

IMPACTS OF HYDROLOGIC CHANGE ON  
GEOCHEMISTRY IN THE UPPER SNAKE RIVER, A HIGH MOUNTAIN ACID ROCK  
DRAINAGE STREAM

by

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B.A., Vassar College, 2005

A thesis submitted to the  
Faculty of the Graduate School of the  
University of Colorado in partial fulfillment  
of the requirement for the degree of  
Master of Science  
Environmental Studies Program

2011

This thesis entitled:  
Impacts of hydrologic change on geochemistry in the Upper Snake River,  
a high mountain acid rock drainage stream  
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has been approved for the Environmental Studies Program

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The final copy of this thesis has been examined by the signatories, and we  
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Of scholarly work in the above mentioned discipline.

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**Impacts of hydrologic change on geochemistry in the Upper Snake River, a high mountain acid rock drainage stream**

Thesis directed by Professor Diane M. McKnight

The Upper Snake River watershed in Colorado is in an alpine catchment impacted by acid rock drainage originating from the natural weathering of pyrite. A compilation of historic low flow stream chemistry data from this site indicates that zinc concentrations have increased six-fold over the past 30 years, with a more rapid increase in the past decade. Over this time period, pH has also decreased substantially (from approximately 4.0 to 2.6). Observed increases in metals concentrations are correlated with earlier snowmelt and peak streamflow. I hypothesize that an increase in zinc concentrations is due to changes in groundwater caused by climate change and associated earlier peak snowmelt (by 2-3 weeks), resulting in a lower groundwater table and new subsurface material being exposed to weathering conditions for the first time. Observed increases in background metals concentrations may pose a growing danger to aquatic ecosystems and as such have implications for mitigation of former mining sites.

The current research further investigates the established source of metal-rich inflows from the northeastern slope of the catchment using a tracer injection study with synoptic sampling. Results of the tracer study indicate two primary zones of trace metals loading. The first is on the steep, rocky, alpine slopes where stream discharge and trace metal loads increase rapidly. This is likely the source of increased weathering and decreasing pH. Discharge and metal loads increase dramatically again through a gently-sloped meadow and through bog iron ore in the bottom of the river valley, which is in the last 60-m reach of the tributary before it

flows into the Upper Snake River. The tracer study indicated a significant increase in hyporheic exchange along this final reach. I hypothesize that decreasing pH over the past three decades reached a threshold, mobilizing zinc sorbed to iron hydroxides in the hyporheic zone, meadow, and bog iron ore. This mobilization of metals from the meadow is likely to have begun over the past several years, during which time the metals concentrations have increased exponentially.

## ACKNOWLEDGEMENTS

Diane McKnight, my dedicated, enthusiastic, and empowering advisor, cannot be thanked enough for her support of this work and of me as an Environmental Studies student and budding hydrologist. In so many ways, working with Diane continues to positively shape me as a student, as a scientist, and as a citizen.

Monumental thanks are also due to Andrew Todd at the USGS in Denver, Colorado for opening up the opportunity for me to be a part of this project. It was Andrew who identified the increasing metals trend and first hypothesized the potential link to climate-induced hydrologic change. I am incredibly grateful to have been able to participate in collecting, analyzing, processing, and interpreting data for this interesting work. I am also grateful to Andrew for his continued support with each step of this thesis and for being such an involved member of my defense committee.

Roger Pielke, Jr. was not only a helpful member of my thesis defense committee, but, along with my other core Environmental Studies professors, Sharon Collinge and Benjamin Hale, instilled in me a sense of confidence that was perhaps the most important part of my graduate studies. From my first day of class through my thesis defense, Roger taught asked my classmates and me to question our own assumptions and encouraged us to appreciate other values and points of view.

Ken Bencala provided invaluable feedback on an early draft of this thesis. I am very thankful for the contribution of his expertise to this thesis. Good advice from a veteran McKnight lab group member and all-star ARD/tracer-study student, Sabre Duren, was instrumental to the maintenance of my sanity during the earlier phases of this work and toward planning my tracer

injection study. My fellow Environmental Studies graduate students and friends who helped with my fieldwork undertaking are awesome troopers; special thanks to Katie Alexander, Emily Graham, and Emily Zakem, for their willingness to lead my fieldwork teams for the tracer study.

Alison Ling and Patrick Robinson were my group-mates for the October 2009 synoptic field study that laid the foundation for my tracer study presented in this thesis. I would not have made it through my several-week long marathon of data processing and writing without the support, ironic mockery, and laughter of office-mates Lee Stanish and Tyler Kohler. Without the calm and clarity of Rachel Gabor, I may not have made it through re-learning math during my first semester of graduate school. And Jane Turner is the best study buddy ever.

Fellow hydrologist and life-adventurer Evan Pugh is a priceless field assistant, stellar graphic designer, and ever-patient reader of very rough first drafts. Grad school (and all those classes together) would not have been the same without him. I would not be the same without him.

The Environmental Protection Agency provided support for this work in the form of laboratory analysis of water samples and the wisdom and experience of Carol Russell. Thanks to Suzanne Anderson for helping to coordinate the availability of the Ion Chromatograph in her laboratory at the Institute of Arctic and Alpine Research. Without the endless patience and assistance of Chrissy Pruett in that lab, my tracer samples would never have been analyzed.

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## OVERVIEW

Recent work has identified a significant increase in metals concentrations over the past 30 years in a high mountain ARD catchment in Colorado. Over this time, increasing solute concentrations have been measured upstream of large-scale historic mining activities (Crouch et al. 2009). Preliminary analysis of available water quality data collected during multiple studies suggested a four-fold increase in zinc concentrations during the seasonal low flow periods of September and October. During the past three decades, metals concentrations have increased concurrently with sulfate concentrations, suggesting that the increases are due at least in part to accelerated weathering of disseminated pyrite within the watershed. The purpose of the current study is to investigate the cause of these increases in metals concentrations by determining the source and timing of the increase in metals concentrations. There are several potential scenarios that could account for this change, none of which are mutually exclusive.

The increasing solute concentrations may be the result of climate-related hydrologic change. Transition to earlier peak snowmelt (observed to be 2-3 weeks in the Colorado Rockies) may result in lower stream flows and drier soils in late summer. Related changes in groundwater could also expose a greater amount of unweathered subsurface material to weathering. Alternatively, accelerated weathering due to warmer summers, resulting in greater thawing beneath any historic mining deposits, may be a contributing source of the increasing metals. These hydrologic changes are not necessarily the result of global climate change; another potential explanation is that a severe drought period in 2002 changed groundwater flow conditions and/or lowered the water table. If climate-related hydrologic change is not driving this increase, it may be that an increase in anthropogenic activity in the Upper Snake River watershed

is the cause of the observed increase in metals concentrations; however, no such increase in activity has been documented.

An examination of available data and archived water samples was conducted to better understand the timing of the increasing trend in solute concentrations. These data were used to investigate any relationship with available hydrologic data. Field experiments were also conducted to delineate the source of the increasing solute concentrations in the Upper Snake River. These analyses aim to identify the scenario most capable of parsimoniously explaining the observed past trends and projecting future changes. Such projections are important because increasing trends in metal concentrations have implications for mitigation and have attracted the attention of water quality specialists and watershed stakeholders.

In understanding and discussing the results of this research, I will use the framework described by McKnight and Bencala (1990) in reference to processes controlling stream solute concentrations:

The most important goal may not be to describe one process occurring in a particular zone but to identify which processes dominate an observed spatial or temporal trend in a particular constituent or set of constituents... The questions are, Which processes are dominant and where do they occur: in the watershed, riparian zone, stream, or substream? ...or several, simultaneous processes?

