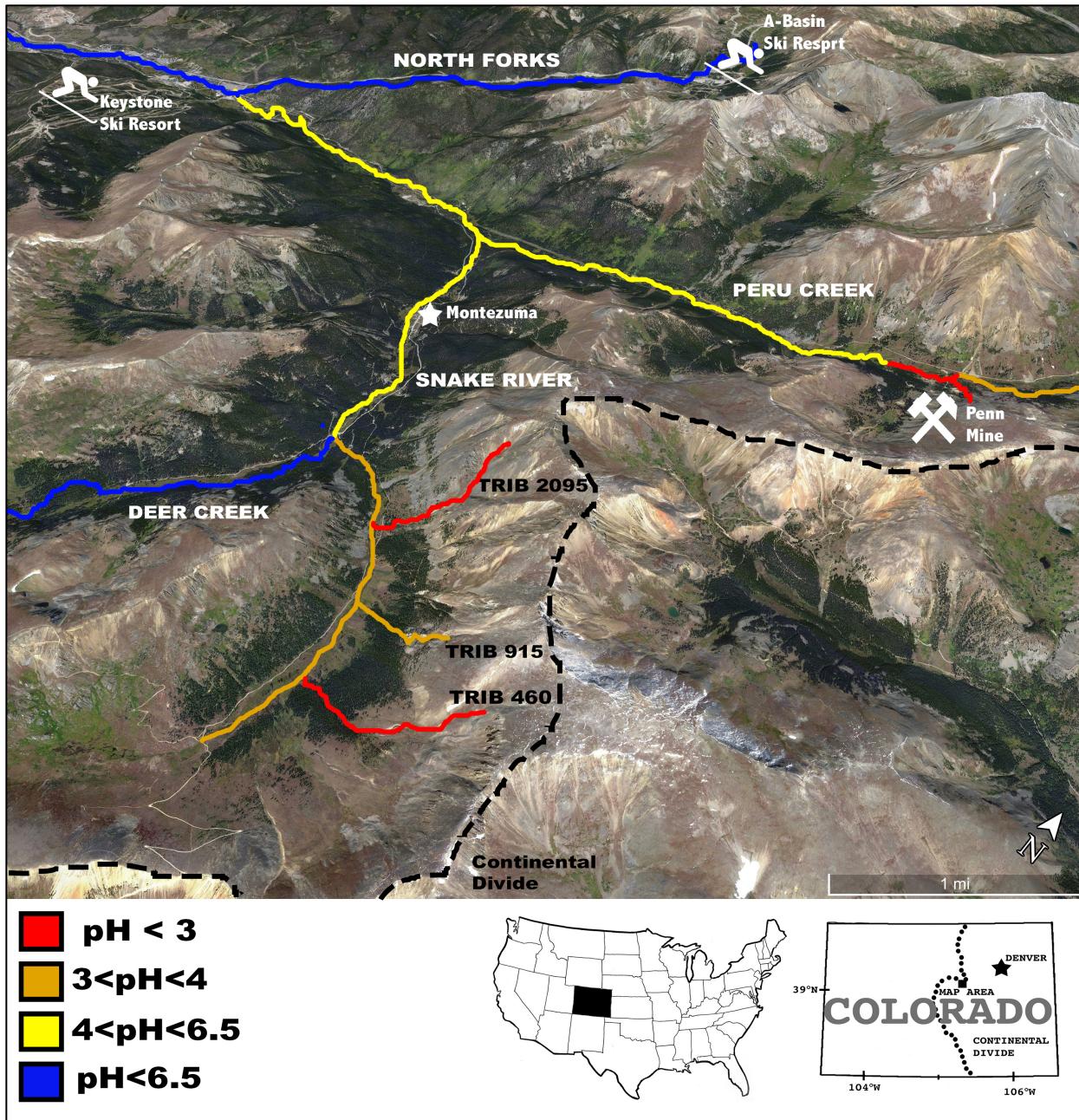


Figure 1: Map of the area and baseflow pH conditions. (Imagery: GoogleEarth)

Over the last 15 years, more frequent drought conditions and earlier occurrence of peak spring snowmelt (Rood et al. 2008), possibly related to climate change (Clow 2010), have significantly reduced water quality in the Snake River during summer low-flow conditions, when metal concentrations are at their highest. Just as this serves to lengthen the period of low

streamflow, accompanied by extremely low pH, similar increases of the duration that surface rock is exposed to weathering which therefore enhance subsurface reactions, acid production, and the dissolution of metals from minerals due to an enlarged oxic zone from a decreasing water table and reduced recharge (Manning et al. 2013). And in the last 20 years, a near fourfold observed increase of zinc concentrations has occurred (Crouch et al. 2009; 2012).

1.3 The Presence of Rare Earth Elements

Recently, discoveries of extremely high concentrations of rare earth elements (REE) have been found throughout this watershed, in both the ARD and AMD impacted areas of the Snake (Rue 2012; Duren 2013). These were an unexpected result of this authors UROP-funded honors thesis project, with determining the sourcing and transport of these elements the focus of additional, master's study. Recent re-analysis of archived samples from the 1990s indicates that REE concentrations have also increased almost fourfold.

An initial observation into the presence of REEs here is that both ARD and AMD portions of this reach are major sources of enrichment. Specially, the Pennsylvania Mine drainage tunnel and Tributary 2095, a small contributing stream at the headwaters of the upper Snake, are responsible for the bulk of these loadings. These two sources are similarly responsible for introducing major quantities of heavy metals at a low pH that allows them to remain dissolved and transported downstream. Once these waters mix with pristine sources further down the reach (Photo 1), the normalizing of low pH conditions force the precipitation of these metals, hence reducing their concentration and localizing impacts.

However, some metals such as zinc are intransigent to these changes in pH and remain in the water column at concentrations toxic to aquatic life as far downstream as the Keystone Ski Resort and likely to the terminus into Dillon Reservoir. The behavior of REEs appears to follows

similar trends to zinc in both their relatively conservative behavior and consistently elevated concentrations down the reach. Unlike zinc, there exists no toxicity standard for REEs, nor is the EPA monitoring them as a water pollutant. Considering that the Snake River discharges directly into Dillon Reservoir, a major source of drinking water for the Denver region, this could represent a threat to public health.

1.4 Objectives and Hypothesis

Through the synthesis of data collected throughout the upper Snake River, continued sampling of this watershed during varying flow conditions over the last 3 years, and re-analysis of achieved samples from the 1990s, valuable observations can be made regarding the sourcing, fate, and transport rare earth elements in the Snake River. Trends in the rising zinc concentrations suggest that mineral weathering processes over the last 30 years are increasing dramatically (Todd et al. 2005), and propose within the context of this thesis play a significant role in the enhanced dissolution of REEs. Through multiple experiments performed at the headwaters of this watershed, where the majority of these solutes are introduced and accompanied by low pH, the association between REEs and other aspects of water chemistry will be explored in an attempt to better elucidate these relationships. The three main chapters of this Master's thesis will investigate the following: 1) long-term trends in REE concentrations at the headwaters of this watershed, 2) effects of flow on the mobilization REEs, 3) behaviour of REEs at their source of enrichment (Trib 2095) against other weathering products and solutes. Through the coupling of data collected across spatial and temporal scales, the objective of this thesis serves to advance the collective understanding of REEs in an aquatic environment and characterize their behaviour in contrast with other important aspects of water quality.

Chapter 2: Background

2.1 Sources of Acid Mine and Rock Drainage

Acid mine drainage (AMD) and acid rock drainage (ARD) are formed from the weathering of pyrite (FeS_2), often contained in mining waste rock or disseminated among the strata of mineralized areas, and the subsequent breakdowns to its basic elemental constituents. In the presence of oxygen and water, acidified by the diffusion of atmospheric CO_2 to form carbonic acid, the breakdown of pyrite can be both chemically and biologically driven. In areas of historic mining, the generation of AMD can occur by the oxidation at surface waste rock and tailings piles as well as underground, in the tunnels and drainage adits themselves. Given the interconnectivity of percolating surface water into the mineshafts, of a fractured geologic environment, countless flow paths, and an extended residence time, the generation of AMD is therefore exceedingly difficult to address.

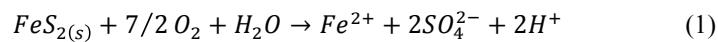
Whereas acid mine drainage can be considered a point source of water pollution, acid rock drainage is a far more diffusive problem. While it is generated in the same processes as AMD, the formation of ARD is contrasted as a natural occurrence in presence of pyrite, disseminated amongst the country rock, a complex variation of co-deposited geologic parent and subsequently stressed materials. In Colorado, the primary source of ARD relate to bands of metalliferous hydrothermal deposits stretching from northern Boulder County to the La Plata Mountains, west of Durango, better known as the Colorado Mineral Belt (CMB) (Tweto and Sims 1963). Nearly all historic mining activity in Colorado occurred within the CMB, and the same geologic conditions that lead to the formation of major gold and silver deposits also resulted in a significant presence of pyrite. Many mine sites, both abandoned and active, are located within the CMB at elevations well over 10,000ft. These high alpine locations promote enhanced

weathering due a variable hydrologic regime and minimal vegetative cover. Though much of these high alpine regions are snow-covered for winter, persisting well into the spring, the melt and subsequent percolation of these waters through these mineralized, oxic zones accordingly leads to the natural generation of acid rock drainage in spring and summer. The secondary presence of additional, co-deposited sulfide minerals such as sphalerite ((Zn,Fe)S), chalcopyrite (CuFeS_2), and galena (PbS) also play an implicit role in the relative dissolution of the heavy metals contained within these ores driven by low acid conditions and their eventual drainage to streams for transport.

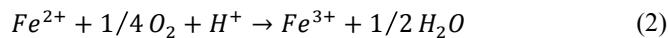
The effects of both ARD and AMD can be exacerbated by extreme flow events, either floods or drought. While the effects of climate change are hard to predict, it is generally accepted that in the central Rock Mountains, where a large amount of the ARD and AMD contamination is located, temperatures and the frequency of extreme weather conditions will increase (Clow 2010; Todd et al. 2012). As a result, the future impacts of AMD and ARD may be greatly different from current observations. Given the advancing of peak spring streamflow by over 2 weeks (Rood et al, 2008) over the last 30 years, the duration in which these high alpine regions are exposed to weathering is also increasing. Exacerbating this further are trends towards drier, warmer summers with more prevalent extreme rain events interspersed by drought (Clow 2010).

2.2 Acid Mine and Rock Drainage Formation:

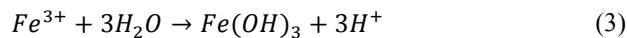
There are several chemical reactions associated with the generation of AMD/ARD (Stumm et al. 1982). The initial chemical process is the oxidation of pyrite to Fe(II) and sulfate at neutral pH:



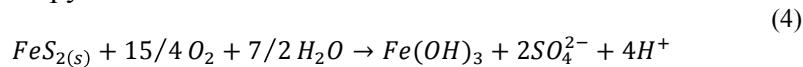
Once enough H⁺ ions are produced to bring the pH down to less than 4, the following step occurs:



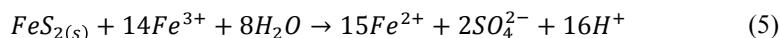
Because Fe(III) is not soluble in water with a pH higher than about 3, it precipitates as an oxyhydroxide:



The overall reaction of pyrite oxidation:



However, the release of more H⁺ ions decreases the pH below 3, allowing for soluble Fe(III), which is subsequently used as the electron acceptor for pyrite oxidation:



Continual release of Fe(III) creates a self-perpetuating process. Pyrite oxidization by Fe(III) occurs at a much greater rate than that of the oxidation of pyrite by O₂, yielding a positive feedback for acid generation. When Fe(III) oxidizes one mole of pyrite, 16 moles of H⁺ ions are generated, compared to the 2 moles of H⁺ ions generated by O₂ in Reaction 1. Therefore, Fe(III) is the essential constituent in the production of AMD/ARD, making Reaction 5 the dominant chemical process. Because of the importance of Fe(III), Reaction 2 is considered the rate-limiting step in the generation of AMD in new mine waste sites because of the slow reaction rate under normal conditions. However, Fe-oxidizing bacteria, such as *Acidithiobacillus ferrooxidans* can increase the rate of Fe(II) oxidation in Reaction 2 by six orders of magnitude, (Brown et al. 2002). As time progresses, the above reactions increase acidity, resulting in the mobilization of heavy metals, also contained in the waste or country rock (Neculita et al. 2007).

2.3 Site Description:

2.3.1 Hydrology

The Snake River is a headwater catchment located high in the Rocky Mountains near the town of Montezuma, it abuts the western slope of the continent divide with base elevation of 10,500 feet and its highest elevation just over 13,000 feet. Though the valley floor is vegetated with tree cover, much of the surrounding topography is steep talus and scree fields of accumulated weathered materials and downcut by a series of high-gradient first order streams. This high alpine location and seasonal flooding due to snowmelt promotes stream channel incision, leading to characteristic v-shaped gulch morphology and a rough substrate from the additional accumulation of slope wash. The major branches of the Snake River watershed are the upper Snake River, Deer Creek, Peru Creek, and the North Forks, which are all 2 and 3rd order streams that are fed by a mixture of perennial and interment 1st order tributaries that drain off the divide. Winter precipitation and eventual snowmelt are the dominant source of stream water and recharge of the saturated-zone groundwater. Depending on this, summer baseflows in the high order portion of this catchment vary between 0.5 and 5 cubic feet per second. Orographic precipitation is common in the summer, leading to flashiness in the hydrograph and enhanced transport of freshly weathered sediments. The topography and the resulting hydraulics further promote the lateral inflow of groundwater into tributaries on the valley floor, causing some of them to gain additional flows from a shallow interface of the vadose and saturated zone.

2.3.2 Geology

The mountains surrounding the Snake River Watershed have differentially weathered over the ages through a mixture of physical, fluvial, and chemical weathering processes. High elevation, steep gradient, varied precipitation and limited vegetative cover all act to shape this

dynamic region. The country rock of the area is predominantly disseminated pyrite, again due to its location in the CMB. Bog iron (limonite) deposits are prevalent, resultant from millions of years of sulphide weathering and the precipitation of hydrated iron oxides in wetlands portions of the valley floor below (Loverling, 1935). The underlying geology of the region is the Idaho Springs Formation, though a mixture of other ore deposits are additionally present which include: Pegmatite, (Precambrian) Swandyke Hornblende Gneiss, (Cretaceous) Hornfels, (Tertiary) Porphyritic Quartz Monazite and Apatite, and (Holocene) glacial and fluvial deposits (Neuerburg and Botinelly, 1972).

Loverling additionally noted numerous outcropping and knobs of weathered quartz monazite on many small peaks and cirque walls throughout the upper Snake and Peru Creek. He further estimated that there exists upwards of 16 square miles of this Montezuma quartz monazite stock at the surface across the quadrangle, representing the largest deposit in the Front Range mineral belt (Loverling and Goddard, 1950).

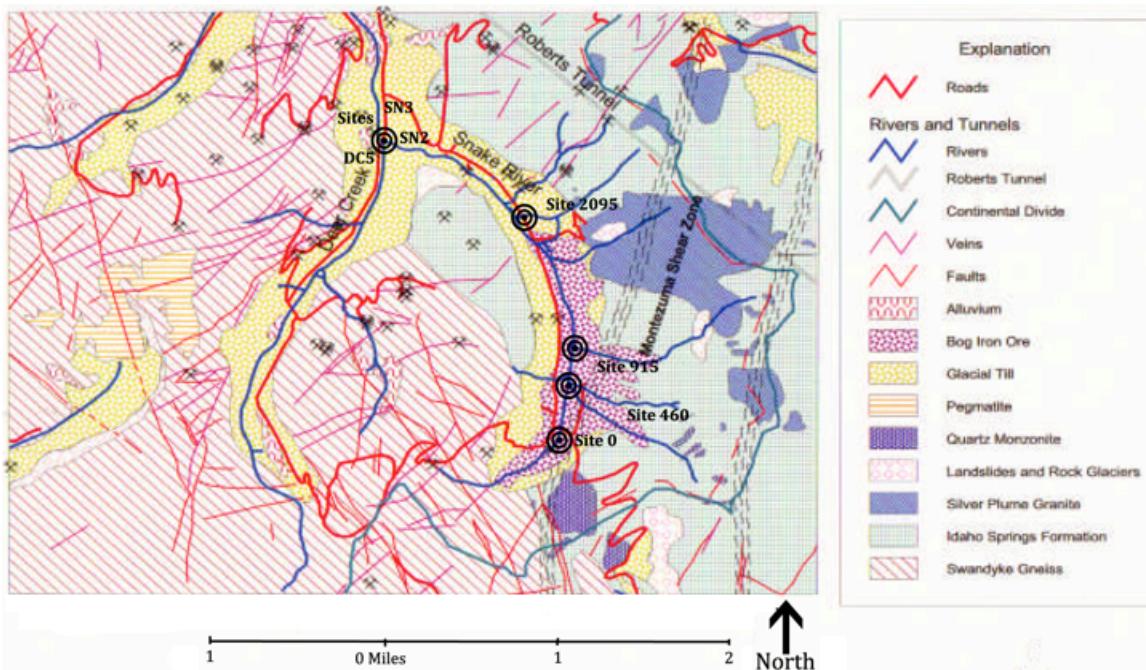


Figure 2: Background Geology of the upper Snake River, including study sites (Adapted from Loverling 1935; Theobald 1963)

2.3.4 Climate and Water Chemistry

Long-term datasets of precipitation, temperature, and river discharge at many sites throughout the Colorado Rockies show decreasing trends in summer flows (Rood et al. 2008) which correlate to other, more recent findings that highlight a snowpack that is melting 2-3 weeks earlier (Clow 2010). Using snow water equivalent measurements from SNOTEL sites nearest to the Snake River, a correlation was shown between advancement of peak stream flow by an earlier melt season and rising metal concentrations in summer months (Todd et al. 2012). The 30-year water chemistry record from the upper Snake River itself further shows that fluctuations from 100-400% of historical average concentrations are occurring during these low-flow months (Crouch et al. 2010). Although accounting for these long-term climate related changes in snowmelt timing and increasing temperatures observed in the Rockies, particularly as they pertain to enhancing oxidizing rates of sulphide minerals, is important in understanding their effects on water chemistry. And there exists additional consideration as to how these might alter the hydrologic regime itself.

Trends in streamflow and water chemistry for the Snake River, with records going back almost 30 years, suggest that these changes in climate alone are not responsible for rising concentrations of dissolved solutes and lowering pH (Todd et al., 2012; Manning et al. 2013). A linear trend in rising zinc concentrations had been observed until 2002, when a historic drought occurred in Colorado and flows reached there lowest on record as well as the highest concentrations of heavy metals ever measured in the Snake. And in the years preceding this event, concentrations of zinc appeared to be trending towards exponential increases (Crouch et al. 2013). Absent data regarding exact changes in the water table or the influence of diminishing recharge into the system, recent studies have rather attempted to model the resultant drop in the

water table from such a drought in the Snake River and found it could indeed enhance ARD/AMD weathering through the expansion of the unsaturated, oxic zone (Manning et al. 2013). Conceptually this makes sense, as sites which are situated high on the Continental Divide and fed by small, 1st order headwater streams, would experience reductions in shallow groundwater and subsequent seasonal recharge as well as an increase in the cross-sectional surface area of the vadose zone, which in turn provides an additional interface for the weathering of primary and secondary minerals by percolating of waters from seasonal precipitation. Considering the potential magnifying effect of climate change on these aspects of AMD/ARD generation and transport, here exists a likely scenario for these exponential increases in stream solute concentrations as connected to the discrete complexities of high alpine catchment hydrology, structural geology, mineralogy, as well as geochemistry occurring in-between. From synthesis of numerous studies conducted within the Snake River Watershed since the 1980 on these topics, there represents a growing body of evidence in support of these inter-connected relationships, from which implications for worsening water quality in the future may prove an even greater challenge.

2.4: Rare Earth Elements

2.4.1 Presence of Rare Earth Elements

The Snake River has been studied as a critically impacted watershed as far back as the 1960s (Theobald et al. 1963) and the processes responsible for rendering acidified, metal-laden waters are still occurring if not worsening altogether. But more recently, it has been discovered that portions of the Snake River contain dissolved concentrations of rare earth elements (REE) several orders of magnitude above what are observed in rivers worldwide (Figure 3). These

patterns in enrichment appear similar to other that of other rivers and suggest a trend in compositional distribution from the minerals in which they disassociate (Goldstein and Jacobson 1988)

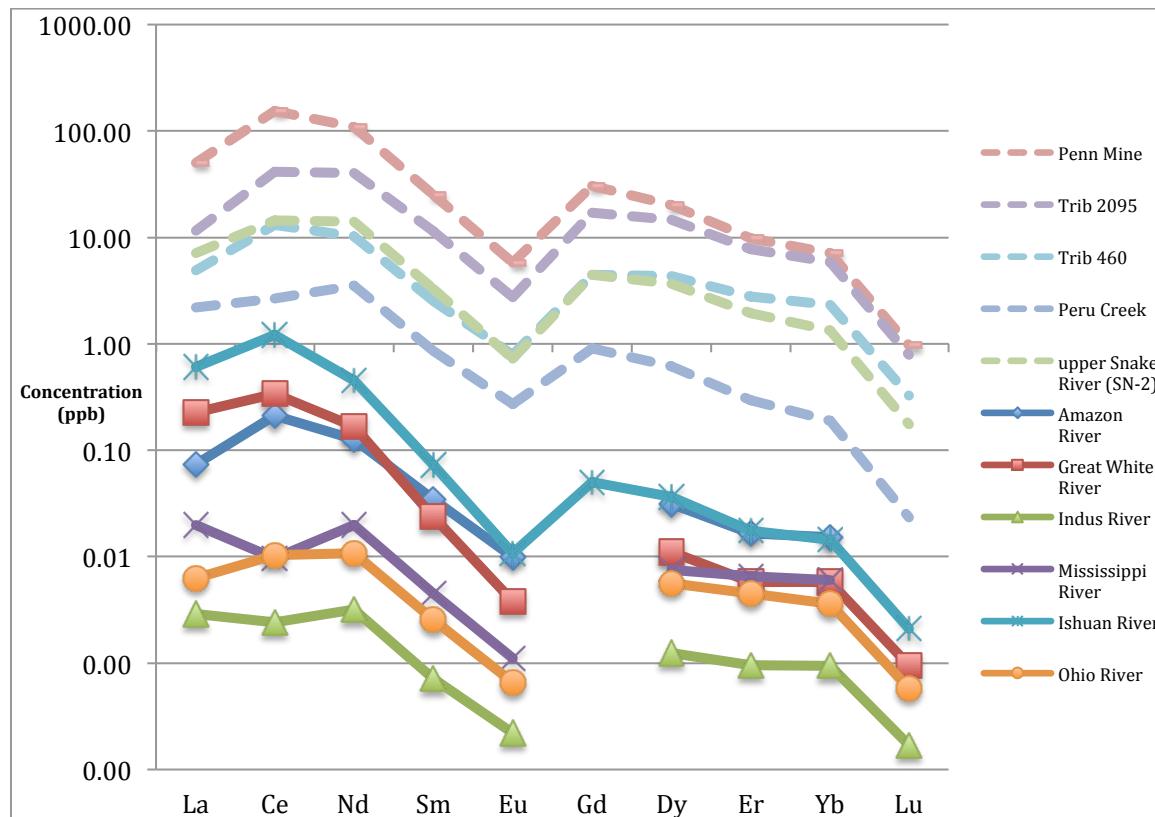


Figure 3: REE concentrations in the Snake River Watershed and other major rivers worldwide (Adapted from Goldstein and Jacobson 1988)

Though REEs are present in the solid phases in many minerals and ores, their amounts are relatively low in comparison to other elements, and their aqueous presence, particularly in surface waters, remain dilute at the parts-per-trillion range. However, groundwaters tend to be more enriched due to percolation or prolonged contact with REE-bearing mineralized zones. Because of this, they are often used as a conservative tracer to estimate surface mixing and groundwater interconnectivity (Goldberg et al. 1963; Cullers and Graf, 1984, Ojiambo et al. 2003. Tang et al. 2006).