The following chapters outline the methodologies employed to execute these research objectives and discuss the results of those studies. Chapter 1 is an introduction to the important topics covered in the rest of the thesis and Chapter 2 is a thorough site description and site history. Chapters 3 and 4 detail two related projects conducted as a part of this work. Chapter 3 describes water quality data collected between 1980 and 2010 (In Appendices A and B I describe the work completed to ensure the robustness of this dataset by closing data gaps and analyzing all archived samples for metals using the same laboratory). The goal of the work described in Chapter 4 is to

identify whether major sources of metals loading to the Upper Snake River are discrete or distributed and to what degree the processes contributing to these metals are in-stream or watershed-based utilizing a tracer-injection study. Chapter 4 includes discussion of metal loading contributions and the application of a transient storage model to quantify in-stream processes. Potential implications of this research, including an assessment of its applications for remediation of mine drainage, are presented in Chapter 5.

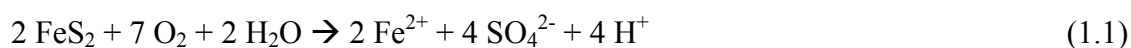
## Chapter 1

### INTRODUCTION

This research is concerned with the geologic weathering process of acid rock drainage (ARD) which occurs naturally throughout the Colorado Rocky Mountains as well as within many other regions of the world. ARD is the oxidation of sulfide minerals (most commonly pyrite,  $\text{FeS}_2$ ) in the presence of oxygen and water to produce sulfuric acid (and iron, in the case of pyrite) and the consequent dissolution of the metal-rich host rock. These processes continue until the pyrite and host-rock are weathered away, which can take tens of thousands of years. The resulting acidic, metal-rich runoff flows into streams, altering stream ecosystems for the long term – with very low pH, high dissolved metals concentrations, and metal oxides precipitated on the stream bed. This same chemical weathering process is accelerated by historic hard rock mining activities and is known as acid mine drainage (AMD), the legacy of which is a major source of pollution and degradation of mountain streams in the American mountain west (Mineral Policy Center 1997), including the Southern Rocky Mountains (Todd 2005). AMD is the result of increased surface areas of rock exposed to oxygen and water in mines, mine tailings, and waste rock piles.

#### 1.1 ACID ROCK DRAINAGE

ARD and AMD are the product of the same series of chemical reactions (Singer and Stumm, 1970; McKnight and Bencala, 1990). Oxidation is initiated when pyrite in the host rock is exposed to  $\text{O}_2$  and  $\text{H}_2\text{O}$  in the environment. Fe is oxidized and  $\text{O}_2$  is reduced, producing ferrous iron and sulfuric acid and reducing the pH of the runoff in nearby streams (Equation 1.1).





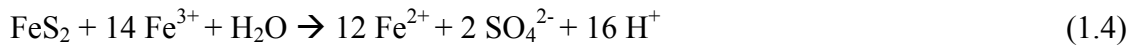
In the second stage of the reaction, ferrous iron is oxidized to ferric iron by acidophilic, chemosynthetic bacteria such as *Thiobacillus ferrooxidans* (Equation 1.2), without which the reaction would proceed too slowly to effect stream ecosystems.



Downstream, when the pH is raised to approximately 3.5 by pristine inflows, the iron precipitates out of the water column as ferric hydroxide onto the bed of the stream (Equation 1.3)



This reaction is accelerated as the ferric iron in the water column oxidizes additional pyrite as shown in Equation 1.4.



The presence of acidity and dissolved metals concentrations in streams and groundwater poses a danger to aquatic ecosystems and, potentially, drinking water supplies. For example, in many ARD-impacted mountain streams, fish populations are not self-sustaining. At low pH, dissolved metals in ARD streams accumulate within fatty tissues of fish resulting in chronic fish toxicity (Todd 2005). When very high metals concentrations are present, the toxic effects can kill the fish before they even have time to accumulate in tissues. The mechanism of acute toxicity is at the gill, where the metal competes with ions that the fish needs, such as calcium and sodium, to maintain its osmotic balance. As the pH becomes more neutral, precipitation of metal oxides on the stream bed hinders the growth of microbes, algae, and invertebrates for many kilometers of streams, also limiting the growth of fish populations and other organisms in higher trophic levels. In fact, metal oxide deposition can have more detrimental effects on stream ecology than the associated low pH and high metals concentrations (McKnight and Feder 1984, Niyogi et al.

1999). However, it is pH and dissolved metals which are regulated under the federal Clean Water Act.

Metals abundant in the sulfide minerals rapidly weathered through ARD include zinc, cadmium, and lead, which remain soluble at neutral pH and therefore remain present in the water column well downstream of other ARD impacts. These conservative metals are transported in solution greater distances downstream than more reactive metals such as iron and aluminum which are lost to the streambed as their respective hydroxide precipitates (Stumm and Morgan 1981).



**Figure 1.2.1.** View downstream at the confluence of the Snake River, an ARD stream (inflow from bottom right) and Deer Creek (a typical mountain stream (inflow from bottom left) showing the change in precipitation of red/orange iron hydroxides at lower pH to the precipitation of white aluminum oxide at  $\text{pH} < 5$ . Photo courtesy of Katie Alexander, left.

## 1.2 IN-STREAM AND WATERSHED GEOCHEMISTRY

Stream chemistry is controlled by both watershed and in-stream processes. Longitudinal in-stream chemical processes are controlled largely by changes in pH due to inflows of water with a higher pH. With downstream increases in pH, hydrous oxides form that may exist as deposits on the streambed or as colloids suspended in the water column. As described above, iron precipitates out of the water column at a pH of approximately 3.5. Above pH 5, aluminum hydroxide begins to precipitate in a reaction similar to that of ferric iron (Equation 1.3). Therefore, the composition of the oxides deposited on streambeds changes with distance downstream with circumneutral inflows that raise the pH of the stream (Figure 1.2.1). More soluble metals, such as zinc, remain dissolved at neutral pH and are transported further downstream with decreasing concentrations due predominantly to dilution by inflows (although some zinc may also be sorbed to iron oxides and organic material along the stream bed). For some metals, such as iron, diel fluctuations due to photochemical processes are also significant drivers of their concentrations in the water column.

The presence of metal oxide precipitates such as iron and aluminum has been found to affect the chemistry of other metals by sorption and co-precipitation (Runkel et al. 1999, McKnight et al. 1992). For example, Kimball et al. (1992) found that concentrations of metals including cadmium, copper, and manganese (and to a lesser degree, zinc) in iron-rich colloids in a first-order AMD-impacted drainage were higher than those reported in surrounding soils. Others have found that dissolved copper concentrations in an ARD-impacted river were controlled by co-precipitation reactions (Johnson 1986). These results suggest that changes in pH may influence metals other than iron and aluminum, which are insoluble at relatively low pH and therefore are first to form precipitates on the streambed.

Because ferric iron hydroxides precipitate out of the water column at relatively low pH, they can collect in regions of anoxic reducing conditions such as meadows, forming thick iron-ore deposits. Deul (1947) investigated natural bog-iron ore deposits present in a valley impacted by ARD and determined that they were produced by acidophilic, chemosynthetic bacteria which derive energy from the oxidization of ferrous to ferric iron (Equation 1.2). The reducing environment of these anoxic zones has historically been a sink for iron hydroxide colloids and the other metals which sorb to this precipitate, such as aluminum and zinc.

On the watershed scale, seasonal hydrologic change drives the occurrence of overland flow, shallow subsurface flow, and groundwater recharge flow paths. In the Rocky Mountains, up to 80% of annual precipitation falls as snow and the hydrograph is dominated by spring melt, which can dilute dissolved metal and sulfate concentrations in streams (Brooks, 2001). As these flows decrease during prolonged dry periods of summer, acidity and metals concentrations in streams resulting from ARD gradually increase due to exposure of more surface area to oxidizing conditions and the subsequent accumulation of soluble salts (Nordstrom 2009; Maest et al., 2004). In-stream solute concentrations spike during the first snowmelt flush and during rainstorms, when accumulated salts and shallow acidic groundwater are flushed out of the system, after which concentrations decrease before slowly rising again during the next dry period (Nordstrom 2009).