Initial investigation of the Snake River Watershed in 2012 (Rue 2012) indicated significant sources of REE surface enrichment in both the ARD-impacted upper Snake and AMD-impacted Peru Creek near the Pennsylvania Mine drainage adit. The prevalence of minerals such as quartz monazite (Loverling 1950), a mixed rare earth phosphate, and underlain by a silver plume granite parent material, another mineral shown elsewhere in Colorado to be REE-bearing (Allaz et al. 2013. Vanfossen et al. 2014), likely plays an implicit role in their presence. The mechanism by which these REEs are mobilized into the streams at these high concentrations relate to the dissolution of these ore bodies or disseminated materials by contact with acid-rich waters rendered from ARD/AMD reactions.

2.4.2 What Are REEs?

In the periodic table, Rare Earth Elements (REE) make up seventeen of the 188 identified chemical elements. Fifteen of them are classified as lathanides, and the remaining two are scandium and yttrium. Most exist in a trivalent (+3) state, making their chemical behaviour somewhat consistent although respective REE electron configuration additionally plays a role. The reason for yttrium to be considered REEs is that it tends to occur in the same geologic ore deposits and exhibit similar trivalent characteristics. REEs are not nearly as "rare" as their name would imply, as in rock-forming minerals, REEs commonly occur in carbonates, oxides, phosphates, and silicates.

Figure 4: Periodic Table, highlighting rare earth elements locations and properties.

The lanthanide classified REEs have atomic numbers 57 through 71 and are the following by atomic number: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Rare earths are often grouped as being a "light-group rare-earth element" (LREE) or "heavy-group rare-earth element" (HREE), with the definition of a LREE and HREE being based on the atomic number and electron configuration of each rare-earth element. The LREE are defined as lanthanum, atomic number 57 through gadolinium, atomic number 64. This is due to lanthanum having no 4f shell electrons; clockwise spinning electrons are added for each lanthanide through gadolinium. Gadolinium has seven clockwise spinning 4f electrons, creating a very stable, half-filled electron shell. The LREE additionally have in common increasing unpaired electrons, from 0 -7. HREE are defined as terbium, atomic number 65 through lutetium, atomic number 71, as well as yttrium, atomic number 39. This is because starting with terbium, counter-clockwise spinning

electrons are added for each lanthanide through lutetium (REEH 2015).

2.5: Preliminary Investigation and Analogous Research

2.5.1 Synoptic Study, upper Snake River

In 2012, synoptic sampling of the tributaries in the upper Snake River revealed one stream in particular, Tributary 2095 had the highest REE concentrations in upper Snake River (Rue 2012). This tributary has also been the topic of prior investigation (Crouch 2010), characterized as major source of other dissolved heavy metals into this upper portions of the reach as well as having extremely low pH thereby enhancing dissolution and transport (Crouch et al. 2013). This detailed tracer study by Caitlin Crouch performed at the origin of this tributary first revealed this stream as having a complex hydrologic regime with two district zones (Figure 5): a high gradient exposed area above vegetated valley floor with a rocky substrate and extreme stream gradient, and a tree covered reach with a sinuous, incised stream channel, a sandy substrate as well as significant lateral inflow of shallow ground, which can be physically observed by both 10 degree decrease of in-stream water temperature and large increase in discharge at noted in the tracer data. The surface flow path of this lower zone is highly dynamic and can change seasonally, with new meandering channels and temporary wetlands forming until a high flow event re-establishes the active channel. This study also detailed that upwards of 80% of zinc loadings present downstream at SN-2 can be sourced to Trib 2095. Later re-analysis in 2013 of archived samples from this experiment further indicated a similar pattern in enrichment of REEs neodymium and yttrium (Table 1).

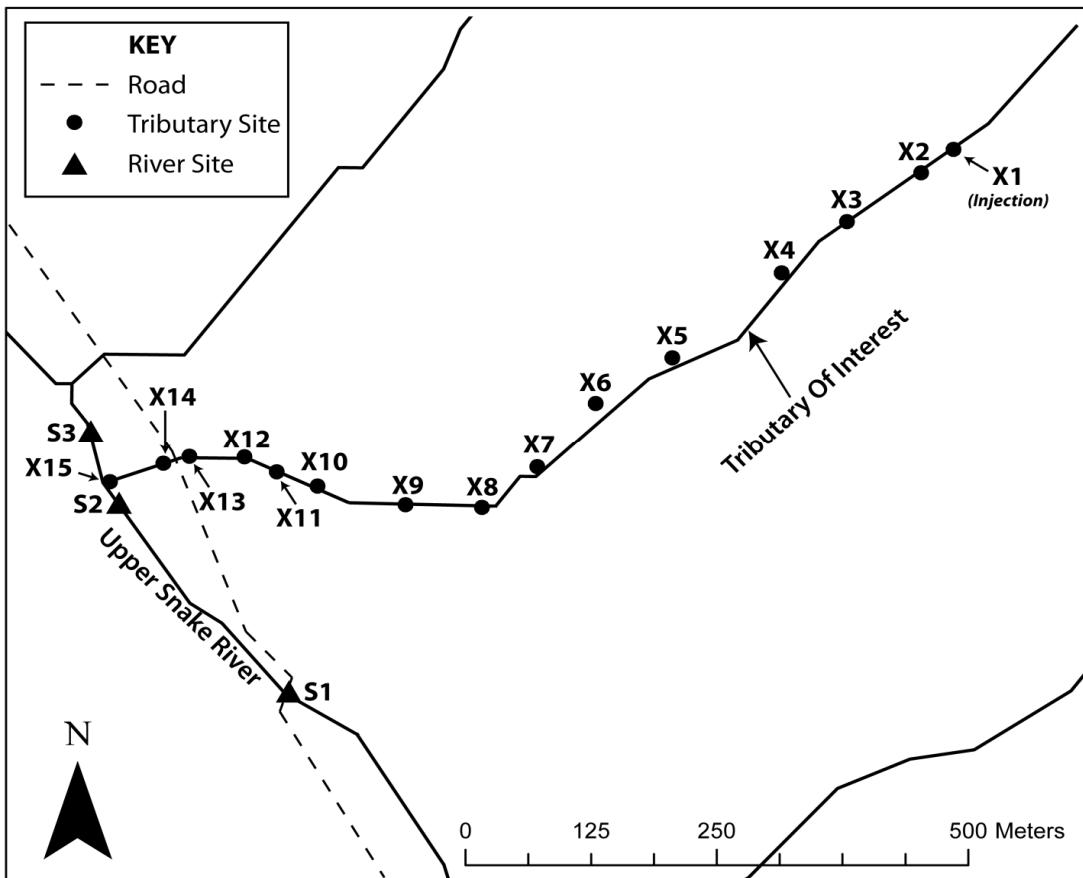


Figure 5: Trib 2095 sample sites during the September 2010 tracer injection study. All sites were sampled for metals analysis during the plateau (Crouch 2010).

Site	Flow(CFS)	Zinc Concentration (ppb)	Nd Concentration (ppb)	Y Concentration (ppb)
X1	0.22	6795	96	160
X2	0.22	8670	99	180
X3	0.22	12697	107	218
X4	0.22	15471	115	256
X5	0.22	15540	115	254
X6	0.28	15177	116	252
X7	0.28	15592	116	253
X8	0.28	14973	116	250
X9	0.28	14530	113	241
X10	0.28	14382	112	238
X11	0.28	15106	116	251
X12	0.28	14311	112	240
X13	0.28	14365	111	238
X14	0.28	14711	115	243
X15	0.74	7874	62	133
S1	*	387	3.50	9
S2	*	399	3.59	9
S3	*	485	4.16	10

Table 1: Flow estimated from 2010 tracer data and zinc data, including 2013 re-analysis for REEs
(Adapted from Crouch 2010)

During 2012 sampling (Figure 6), other tributaries tested further upstream and closer to the headwaters of the Snake had elevated metal concentrations and low pH, however both trace metal and REE concentrations were both considerably lower than Trib 2095 (Table 1, Table 2). In order to contrast streams dominated by watershed or in stream processes, sulfate becomes another an important consideration by both its relatively aqueous conservative behaviour (Bencala et al. 1987; 1991) and generation from ARD/AMD reactions. The presence of sulfate both serves as proxy for sulfide weathering processes and allows for relative estimates of flow contributions by dilution. Data from synoptic sampling indicated that Trib 460, like Trib 2095 is introducing solutes generated from geochemical weathering, although to a much lesser degree of enrichment and at a higher pH.

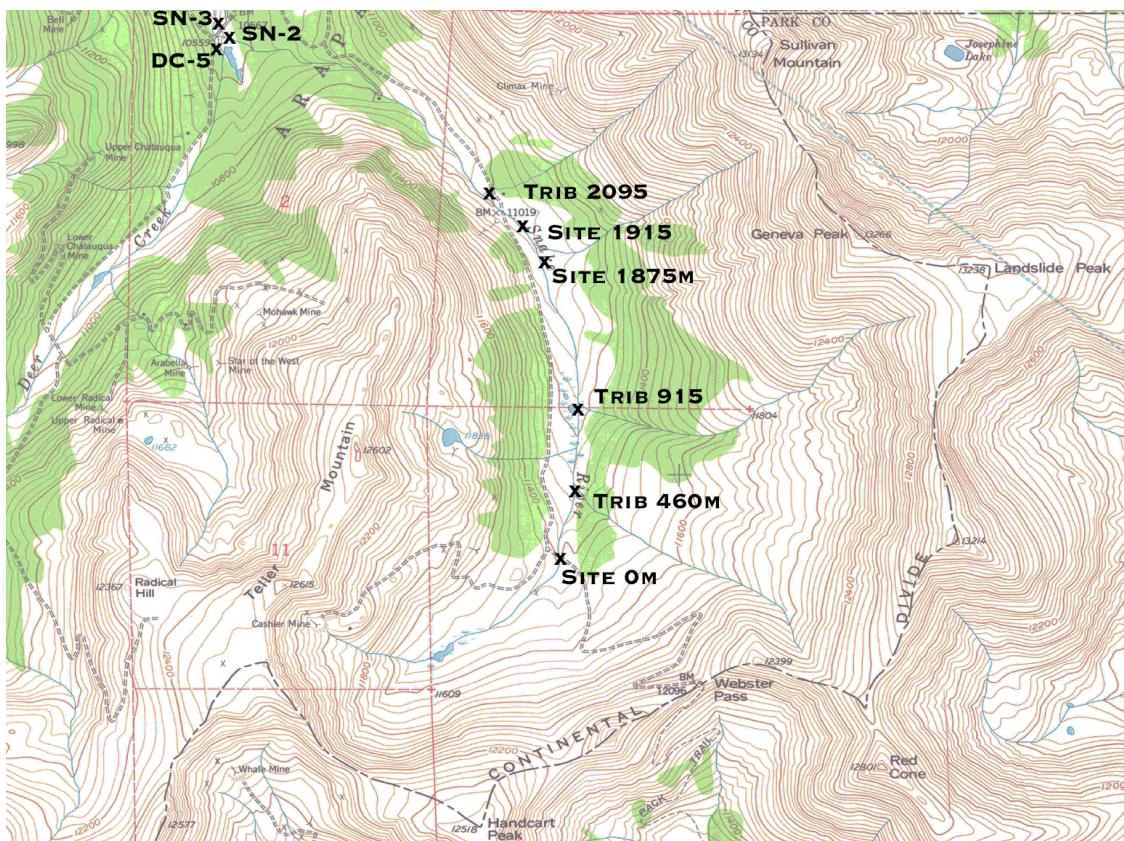


Figure 6: USGS Topographic Map, Montezuma Quadrangle, 1:24000, Upper Snake River study sites adapted from Belanger 2002 and overlaid on map

	Copper (ppb)		Iron (ppb)		Aluminum (ppb)		Zinc (ppb)		Sulfate (ppb)		pH	TDS
	9/22/12	9/29/12	9/22/12	9/29/12	9/22/12	9/29/12	9/22/12	9/29/12	9/22/12	9/29/12	9/29/12	9/29/12
Site 0m	*	1.31	*	2549	*	1344	*	119	*	88.9	4.34	110
Site 450	*	1.32	*	3182	*	2812	*	204	*	94.3	3.73	140
Trib 460	*	24.61	*	24037	*	23904	*	1082	*	378	3.18	450
Site 485	*	3.60	*	4493	*	5178	*	264	*	123	3.66	160
Site 900	*	5.42	*	5757	*	7192	*	344	*	145.8	3.56	200
Trib 915	*	117.98	*	7553	*	6877	*	759	*	135.9	3.58	200
Site 940	*	34.65	*	5739	*	6927	*	439	*	139.4	3.58	200
Site 1875	32.19	32.74	2123	2119	8245	7863	439	429	145	144	3.55	210
Site 1935	33.41	31.28	2133	2360	8173	8019	456	463	145	146	3.56	210
Site 2085	36.16	30.11	2380	2263	9082	8507	521	494	148	145	3.55	210
Trib 2095	76.52	70.75	14872	17376	42943	43622	4880	5141	513	544	3.02	1100
Site 2120	37.12	32.68	2640	2876	12097	11251	904	876	192	183	3.55	240
SN-2	48.68	36.93	1317	1316	13372	12963	1585	1474	203	206	3.65	310
Deer Creek	2.92	0.29	147	188	6.9	6.5	51	37	24	26	7.75	60
SN-3	23.64	23.55	601	1112	7810	8101	924	792	129	133	4.83	140

Table 2: Major metals and sulfate concentrations, pH, and TDS of the upper Snake River

	Neodymium (ppb)		Dysprosium (ppb)		Gandolinium (ppb)		Lanthanum (ppb)		Yttrium (ppb)		Samarium (ppb)	
	9/22/12	9/29/12	9/22/12	9/29/12	9/22/12	9/29/12	9/22/12	9/29/12	9/22/12	9/29/12	9/22/12	9/29/12
Site 0m	*	0.40	*	0.17	*	0.18	*	0.39	*	1.56	*	0.12
Site 450	*	1.07	*	0.40	*	0.41	*	0.76	*	3.09	*	0.29
Trib 460	*	10.18	*	4.36	*	4.48	*	4.90	*	37.91	*	2.53
Site 485	*	1.98	*	0.78	*	0.83	*	1.22	*	6.26	*	0.49
Site 900	*	2.87	*	1.14	*	1.21	*	1.72	*	9.34	*	0.71
Trib 915	*	6.99	*	1.84	*	2.32	*	3.12	*	13.63	*	1.53
Site 940	*	3.85	*	1.30	*	1.47	*	2.09	*	10.24	*	0.92
Site 1875	5.51	4.83	1.89	1.73	2.12	1.95	2.60	2.43	13.48	12.78	1.38	1.21
Site 1935	5.14	4.95	1.81	1.79	2.08	2.03	2.54	2.52	13.21	13.32	1.33	1.27
Site 2085	5.91	5.27	2.12	1.93	2.40	2.11	2.89	2.56	14.85	13.82	1.57	1.39
Trib 2095	40.96	39.99	13.89	14.56	16.67	17.07	11.60	11.55	89.71	90.41	11.29	11.44
Site 2120	9.81	8.88	3.27	3.17	3.76	3.54	3.89	3.56	22.48	20.76	2.56	2.36
SN-2	14.83	14.13	3.56	3.68	4.45	4.43	7.37	7.11	27.31	26.42	3.32	3.30
Deer Creek	0.03	0.03	DL	0.01	0.01	0.01	0.04	0.04	0.03	0.04	0.02	0.04
SN-3	9.02	8.85	2.34	2.26	2.96	2.78	4.65	4.49	17.08	16.81	2.13	2.10

Table 3: Major REE concentrations in the upper Snake River

2.5.2 Analogous Research

To better understand the role of REEs in the upper Snake River, Trib 2095 was targeted for further study. From the hydrologic observations made by Caitlin Crouch (2010) in her tracer study, a more focused evaluation was planned on the interface between the upper and lower zone. Relevant research performed nearby in Peru Creek in 2011 by Sabre Duren centred on the diel cycling of trace metals, and served as a framework for this additional work and 2004 Peru Creek samples were re-run for REEs. The result of this re-analysis was striking; portions of Peru Creek both at the mining portal and the wetlands below had REE concentrations higher than that of Trib 2095 (Duren 2013). Supplemental to concentrations of neodymium present in Peru Creek beyond 200 ug/L as well as trace metal concentrations well exceeding those observed in the upper Snake River, was the observation of a highly dynamic system driven by photochemistry

within the wetland and its role in mobilizing metals.

The 2004 Peru Creek diel date regarding the reactive iron species, trace metal, dissolved organic carbon (DOC), as well as newly-analysed REE concentrations made evident a complex reactions pathways possibly responsible for enhancing their transport. Contrasting behaviour was observed between the wetlands and the main channel of Peru Creek; with stream concentrations of Fe^{2+} increasing corresponding to light intensity, whereas in the wetlands Fe^{2+} concentrations decrease over the course of the day. This increase in in-stream Fe^{2+} is congruent with numerous studies that highlight the aqueous photoreduction of Fe^{3+} to Fe^{2+} (McKnight et al. 1988; McKnight and Bencala 1988; McKnight and Bencala 1989; Kimball et al. 1992; Runkel et al. 1996; Broshears et al. 1996; Hrncir and McKnight 1998; McKnight et al. 2001, Scott et al. 2003). However, in the wetlands the decreasing Fe^{2+} is related to its oxidization by H_2O_2 , generated from the photodecay of dissolved organic matter (DOM) or better known as a photo-fenton reaction. In this regard, the photo-fenton reaction is outcompeting photo reduction pathways in the wetland and the decreasing Fe^{2+} concentrations are indicative of the cycling of Fe^{3+} to Fe^{2+} via photoreduction followed by its rapid oxidation by H_2O_2 back into Fe^{3+} .

Related to this redox speciation and cycling of iron in Peru Creek, are the release of trace metals and REEs. The co-precipitation and sorption, specifically in a low pH, of trace metals is a known processes as well as the photoreduction of iron oxides in their remobilization (McKnight and Bencala 1988; Fukushima and Tatsumi 2001, McKnight et al. 2001b, Duren et al. 2004. Gammons 2014). However, the "pulsing" of REEs as observed in Duren's Peru Creek diel experiment presents a conceptual challenge, as it is not congruent with results of other study. Rare earth elements are thought to behave conservatively in low pH systems, and in the formation of iron oxides they are not preferentially scavenged or sorbed due to competitive

binding of more favorable solutes, ligands, and/or metals (Verplanck et al. 2004). As with many other cations, REEs in an aqueous environment are in constant competition to form stable complexes or otherwise be incorporated in solid phases, which often requires the presence of inorganic ligands in mediating this partitioning (Stumm and Morgan 1988; Drever 1997, Verplanck 2013). In alkaline systems, for example, carbonate plays a significant role in the cycling of REEs between free-ion, complexed, and colloidal forms (Quinn et al. 2006; Pourett et al. 2007). But in less alkaline environmental, such as an ARD/AMD system, sulfate is rather the dominant complexing ligand for REEs because of its continued generation by weathering processes and therefore explains its relatively conservative behavior as well as resistance to partitioning by sorbtion or co-precipitation (Sholkovitz et al. 1993; Sholkovitz 1995).

2.5.3 The Role of Dissolved Organic Material

Dissolved organic matter (DOM) plays an important role in the conceptual explanation for how REEs are being incorporated into colloidal or precipitated iron oxide solids that are then remobilized through photoreduction. And while the coupling of redox cycling of iron to DOM and its photolysis (Voekler et al. 1997; McKnight et al. 2001a) is widely acknowledged, the role of DOM in forming organometallic substances is far less understood, as are the sorptive qualities of these complexes. Some of this can be related to the long held belief of DOM as a homologous pool of organic ligands with similar traits, however with the advancement of analytical techniques and advanced characterization methods, we now know this is untrue. DOM exists rather as a macromolecule composed of a highly diverse assemblage of smaller organic moieties with varied source, molecular weight, and lability (McKnight et al. 2001c, Peuravuori 2005, Peuravuori et al 2007). While some fractions of this pool are chargeless and refractive, some of the major constituents (40-50%) of the DOM pool such as humic acids (HA) and fulvic acids

(FA) play an important role beyond photochemical reactions to that of being complexing agents for strong-binding metals as well (Chin et al. 1997; Drexel et al. 2002, Craven et al. 2012).

This is especially the case in the Snake River, where humic substances are shown to be preferential sorbed to aluminum and iron oxides (McKnight et al. 1992). The seemingly ubiquitous nature of humic and fulvic acids, as a significant portion of this dissolved organic carbon (DOC) pool, relate to their importance as potential ligands in an aqueous environment. To better evaluate the behaviour of REEs in the Snake River, it prove paramount to understand how they might speciate or complex in the presence of certain fractions of dissolved organic material and metals, as highlighted in the paper “Effects of Fe competition on REE binding on humic acid: origin of REE pattern variability in organic water” by Melanie Davranche (2013).

These recent studies have shown conclusive patterns to occur with the selective enrichment of HA binding sites in respect to pH (Marsac et al. 2012; Davranche et al. 2013, Migaszewski et al. 2014). For example, at pH 3 and with high REE/HA concentrations, high enrichment occurred in the middleweight (MREE) fraction towards the weak carboxylic sites, where as at pH 6 this shifts towards the multidentate sites. Heavy weight REEs (HREE) on the other hand exhibit an opposite pattern in that at pH 3 they favour multidentate sites and at pH 6 the stronger phenolic groups. This selectivity of certain REE fractions towards the weak and strong acid components of a HA molecule start to illuminate the complexity of studying this issue, as certain humic acids with a higher aromaticity would have a more phenolic groups that in turn would bind HREEs disproportionately.

However, the binding between humic acids and rare earth elements is largely shown to be controlled by pH, where as the fractionation of them has a great deal to do with the major cation concentrations and the competition for HA binding sites between REEs and major strong metal-

binding cations such as aluminium and iron. Because pH also plays a role in the reactivity and speciation of these cations, its role cannot be stressed enough as the primary control on REE-HA binding (Tanizaki et al. 1992; Johannesson et al. 1996. Ingri et al. 2000). But the preferential fractionation of light, middle, and heavy weighted REEs to multidentate or weak carboxylic HA sites is not alone determined by their properties, or pH, but also in relation to those which are being competed for by other metals as well as ligands.

As previously discussed, significant effort has been devoted to understanding the role of inorganic ligands in their role as complexing agents, but much less has been made in regard to accounting for these ubiquitous substances found in nearly all natural waters on Earth. Though in recent years it has become a more active topic for study, furthered by development of geochemical models suitable for understanding the complexity of DOC fractional behaviour. (Tang et al. 2003; Gammons 2005a, Pourret et al. 2007). Similarly, a great deal of work has gone into understanding the binding of metals by HA, but there exists a much lesser body of knowledge surrounding how REEs are bound. Part of this stems from the complex structure of humic substances and the sheer amount of binding sites they might exist, although due to the similar trivalent properties of REEs they become attenuated to sites which suit their respective structure. Accordingly, fractionation and portioning of them in regard to atomic weight further highlight a pattern of enrichment towards sites strongly favoured.

But again we must presume that competition with metal cations for binding sites is occurring, and therefore must be evaluated as well. Marsac (2012) showed the competitive effects of aluminium on REE-HA binding demonstrated that Al^{3+} was strongly bound to multidentate sites at low pH(3) with REE/HA concentrations and that at a higher pH(6) with correspondingly high concentrations of REE/HA this shifted toward carboxyl sites. The primary

reason for this differentiation was the competition between the HREE and LREE fractions with their respectively preferred binding sites. As more studies focus on REE-HA binding, there exist evidence to suggest specific REE themselves undergo fractionation depending on other metals that are competing for the same sites and that complexes could show increased sorption potential even at low pH.

Subsequently, it become tantamount to evaluate these competing complexation behaviour in other metals with similar known properties such as iron, which in the case of the 2013 Davranche paper and its relationship to an AMD-impacted area such as the Snake River proves a critical component to the geochemical puzzle. Here the combined approach of modelling and experiment yield, parallel to the methodologies used for the aforementioned Marsec paper that focused on aluminium, produced corollary results. At a low pH(3), iron strongly competes for multidentate HA sites with the HREE fraction. At high pH(6), this changes and iron instead competes with all REE for HA binding sites, with equal affinity for carboxylic and phenolic sites.

In the early 2000s, there became a growing body of literature to reassess previously modelling experiments regarding organometallic complexing behaviour and expand this data to that which is observed in real world natural waters (Tang and Johannessen 2003; Davranche et al. 2004, Yamamoto et al. 2005, Tang and Johannessen 2005a) These prior studies were part of a movement away from characterizing the dissolved organic matter as a homogenous pool of available ligands, and all similarly used the fractional constituents that were separated by molecular weight through accepted separation (ultrafiltration) techniques that in turn allowed them to be correlated. As highlighted in the paper, though the original model was somewhat accurate as a predictive tool for estimating the complexing RE-HA behaviour between, it is

inherently flawed through the parameterized assuming the humic fraction is the only capable of metal binding (Tang et al, 2006).

In 2003, Tang and Johannessen (2003) compared model and field data from other studies to show there could exist upwards of a 20% difference between predicted versus experimental data across the 14 REE species. Though it was carefully noted that these difference tend to shrink to around 10% when accounting for partitioning of REE towards humic and fulvic fractions. This comparative research began to tease out the selective partitioning of REEs in regard to DOC and pH conditions playing a role in their sorptive preferences, which were also influenced by the presence of other strong solution ligands. In Cameroon, for example, both extremely high DOC and low pH overwhelmingly promote organic REE complexation due a lack of available competing ligands, where as the model predicted a much lesser amount (Taniziki et al. 1992). The less-acidic sites such as those in Japan saw higher HREE complexation with the FA fraction that suggest LREE are more strongly associated with the larger, less soluble HA (Viers et al. 1997). This was a trend observed across all site data well. In the Sweden sites, which were characterized by a circumneutral pH, two more interesting trends were evident; a near complete complexation occurred with the ultrafiltered organic material and REE enrichment was more favoured towards the humic, colloidal phases (Ingri et al. 2000). From attenuating the model to the experimental results from these 3 sites and including known inorganic ligands for HA bindings sites, these simulations indicate that in circumneutral pH indeed the dominant complexation will occur with dissolved organic material. And that these humate complexes, in terms of fractionated species, will vary with pH conditions; values between 5.4-7.9 will favour LREEs and between 4.8-6.7 that of HREEs. However, the model still suggests there will remain a strong competition with inorganic ligands. Carbonate for

example, displays an affinity towards higher molecular weight REEs, as does the fulvic acid portion of the DOM pool, which makes these overall more evenly distributed between organic and inorganic complexes whereas LREEs are preferentially enriched as colloids (Yamamoto et al. 2005; Verplanck 2013). In less alkaline natural waters, likely inorganic ligands such as sulfate would be the more common complexing agent.

Field and lab experiments testing of REEs on the sorption of Carrizo sand would later underline this relationship further, identifying that sorption was highly enhanced by the presence of strong complexing ligands such as carbonate or humic substances at pH<4 and that this decreased above pH 4 (Tang and Johannesson, 2005; 2006). In terms of partitioning, also shown were the preferential sorption of HREEs in solutions lacking these ligands and the favouring of LREEs removal in those doped with carbonate ions. These become important concepts in identifying the enhancement of fractionating behaviour of REEs themselves in the presence of competing strong ligands, as prior study indicated a general REE concentration decrease in more neutralizing pH conditions (Johannesson et al. 1995). Although the homogenous nature of sand in regard to estimating surface interactions provide only a basic framework in how these behaviours might translate to sorption or scavenging by metal oxides.

Translation of this research to the Snake River would suggest that the primary inorganic ligand complexing with REEs would be sulfate, due to its constant generation from AMD/ARD weathering processes and biogeochemical cycling between hydrogen sulfide (Crouch 2011; Verplanck et al. 2004, Bencala et al. 1991). DOC values varying from 1 and 1.5 mg/L put these at the low end of world average river waters (Tang et al, 2004) but this amount is sufficient to at least suggest dissolved organic carbon is playing a role in altering the aqueous phases of REEs away from free ions to that of more stable inorganic and organic complexes, some of which

would be colloidal. But as Trib 2095 is at extremely low pH condition, with a host of metals such aluminium and highly reactive (dissolved) iron species in high concentration, competition between them and REEs for binding sites on humic/fulvic fractions could be also playing a role in the preferential formation of these complexes with inorganic ligands. In contrast with Peru Creek, and the major wetland below the mine portal, the elevated DOC concentration coupled to an increased residence time would strongly favour the formation of REE-DOM which could be sequestered and released by the photochemical cycling of iron. Related to this preference of REEs for an organic ligand (DOM) against an inorganic (sulfate), could additionally indicate a relatively limited availability of sulfate due to its microbial-mediated reduction to hydrogen sulfide in mine workings (Druschel et al. 2004; Roesler et al. 2007). In Trib 2095, for example, a low residence time, lesser DOM input, and continued enrichment of sulfate would favour this inorganic REE-SO₄ complexation, which would be expected to act more conservatively in this system.

2.5.4: Iron & REEs

As we have explored relevant research regarding aqueous behaviour of REEs in terms of complexation with dissolved organic matter and the competition with other dissolved strong binding metals (Fe, Al), it becomes tantamount to shift a critical eye towards their loss and portioning in the solid phases from oxidative dissolution processes known to be occurring in acid mine waters. As an important analogue for this study, we look at the Verplanck (2004) study “*Rare earth element partitioning between hydrous ferric oxides and acid mine water during oxidation*” due to its focus on REE geochemistry and behaviour in extremely low pH conditions by evaluating, both through lab experiment and field data, the effects of iron oxidation on dissolved REE concentrations in acidic mine waters ranging from pH 1.6 to 6. We have

previously discussed the possible transformations and partitioning that can occur to free REE ions in solution, but in order to understand the entire geochemical “picture” their fate and transport it is necessary to account for activities that might serve to remove them from the water column.

Sites evaluated in this paper were all AMD impacted streams that also contained elevated concentrations of REEs, with varying pH conditions and inflows of neutralizing waters. This provides an excellent diverse dataset in which to observe the behaviour of REEs in different aqueous, acidic conditions. Through the spatial tracing of simultaneous metal loadings of aluminium, iron, and as well as REEs it is possible to quantify losses due to precipitation through a mass imbalance. Simultaneous filtered and filtered samples were also collected to differentiate changes from aqueous, dissolved phases to colloids and solids, which bolsters the ability to quantify a total mass balance.

These study results from the Big Colorado Mine effluent highlighted an interest trend in iron by that within a 100m of the outflow, 73% of iron(II) had oxidized and precipitated, where as aluminium and REEs showed no appreciable losses. It's important to note that the pH conditions of this site see continuing decrease in pH as distance furthers from the portal, starting at pH 4 and going as low as 3.2 after 100 meters. This suggests a abundant production of protons beyond what can be consumed by ferrous iron oxidation, which points to the hydrolysis of ferric iron to iron hydroxides as the dominant reaction for this pH drop, further indicating precipitation. Despite these significant losses in dissolved iron and changes in species, no complexation or co-precipitation of other metals or REEs seemingly occurred.

Samples from the Crystal Mine adit, on the other hand, show a much more surprising trend in metal and REE behaviour. Unlike the Colorado Big Mine, pH conditions here increase

in distance from the mine outflow, beginning at 5.1 and ending near neutral (6.6), likely due to additional inputs of shallow circumneutral groundwater. Between the first and second portion of the reach, there are losses in the dissolved fraction of aluminium, iron, but total mass loads remain the same, which indicates that precipitation is occurring but that these solids are not depositing and are instead being transported within the water column. REE concentrations also decrease in this stretch, however this is attributed to dilution, as there is no change between in the dissolved (filtered) fraction. Further downstream, as pH conditions to rise, a much larger mass imbalance appears in the dissolved fractions of aluminium, iron, as well as REEs. But again, total loads appear relatively stable, which indicates that above pH 5 that REEs are no longer conserved and are being co-precipitated or complexed as colloids. Additionally worth noting is that fractionating of differing REE also becomes evident in these co-precipitated losses, as they become much more heavily enriched in HREEs.

To better interpret the field data results, lab experiments were performed using collected samples that varied from pH 2.6 to 5.3 that were then allowed to oxidize to the walls of the container. Both the precipitates and the remaining solution were analysed to observe changes in the solid and aqueous fractions, pH, mineralogy of the precipitates, and the partitioning of REEs if occurred. These results well correlated to that which was observed in the field and the known mineralogy of iron precipitates, though the preferential enrichment of HREE was less evident. Possible explanation for this related to the stability of REEs complexed with sulfate, the dominant ligand present and an important process referenced in other literature, which would resist the selective adsorption of HREEs over LREEs.

This is coincidentally the most striking aspect of acid mine drainage; the rusty orange coating of hydrous ferric oxides on a streambed that immediately alerts the casual observer to a

problem. This equates to a transition of an aqueous phase ferric iron to the insoluble solid iron (III) hydroxide, which can scavenge a host of other ions in the process. It has also been experimentally shown that the type of HFO also plays a role in its sorptive capacity, which is determined by the environmental conditions under which it formed (Nordstrom 1985; Nordstrom 2011); for example schwertmannite, a common HFO formed in ARD systems, has a much higher capacity for the adsorption than goethite, which forms under a higher pH condition. A host of studies have focused on how these hydrous ferric oxides (HFO) precipitates serve to remove a host of other metals, anions, and even dissolved organic material from solution through strong metal binding (McKnight et al. 1992; Gammons 2005a, Wood, S.A. 2006. Parker et al. 2008.), further underlining this remains a highly pH dependent processes, with both the efficiency and specificity being primarily determined by this parameter.

2.5.5 Summary

In summation we see that there are complicated, competing ligand interaction with REEs in terms of the formation of more stable aqueous complexes over that of free ion species as well as their removal from solid phase iron scavenging. Albeit it is still possible to make a host of conclusions from this data that proves very useful in interpreting data from the Snake River: at pH values below 5.1 REEs behave very conservatively and it is therefore possible to use their concentrations as a geochemical proxies for their mineral sourcing, however between pH 5.1-6.7 both removal and fractionation occur, and can be heavily skewed towards the HREE depending on the presence of competing, stabilizing ligands such as carbonate, sulfate, or humic substances (Verplanck et al. 2004; Tang and Johannesson 2005, Gammons et al. 2005b). However, these REE complexes have potential so show enhanced sorptive qualities depending if these interactions facilitate ligand-to-metal or metal-to-ligand charge transfer (LMCT, MLCT)

(Voelker et al. 1997; Chen 2015).

Through the previous synthesis of research, a picture begins to take shape about the various reactions occurring in the Snake River Watershed. It is only possible to gain such insight through the evaluation of literature that has studied the behaviour of REEs in a host of differing pH environments, undergoing competitive scavenging by other metals, precipatory processes, and in the presence of ample complexing agents such as organic and inorganic ligands (Table X). Particularly important is the study of sites that might be analogous to the Snake River, a crucial aspect requiring the inclusion of pioneering work by Phillip Verplanck.

	low pH	high pH
<i>Preferred REE phase</i>	Free ion or complex	colloidal and solid
<i>REE Behavior</i>	Conservative	Non-Conservative
<i>Dissolved REE enrichment</i>	HREE	LREE
<i>Preferred DOM binding</i>	HREE-FA	LREE-HA
<i>Preferred Ligand</i>	Sulfate & DOM	Carbonate
<i>DOM-REE Fractionation</i>	LREE	HREE

Table 4: Contrast of REE behavior by pH (Goldstein and Jacobsen 1988; Tang and Johannesson 2004, 2005a, 2006; Verplanck et al., 2004; Gammons et al. 2005b, Marsac et al. 2012; Davranche et al. 2013. Migaszewski et al. 2014, Verplanck 2014)

Chapter 3: Field Sample Collection & Analytical Methods

3.1 Water Sample Collection:

3.1.1 Major Cations and Anions

Major cation and anion water sample collection were done according to the Colorado Department of Public Health and Environments methodologies and standards for testing surface water (CDPHE, 2001) as well as EPA Method 200.8. Samples were collected in 60ml HDPE plastic containers, with a sample volume of no more than 50ml. Prior to collection, each container was first bathed overnight in a 3% mixture of reagent-grade nitric acid in ultra-pure deionized water, followed by three flushes of ultra-pure deionized water after of which they will be left to dry. During collection, samples were collected in with .45 um nylon filters to prevent colloidal or eigencolloids contamination. After collection, samples were labelled with their respective pH, total dissolved solids, and then acidified with trace-metal-grade nitric acid to a value near or less than 1.5 for laboratory analysis. For each collection, field blank were prepared using ultra-pure deionized water, also acidified to the same value, to quantify any further possible contamination from containers or acids used. For the diel experiment, major cations and anions were sampled hourly Sites A, B, and C. For the tracer experiment, all sites were sampled once, before the commencement of conservative tracer injection. For synoptic and longitudinal investigation, samples were collected in relation to previously study sites and locations (McKnight et al. 1988; Boyer 1999, Belanger 2002, Todd 2006, Crouch 2010, Rue 2012).

3.1.2 Dissolved Organic Carbon

Dissolved organic carbon (DOC) samples were collected following EPA Method 415.1. Prior to collection, glass amber bottles was pre-rinsed then bathed overnight in a 5% mixture of

reagent-grade hydrochloric in ultra-pure deionized water, followed by three flushes of ultra-pure deionized water after which they were combusted at 500°C to remove any residual carbon contamination. Upon collection, all waters were filtered through a Whatman GF/F filter with a nominal pore size of 0.7 microns. For the diel experiment, only Site A was sampled for DOC and bi-hourly. During the tracer experiment, initial DOC samples were collected at each site. In the synoptic and longitudinal studies, DOC samples were not collected.

3.1.3 Isotopes

Isotopes samples were collected in 10mL glass vials with a teflon cap. Prior to collection, all vials were triple rinsed in ultra-pure DI and dried. In the field, samples were collected unfiltered and devoid of headspace within the vial to prevent further fractionation of O¹⁸ isotopes.

3.2 Field Meters and Instruments

For synoptic and longitudinal sampling, total dissolved solids were obtained using an Oakton TDSTestr field probe calibrated to a Hanna Instruments stock solution (HI 7032) of 1385ppm. To test pH, an Oakton pHTestr 30 was used and were was calibrated daily using 3 standards (triple point), and rinsed between samplings.

The YSI Model 63 multiparameter field probe was used to collect temperature, TDS, and pH data for both diel and tracer experiments. Before field deployment, it was calibrated using the HI-7032 conductivity standard and exhibited an acceptable less-than-5% margin of error. For pH, a triple point calibration was made using Fischer Scientific buffer stock solutions of pH 4, 7, and 10 standards. However, the pH portion of the probe also broke halfway through the diel

study (12am), leaving a gap in data collected.

For quantifying iron species during the diel experiment, a Hach DR-2800 Field Spectrophotometer was used on-site to measure ferrous (Fe^{2+}) iron via the Phenanthroline Method adapted from *Standard Methods for the Examination of Water and Wastewater* (15th ed. 201 1980). Total iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$) was measured by ICP-MS by the LEGS lab, with ferric iron concentrations then estimated by subtracting Fe^{2+} from Fe^{total} . Reactive iron species were only measured during the diel study at Site A, however total iron was measured at all sites by cation samples collected.

Discharge measurements were collected using a Model 6205 Pygmy Meter and USGS Midsection method (Ratz et al, 1982). Stream transects were chose by both morphology and location of previous measurement or prior study (Boyer 1999, Belanger 2002, Todd 2006, Crouch 2010, Rue 2012). Supplemental streamflow data from the Snake River gauge at Keystone (#09047500) was available via the USGS National Water Information System web interface.

3.3 Tracer Injectate

Sodium chloride (NaCl) and Lithium Bromide (LiBr) were chosen as the conservative salts for the dual injection tracer experiment (Kimball et al, 1988). In the main stem of the Snake River, LiBr was chosen as the additive tracer, with NaCl for Trib 2095. To create LiBr tracer sufficient to increase in-stream concentration by at least an order of magnitude, it was estimated that at an high estimated discharge of 5 cfs this would require 500 grams dissolved in 20L of DI water. Final concentrations for the LiBr injectate were measured as 1.8 grams/liter of lithium and 25 grams/liter of bromide. In Trib2095, given the challenge of lateral inflow contributing

additional solutes and volume at an estimated discharge of less than 1cfs, this required 2.2 kilograms of NaCl dissolved into 20L of water to a final measured concentration of 69 grams/liter of sodium and 46 grams/liter of chloride

3.4 Sample Analysis:

Cation, anion, and tracer samples were delivered filtered and acidified for analysis to the Laboratory for Environmental and Geological Studies (LEGS), located within CU-Boulder Geology Department. Cation data were provided via Inductively Coupled Mass Spectrometry (ICP-MS) on a Varian Model X. Anion data, specifically sulfate, were provided via Ion Chromatography (IC) analysis on a Dionex Series 4500I.

Isotopes and DOC data were provide by the Kiowa Environmental Chemistry Lab at the Institute for Arctic and Alpine Research (INSTAAR). DOC was measured using a Shimadzu Total Carbon Analyzer, Model TOC-L. Isotopes, specifically Oxygen-18 and Deuterium, were measured by a Picarro Cavity Ringdown Spectrometer, Model L2130-i.

Chapter 4: Longitudinal and Synoptic Sampling

4.1 Introduction

In order to better understand the relative contributions of trace metals and REE in the Snake River Watershed as well as the temporal trends in these concentrations in correspondence to flow conditions, a longitudinal survey was conducted in early summer of 2013. Given the wealth of information available on rising solute enrichment trends during late summer baseflow, there remain outstanding questions as to how extreme or flood stage events influence their fate and transport. Because stream alluvium and sediment are major sources of metals due to precipitation and sorption processes occurring, yearly spring snowmelt has high potential to mass mobilize these materials and depending on input there exists potential to alter channel morphology.

In the Snake River, spring melt begins in late April and high flows can persist as late as July depending on the last snowfall. Promoting this melt are frequent afternoon thunderstorms that are driven by the orographic effect of the nearby Continental Divide. With both upper portions of Peru Creek and the Snake River are fed by a series of intermittent and perennial streams in a pronounced alpine environment, this results in a flashy hydrologic regime that can be greatly influenced by precipitation events, even those of short duration but high intensity. Ecological evidence of these flushing events was noted by a large 2007 rainstorm event resulting in the mass killing of all fish present in the lower portion of the Snake River, caused by the spiking of dissolved metal concentrations at least an order of magnitude above background, which is already borderline toxic level (Todd et al. 2006; Berwyn 2007)

In 2013, late April and early May snowfall and high temperatures in towards the end of the month into June had the Snake River running at near-historically high flow. This resultant

flooding was sufficient to destabilize and undercut the streambank, mass mobilize sediments, and also wash out the major road to Montezuma that required the evacuation of the town.