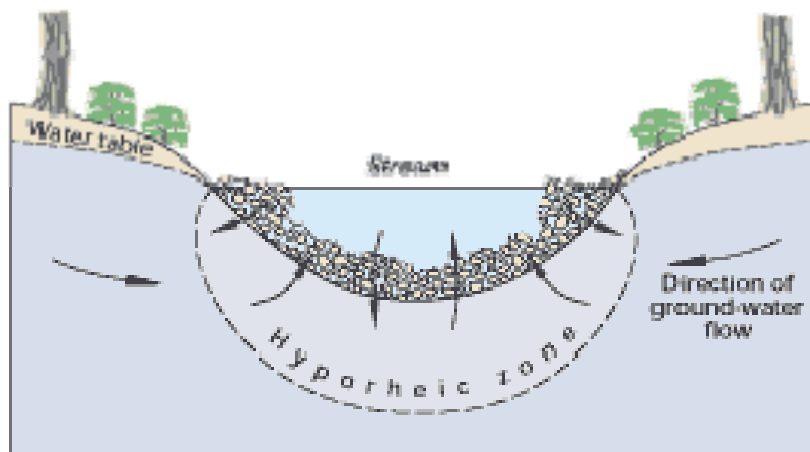
Liu et al. (2004) outline a conceptual model of the relationship between snowmelt, groundwater, and surface water flows in two alpine catchments that is useful for understanding the potential flowpaths of snowmelt and sources of annual streamflow. The conceptual model has three distinct phases which are consistent with Nordstrom (2009): initiation of snowmelt, rising limb of hydrograph and maximum discharge, and the recession limb of the hydrograph to

low flow conditions. In the first stage, soils become saturated resulting in overland flow to the stream channel. When soil becomes saturated, water-dependent chemical reactions such as ARD are initiated and solute concentrations in streams increase. The second stage is characterized by dilution of solute concentrations in the stream as snow melts and flow increases. Liu et al. (2004) estimate that much of the near-stream subsurface flow of snowmelt is routed directly to the stream channel within a matter of hours and that a much smaller portion of the water is likely to follow deeper, more vertical pathways into the bedrock and mix with groundwater before it flows into the stream. They note that in some systems, in the second stage flow into streams can be dominated by groundwater delivered by a process of displacement by snowmelt inputs (McGlynn et al. 2002). Water flowing through and beneath talus is also a significant contributor to streamflow during the snowmelt peak, but may be significantly limited in some regions by the impacts of frozen ground, about which little is known (Liu et al. 2004). In stage three of the snowmelt-streamflow model, the hydrograph shifts to flow dominated by groundwater (from fractured bedrock storage) by late September.

Belanger (2002) found that in mid-summer, subsurface inflows can be more significant contributors to overall metal loads in ARD watersheds than surface tributary flows. Although lateral inflow dissolved metals concentrations were estimated to be lower than tributary inflows, high lateral discharge generated higher dissolved metals loads (Belanger 2002). This finding was attributed to waters reacting more intensely with the subsurface rock, soils, and sediment due to the ratio of rock-surface to water volume, and the likely stronger oxidizing conditions. For this same reason, water exchange with the hyporheic zone likely plays a significant role in metals loading in ARD streams.

### 1.3 MODELING HYPORHEIC EXCHANGE

The hyporheic zone is a region of surface and shallow groundwater water exchange beneath and alongside a stream bed. As such, the hyporheic zone has at least two significant effects on stream chemistry. First, the water is exposed to greater surface area of mineralized rocks and sediment, increasing the potential for chemical reactions. Additionally, the hyporheic zone acts as a temporary storage area surrounding the main channel, where solutes flow through porous media that increases travel time downstream (Figure 1.3.1). These two effects are coupled in that solute transport rates must be slower than reaction rates in order for biogeochemical interactions to have a major effect on water quality (Kimball et al. 1994).

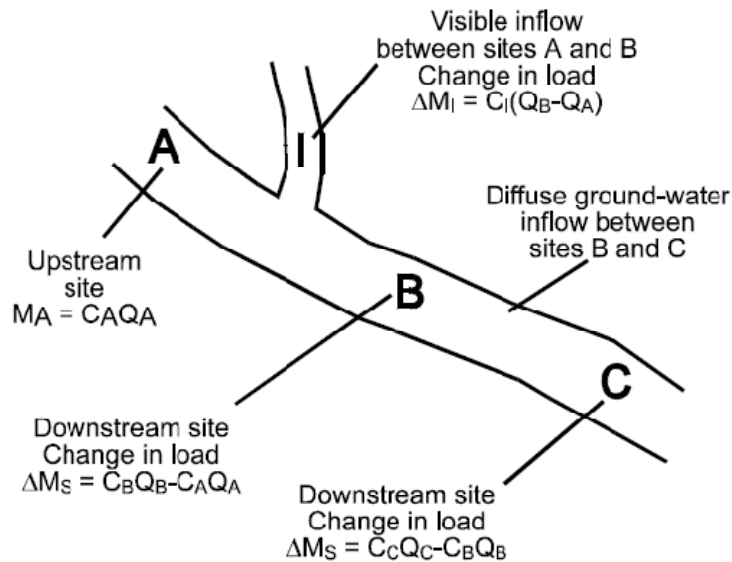


**Figure 1.3.1** This figure illustrates stream flow and exchange with the hyporheic zone. The hyporheic zone is present in streams gaining groundwater (as shown) and is also present in streams that are losing water to groundwater. (Ground Water and Surface Water A Single Resource By T.C. Winter, J.W. Harvey, O.L. Franke, and W.M. Alley Online at [pubs.usgs.gov/circ/circ1139/htdocs/natural\\_processes\\_of\\_ground.htm](https://pubs.usgs.gov/circ/circ1139/htdocs/natural_processes_of_ground.htm))

Hydrologic processes that affect the fate and transport of solutes in a stream channel include advection, dispersion, and transient storage in the main channel or the hyporheic zone (Runkel 1998). Advection refers to the downstream flow of water due to gravity, while dispersion refers to solute spreading resulting from both molecular diffusion and shear stresses within the flow. Transient storage in the main channel increases solute residence times in the system when solutes are held in eddies and slow-moving pools in the stream or in wetland areas

adjacent to the channel. These advective, dispersive, and transient storage properties differ between stream systems. Conservative solute transport models can be coupled with field data from a tracer injection study to quantify these properties and understand the effective size of the hyporheic zone and the degree of exchange with the stream channel.

A One-dimensional Transport with Inflow and Storage model (known as OTIS) was developed by the USGS to model solute transport in streams and rivers (Runkel 1998), largely in response to a need for deeper understanding of sources and fates of metals associated with AMD (Kimball 1997). OTIS is based on a conceptual model of water flow between the advective stream channel and relatively stagnant storage zones. In addition to modeling the hydrologic parameters of advection, dispersion, and transient storage, OTIS can simulate the effects of first-order decay and sorption for chemically reactive solutes. Although the model is one-dimensional in that it assumes that solute concentration changes only longitudinally and does not vary with width or depth, it also accounts for lateral inflow from overland flow, unsaturated subsurface flow, and groundwater inflows. OTIS uses four hydrologic parameters to describe the main channel and storage zone: cross sectional area of channel ( $A$ ), cross sectional area of hyporheic zone ( $A_s$ ), dispersion ( $D$ ) and the hyporheic exchange coefficient ( $\alpha$ ). These parameters can be manually adjusted through trial and error or OTIS-P (with parameter estimation) can be employed to estimate these parameters through several iterations using nonlinear regression statistics. Once the hydrologic parameters are determined, chemical reactions associated with sorption and decay can be modeled for applications such as quantifying trace metal removal from streams.



**Figure 1.3.2:** Conceptual illustration of sampling sites used to calculate groundwater inflow and downstream changes in discharge and load (Kimball 1997).

In a tracer-injection study, a conservative (non-reactive) tracer such as a salt is pumped into a stream at a known concentration and rate. Frequent (3-5 minute intervals) measurements are taken from several downstream sites as the tracer pulse moves downstream. Analysis of these samples allows for plotting “breakthrough curves” for each site that track the movement of the tracer downstream. The breakthrough curve is interpreted in three parts: the “rising limb” as the tracer moves downstream and concentrations increase; the “plateau” when the tracer has saturated the storage zones and maximum concentrations are achieved; and, finally, the “falling limb” of the breakthrough curve represents the decrease in tracer concentrations after the pump is turned off. These studies are often used to quantify sources of metal loading from ARD (Kimball 1997, Kimball et al. 2001, Bencala et al. 1990, Kimball et al. 2002) because clean-up of old mines requires knowledge of the most significant metals sources, which is a function of both the metal concentration and discharge. Multiplying the source discharge by the concentration yields a value of the total mass of the metal flowing in the stream, known also as the load. The significance of using the tracer is that it allows for reliable discharge measurements of the stream



and any inflows or outflows. This is important in mountain streams with rough cobbled beds that are otherwise difficult to accurately measure. Discharge is calculated as a function of the dilution of the conservative tracer. In order to determine metal load, synoptic samples are taken during the plateau of the tracer study in both the main stem of the stream and any inflows to provide spatially detailed concentration data in the stream system. The difference in discharge between two stream sites represents the totally inflow in that stream segment.

In OTIS, the cross-sectional area of the channel is used with the discharge (calculated from plateau tracer concentrations) to describe the stream velocity – and therefore the lag-time between the rising and falling limbs of the breakthrough curves for downstream sampling locations. The hyporheic zone cross-sectional area and exchange coefficients determine the shape of the rising and falling limbs and represent the amount of mixing that occurs between the main channel and storage zones. Of particular significance to learning about properties of the hyporheic zone is the curvature of the “tail”, the final portion of the falling limb which represents outflow of the tracer stored in the hyporheic zone during the injection period.

#### **1.4 SNOW HYDROLOGY AND CLIMATE**

Previous studies about the timing of snowmelt have been concerned primarily with implications for the *quantity* of water available throughout the rest of the year (Clow 2010, Regonda et al. 2005, Ray et al. 2009). Concerns about potential implications of earlier snowmelt have included reservoir operation (flood risk, municipal use), water rights (agriculture, drinking water, etc), forest ecology (wildfire severity, pine beetle epidemic), stream ecology and fisheries, and recreation (Ray et al. 2009). It has been previously noted that water *quality* may also be sensitive to changes in precipitation and hydrograph timing (which were noted to potentially affect sediment load and pollution) as well as water temperature (Ray et al. 2009); however, the

mechanisms and consequences of any such impacts have been only superficially explored.

Nordstrom (2009) described ways in which climate change may influence stream water quality by impacting geochemistry and weathering processes. In the current study, the foremost interest is that earlier snowmelt may result in the acceleration of natural chemical weathering processes and therefore affect water quality. Potential effect of the lack of late-season dilution is also addressed.

Snowmelt timing in the mountainous western United States has been found to be strongly influenced by winter and spring climate (Cayan et al. 2001, McCabe and Clark 2005, Stewart et al. 2005, Clow 2010). In particular, air temperature (Cayan et al. 2001, Stewart et al. 2005), precipitation, and maximum snow water equivalent (SWE) (Clow 2010, Mote 2006) affect snowmelt and streamflow timing. Air temperature in the Northern Hemisphere has been found to increase approximately 0.34 °C per decade during 1979-2005 (Folland et al. 2001) while warming in the Colorado Rockies has been observed to be twice that during the same period, with the greatest temperature increases occurring in November-January (Clow 2010; Ray et al. 2008). In areas of historic mining, warmer spring and summer temperatures as well as earlier snowmelt may result in greater thawing in and around historic mines and mining deposits, increasing the potential for chemical weathering and production of ARD. Indeed, April 1 SWE, maximum SWE, and winter precipitation rates in Colorado have decreased over the past few decades (Mote 2006, Knowles et al. 2006, Stewart et al. 2004, Knowles and Cayan 2004) as the result of changing climate patterns thought to have anthropogenic origins. Climate in the western United States is impacted over periods of several years by the El Nino Southern Oscillation (ENSO) and over periods of 1-2 decades by the Pacific Decadal Oscillation (PDO).

The complexity of these climate patterns and the irregularity of climate in the Southern Rockies can make detection of precipitation and snowmelt trends difficult, especially over the period of record available at most SNOTEL sites (22 years) and many stream gauges. Snowmelt timing in this region exhibits substantial inter-annual variability (Clow 2010, Ray et al. 2008) and is impacted by short-term global climate oscillations (Mann et al. 1995). While specific relationships between Colorado climate and cyclical oceanic and atmospheric patterns are not well described (Cayan 1996, McCabe and Dettinger 1999, Rajagopalan et al. 1997), streamflow timing in the western United States has been found to scale with Pacific climate indices such as ENSO and PDO (Stewart et al. 2005, Regonda et al. 2005). Moreover, recent studies suggest that 60% of these regional changes in climate and climate-driven hydrology are the result of anthropogenic greenhouse warming (Barnett et al. 2008, Hidalgo et al. 2009).

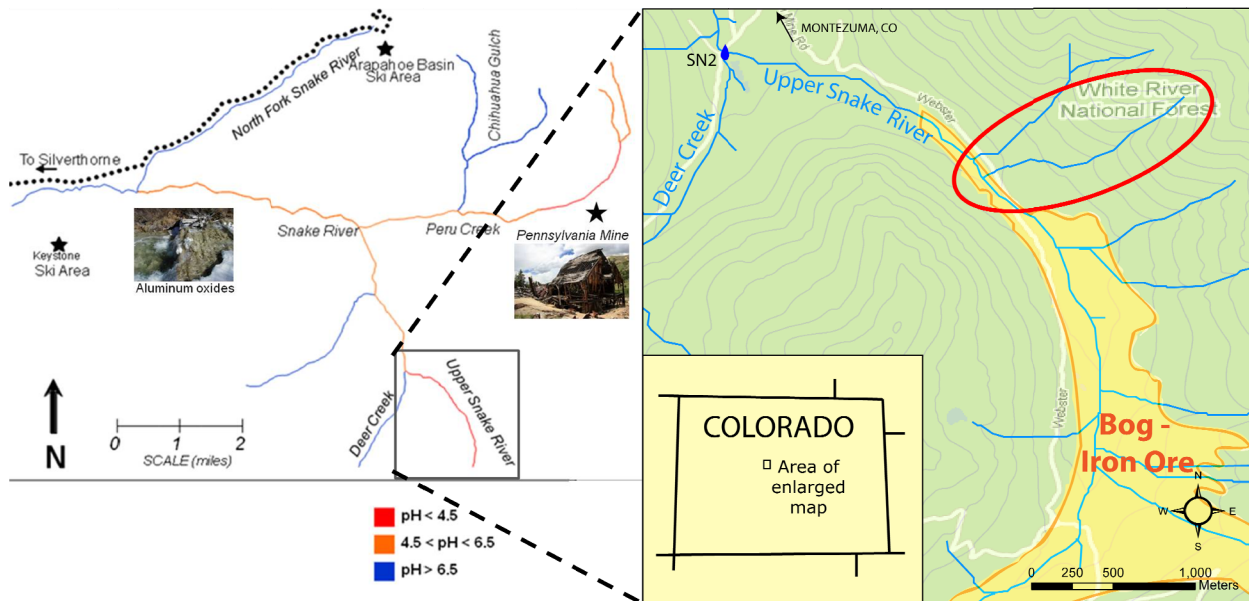
Several previous studies had found only minor significant changes in maximum SWE and the timing of snowmelt (Regonda et al. 2005, Stewart et al. 2005, Knowles et al. 2006, Mote 2006) and attributed this absence of significant trends in part to Colorado's cold climate and high elevations. However, these studies used simple linear regression analysis as their primary statistical technique. Using a regional statistical analysis method (Kendall analysis), Clow (2010) found that snowmelt timing (measured from SNOTEL SWE data) and streamflow timing (using gauge discharge records) in the Colorado Rockies has advanced approximately 2-3 weeks earlier over the past 3 decades. Streamflow timing in the region that includes the current study site in the Snake River watershed was found to be 4.0-5.9 days earlier per decade (Clow 2010). Spring air temperatures, in particular, have been found to be significantly correlated with earlier snowmelt (Clow 2010, Stewart 2005). Despite a decrease in April 1 SWE and annual maximum SWE, the time at which 80% of the year's water had passed by the stream gauge was found to be