Accordingly, it was not possible to reach Peru Creek or the upper Snake River during this time.

But on June 6th, it was possible to access the river near Keystone where the USGS gauge is located, so sample were instead collected here and at the confluence of the North Forks with the Snake. It would be 5 more weeks until the roads were rebuilt and these areas were reachable again. So on July 13th, we comprehensively sampled the upper portions of the reach and measured discharge as well to provide estimates for total metal loadings from all major tributaries.

To better interpret the synoptic samples and observe overall trends in changes to water chemistry, archived samples from previous study that have been stored at INSTAAR were re-tested. By parsing this large set of historical samples, specific ones were chosen for their similarity of flow conditions and date. The 56-year flow record for the Snake River at the Keystone gauge guided these decisions, as it represents the most contiguous record for the watershed and given the relatively similar contributions of all tributaries to overall watershed streamflow (Boyer et al. 1999), provides at least a framework in which to compare samples from the mid 1990s to today.

4.2 Specific Methods:

Major cation and anion water sample collection followed Colorado Department of Public Health and Environments methodologies and standards for testing surface water (CDPHE 2001) as well as EPA Method 200.8. Prior to collection, HDPE bottles were bathed in a reagent-grade 5% nitric acid bath, tripled rinsed with DI, and then dried. During collection, samples were collected with .45 um nylon filter and then acidified with trace-metal-grade nitric acid to a value

near or less than 1.5 for later laboratory analysis. Field blanks were also prepared using identical bottles and procedure to quantify any sources of contamination or error.

Discharge measurements were collected using a Model 6205 Pygmy Meter and calculated by the USGS Midsection Method (Ratz et al. 1982). Stream transects were chosen by both morphologic constraints and location of previous measurement or prior study (Boyer 1999, Belanger 2002, Todd 2006, Crouch 2010, Rue 2012). Supplemental streamflow data from the Snake River gauge at Keystone (#09047500) was available via the USGS National Water Information System web interface.

4.3 Results

4.3.1 Synoptic Sampling at the Keystone Gauge; June 6th and July 13th, 2014

Because these samples were filtered, here we can only conclusively observe the dissolved fraction. By this it appears that during high flow events, trace metals such as iron and zinc increase loadings by a factor of between 3 and 4, whereas lead is almost 7x higher. While aluminium loadings only double, it has the largest TMDL making it the predominant contributor of trace metals to the water column. With noted zones of aluminium oxide deposition in both the lower portion of Peru Creek and the Snake River at SN-3, this also suggests remobilization of these solid phases into the dissolved, colloidal fractions within water column as well. And while it appears that REEs remain in low concentrations and loadings in contrast with these metals, its important to quantify that here these amounts still represents at least 3 orders of magnitude more than in average surface or groundwaters.

Keystone Gauge	6/7/14	Zinc	Iron	Aluminum	Lead	Neodymium	Yttrium
535 CFS	Concentration(ppb)	185.43	195.25	250.33	2.77	0.851	0.52
6/7/14	TMDL (Kg)	242.72	255.56	327.66	3.63	1.11	0.68
Keystone Gauge	7/13/14	Zinc	Iron	Aluminum	Lead	Neodymium	Yttrium
172 CFS	Concentration(ppb)	159.65	189.2	375.59	1.21	0.995	1.03
7/13/14	TMDL (Kg)	67.18	79.62	158.06	0.51	0.42	0.44

Table 5: Solute and REE concentrations at the Keystone Gauge, 6/7/14 & 7/13/14

4.3.2 : Longitudinal Sampling of the Snake River: July 13th, 2014

On July 13th, a sampling campaign of the major tributaries of the Snake River watershed was done to evaluate trace metal loadings relative to contributing tributaries (Figure 6). To quantify this, water samples were collected at selected sites along with pygmy meter measurements taken at the confluence of Deer Creek and the upper Snake River, Peru Creek and the Snake River, and the North Forks with the Snake River. However, it was not possible to measure discharge at the portion of the Snake River below the confluence with Peru Creek and above the North Forks, though water chemistry samples were still collected. Even so, these synoptic scale data provide important information regarding the major source of trace metals as well as their fate and transport downstream.

In the case of the Snake River, Peru Creek and the upper Snake River (SN-2) are the major contributors of both metals as well as REEs. Both exhibit extremely high loadings of zinc, iron, aluminium, neodymium, and yttrium, although these amounts decrease significantly upon mixing with more pH neutral waters and in differing amounts seemingly related to their respective solubility. But both concentration and loading data reflect similar losses of trace metals such as iron and aluminium by a factor of 2 within the river, whereas zinc and REEs display a remarkably similar trend in these decreases by a factor of 3 (Table 6). The noted visual presence of both iron and aluminium oxide in the confluence zone of the upper Snake with Peru Creek and supported by data showing decreasing mass loadings do not appear to influence REEs and therefore experimentally demonstrate that they are not being scavenged by the formation of these precipitates. In Peru Creek, other circumneutral flows also increase pH and result in significant aluminium oxide deposition, and again REE loadings appear unaffected. These observations of REEs intransigence to metal oxide scavenging below pH values of 6.5 are additionally in agreement with other related field studies (Verplanck et al. 2004). And assuming

relative conservative behaviour zinc, losses in loadings between sites SN-2 and SN-3 suggest cation scavenging is in fact occurring by the strong-metal binding of both aluminium and iron.

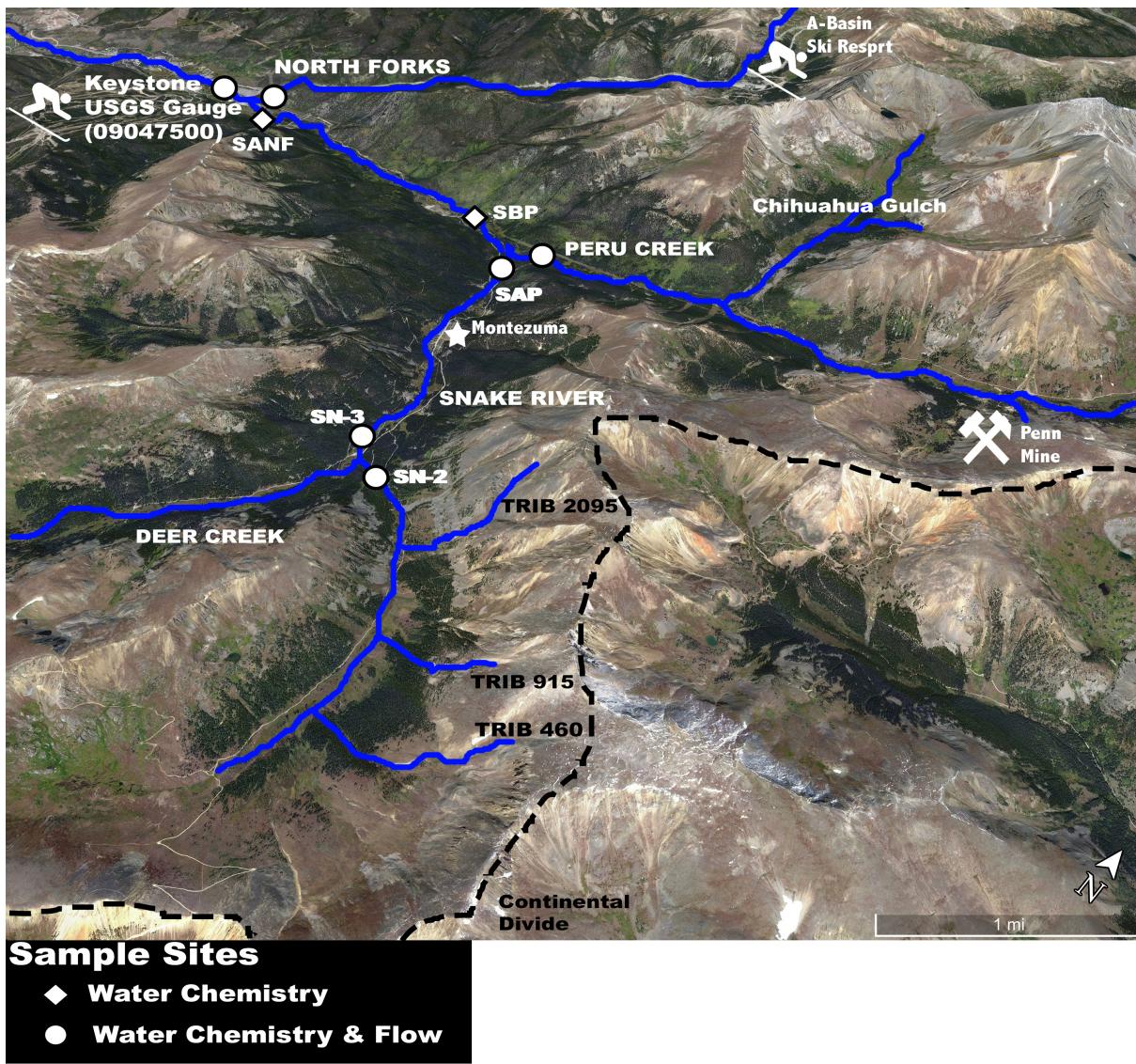


Figure 7: Sampling site map across the Snake River Watershed, 7/13/14 (Imagery: GoogleEarth)

7/13/14	Zinc (mg/s)	Fe (mg/s)	Al (mg/s)	Nd (mg/s)	Y (mg/s)
SN-2	323.09	577.15	2615.76	2.89	4.77
SN-3	288.81	564.45	1602.84	2.56	4.15
Snake Above Peru	341.69	387.47	1130.8	1.53	2.3
Peru Creek	2264.68	1449.32	3841.48	14.42	15.84
Snake Below Peru	*	*	*	*	*
Snake Above North Forks	*	*	*	*	*
North Forks	4.18	224.5	54.23	0.4	Below DL
Keystone Gauge	777.57	921.5	1829.31	4.82	5.04

Table 6: Metal and REE loadings across sites, 7/13/14

7/13/14	Flow (cfs)	Zn (ppb)	Fe (ppb)	Al (ppb)	Nd (ppb)	Y (ppb)
<u>SN-2</u>	20	570.49	1019.09	4618.75	5.11	8.43
<u>SN-3</u>	33	309.07	604.04	1715.27	2.74	4.44
<u>Snake above Peru</u>	35	344.76	390.95	1140.97	1.54	2.32
<u>Peru Creek</u>	95	841.86	538.76	1428.01	5.36	5.88
<u>Snake below Peru</u>	*	548.52	359.4	1163.11	2.88	3.51
<u>Snake above North Forks</u>	*	555.00	337.59	984.20	2.13	2.61
<u>North Forks</u>	70	2.11	113.26	27.36	0.2	Below DL
<u>Keystone Gauge</u>	172	159.65	189.2	375.59	0.99	1.03

Table 7: Metal and REE concentrations, 7/13/14

4.3.3 : Historical Trends at Sites SN-2 and SN-3

At SN-2, high flow conditions likely existed in June of 1995 and 1996 according to streamgauge data at Keystone (Table 7). Neodymium and yttrium, rare earth elements observed in largest concentration, fluctuated between 1 and 4 ppb, with relative increases to the amount of flow. Zinc shows similar trends to this, with increases relative to higher flows. Although it appears that at above 600cfs, these extremely high flows tend to dilute concentrations of these solutes. In 2013, at significantly lower flow conditions on May 29th, nearly double the amounts of neodymium and yttrium were observed. As summer progressed, and discharge approached baseline, these concentrations appeared to increase in proportion to declining flows. This tentatively suggests that loadings of REEs remains constant and that changes to flow are predominantly what are controlling concentrations, though it is not possible to quantify this against 1995/1996 data because of gaps in sample archive.

However, a more complete record is available for SN-3, which is just below the inflow of Deer Creek (Table 8). And although dilution of the upper Snake River by these pristine waters causes precipitation of pH-sensitive metals such as iron and aluminium (Boyer et al. 1999), conservative solutes such as zinc remain dissolved in the water column (Runkel et al. 1996). Even after the confluence, pH remains acidic and in such conditions REEs also behave

conservatively (Johannesson et al. 1995; Verplank et al. 2004). Thereby allowing the use of this more temporally heterogeneous dataset from SN-3 (Table 9), it is apparent that in baseline, low flow conditions that both REE and zinc concentrations have increased significantly between 1996 and 2013. Furthering this observation is that neodymium and yttrium loadings have increasing by almost factor of 4, which is congruent with other study that correlated a similar increase in zinc concentrations in correspondence with enhanced sulfide weathering (Crouch 2010). These mirroring trends of rising zinc concentrations with REEs provides further evidence that mineral dissolution are the primary means of solute enrichment in the upper Snake River, with rates increasing relative to changes in climate and the hydrologic regime. If such changes persist, or worsen in the coming years, will liberate more rare earth metals to be mobilized greater distances down the reach.

Site SN-2	Flow at Keystone Gauge (CFS)	Nd (ppb)	Y (ppb)	Zn (ppb)
6/20/95	736	1.60	2.77	243
6/27/95	671	1.01	2.61	200
6/13/96	578	2.12	4.07	427
6/19/96	457	1.90	3.66	383
5/29/13	176	4.73	7.24	455.15
7/13/13	116	6.07	9.83	693.15
9/21/13	80	10.31	19.997	1058.9
10/12/13	52	9.32	15.472	934.2

Table 8: Historical Neodymium, Yttrium, and Zinc concentrations at site SN-2

Site SN-3	Flow at Keystone Gauge (CFS)	Nd (ppb)	Y (ppb)	Zn (ppb)
5/31/96	198	0.79	1.8	211
7/9/96	227	0.4	0.81	167
9/9/96	35	1.42	3.1	312
5/29/13	180	2.96	4.48	292
7/13/13	116	2.87	4.72	360
9/21/13	80	5.86	10.82	617
10/12/13	52	5.34	9.17	546

Table 9: Historical Neodymium, Yttrium, and Zinc concentrations at site SN-2

4.4 Discussion:

4.4.1 : Keystone gauge, the effects of extreme flow

During flood stage conditions of 535CFS at the Keystone Gauge, concentrations of trace metals and REEs appear relatively similar to those measured a month later. But concentration data are inherently flawed, as not accounting for total volumes of water. In this regard, a total mass load can be calculated using discharge and concentration. To better highlight the total mass that is being transported downstream, a Total Maximum Daily Load (TMDL) is then estimated using loading data interpolated over 24 hours. In comparing TMDL values in these two flow conditions, it becomes clear that significantly more solutes are being transported during flood stage. However, given the turbidity of the Snake River during high flows it is likely that more material still is being mobilized and transported in solid and colloidal phases due the sorption with suspended and wash load sediments, hyporheic zone flushing, and saltation of streambed coble covered in surface metal oxide precipitates. The fate of these materials all suspended differently in the water column, then settling out relative to size further downstream as alluvial deposit at the terminus of the Snake River into Dillon Reservoir and suggest cumulative enrichment here of sediments in metals as well as REEs.

A secondary observation to these data is the exceedance of EPA Aquatic Life Toxicity Standards by zinc and lead. This highlights the potential of high flows generated from yearly spring snowmelt to disrupt the aquatic ecosystem by killing most benthic microorganisms and fish. And again, because the Snake River terminates into Dillon Reservoir, there are further implications for these inflows of acutely toxic waters and sediment on aquatic organism habitat there. As shown in prior study that in late-summer baseflow conditions these concentrations are well beyond these standards (Todd et al. 2005; Todd 2006), it is now is clear by this data that

even in spring runoff conditions the dilution of heavy metals by melt water, its major contributor of flow, is no longer adequate to maintain a marginally aquatic ecosystem.

4.4.2 Longitudinal Sampling

While concentration data highlights advective and dispersive behaviour of solutes in solution, loading data are crucial in an ability to resolve changes in within the water column (Table 5). Losses from sediment sorption, hyporheic cycling, precipitation, dissolution, and colloidal complexation all play a role in altering this mass balance, where as concentration data can only estimate dilution of solutes and does not account for these changes. And despite the inherent error in measuring discharge with a pygmy meter, the ability to estimate these changes in total dissolved fractions remain helpful on a watershed scale to clarify the predominant contributors of both trace metals and REEs.

The secondary observation by this longitudinal survey is the lack of data regarding the fractionation of trace metals and REEs between dissolved, colloidal, and solid phases. And though measuring flow as well as solute concentration helps elucidate the portion remaining within the more labile dissolved fraction, the constant spiralling of these metals between aqueous, intermediate, and solid states makes it difficult to completely account for them in a perspective of mass balance. In this regard, it remains paramount to acknowledge such outstanding questions so that future investigations can possibly address them.

4.4.3 Historical Trends at Sites SN-2 and SN-3

While trends in streamflow and water chemistry vary significantly year to year, due to host of hydrologic, meteorological, climate related factors, stochastic events such as intense rainstorm have equal potential to influence these aspects as well. Accordingly, it proves difficult

to make long-term observations regarding changes to weathering rates, acid production, and mobilization of metals in this watershed due to its flashy regime. However, given the availability of a 56-year discharge record from the Keystone streamgauge, is it possible to contrast solute concentrations from archived samples against analogous flow conditions.

Stored at the Institute for Arctic and Alpine Research (INSTAAR) are a library of water samples stored from many prior studies of the Snake River. These have served as important historical snapshots regarding the changing water chemistry. And through the synthesis of this long-term record the acknowledgment that concentrations of metals such as zinc are exponentially increasing. (Todd et al. 2012). For the purpose of this thesis, these samples provide an opportunity for re-analysis to investigate the presence rare earth element as well as trends in concentration. Specifically, sites SN-2 and SN-3 were chosen for this examination because they are among the oldest, most repeated sampling locations in the Snake River. Using these spatially homogenous data, it indeed appears enrichment of REEs are increasing at the now-exponential rate observed with that of zinc and supports the conceptual explanation that the enhanced generation of acid related to reductions in the water table as well as changes to the hydrologic regime are the responsible mechanisms.

Chapter 6: Dual Injection Tracer Experiment in Trib 2095

6.1 Introduction

On September 20th, 2014, a dual injection tracer experiment was performed in the upper Snake River at Tributary 2095. Two injection points were chosen; one above the area of groundwater inflow in the tributary itself and the other above its confluence with the main stem of the Snake. Two conservative tracers, Sodium Chloride (NaCl) and Lithium Bromide (LiBr) were used to track the changes in flow between these differing hydrologic regimes. The reason for this experiment were twofold; while previous investigation focused on tributary itself (Crouch 2010) there exists no data regarding the flow of the Snake River itself along this short portion of the reach in terms of quantifying groundwater inputs and accordingly from a mass balance perspective there exist an incomplete understanding of how loadings are changing from these dynamic mixing processes. Therefore the purpose of this study is to expand beyond the tentative observations from the previously discussed experiments to collect precise hydrologic data that allows a better resolution regarding the contrasting of behaviour of pH-sensitive heavy metals such as iron with more conservative elements such as sulfate, zinc, and REEs in a stream responsible for their significant sourcing in this watershed.

Five sampling sites were chosen by proximity to injection sites and areas of known changes in flow (Figure 1). Samples were collected at each site with an interval of 5 minutes for the first 30 minutes after the start of injection, then switching to every 10 minutes for 30 minutes, and again back to a 5 minute interval after turning off of the pumps. This ensured a high resolution in the arrival and decay period of the tracer, with less samples collected during the steady state phase when such precision is unnecessary. Graduate students from Applied Stream Ecology assisted in this experiment, stationed across the many sites, and were instrumental to its success.

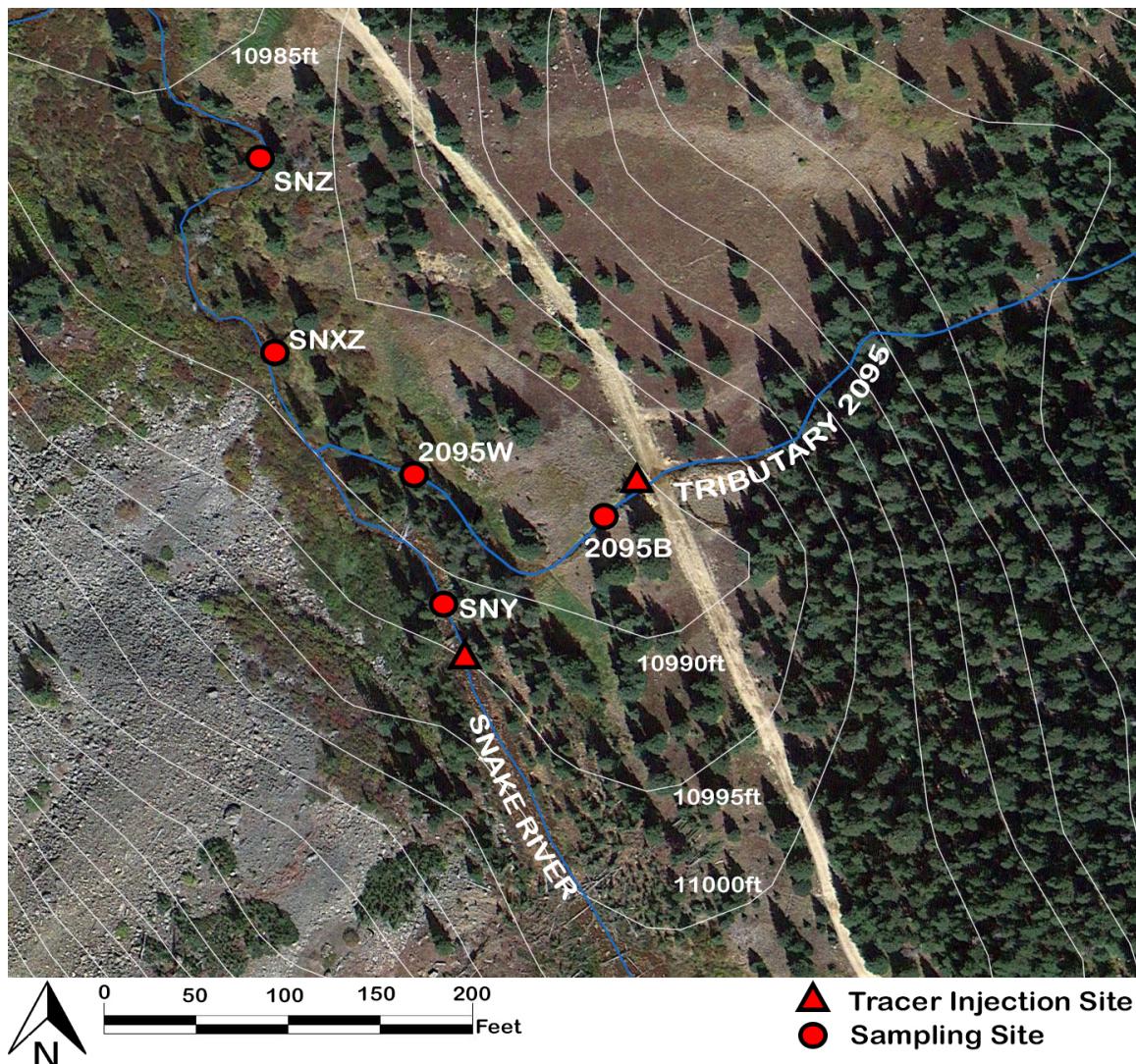


Figure 8: Tracer Injection Experiment Site, Trib 2095 (Imagery: GoogleEarth, Topographics: USGS NED)

6.2 Specific Methods

6.2.1 Cations and Anions

Procedures for bottle prep, sample collection, filtration, and acidification followed joint EPA and CDPHE standardized protocols as outlined in Chapter 3. Prior to commencement of injection, background solute concentrations were collected at each site to allow for baseline data from which to identify the tracer addition as well as the loadings to be calculated for metals and REEs. Field blanks were also prepared to quantify any additional contributions of contaminants during collection or processing, and all samples were again delivered to LEGS for lab analysis by mass

spectroscopy (ICP-MS) and ion chromatography.