later relative to the initiation of melt, suggesting a decrease in winter precipitation and a corresponding increase in the importance of spring and summer rain to the hydrograph (Clow 2010).

## Chapter 2

### SITE DESCRIPTION

The Snake River watershed in Summit County, Colorado has its headwaters in the highly mineralized and glaciated alpine terrain found along the western slope of the Continental Divide (Figure 2.1.1). The snowmelt dominated Snake River drains more than 60 square miles, running for approximately fifteen miles: through the town of Keystone and then into Dillon Reservoir, the largest water storage facility in the Denver Water system. The upper portions of the watershed is largely undeveloped except for the town of Montezuma, located about two miles downstream from the confluence of the Upper Snake River and Deer Creek and the Arapahoe basin ski resort along the North Fork.



**Figure 2.1.1.** The Upper Snake River within the broader Snake River Watershed. The blue water drop indicates the location of the Snake River above Deer Creek (SN2), the long-term sampling site. The red oval indicates the site of the tributary of interest and the September 2010 tracer study.

As a result of both historic mining activity and natural biogeochemical processes, a large percentage of the Snake River Watershed is impacted by acid rock drainage. In the late 1990s

and early 2000s the Snake River was identified on Colorado's 303(d) list of impaired water bodies due to high concentrations of zinc, cadmium, copper, lead, and manganese resulting from both natural weathering and historic mining in the watershed (CDPHE 2008). TMDL requirements have now been developed for the watershed, which is therefore set for water quality monitoring and, eventually, mitigation. Section 303(d) of the Federal Clean Water Act requires States to periodically submit a list of impaired water bodies to the U.S. Environmental Protection Agency (EPA). Due to their presence on the 303(d) list, metals given the most focus in this analysis are zinc, cadmium, copper, and manganese.

Large sections of the Snake River and its tributaries are coated in metal hydroxides – primarily iron and aluminum hydroxides – that precipitate out of solution as flow from pristine tributaries raises the pH of the stream water. Northern portions of the Snake River watershed receive inflow from numerous abandoned mines (Figure 2.1.1). The Pennsylvania Mine, located in the northeastern portion of the watershed, has been found to be one of largest sources of metals and acidity within the watershed (McKnight and Bencala 1990).

The presence of acid rock weathering in the Snake River Watershed is a result of its geology. This region of the central Rocky Mountains is characterized by steep-sided glacial valleys covered in relatively thick glacial till deposits underlain by predominantly metamorphic granitic rocks (of hydrothermal metamorphism). The Snake River Watershed is largely underlain by crystalline rocks of varying mineralogy and metamorphism from nearly monomineralic schists to highly complex gneisses. The most common of these crystalline rocks are quartz-biotite blend schists and gneisses made predominately of quartz, microcline, plagioclase, and biotite (Wood 2005). Also present in the region are numerous crystalline stocks, dikes, and sills as well as ferricrete deposits.

## ***2.2 The Upper Snake River***

The Upper Snake River, defined as upstream of Deer Creek – the location of the study sites in this analysis – drains approximately 11.8 km<sup>2</sup> on the southeastern portion of the Snake River watershed. Stream gradients in the study area are very steep and stream velocities are rapid. Because it is a snowmelt-dominated stream, there is considerable variation in discharge between low-flow and high-flow regimes. Flow in the Upper Snake River between April and July ranges on average from a low of approximately 0.1-0.2 m<sup>3</sup>sec<sup>-1</sup> to a high that averages near 6 m<sup>3</sup>sec<sup>-1</sup> and regularly gets above 9 m<sup>3</sup>sec<sup>-1</sup> (Boyer et al. 1999). The Snake River at Montezuma (the closest stream gage to the site, USGS gage #09047500) has an average annual stream flow of 1.9 m<sup>3</sup>sec<sup>-1</sup> (measured over the past 30 years) of which the Upper Snake River accounts for approximately 20% (Boyer et al. 1999). The elevation of the long-term sampling site at the confluence of the Upper Snake River and Deer Creek is 3,219 meters above sea level. The highest point in the Upper Snake River watershed is above 4,020 meters on Geneva Peak. At elevations such as those at the study site, the valley floor is covered in wetlands and shrubs and the valley sides have unvegetated ridges and peaks (Figure 2.1.2).

This study investigates increasing metals concentrations in the Upper Snake River. The location of the site where increasing metals concentrations were measured is immediately upstream of its confluence with Deer Creek. The geochemistry of the confluence has been studied extensively because the inflow of Deer Creek, a relatively pristine stream of approximately equal flow to the Upper Snake River, raises the pH and causes precipitation of aluminum and iron hydroxides on the stream bed below the confluence (Theobald 1963). Previous studies have shown that loading of iron, aluminum, and manganese decreases below the

confluence due to precipitation but that loads of other heavy metals remain high because they remain in solution at higher pH (Theobald 1963, Todd et al. 2005).



**Figure 2.1.2.** View from the site of the tracer injection study, southwest up the Upper Snake River valley toward Webster Pass and the continental divide. Photo courtesy of Patrick Robinson.

Pyrite, the most abundant sulfide mineral in the Upper Snake River valley, occurs disseminated in large-grained metamorphic rocks such as the gneisses described above. Pyrite is also the most common mineral in the veins of mined ore and is present in contact-metamorphic deposits near large stocks as well as in hydrothermally altered rocks of the Upper Snake River valley (Lovering 1935). Other sulfides present in the region are galena ( $\text{PbS}$ ), sphalerite ( $\text{ZnS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), bismuthinite ( $\text{Bi}_2\text{S}_3$ ), and molybdenite ( $\text{MoS}_2$ ). However, the total pyrite disseminated in the rocks of the Upper Snake River valley is much greater than the total quantity



in the veins (Theobald 1963). As a result of the presence of this disseminated pyrite, the headwater tributaries on the eastern side of the Upper Snake River watershed have been characterized as a natural source of acidic and metal-enriched streamwater and groundwater (Theobald 1963, Belanger 2002). This source is an important finding because the previously identified influential mines were on the western site of the catchment (Wilson and LaRock 1992). The Upper Snake River also runs through a naturally occurring ferricrete deposit (iron-ore, Figure 2.1.1).

Crouch (2009) and Belanger (2002) found that metals increase downstream in the main stem of the Upper Snake River (with the exception of iron, which was observed to decrease downstream in both studies). Belanger (2002) and Bencala et al. (1990) determined that loading of some metals to the Upper Snake River was predominately from distributed lateral inflows, which have a significant influence on stream chemistry. For some of these subsurface inflows, concentrations were estimated to be lower than those in tributaries but high lateral discharge generated higher dissolved metals loads (Belanger 2002).

## **Chapter 3**

### **POTENTIAL IMPACTS OF CLIMATE-DRIVEN HYDROLOGIC CHANGE ON STREAM CHEMISTRY**

#### **3.1 BACKGROUND**

Andrew Todd at the United States Geological Survey (USGS) observed an increasing trend in low-flow zinc concentrations between water years 1979 and 2008 (Crouch 2009). Data is available from many of these years and archived water samples were available for a subset of these years. The purpose of the work described in this chapter was to compile the most accurate and representative data from the water quality samples and analyses available to establish the observed trend during September low flow over the past 30 years, 1980-2010. Questions addressed in this section include: Are metals concentrations increasing in the Upper Snake River? If so, over what time scale has the change occurred? (Quickly over the past 10 years since the 2002 drought? Steadily over the past 30 years?) Samples from this data set had been analyzed in several different labs and with different analytic techniques. Available water samples were (re)analyzed to 1) ensure that the laboratory analysis techniques are the same for as many samples as possible and 2) to fill in a data gap in the mid-1990s with archived samples that had not been previously analyzed. For a description of this evaluation, see Appendices A and B.

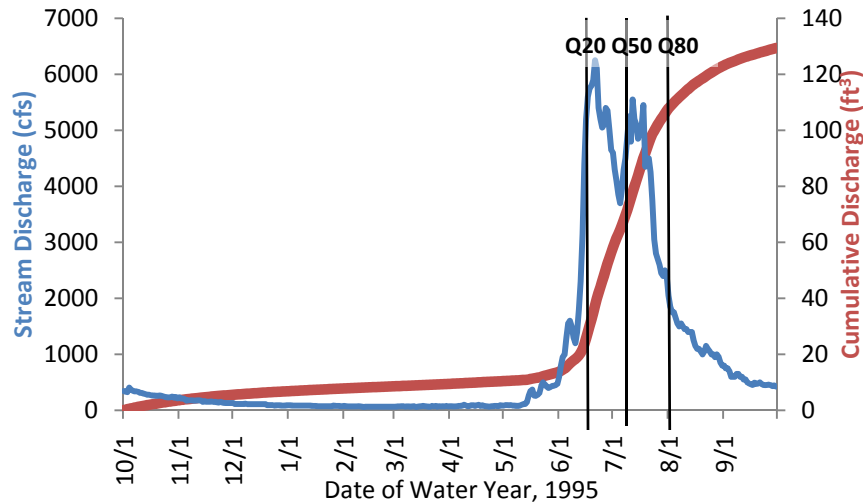
#### **3.2 DATA ANALYSIS**

Because annual spring snowmelt flows in ARD watersheds are characterized by high acidity and metals concentrations known as the “first flush” (Nordstrom 1977, Younger and Blachere 2004, Green et al. 2006), the focus of this study is on changes in acidity and metals concentrations during the low flow period of September through December when the snow has melted and the source of flow is groundwater, which is more comparable between years. Yearly

streamflow and snowmelt data were compared with low-flow water quality characteristics. Streamflow data were used as a proxy to estimate changes in the timing of snowmelt and SNOTEL data were used to directly measure snowmelt timing. All relationships and correlations were described by linear regression analysis and ANOVA.

### ***3.2.1 Streamflow Methodology***

Streamflow data were analyzed as a proxy for snowmelt timing and to estimate changes in the timing of snowmelt from year to year. Streamflow analysis techniques were modeled after Clow (2010). Data were processed for quality and completeness and yearly hydrographs and cumulative discharge curves were constructed. On the cumulative discharge curve, the changes in slope which occur at 20%, 50%, and 80% of the year's total streamflow approximate the beginning, midpoint, and end of snowmelt runoff (Clow 2010). Based on this cumulative discharge curve, days representing the onset of flow, peak flow, and end of melt were recorded as Q20, Q50, and Q80 (Figure 3.2.1). Days were recorded as the day of the water year between Oct 1 and Sept 30 of the following year. Because these are snowmelt-dominated systems, these methods should be consistently representative in most water years. Similar methods have been used by Stewart et al. (2005) and McCabe and Clark (2005).



**Figure 3.2.1** Illustration of Q20, Q50, and Q80 as the day of the water year on which 20%, 50%, and 80% of the cumulative discharge has passed the gage. In the snowmelt-dominated hydrographs of the Southern Rockies, these values generally capture the start of the snowmelt pulse (Q20), its peak (Q50), and its end (Q80).

### 3.2.2 Snowmelt Methodology

Snow accumulation and melt data were collected from the Loveland and Grizzly Peak SNOTEL sites. The Grizzly Peak site is the only site in the vicinity with a water record longer than 15 years (the record starts in 1979). Analysis was again modeled after Clow (2010). The first step was to review data for quality and completeness and to identify the day of maximum snow water equivalent (SWE) for each year of record. Day of peak SWE was used for a value of maximum accumulation as a proxy for snowmelt onset. Additionally, day of snow depletion was recorded for each year at each site because this is the day on which snowmelt is no longer entering the subsurface.

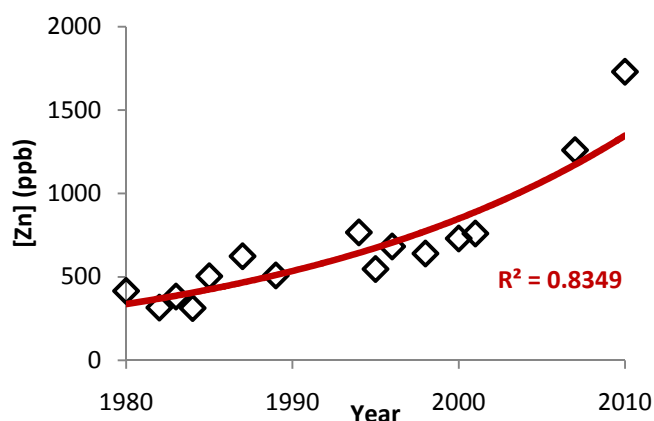
## 3.2 RESULTS AND DISCUSSION

Dissolved metals concentrations have been observed to increase over the past three decades (Crouch 2009) at the long-term study site, SN2, on the Upper Snake River (Figure 2.1.1). This section describes this trend using the full data set constructed from a long term data record and archived samples (Appendix C) and compares this trend with hydrological parameters

to try to gain a better understanding of causes of these increasing solute concentrations. The purpose of this chapter is to use the new, complete data set established in Appendices A and B to analyze the increasing trends in metals concentrations with other available hydrologic and climate data in an effort to determine the cause of this trend. The focus here is on increasing trends in zinc because concentrations remain at the levels that most significantly exceed metal-specific aquatic life criteria farther downstream than the other constituents.

### 3.3.1 Stream Chemistry Trends

Dissolved zinc concentrations during the low-flow period have increased in the Upper Snake River and this increase has become exponential over the past decade ( $p < 0.001$ ).



**Figure 3.3.1** Dissolved zinc concentrations have increase in the Upper Snake River. This increase was linear until the early 2000s when it began to increase more quickly and has become a significant exponential increase ( $p < 0.001$ ).