6.2.2 Tracer Injectate and Addition

Using coarse discharge data collected previously by pygmy meter and background conservative solute (Na, Li, Br, Cl) concentrations from the diel experiment, concentrations of the two injectates required to result in at least a magnitudinal increase were estimated. The choice of selecting LiBr for the main stem of the Snake River was due to the relatively low background concentrations of both elements, which would allow a lesser solute addition and a clearer signal to noise ratio. The use of NaCl for injection into Trib 2095 rather required a much larger amount of salt to be used due to both the high background concentrations and increasing amount of these elements by groundwater inflows.

To achieve target injectate strengths, 500 grams of Lithium Bromide was dissolved in 20L of ultrapure DI water that resulted in verified concentration of 18 grams/liter of L of lithium and 24 grams/liter of bromide. For Sodium Chloride, 2.4 kilograms were dissolved in 20L of ultrapure DI water to yield a verified concentration of 46 grams/liter of sodium and 69 grams/liter of chloride. Two samples of each injectate were taken at the beginning and end of the experiment to quantify any changes in the concentration of the solutes over the course of injection, however no variation was observed.

6.2.3 Field Equipment

Two Millipore model field pumps, powered by 12V battery, were used to inject controlled volume of 300mL per minute, which was verified every 20 minutes. No errors or failures in the pump or battery were noted, and fluctuations in pump injection volume varied by less than 5%.

Multimeter YSI probes (conductivity, pH) were also used to monitor the arrival, stabilizing, and decay of the tracer pulse, though these were only used as a diagnostic tool to identify the tracers reaching of steady state concentration. Though given the extremely high solute concentration of both the Snake River and Trib 2095, these pulses were difficult to resolve beyond the fluctuations of the meter itself.

6.3 Results

6.3.1 NaCl Tracer Data

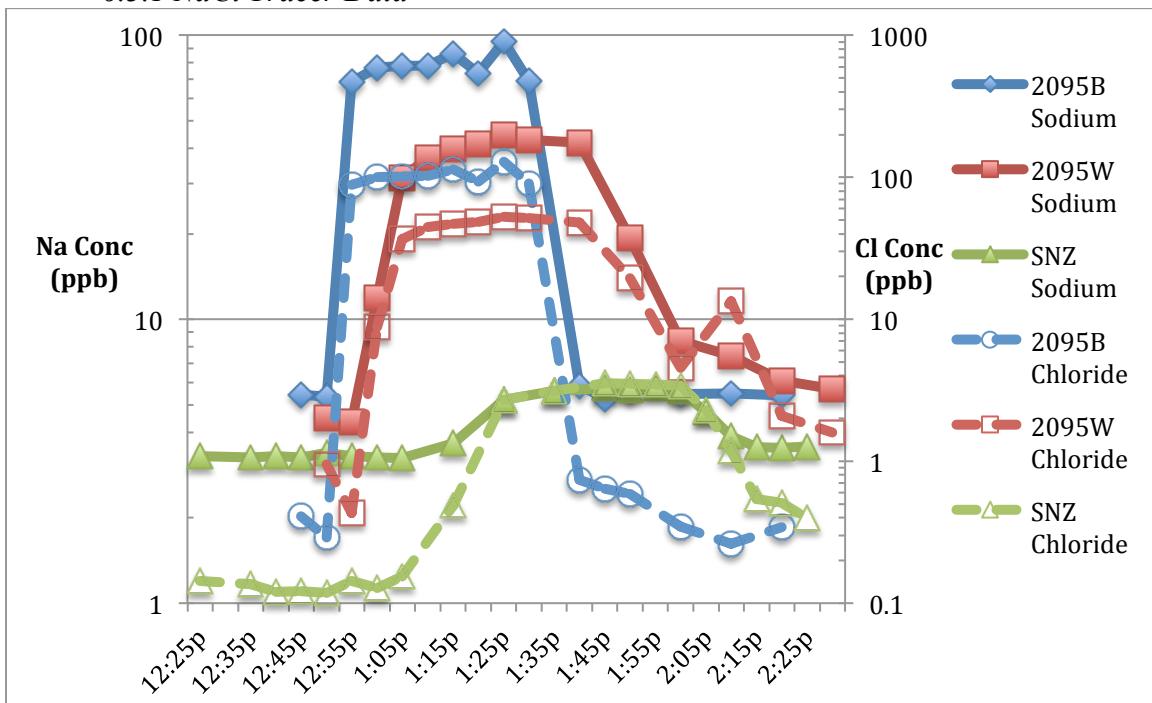


Figure 9: Sodium and Chloride tracer data across sample sites, 9/20/14

6.3.2 LiBr Tracer Data

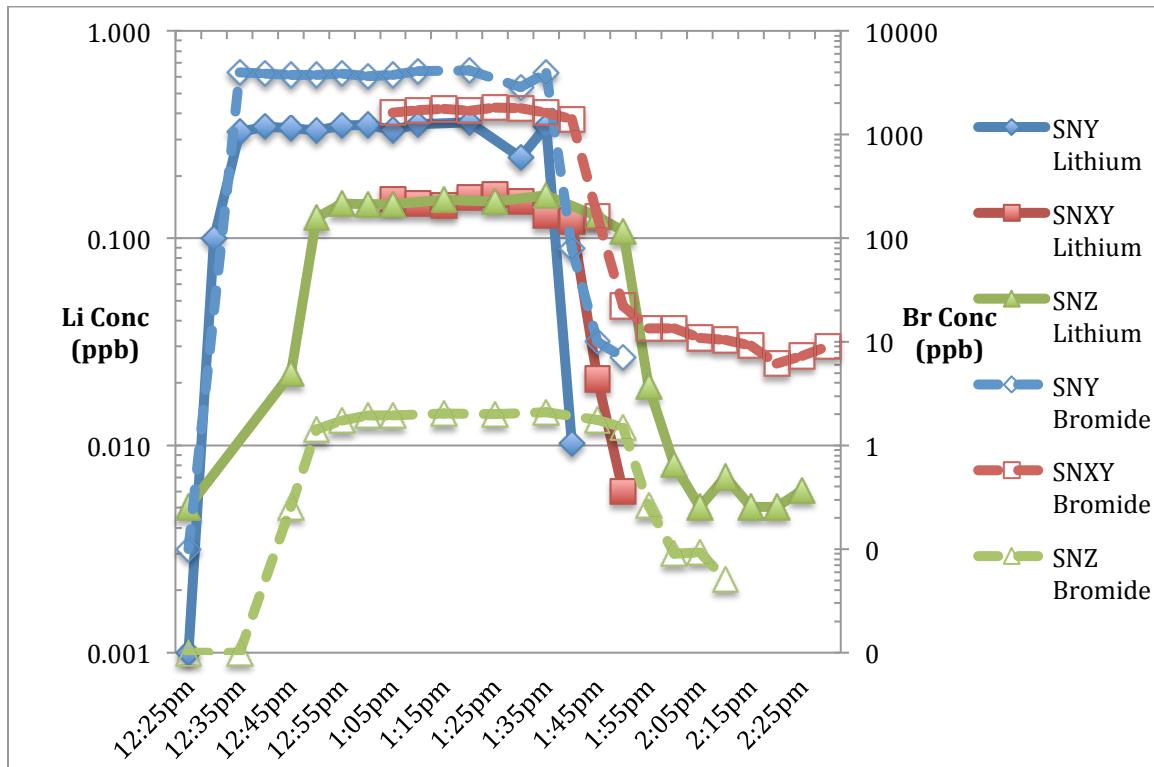


Figure 10: Lithium and bromide tracer data across sample sites, 9/20/14

6.3.3 Flow Data and Loadings

Flow data calculated from this dual injection tracer reveals a much more complex flow path than previously known. While the path of Trib 2095 into the main stem of the Snake is sinuous, with small diversions into temporary wetlands and a diffuse channel with the seep of additional of shallow groundwater inflow that double its discharge, the Snake River is itself is also gaining flows from these groundwaters by the equivalent amount. This data alone greatly enhances understanding of the interconnectivity of these two streams as well as the highlighting the hydrologic complexity of this high alpine catchment. These data also suggests a coupled hyporheic zones with high potential for redox reactions by mixing of contrasting surface and groundwater.

Site	SNY	20995B	2095W	SNXZ	SNZ
Flow (CFS)	1.14	0.11	0.23	2.40	2.70
Iron (mg/s)	77.82	237.39	196.79	249.73	331.04
Zinc (mg/s)	14.12	57.94	57.85	65.94	108.23
Sulfate (mg/s)	4.19	4.77	4.69	11.30	16.36
Neodymium (mg/s)	0.12	0.33	0.32	0.48	0.84
Yttrium (mg/s)	0.29	0.75	0.70	1.11	1.78

Table 10: Flow data and loadings across sample sites, 9/20/14



Photo 2: Temporary wetland of Trib 2095, noted iron oxide deposition (D. Castendyke)

Prior investigation revealed that Trib 2095 is responsible for upwards of 80% of zinc loadings in the upper Snake (Crouch et al. 2013), which is further supported by data from this experiment. These loadings also congruently exhibit conservative behaviour through the Trib 2095 wetlands, however these loadings appear to be rising even at increasing distances from this mixing zone, suggested a alternative or secondary flow paths within the wetland area

contributing solutes well below the confluence.

Related to intransigence of zinc and consistent loadings through Trib 2095, are the mirroring behaviour of rare earth elements. Neodymium and yttrium, the REEs of highest concentration, remain largely conserved and these loadings increase in trends similar to zinc. Again, this reveals that Trib 2095 is the dominant contributor of these solutes and hence a major point source of enrichment by weathering products. The exact mechanism by which REE loadings increase below the inflow of Trib 2095 remain unknown, but conceptually could represent the slow, advective transport of wetland waters through the hyporeic zones into the main channel.

6.4 Discussion

6.4.1 Flow Data

Due to its location on the Continental Divide, in an area characterized with high relief, the resulting hydraulics from this elevation gradient appear to promote a significant gaining of flows within both Trib 2095 and the Snake River. Incorporating observations from the diel experiment, relatively steady-state solute concentrations and dynamic surface flow contributions likely result in enhanced loading during daytime periods and decrease over the night. Therefore, it is rather these near-surface groundwaters with the greater potential to mobilize metals, particularly as a consistent contributor of flow. Related to this is the important observation that both Trib 2095 and the Snake River itself gains significant flow from this shallow groundwater, the later fact only discovered through the use of a second tracer.

6.4.2 Major Metals and REE Loadings

Coupling flow data to samples collected at each site for major cations and anions

provides a critical evaluation regarding the role of Trib 2095 in altering water chemistry in the headwaters of the Snake River. Through a mass balance approach, it proves possible to quantifying loadings of metals and REEs as well their contrary behaviour.

Where as solutes such as zinc, sulfate, and REEs exhibit a conservative behavior similar to that of the injected tracers, the decreasing loadings of iron in Trib 2095 indicate its sequestration in the wetland upon mixing with lateral inflows. Intuitively, this underlines partitioning of dissolved iron into solid phases, with biotic and abiotic processes possibly playing a role.

Although these loadings temporarily decrease in this area, visually noted as an area rich in iron precipitates in the loamy soils, these amounts increase dramatically at further distances from the Trib 2095 confluence again suggesting their reduction from solids back into a dissolved phases that is being advected back into the Snake through subsurface pathways. This provides additional evidence of a complex redox environment the lower, wetland portion of Trib 2095 that is cycling metals such as iron between mobile and non-mobile phases, though whether or not this is microbial or physically mediated process is outstanding question for further investigation.

Chapter 6: Diel Experiment in Trib 2095

6.1 Introduction

On August 21nd and 22nd, a diel experiment was performed at Trib 2095 to observe trends in trace metals, solute, and REE concentrations. Sites were selected by synthesis of previous study data (Crouch 2010) to include the two previously identified distinct flow regimes as well as main stem of the upper Snake River, below its confluence. Figure 7 illustrates the conceptual layout of the sites as well as the analytes collected at each over the 24-hour duration of the experiment.

Site A, representing the portion of Trib 2095 dominated by surface processes and flows, was sampled for major cations, anions, DOC, isotopes, and Fe^{2+} . Site B, located 20 meters downstream, is an area of known inflow of shallow groundwater into the stream channel with a observable water temperature drop of almost 10°C and was sampled for major cations, anions, and isotopes. Site C, located 25 meters downstream of the confluence of Trib 2095 and was chosen to provide information on the steady state behaviour of the main channel of the upper Snake River and also was sampled for major cations, anions, and isotopes. Given logistical, manpower, and equipment constraints, it was not possible to sample all sites for all analytes and accordingly Site A was prioritized to collect the more detailed data so that it might be possible to quantify the diluting aspects on water chemistry of lateral inflow.

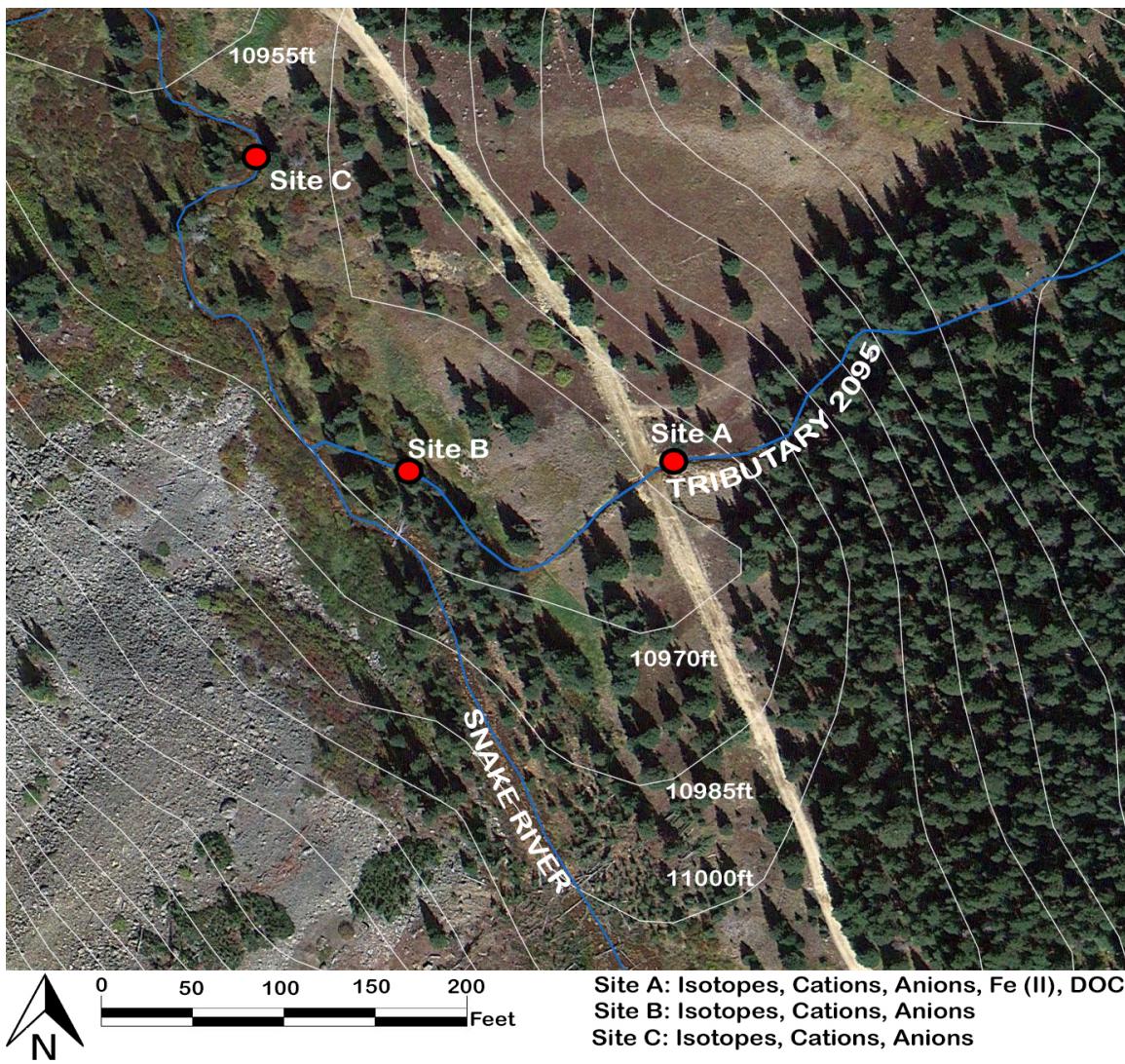


Figure 11: Diel Experiment Site, Trib 2095 (Imagery: GoogleEarth, Topographics: USGS NED)

6.2 Specific Methods

6.2.1 Cations and Anions

Water samples were collected in 125mL HDPE bottles, filtered through a .45 µm filter, and acidified below pH 2 with trace-metal-grade nitric acid for later analysis by the LEGS lab, with bottle labelled by its site and time, as well as the date.. Procedures mirrored CDPHE and EPA surface water sampling protocols, and prior to study all sample bottles were bathed in a 5% nitric acid bath and rinsed 3x with ultra pure DI water to minimize contamination Field blanks

were also prepared to quantify any additional contributions of contaminants during collection.

6.2.2 Isotopes

Isotopes were collected in 15mL glass vials, filled to the top with minimal headspace, tightly screwed camp, and a clear label of time/location/date. These samples were not filtered or acidified, following established isotope collection protocols, and were cold stored up until analysis by the Kiowa Environmental Chemistry Lab. Prior to collection, vials were cleaned in a 5% HCl acid bath, rinsed 3x and then dried.

6.2.3 Reactive Iron (Fe^{2+})

Ferrous iron concentrations were measured in situ using a Hach DR-2800 Field Spectrophotometer. Using the reagent kits to measure Fe^{2+} via the Phenanthroline Method, Site A was sampled every hour. Combining this with total iron concentration data from yielded from later ICP-MS measurement of water samples then allowed for solving for ferric iron (Fe^{3+}) using the following equation.

$$Fe^{ferric} = Fe^{total} - Fe^{2+}$$

6.2.4 Field Measurements

The monitoring of pH, conductivity, dissolved oxygen, and temperature over the course of the experiment was done using a YSI Model 63 multiparameter field meters. Prior to use, this meter was calibrated for pH using a triple point (4,7,10) standard and conductivity precision was tested against a standard. A handheld Oakton pH was meter was later used when probe broke on the YSI, however it this data proved less accurate.

6.3 Results

6.3.1 Field Measurements

Trends in isotope ratios over 24 hours experiment between these sites do highlight these distinct flow regimes and behaviour. Firstly, that ratios of ^{18}O and deuterium become increasingly enriched in light isotopes at all sites during periods of warm temperatures. This could be reflexive of the decrease viscosity of warmer waters preferentially percolating a larger amount in the high alpine portions of the reach and in turn suppressing the emergence of colder, dense groundwaters on the valley floor. When air temperatures fall as the sun goes down, these ratios at all sites quickly fall towards more depleted values and suggest increased contrast in ground over surface waters. And while Site B is implicitly affected by these changes at Site A, as a source of more significant, depleted groundwater inflow the increase of heavy isotopes is therefore dampened. Accordingly, Site B appears to have a more steady state behavior where as A & C appear to be tightly coupled to surface processes. In further support of this concept, the occurrence of a rainstorm at 8am made a drastic contribution of heavier isotopes to streamflow at these sites that continued until the end of the experiment. This demonstrates both the flashiness of the tributary and Snake River alike, and dynamic relationship that oxygen isotope values have with temperature and precipitation, even on short timescales.