Samples used to illustrate this trend include data from a long-term record at the site as well as archived samples from 1994-1996 that provide data for years that had not been previously described (Appendix A). Measured zinc concentrations have increased at an average rate of  $35.7 \mu\text{g L}^{-1}\text{year}^{-1}$  over the past 30 years ( $p < 0.001$ , Figure 3.5.1). There has been an approximately five-fold increase in low-flow September zinc concentrations over the past 30 years from concentrations of between  $300\text{-}400 \mu\text{g L}^{-1}$  in the early 1980s to concentrations exceeding  $1700 \mu\text{g L}^{-1}$  in 2010. Additionally, in their 1963 paper, Theobald et al. reported zinc concentrations

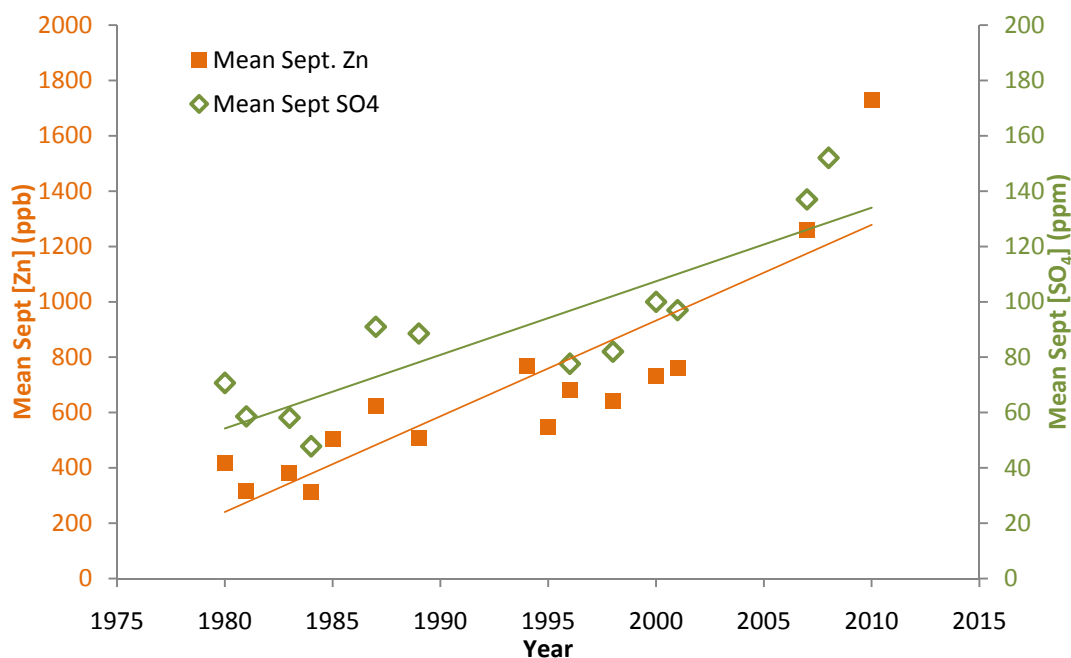
immediately above the confluence with Deer Creek to be at  $350 \mu\text{g L}^{-1}$ , consistent with the observation that concentrations began rising in the late 1980s. The full data set is presented in Appendix C (Figure C.1).

**Table 3.3.1** Trends in stream chemistry with time, mean September values ( $\mu\text{g L}^{-1}$ ). Raw data are presented in Appendix C, Table C.1 or \*Table C.2.

Analyte	Study period increase	Available record	$\mu\text{g L}^{-1}\text{year}^{-1}$	p-value
Al	262%	1994-2010*	256	0.0004
Cd	840%	1980-2010	0.24	0.0005
Cu	129%	1980-2010	0.71	0.0008
Fe	209%	1994-2010*	34.9	0.0129
Mn	280%	1980-2010	64.4	0.0003
Zn	300%	1980-2010	35.7	0.0001
SO <sub>4</sub>	115%	1980-2010	2.90	0.0003

The concentrations of the solutes of interest (Zn, Cd, Cu, Mn, Al, Fe, and SO<sub>4</sub>) increased significantly ( $p < 0.05$ ) over the study period for which data for each were available (Table 3.5.1, Appendix C). Of the seven relevant analytes that are examined in more detail here, cadmium exhibits the greatest percent increase over the 30 year study period, increasing from  $1 \mu\text{g L}^{-1}$  in 1980 to  $9.4 \mu\text{g L}^{-1}$  in 2010. Aluminum, copper, and manganese increased by 262% ( $3,290 \mu\text{g L}^{-1}$  to  $11,900 \mu\text{g L}^{-1}$ ), 129% ( $18 \mu\text{g L}^{-1}$  to  $41 \mu\text{g L}^{-1}$ ), and 280% ( $933 \mu\text{g L}^{-1}$  to  $3,550 \mu\text{g L}^{-1}$ ) respectively. Despite the observed precipitation of iron on the streambed, concentrations over the study period increased 209%, from  $664 \mu\text{g L}^{-1}$  to  $2055 \mu\text{g L}^{-1}$ . Iron is very reactive and subject to photochemical diel fluctuations (McKnight et al. 1988), complicating the understanding of its changing concentrations. Compounding this issue is that the time of day when these samples were collected is unknown and is likely to have varied substantially. The resulting uncertainty potentially explains the increasing iron trend having a much lower statistical significance than the other solutes.

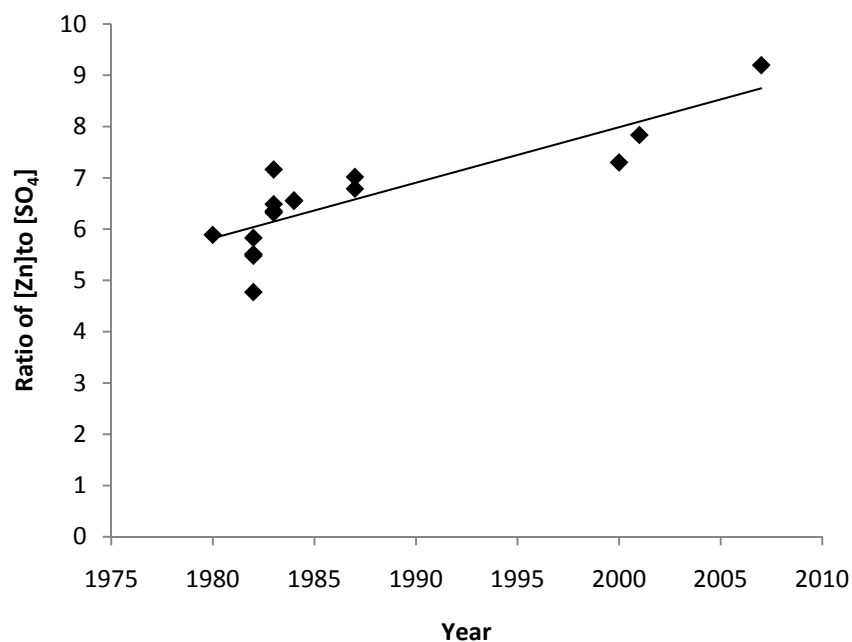
It is well established that in ARD environments,  $\text{SO}_4$  is mobilized in proportion to metals and acidity and remains relatively conservative at low pH (Sullivan and Drever 2001, Bencala et al. 1987). Both Theobald (1963) and Kimball et al. (1994) demonstrated this relationship between  $\text{SO}_4$  and  $\text{Fe}^{2+}$ ,  $\text{H}^+$ , Al, and other metals at the confluence of the Snake River and Deer Creek by showing minor losses of sulfate to iron oxides below the confluence. Figure 3.3.2 illustrates simultaneous increasing trends in dissolved zinc and sulfate over the past 30 years, indicating that these water quality changes are driven primarily by accelerated chemical weathering in the watershed.



**Figure 3.3.2** Low-flow dissolved zinc concentrations indicate an approximately 300% increase between 1980 and 2007 (years for which both  $\text{SO}_4$  and Zn data exist) period along with a corresponding 150% increase in  $\text{SO}_4$ .