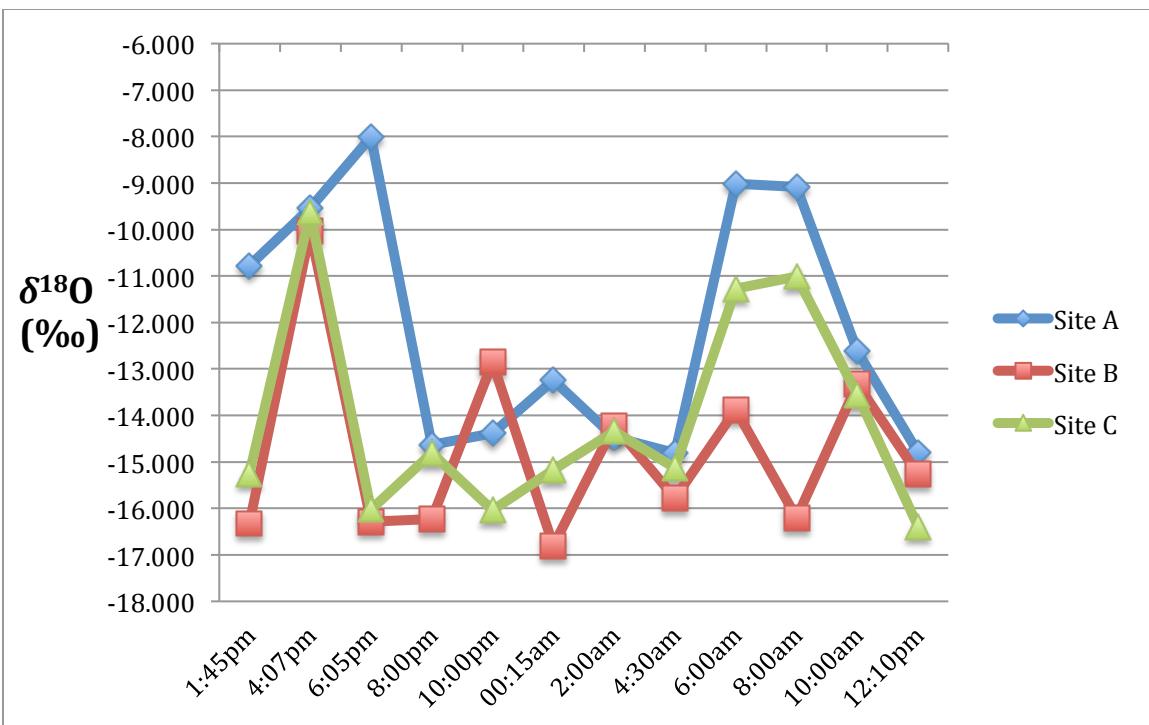


Figure 12: Ratios of $\delta^{18}\text{O}$ at Sites A, B, and C. 8/21-8/22

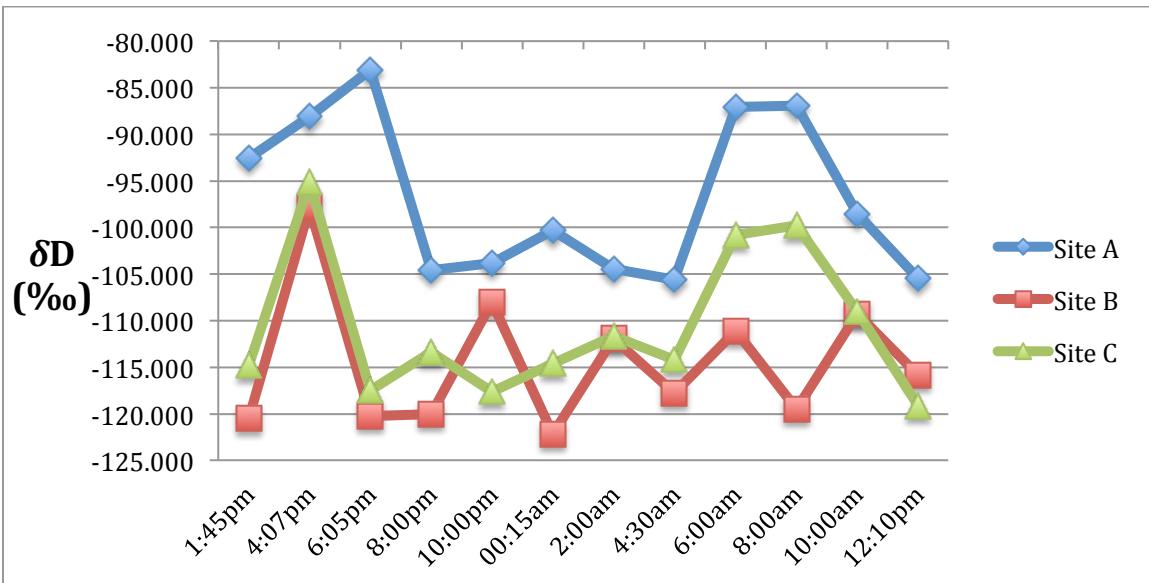


Figure 13: Ratios of δ Deuterium at Sites A, B, and C. 8/21-8/22

Water temperature data, despite its simplicity, showed the important trend of changes over the course of day and night due to air temperature as well as input of solar radiation. Despite vastly differences in flow between Sites A (Trib 2095) and C (main stem of Snake River), the

near mirroring of water temperature trends highlight that daytime heating and ambient air temperature in turn drive water temperature. In contrast, Site B, with noted inflows of shallow groundwater in previous studies, appeared relatively intransigent over the 24 hours and suggesting that despite higher water temperatures above at Site A, which is dominate by surface flow, that at night when these contributions decrease so does the amount of heat to influence Site B. It also posits that groundwater inflow is the major control on water temperature at this site as well.

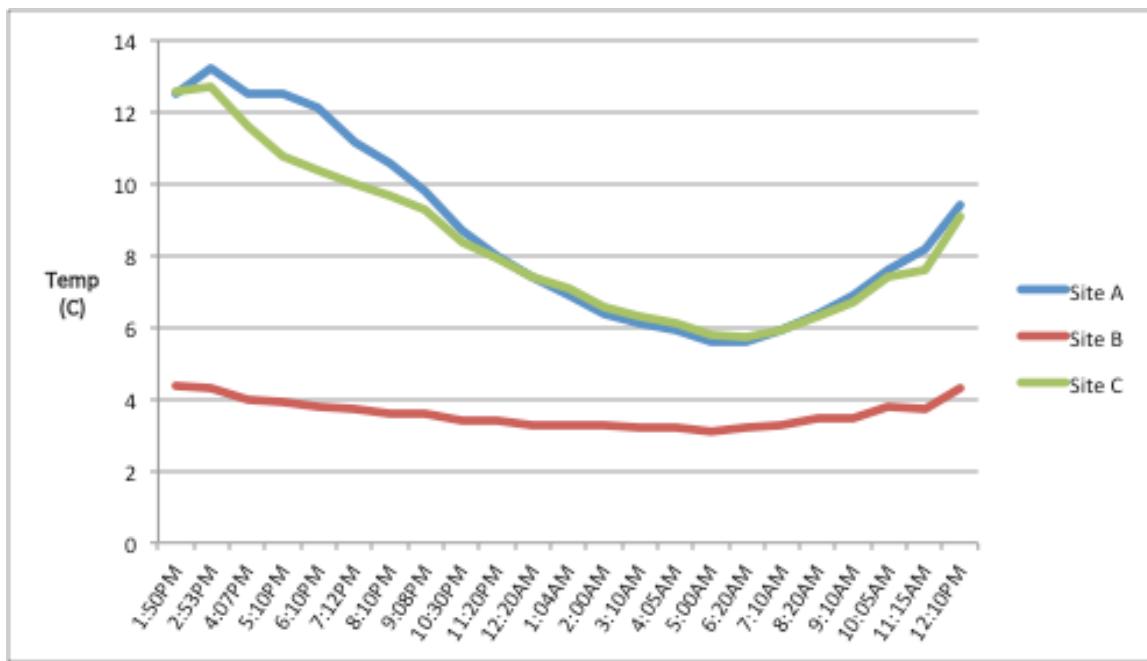


Figure 14: Water temperature at Sites A, B, and C. 8/21-8/22

While it important to monitor the physical characteristics of stream chemistry to observe any changes that might effect solute concentrations, it became clear that tracking parameters such as pH and conductivity become difficult using field meters. The YSI pH probe broke halfway through the experiment, making its data both non-contiguous and with the use of a secondary probe, impossible to compare (Figure 8).

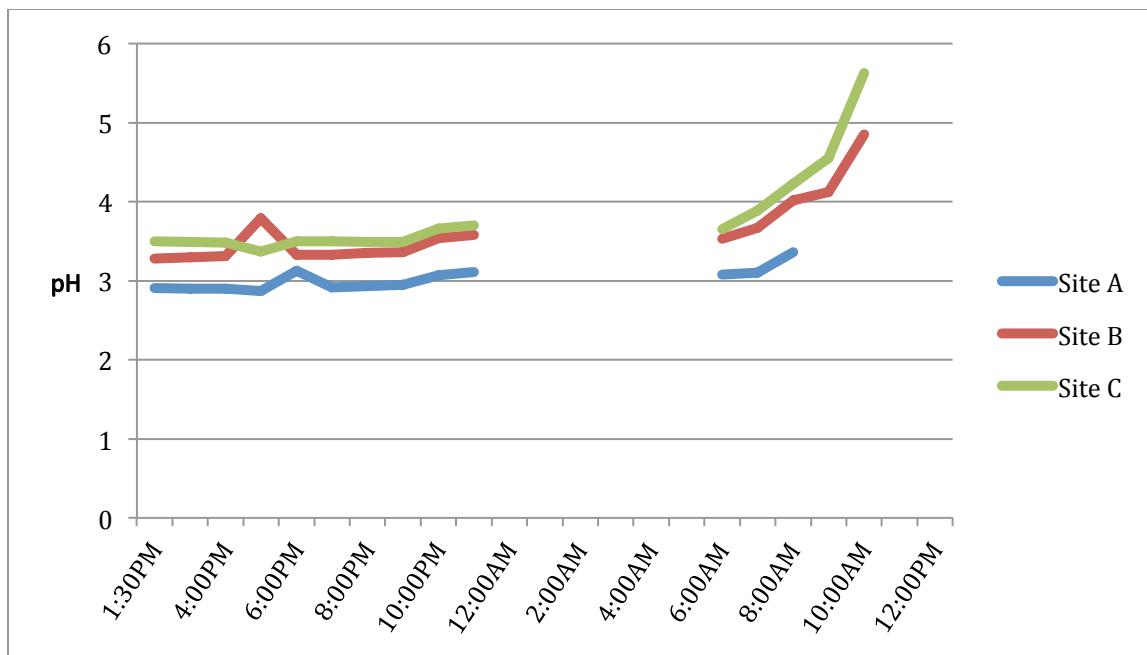


Figure 15: pH conditions at Sites A, B, and C. 8/21-8/22

While conductivity measurements are relatively simple, a major drop in concentrations of dissolved solids present at Site A occurred at 11:20pm, however the next measurement an hour later showed a return to its relative state. Possibly related to this are field notes that document a significant drop in flow in Trib 2095 during this time, perhaps exposing the probe and making a for a flawed measurement. Given the extremely high amount of total dissolved solids present in this part of the tributary, the variability in the record here could be related to instrument drift due to lack of observed changes in Site B located 20m downstream (Figure 9). Located in the main stem of the Snake, data from Site C lends additional credibility to this idea as in-stream specific conductivity measurements here showed little variance over the 24hr experiment, further suggesting a relatively steady state.

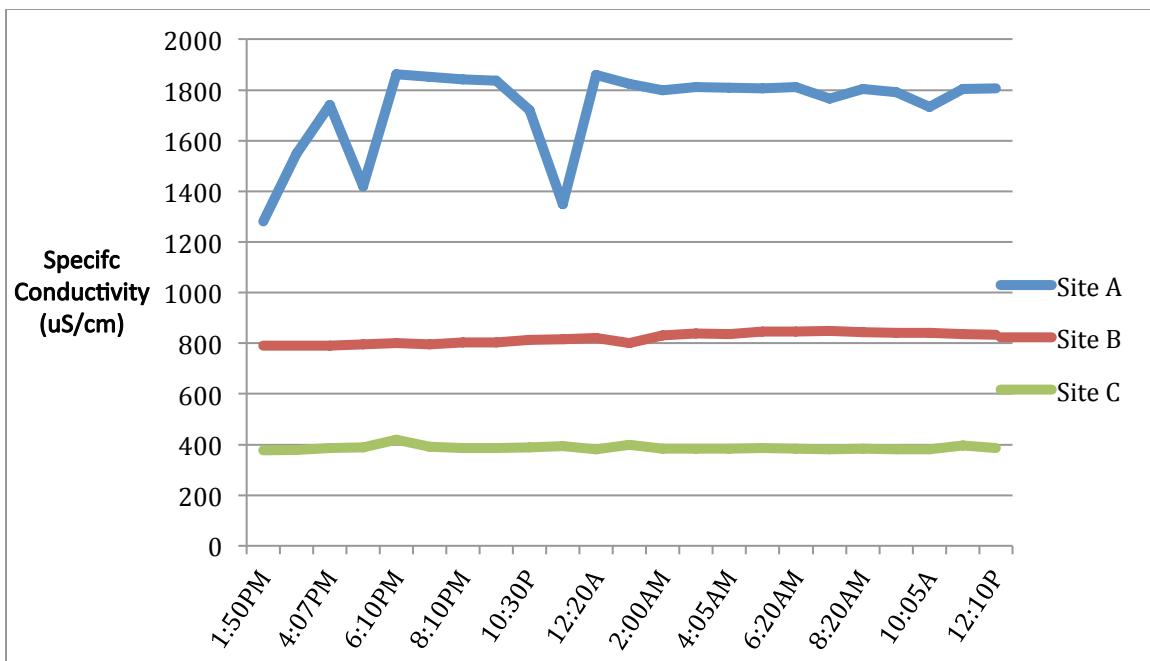


Figure 16: Specific conductance at Sites A, B, and C. 8/21-8/22

Trends in observed dissolve oxygen indicate that Site A & C exhibiting rising concentrations in relation to decreasing water temperatures, which is fundamentally a physical relationship as more oxygen can kinetically dissolve into colder waters. Site B in contrast shows decreasing concentrations at the nighttime, during periods of dwindling surface flow contributions, which also relate to reduced turbulence mixing in the stream. These trends of changing water temperature to dissolved oxygen further highlight the dynamic changes that contrast to portions of the tributary with dominant groundwater inflows that dampen diel fluctuations against those with primarily surface flows which experience daytime heating and nighttime cooling which alter oxygen storage capacity of this relatively well-mixed 1st order stream.

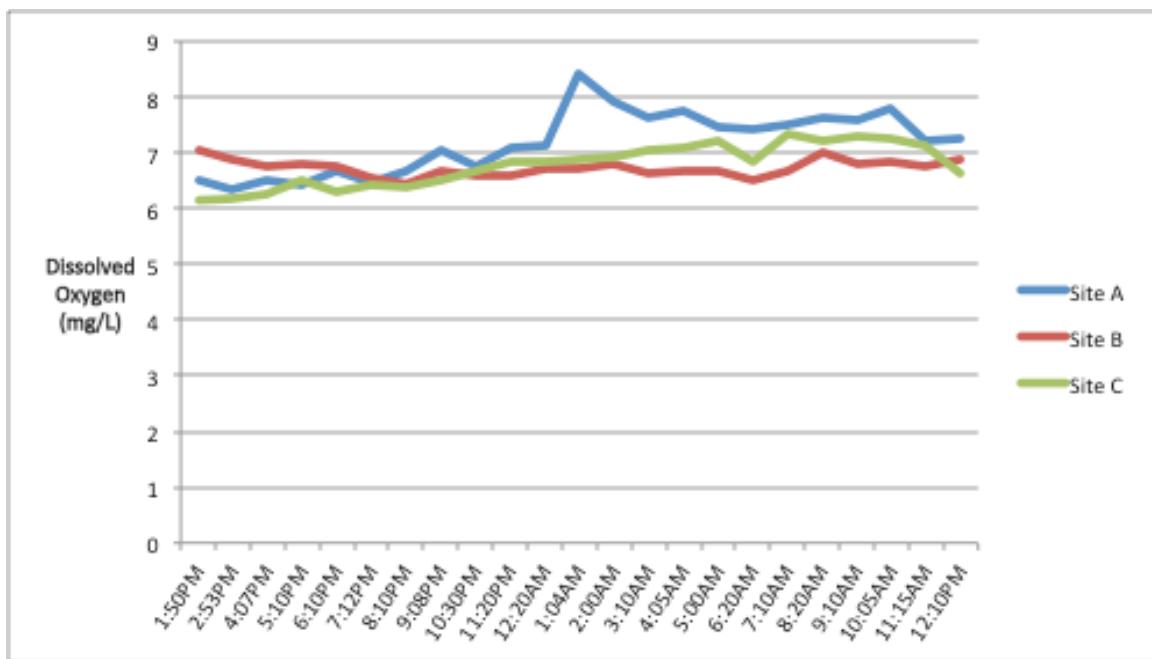


Figure 17: Dissolved oxygen at Sites A, B, and C. 8/21-8/22

6.3.2 : Iron

Data collected regarding ferrous concentrations at Site A show that effectively these amounts double during the day than at night, and as soon as the sun is up, Fe^{2+} is being generated from exposure of HFOs being exposed to both incident and direct sunlight. This observation congruent with previous study both in the Snake River (McKnight and Bencala 1988a) and a host of other AMD/ARD impacted watersheds (McKnight et al. 1988b; McKnight et al. 1989, Kimball et al. 1992, McKnight el al. 2001b). Lacking data of how ferrous iron concentrations change at Site B with lateral inflow changing pH, the in-stream redox conditions remain unknown. However, total in comparison of total iron concentrations 3 across these sites it appears that Trib 2095 sites have a relatively steady state of enrichment of iron. The Snake River shows a much more dynamic environment, possibly driven by competing mechanisms of microbial and photo-mediated dissolution of iron.

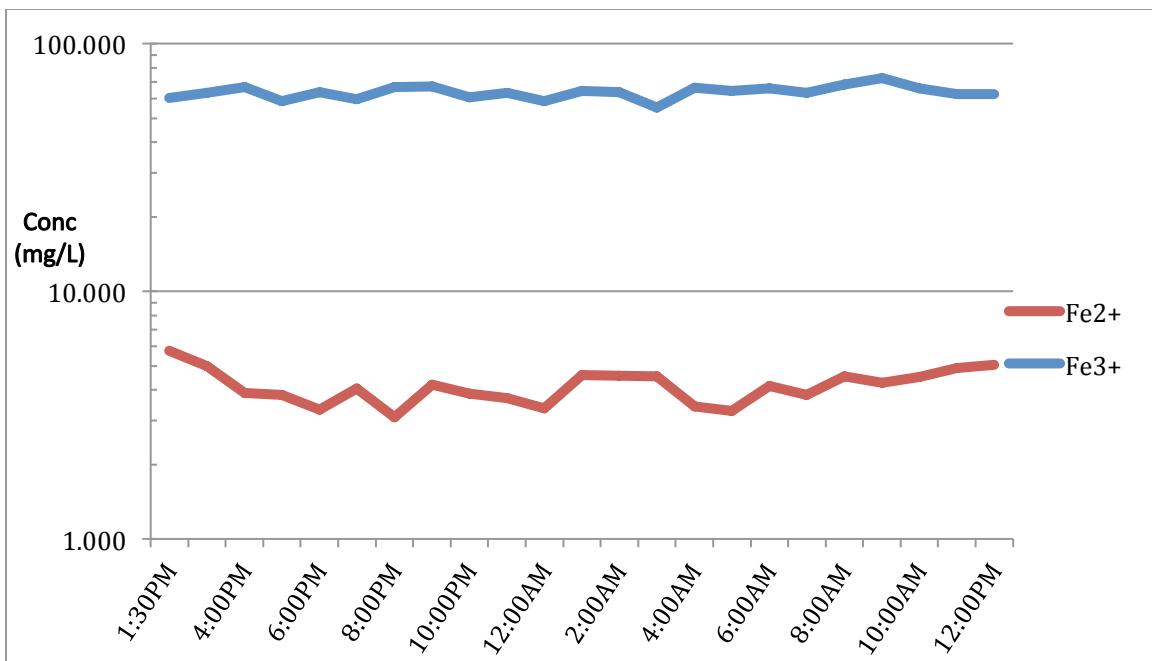


Figure 18: Ferric and ferrous iron concentrations, Site A, 8/21-8/22

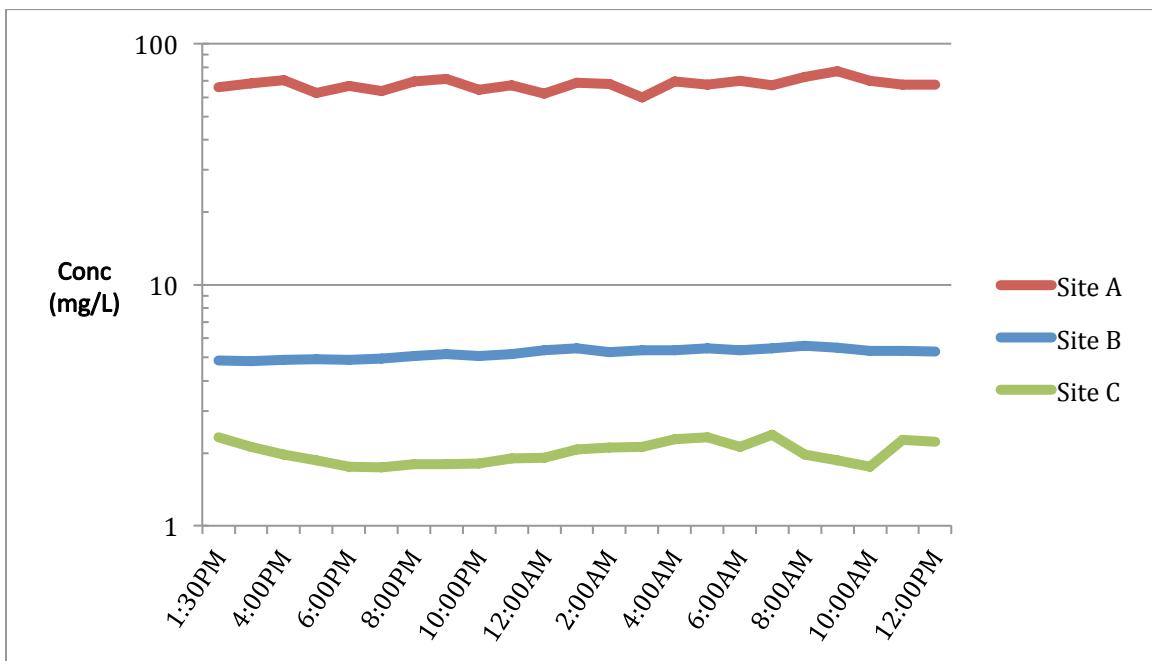


Figure 19: Total iron concentrations at Sites A, B, and C. 8/21-8/22

6.3.3 : Sulfate

Diel trends in sulfate at Site B and Site C suggest a relatively steady state behaviour.

While lateral inflow contributions by groundwater at Site B display a diluting effect and an

overall reduction in concentration, data from the previous chapters tracer experiment highlighted that sulfate loadings through the wetland remain steady. Variability in sulfate at Site A in regard to the small increases in concentrations observed at night could partly be explained by the concentrating effect of reduced surface flows but the most likely reason is stochastic variability in measurement. In support of this, statistical analysis on Site A data at a 95% confidence interval reveals a T-value=0.002009 and a P-Value is 0.998416, indicative of a non-significant variation in measurement.

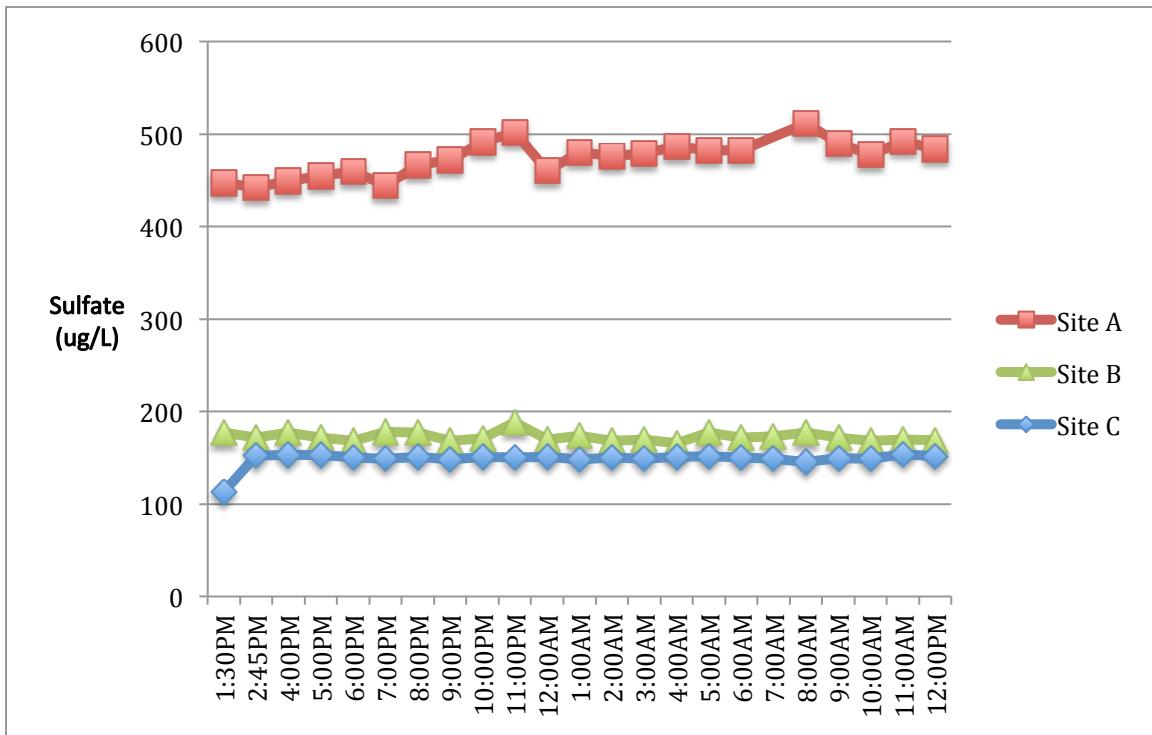


Figure 20: Sulfate concentrations at Sites A, B, and C. 8/21-8/22

6.3.4 : Zinc

Accordingly, in terms of the fate and transport, observing the point source enrichment of zinc over 24 hour is important in understanding the steady state behaviour of watershed as a whole. Over the course of this experiment, data shows that concentrations of zinc at Site A, B, and C remained relatively stable. Slight increases at night-time in Site A, and to a lesser degree

at Site B, could be reflective of the concentrating effect by the reduced surface flows observed over these times. And though sites B & C exhibit steady zinc trends, the fluctuations over 24 hours at Site A likely do not reflect changes to water chemistry and rather indicate the stochastic variability in solutes at high concentration as well as the biased representativeness of a single hourly sample for detecting changes in this turbulent, mixing stream. Statistically and at a 95% confidence interval with a t-value of 0.002306 and p-value of 0.998181, the variations are insignificant.

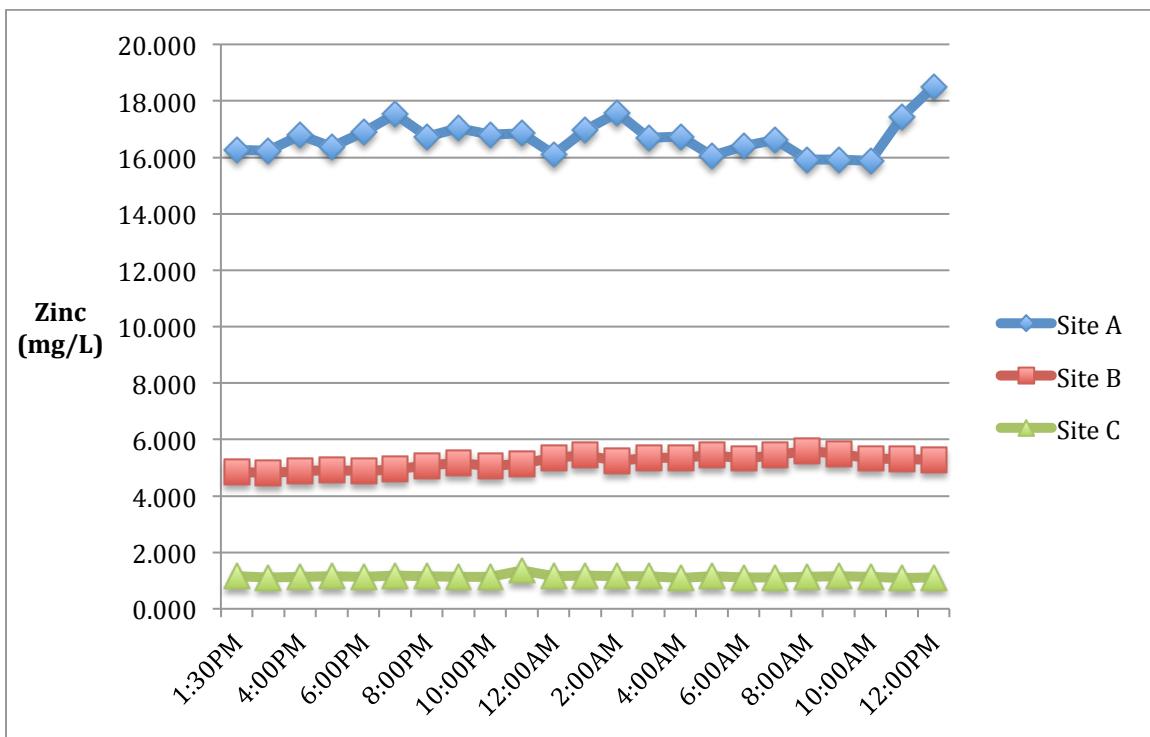


Figure 21: Zinc concentrations at Sites A, B, and C. 8/21-8/22

6.3.5 : REEs

Similar to that of zinc, another pH-insensitive element, trends in concentrations of neodymium and yttrium in Site B & C remain uniform over the 24 hour experiment. Though there appear variation in concentration of these REEs at Site A, again similar to zinc, the dynamic hydrology observed here and decreasing night-time flow could play a role as well as

sampling bias. In as support of these variations, are that at a 95% confidence level the p-value = 0.999923 and T-value=9.8E-05, and therefore these trends in these data are also not statistically significant. Collectively across these three sites, these data suggest that REEs are being introduced into Trib 2095 and then the main stem of the upper Snake at a relatively steady-state of enrichment and that the behaviour of the solutes has relatively little effect.

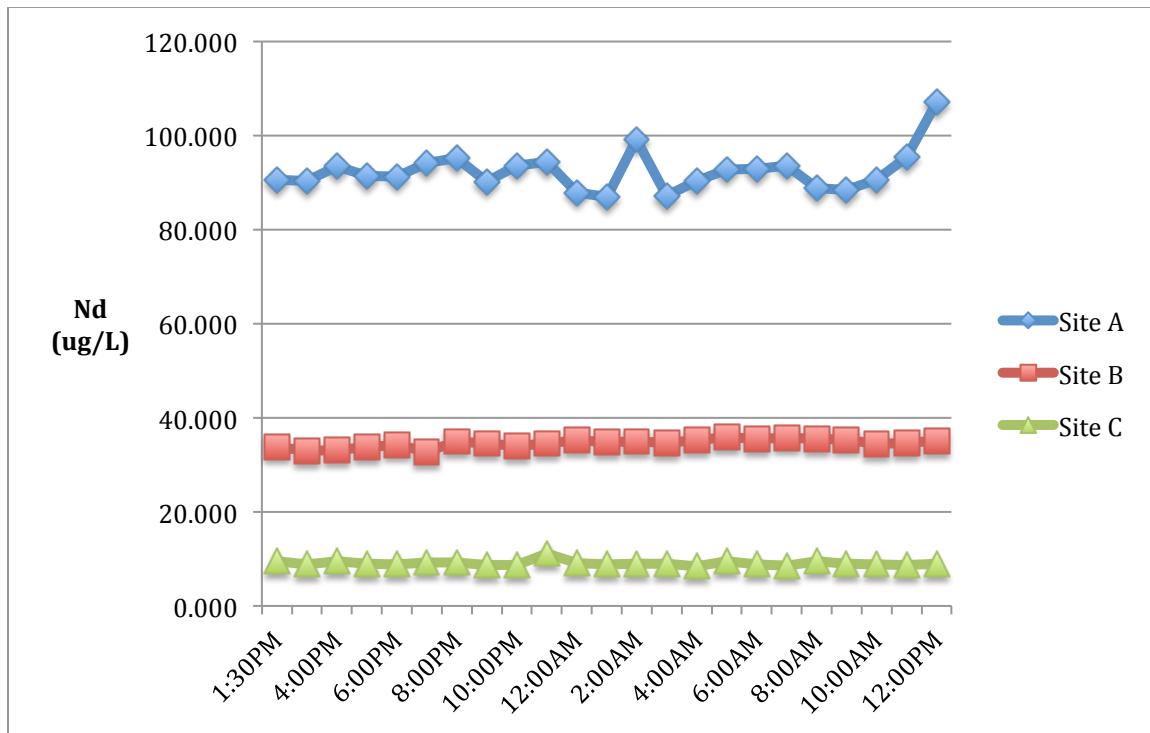


Figure 22: Neodymium concentrations at Sites A, B, and C. 8/21-8/22

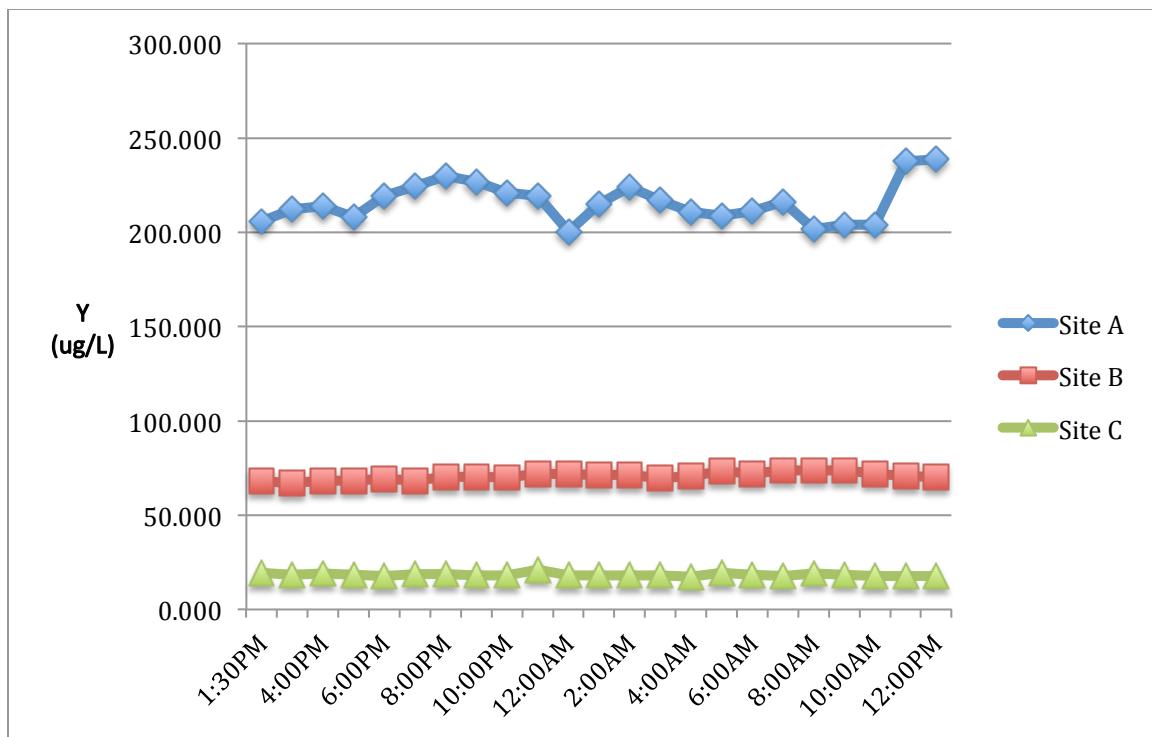


Figure 23: Yttrium concentrations at Sites A, B, and C. 8/21-8/22

6.3.6 : DOC

Dissolved organic carbon was monitored over the course the 24 experiment at Site A only. Logistical challenges limited the amount of sample that could be collected in the hourly interval, so DOC was measured here every 2 hours. From this coarse data record, it is therefore only possible to observe general trends in DOC concentrations and estimate how might they influence other aspects of water chemistry. The most important observation from these data were a near 50% increase of DOC concentrations between the day and night. Multiple mechanisms are likely responsible for this trend; decreased co-precipitation with iron oxides forming from photoreduction, and the concentrating effect from decreased nighttime flows, both trends which have been observed in other AMD/ARD-impacted watershed such as St Kevin's Gulch (McKnight et al. 1990). The overall DOC concentrations observed varied from between 0.9 and 1.5 mg/L, and while

this amount represents a relatively small fraction of total dissolved solutes, its crucial role as a reactive moiety in regard to both iron chemistry and electron shuttling potential in other biogeochemical transformation deserves acknowledgment.

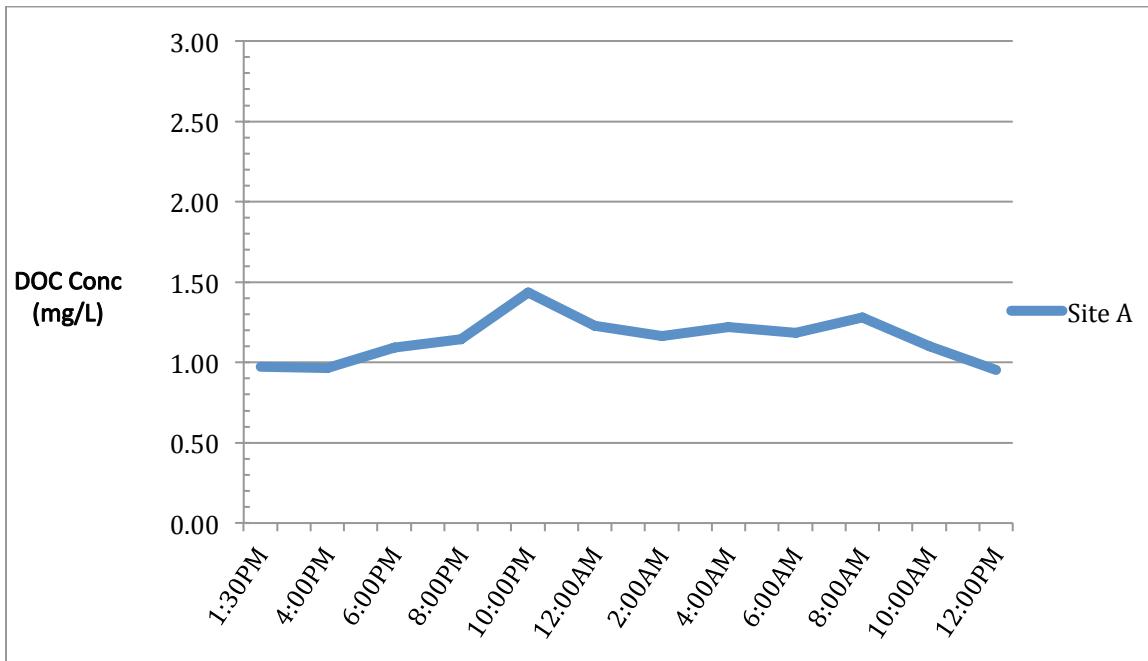


Figure 24: Dissolved organic carbon concentrations at Sites A, B, and C. 8/21-8/22

5.4 Discussion

5.4.1 Isotopes

Stable oxygen isotopes are a more indirect method for monitoring flow conditions, though in dynamic, flashy catchments such as the Snake River they clarify the respective contributions of surface and groundwaters to the hydrograph. Given challenges in measuring discharge in rocky, sinuous, shallow 1st order streams, in the absence of conservative tracer injection, isotope data can provide valuable estimates both in terms of sourcing and gains in flow that might otherwise prove difficult to quantify (Kendall and McDonnell 1998). In the case of Trib 2095, the interface of shallow ground water with surface flows at Site B in the valley flow

can be observed as a 5 degree decrease in water temperature and a rise in conservative solutes such as sulfate as well as sodium. Lesser understood is its interconnectivity of the main stem of the Snake River, and whether not ^{18}O and deuterium values reflect mixing of two discrete isotopic signatures.

Levels of both ^{18}O and deuterium isotope depletion show agreement that groundwater is a major contributor to baseflow in the upper Snake. While the surface-dominated portion of Trib2095 (Site A) display patterns of increased enrichment of lighter isotopes, these ratios fall upwards of 20% and become markedly more depleted by inputs of groundwater at Site B. The Snake River (Site C), reflects mixing of these discrete two components, though it remains skewed towards heavy isotopes. Given a distance of flow of 2095 meters from the headwaters of this reach, some of this could be attributed to the evaporative effect depleting both ^{18}O and deuterium, though without samples from up the valley for contrast this observation is not conclusive. Further complicating matters in interpreting isotopic data from this watershed is its abutment to the Continental Divide, with precipitation inputs that are increasingly depleted due to the coupled continental and orographic fractionation, as well as snowmelt being the dominant source of groundwater recharge that declines over the summer months (Kendall and McDonald 1998).

5.4.2 Iron

Iron chemistry and speciation remains an critical aspect of understanding ARD/AMD systems. The low pH of these environments allows for the enhanced solubility of reactive iron species (Fe^{2+}) not only increases mineral dissolution but directly affect the secondary weathering of pyrite. For example, as discussed in Peru Creek (Duren 2013), the cycling for reactive, dissolved ferrous iron to precipitate as ferric hydroxides in the streams is shown to be highly

related to uv radiation and the peaking in these concentrations, where as in the wetlands it has potential to photoreduce ferric iron into ferrous iron. These complex reaction pathways are often reversible and depending on pH, can drive precipatory processes or in reverse the reductive dissolution of these solid phases.

With pH as the "master variable" affecting the increased solubility of iron, portions of Trib 2095 with the lowest pH (Site A) contain the highest level of iron. However, with mixing of these water with lateral inflow at Site B, the increase of pH results in the precipitation of a significant fraction. Although it is also distinctly possible that these loadings additionally decrease in the vegetated, bog iron deposits through which Site B flows because of diverse metacommunities of microorganism that are using iron to meet their chemotrophic needs (Lovely 1997; Emersen et al. 1999

With greater accuracy of pH conditions in Trib2095 and data from other sites regarding the speciation of iron between $\text{Fe}^{2+}/\text{Fe}^{3+}$ forms as well as cycling between free-ion, complexed, colloidal, and solid forms, it would be possible to elucidate the reactions responsible for the diel patterns observed across these site. In the absence of flow data for this experiment, it is also not possible to evaluate these alterations from a mass balance approach. Related to these concerns are the competing processes of that driven or mediated by a host of both abiotic and biotic factors, some of which an unquantifiable. This hints at the inherent difficulty in clearly defining mechanisms responsible for iron behaviour in this system, particularly given the reversibility of these reactions by these competing or compounding factors, by which pH can play a primary or secondary role.

5.4.3 Sulfate

As previous detailed in the weathering reaction of pyrite, the liberation of sulfate and its role in lowering pH conditions which in turn drive secondary, positive feedback reactions, serve an important proxy by which stream can be identified by such processes influencing water chemistry. In the upper Snake River, trends in sulfate concentration of the three perennial streams (Trib 460, Trib 900, Trib 2095) identify Trib 2095 and Trib 460 as the dominated by solutes generated from sulfide weathering processes, with Trib 2095 having the highest contributions of sulfate, heavy metals, and rare earth elements as well. Well correlated to these trends are lower pH values relative to these higher solute concentrations, further clarifying this Trib 2095 as the preeminent point source of enrichment.

5.5.4 Zinc

The role of zinc is both as analogue for conservative metals that remain intransigent to changes to pH and a proxy for mineral dissolution processes. In Trib 2095, zinc concentration are the highest among any site sampled in these headwaters and has been shown to contribute upwards of 80% of total loadings to the upper Snake River (Crouch 2011). The enhanced addition of zinc in this tributary relates to the extremely low pH conditions throughout the upper, high-coverage portion of the stream. While inflows from shallow groundwater in the lower, vegetated section in the valley floor and mixing with the Snake as well circumneutral sources downstream such as Deer Creek increase these values to limit the solubility of pH-sensitive heavy metals and hence their mobilization, zinc remains dissolved and is thus majorly impacting the aquatic ecosystem all the way to Dillon Reservoir (Todd et al. 2006)

5.5.5 Rare Earth Elements

Observations regarding the behaviour of rare earth elements on a diel timescale from sites of major enrichment provide data that is most central to hypothesis of this thesis. Corroborating the results of numerous other studies regarding the relative intransigence of REEs in low pH systems proves paramount (Sholkovitz 1995; Johannesson et al. 1996, Verplanck et al. 2004, Parker et al. 2008, Migaszewski et al. 2014), particularly with how this lies in contrast with data from Peru Creek (Duren 2014), another major source of enrichment. For the sake of brevity, the review of diel REE data will be limited to neodymium and yttrium as those of greatest concentration in Trib 2095. Trends in total REE concentrations normalized to North American Shale Composite (NASC) standards and data regarding the fractionation of HREE/LREEs on a watershed scale

5.5.6 Dissolved Organic Carbon

In aquatic environments, the concentrations of dissolved organic carbon can be effected by preferential scavenging by oxide precipitation (McKnight et al. 1990; 1992a, 1992b), sorptive interactions with streambed sediments as well as within the hyporheic zone (Hornberger et al. 1994; Miller et al. 2006), or by becoming incorporated as an organic ligand in suspended colloidal or solid phased materials (Waite and Morel 1984). Its decay through photo-fenton reaction and the generation of a hydrogen peroxide intermediary product also influences the cycling of ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron (Voelker et al. 1997; Scott et al. 2003). Therefore quantifying its amount in AMD/ARD systems is relevant to understanding dominant in-stream processes as well as controls on its partitioning, sequestration and spiralling in relation to other solutes.

Chapter 7: Synthesis & Conclusions

7.1 Spatial and Temporal Trends

7.1.1 Spatial Sampling

Concentration data of solutes collected at the Keystone Gauge during extreme and average flows reveal that during peak runoff, loadings are increased unilaterally across all elements of interest. In particular, iron and aluminium observed the largest gains as evident by interpolated TMDL data. Other, trace metals such as zinc, lead, as well as REEs, followed a similar, though lesser trend of increasing loads relative to flow. This contrasting enrichment of solutes seemingly reflect their pH sensitivity and due to the sediments being concentrated in precipitate oxides such as aluminium and iron forming from circumneutral inflows, they are accordingly available to be re-mobilized during high flow events as streambed sheer stress increase and force a quantity of these solid phases to redissolve through the fast kinetics of turbulent mixing. These data also indicate that in years of an above-average snowpack, or late season snowfall, enrichment and transport into Dillon Reservoir is thereby greatly enhanced. And although observations from this study are limited to dissolved phases, suspended solids likely represent an even larger fraction of transported materials and influx of metal-rich sediments deposited at the mouth of Dillon Reservoir.

The coupled influence of a changing climate on the Rocky Mountain region, particularly the Snake River and its high alpine location are twofold; alteration to the hydrologic regime by the advancement of peak spring melt, more frequent of drought and reduction in groundwater recharge are enhancing sulfide weathering rates, where as the more intense weather events are promoting the increased erosion rates of the exposed, mineralized material and also result in transport of these freshly weathered sediments down the catchment.

The ecological impact of these high flows flushing out metal-rich sediments and solids on the watershed are that they make an already marginal habitat even more toxic. And if these high flow conditions increase in duration or frequency, from a late season snowfall or a wetter spring, so does its potential for altering richness and diversity of aquatic organisms at further distances downstream, possibly in Dillon Reservoir itself. As mass fish kills have already occurred in portions of the Snake River near Keystone due to intense rain events further up the reach at areas such as the Pennsylvania Mine, this has necessitated the involvement of the Colorado Department of Wildlife to continually stock this river with trout. However, as previous study has shown (Todd et al. 2006), the lifespan of fish in this watershed remains short due to asphyxiation by the toxic aggregation of zinc in gill tissue. But beyond these local impacts to the stream, the increased loading of metals into the water column and sediments of Dillon Reservoir has potential to alter the ecology of this lake as well, particularly at the terminus of the Snake River, which could have grave implications considering that littoral food webs of alpine lakes are often dependent on major stream and river inflows.

Loadings of heavy metals and REEs intuitively follow a pattern related to their proximity to sources of enrichment. Sites closer to the headwaters of the reach where AMD and ARD processes are mobilizing these materials therefore have both higher concentrations and loads. In the data, we observed that at increasing distances from these point sources, these amounts decrease. Reasons for these decreases appear relative to the properties of the solute of interest, how changes in pH might influence their behaviour or solubility, and addition of new solutes that might serve as important ligands in facilitating or preventing phase partitioning. Iron loadings appear to change congruent to stream pH, as do aluminium, although iron becomes increasing

insoluble above pH 3.5 where as with aluminium this occurs above pH 5, which alters their respective dissolved losses. And while zinc shows intransigent behaviour regardless of pH throughout this reach, REEs appear to only act conservatively at low pH and become both fractionated as well as partitioned by the coupled influence of increasing pH and available ligands to facilitate these transitions. However, absent data to quantify changes in the colloidal (.45um-10um) and solid fractions (10um <) relative to the dissolved (.45um<), these changes remain an outstanding, conceptual question.

7.1.3 Temporal Trends

While significant variation in solute concentrations exist between early-summer high flows and later-summer, low baseflows simply by dilution, the re-analysis of archived samples from 1995 and 1996 for REEs indicate that regardless of flow conditions the weathering reactions responsible for their enrichment are increasing. This also agrees with recent research in this watershed connecting the changes in climate and reduced groundwater recharge with enhanced mineral weathering resulting in exponential increases in stream zinc concentrations (Crouch et al. 2013; Manning et al. 2014). While such changes in zinc concentrations at sites SN-2 and SN-3 in dates from 1995-1996 and those in 2013-2014 well reflect this trend, REEs appear to be following a strikingly similar pattern and provides additional credibility to the concept that enhanced mineral dissolution are the responsible mechanisms. The implications for these coupled increases in solutes are that if indeed the observed changes to climate and the hydrologic regime of the Rocky Mountains continue or worsen, the effects will exacerbate the generation of AMD/ARB and therefore reduce water quality throughout the entire catchment, thereby enhance the subsequent transport of metals and rare earth elements into Dillon Reservoir.

7.2 Diel Study in Trib 2095

7.2.1 Non Conservative Solutes

Over the 24 hour experiment, non-conservative solutes such as iron displayed a dynamic behaviour in relation to a host of environmental factors. The photo-decay of ferrous iron was revealed as highly depended on incident and direct uv light, reaching its lowest concentration at night and doubling that amount as soon as the sun rose. While ferrous iron concentrations fluctuated over a diel timescale, total iron concentrations in Trib 2095 appeared in relative steady state over the course of the experiment. This lie in contrast with the main stem of the upper Snake River, which observed decreasing concentrations in the transition from afternoon to evening. This trend reversed at night and these amounts began to increase again, although this appears a flow-related effect given the concurrent increases in heavy oxygen isotopes and the concentrating effect this would have on steady-state solutes.

The effect of groundwater inflow in Trib 2095 appears to play a major role in the observed precipitation of iron oxides in the wetland portion of the stream. While the sequestration of these HFOs in this zone represents a loss from in-stream concentrations, the aggregation of iron in the loamy soils here of a wetted, oxic zone create conditions for mass mobilization of this material by the flashy hydrologic regime (Photo 3). There likely also exists a level of inter-connectivity of this marsh-like area with the stream channel given the overlap of the saturated and hyporheic zones. Such an environment additionally provides an additional interface for redox reactions, in which iron can be cycling between solid and aqueous phases by both biotic and abiotic factors.



Photo 3: Dynamic stream channel and wetland of Trib 2095, noted iron oxide deposition (D. Castendyk)

7.2.2 Conservative Solutes

The presence of conservative solutes such as sulfate in this system is an important geochemical proxy for pyrite weathering processes rendering both acid conditions and additional mineral dissolution. Secondary products such as zinc, also provide valuable insight over diel timescales in terms of quantifying this enrichment processes as steady-state or dynamic.

Concentration data of these solutes over the course of 24-hours at all 3 sites highlight that in these environments, this flux appears somewhat constant. Considering the dynamic flow conditions of Trib 2095, the state of equilibrium that conservative or intransigent elements observe here further clarify an aqueous environment that is driven by weathering reactions with changes in concentration by groundwater inflow further providing a crucial estimates of relative flow contributions by the dilution of these steady-state solutes.

7.2.3 Dissolved Organic Carbon

The collection of coarse data regarding dissolved organic carbon concentration helped contrast the changing flow conditions and in-stream processes acting to sequester/sorb these reactive moieties over the 24-hour experiment. The equivalent doubling of daytime versus nighttime amounts can likely be explained by three likely mechanisms; the concentrating effect of decreased surface flow, reduced sorption and scavenging by iron oxide formation, and possible enhanced microbial respiration activity. However, in the absence of DOC data from the wetlands portion of Trib 2095 and the Snake River, how these concentrations change in respect to environmental conditions, particularly in contrast with conservative and non-conservative are unknown.

7.2.4 Oxygen Isotopes

Deuterium and ^{18}O isotopes were among the most valuable secondary data products collected over the experiment. The distinct differences in ratios of oxygen isotopes by surface and sub-surface waters helped identify relative both contributions of each to flow as well as parse out the influence of a precipitation event. Trends in the enrichment of light isotopes appeared highly correlated to warm air temperature and periods of direct sun exposure, where as

stream concentrations become heavily depleted during the night when surface contributions decrease and subsurface water become a dominant contributor. All 3 sites followed this general behaviour, although Site B and its constant groundwater inflow appeared to dampen these fluctuations. Levels of depleted light oxygen isotopes in the main stem of the Snake also suggest the gaining of flow via groundwater pathways, as evident by the similar ratios between these sites. The occurrence of a rainstorm at 8am was further evidence regarding the flashiness of the hydrologic regime in this region, with the input of isotopically-heavy rain decreasing deuterium and ^{18}O isotopes ratios at all sites for the remainder of the experiment

7.3 Dual Injection Tracer experiment; Trib 2095 & upper Snake River

7.3.1 Flow Data

Estimates of flow as provided by the addition of conservative tracers to Tributary 2095 and the upper Snake River both confirm findings of previous study regarding the relative contributions of groundwater to the wetland portion of Trib 2095 and expand our understanding of the upper Snake River itself by the discovery that it gains flow by a near equivalent amount. The near doubling of discharge above the LiBr injection point and Site SNXZ highlight this observation, and the increase in total flow at Site SNZ below the confluence with Trib 2095 are also in agreement with NaCl tracer data. This further underlines the complex hydrology of this portion of the reach, detailing the effect of an extreme elevation gradient and the resultant hydraulic resulting on gains of flow to both first and second order streams.

7.3.2 Solute Mass Loadings

Mass loading data from all sites indicate both corollary and contrasting trends regarding the influence on Trib 2095 on the upper Snake River, as well as the underlining their inter-

connectivity. Loadings for iron decrease with the wetland portion of Trib 2095, suggesting precipitation occurring from the pH normalizing effect of shallow groundwater inflows. Whereas loadings for conservative elements such as zinc and sulfate remain steady. REEs similarly behave conservatively, and loadings do not change considerably within this zone. Upon the confluence with the Snake River, the large increases in loadings of these solutes at sites both near and distant to the mixing zone again implicitly stress the role Trib 2095 as a major source for contaminants to the headwaters of this reach. The rise of these loadings between sites SNXZ and SNZ also suggests that alternate flow paths or advection of wetland waters are contributing additional solutes to the main channel of the Snake. Considering the contributions of groundwater flows to both regimes and the elevation gradient in-between, the mobilizing of evapoconcentrated solutes and bog iron deposits entrained in the slow, sinuous wetland area, these increases are conceptually congruent.

Coupled flow and water chemistry data collected by this tracer experiment has provided a wealth of greater detail as to the flowpaths as well as additions of reactive and nonreactive solutes to the upper Snake River. Its role as a major source of metals has both been confirmed and expands a previously incomplete understanding regarding the connectivity as well as advected solute contributions by the Trib 2095 wetlands. The discoveries yielded from this study have demonstrated both the contrasting hydrologic regimes of this small, first order watershed as well as explaining the dominant enrichment sources of REEs to the Snake River.

7.5 Other Considerations

In addition to precipitation processes known to be occurring here, other primary data collected for this thesis shows that pH, reactive iron species formation and photochemistry can act as controls on the sequestration and release of other metals on both synoptic and diel

timescales (McKnight 1988, Belanger 2002, Crouch 2012, Duren 2013). However, many reactions affecting these parameters are not simply abiotically driven, which brings about another looming question; how to quantify the role of competing biologically driven chemical processes. Because the cycling of iron and rampant changes in aqueous speciation cannot simply be explained by kinetic mechanisms, as highlighted in the previously-detailed reaction pathways, acidophilic organisms must play a major role in enhancing ARD/ARD weathering processes and accordingly exist in competition with other microorganisms to meet their respective chemotrophic needs. For example, in high concentrations of ferric iron under the assumption it is the dominant electron acceptor, the reaction pathway of sulfate to elemental sulphur or hydrogen sulfide is likely less preferred and therefore bacteria metacommunity could be skewed more towards those suited to cycle iron (Druschel et al. 2004), resulting in increased available these strong sulfate ligands for complexing interactions. Another consideration are the presence of siderophores, a microorganism excretion, that been shown to have the highest binding affinity for Fe^{3+} , have a pronounced effect on the solubility and dissolution of iron (Kraemer 2003). It is these biological processes and their role in facilitating or preventing reactions remain perhaps the most outstanding questions in relevant research on this topic to day and well as within the field of geochemistry And though these biotic controls are an important acknowledgment, given the inherent challenges and costs of quantifying these microbial community contributions, investigation for this thesis focused on the physical characteristics of the Snake River and the resulting aspects of water chemistry likely most directly related to REEs.

7.4 Rare Earth Element Sourcing and Watershed Behaviour

7.4.1 Experimental Synthesis

Detailed in this thesis through a series of experiments and the focused sampling of this watershed across temporal as well as spatial scales, major sources of REE enrichment are confirmed to be Trib 2095 in the upper Snake River and the Pennsylvania Mine drainage adit in Peru Creek. While these respective contributions differ, as do the contrasting ARD/AMD mechanisms responsible in their dissolution, relative concentrations and distributions of REEs by mass weight appear strikingly similar. And despite different locations, this suggests a shared relationship with the minerals responsible for their presence.

7.4.2 REE Enrichment

With prevalent deposits of monazite, noted in the earliest surveys of this region by Loverling, this becomes most likely source of REE enrichment in the Snake River Watershed. Though of the 4 different forms, whether these are sourced from monazite-(Ce), monazite-(La), monazite-(Nd), or monazite-(Sm) are an outstanding question. However, considering high concentrations of cerium, dysprosium, gadolinium, lanthanum, neodymium, and samarium, these monazite stocks appear compositionally diverse and perhaps due to site-specific nuances in hydrothermal deposition and fractionating fluid-rock interactions.

Another puzzling observation was that although yttrium is not considered technically a rare earth element, it abundantly appeared in water samples in as high of concentration as other REEs and at some sites in exceedance of even neodymium. This posits the possibility of xenotime, a yttrium-phosphate (YPO_4) as another accessory mineral present among other phosphates such as apatite. Although without a more comprehensive survey, the last of which dates back to the 1950s, our understanding of the complex geologic environment and all mineral

phases present in the Montezuma quadrangle will remain poor.

7.4.3 REE Fractionation & Partitioning

While aqueous concentrations of REEs and trends in enrichment from the Penn Mine and Trib 2095 appear overwhelming similar when normalized to NASC standards (Figure 1), when compared in terms of fractional composition by weight (LREE/HREE) these areas appear distinctly different (Figure 2). This suggested that from the Penn Mine an enrichment of heavy rare earth elements (HREE) is occurring over that of the upper Snake River. In support of this and shown by Jacobson & Goldstein (1988), younger rocks tend to show a lower La/Yb ratio, which differentiates that the source minerals of REE enrichment in Peru Creek are chronometrically older. This is conceptually supported by the deep, fractured flowpath of water through to mine that eventually drains out the bottom adit and contrasted against the shallow, near-surface weathering processes occurring in the upper Snake River.

Site	La/Yb	La/Yb N
<i>Amazon River*</i>	4.80	0.38
<i>Great White River*</i>	39.50	3.10
<i>Indus River*</i>	3.10	0.24
<i>Mississippi River*</i>	3.25	0.25
<i>Ishuan River*</i>	42.30	3.30
Snake River Watershed		
<i>Trib 460</i>	2.11	0.17
<i>Trib 2095</i>	1.95	0.15
<i>SN-2 (above Deer Creek)</i>	5.34	0.42
<i>SN-3 (below Deer Creek)</i>	5.08	0.40
<i>Snake Above Peru</i>	5.14	0.40
<i>Penn Mine Adit</i>	11.71	0.92
<i>Peru Creek</i>	7.00	0.55
<i>Snake below Peru</i>	7.64	0.60
<i>Snake above North Forks</i>	8.25	0.65
<i>Snake River @ Keystone</i>	7.00	0.55

* Denotes data from Jacobson & Goldstein 1988

Table 11: La/Yb Ratios (HREE/LREE) for worldwide rivers and the Snake River Watershed, normalized to North American Shale Composite (NASC)

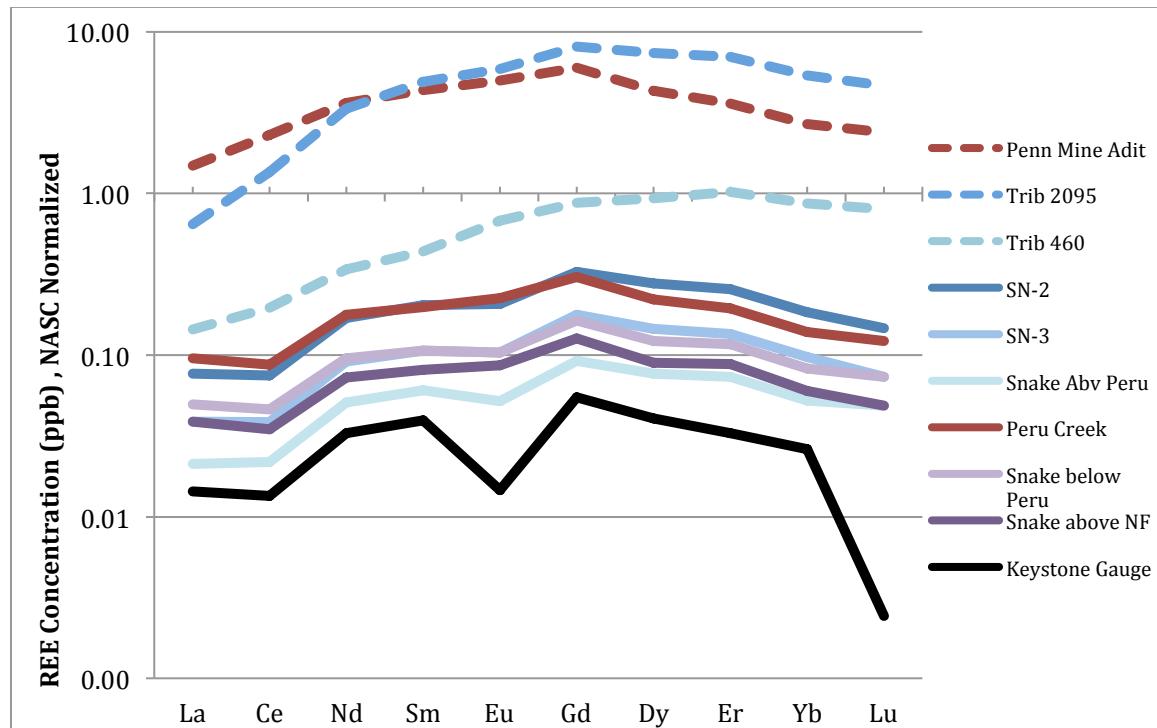


Figure 25: Synoptic Snake River REE Concentrations, normalized to NASC

As shown in a host of other cited research and well reflected in these data, patterns of instream REE enrichment and LREE/HREE ratios appear to be highly sensitive to changes in water chemistry. In the case of the Snake River, as pH conditions normalize further down the reach these patterns change significantly; first, by decrease ratios of LREE, indicative of enhanced sorption or partitioning to colloidal or solid phases, and secondly, the development of a europium anomaly. Because europium is one of the few REEs, along with cerium, with a secondary valence state ($2+$), at an increasing pH these $2+$ ions behave more similarly to calcium, similar in both size and charge, and therefore this anomaly represents depletion of Eu^{2+} as it becomes differentially phased or cation-exchanged with calcium, over that of the more intransigent trivalent form. This observed enrichment of dissolved REEs towards the heavier elements and partitioning of those with divalent states across increasing pH conditions is also

congruent with other study.

7.6 Applications and Conclusions

Rare earth elements remain ubiquitous natural waters by mobilization from mineral dissolution (Jacobson & Goldstein 1988), however the rates responsible for this presence are both diffuse and mediated factors such as pH. Accordingly, their concentrations in the major rivers and seawater are exceedingly low and lie in the part-per-trillion range. Due to these trace amounts, there have been no studies to estimate the toxicity of REEs on aquatic organisms, ecosystems, nor an exposure thresholds for impacts on human health, therefore these concerns have no basis from which to be evaluated. While at low, ppt concentrations it would be impossible to quantify these effects in the environment, it would be possible to evaluate them in the amounts that other heavy metals are studied. For example, aquatic life acute toxicity standards for heavy metals such as lead and cadmium are between 1-20 ug/L (ppb), and standards for clean water fit for human consumption fall even lower (EPA 2013).

In this regard, the Snake River is an unique watershed; two distinct regions impacted separately by ARD and AMD that are generating exceedingly low pH condition that greatly enhance the dissolution of both metal and REE-bearing minerals as well as subsequent transport. With concentrations a 1000x higher than average and loadings that persist above the 1 part-per-billion range below the Keystone streamgauge, this intuitively begs the question regarding levels of REEs in Dillon Reservoir, a major water source for the City of Denver. Are sediments here enriched by REEs? Have increases in mineral weathering rates affected this? These revelation remains perhaps the most outstanding questions of research presented, and draws a critical eye to the need for continued investigation, particularly of Dillon Reservoir, which lies a mere 5 miles below the Keystone Ski Resort and ultimately where many solutes tracked by this study likely

end up. Of additional concern are the impacts to the residents of Montezuma, whom depend on shallow bore wells and remain vulnerable to infiltration of contaminated surface waters. As to date no survey has occurred to investigate the possible presence of metals or REEs in these domestic water sources.

While the focus of this thesis has been to understand the source and transport of rare earth elements within the Snake River, the scope of investigation was limited to evaluating that which was dissolved in the water column. Though the most labile fraction, information regarding the partitioning to colloidal and solid phases remains crucial to understanding to ultimate fate of these materials. And although spatial-distributed loading data highlight that losses are indeed occurring at distances downstream, to what phases and in what exact amount are unknown. The contrasting behaviour REEs between Peru Creek as observed by Duren (2014) and that reported in the upper Snake also deserve closer study, particularly the role of dissolved organic matter possibly facilitating REE scavenging by iron oxides and their photo-mediated desorption which runs contrary to other research. It is the opinion of this author that continued study should seek to clarify these remaining questions and further seek to quantify the following conclusions of this thesis; the Pennsylvania Mine and Trib 2095 remain the dominant contributors of rare earth elements in this watershed, trends in enrichment are increasing at rates observed in other elements such as zinc, and that elevated, increasing concentrations persist as far downstream as the Keystone streamgauge.

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