Linear analysis of covariance (for zinc and sulfate normalized to percent change from 1980 values) was used to determine if zinc and sulfate have increased in proportion with one another for the years for which zinc and sulfate data both exist. Results suggest that dissolved zinc concentrations are increasing faster than sulfate by about 10% per year (Figure 3.3.3). This suggests that some portion of the increases in zinc – and possibly other solutes – may be derived

from a different source than the increases in sulfate. Because the increase in dissolved metals is not parallel with sulfate concentrations, the greater increase in metals may be due to in stream biogeochemistry rather than watershed processes. The increase in sulfate concentrations does suggest that there is also an acceleration of natural weathering in the watershed. This conclusion assumes that sulfide minerals with similar relative amounts of trace metals are being eroded through time.

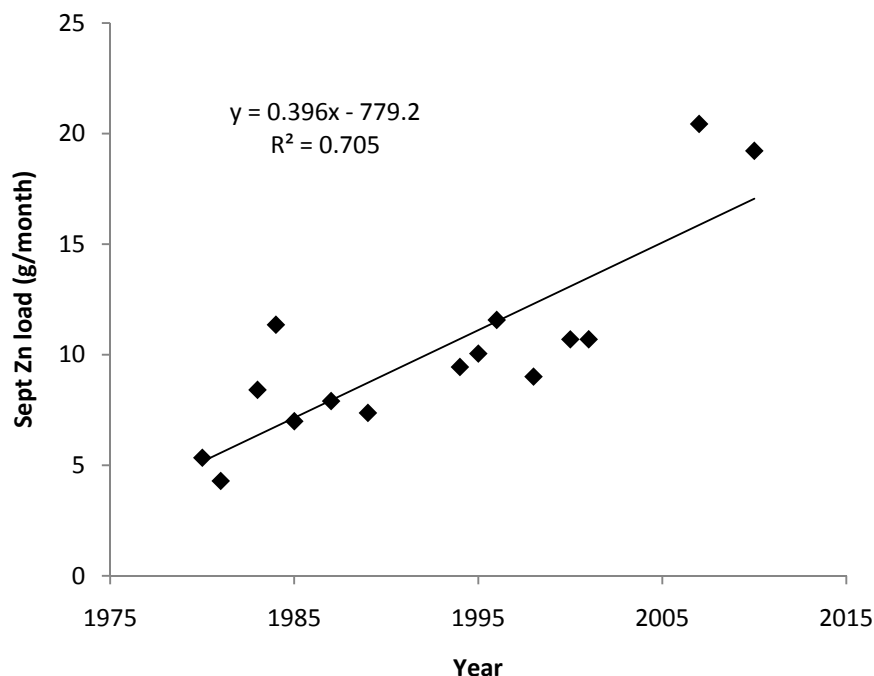


**Figure 3.3.3:** The ratio between the concentration of zinc and sulfate has increased over the past 30 years ( $R^2 = 0.72$ ,  $p < 0.0001$ ). On average, zinc concentrations exhibit a 10% greater annual increase than sulfate each year. (This analysis was performed for days on which both dissolved zinc and sulfate were collected.)

These significant increases in solute concentrations would result in additional strain on already degraded downstream stream ecosystems including macroinvertebrate and fish populations. Dissolved metals concentrations are used to predict acute and chronic toxicity effects and assess attainment of the aquatic life designated use. To help quantify the magnitude of any effects of decreasing discharge on concentration, September mean zinc loads were also



plotted against time to establish if the same trend exists (Figure 3.3.4). Zinc loads were estimated using a discharge equivalent to 20% of the flow at the Montezuma gage (Boyer et al. 1999).



**Figure 3.3.4** Mean September dissolved zinc loads indicate a nearly 400% increase in zinc load over the past three decades, similar to the percent increase as zinc concentrations.

Dissolved zinc loads exhibit an approximately 400% increase from 1980 to 2010. The fact that zinc loads have increased at nearly the same rate as the concentration of dissolved zinc suggests that the effect of decreasing low-flow stream discharge is not the cause of the increasing concentrations.

### 3.3.2 Snowmelt and Streamflow Timing

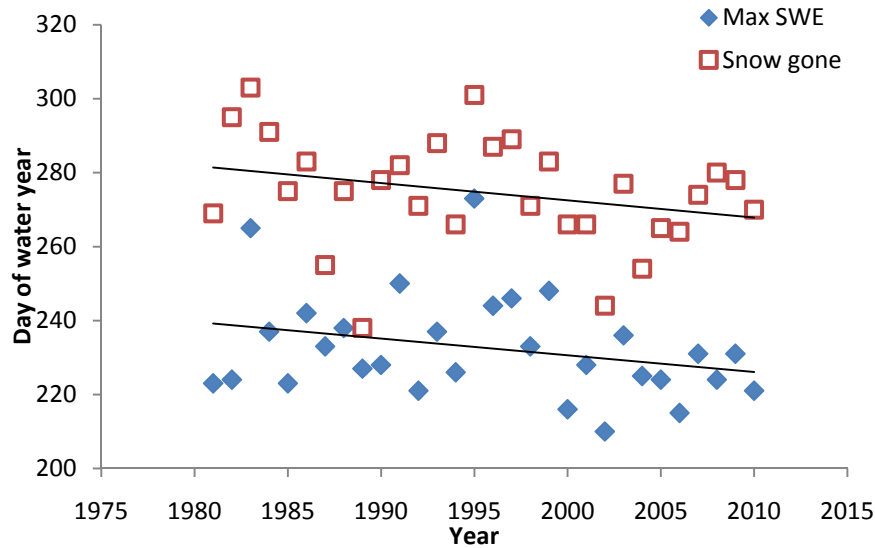
An analysis of snowmelt timing from the Grizzly Peak and Loveland Pass SNOTEL sites along the continental divide, near the perimeter of the Snake River Watershed, suggests that maximum accumulation and snowmelt have advanced over the past three decades. At both SNOTEL sites used in this analysis, earlier timing was detected (Table 3.3.2, Figure 3.3.5), consistent with a recent, larger-scale state-wide investigation (Clow 2010).

**Table 3.3.2** Maximum SWE and termination of snowmelt: the slope of the linear regression, given with significance (p-value) in parentheses.

	Advancement of Snowmelt (days per decade)	
	Max SWE	Snow gone
Grizzly Peak	4.5 (0.13)	4.7 (0.14)
Loveland Pass	15.1 (0.02)	10.8 (0.13)

At the Grizzly Peak SNOTEL site near the Snake River Watershed, both maximum SWE and the Julian day on which all the snow is depleted occur approximately 15 days earlier than they did three decades ago. Snow accumulation and melt in the Snake River Watershed have advanced by nearly 5 days per decade; however, neither of these values is significant at less than 13% probability of error. At Loveland Pass, maximum SWE and the termination of snowmelt also appear to be occurring earlier (Table 3.3.2, Figure 3.3.5). A significant trend in maximum SWE was detected that indicates an advance of 15 days per decade. However, it should be noted that these data were collected over only 15 years and are subject to magnification of a decadal climate cycle signal which may currently be swinging toward advancement of snowmelt.

Consistent with the results of snowmelt timing from the SNOTEL sites, results of the streamflow analysis support the contention that snowmelt (measured as the bulk of streamflow) is occurring earlier in the Rocky Mountains when compared to 30 years ago (Table 3.3.3). Analysis of the streamflow trend yields a negative slope, indicating the advancement of the snowmelt pulse with time. Over the same period, streamflow timing varied from year to year by as much as two months in the Snake River watershed (Figure 3.3.6). The Snake River flowing at the Montezuma gage has shown statistically significant advances (between 1-5 days per decade) in the onset and conclusion of the spring snowmelt pulse over both the intervals of the past 30 and past 50 years.



**Figure 3.3.5** Data from the Grizzly Peak SNOTEL site illustrate the trend toward earlier snow accumulation (Max SWE) and melt (Snow gone) over the past 30 years ( $p < 0.14$ ). Analysis shows negatives slopes, suggesting that the peak and end of the snow season may be occurring earlier at this location in Colorado.

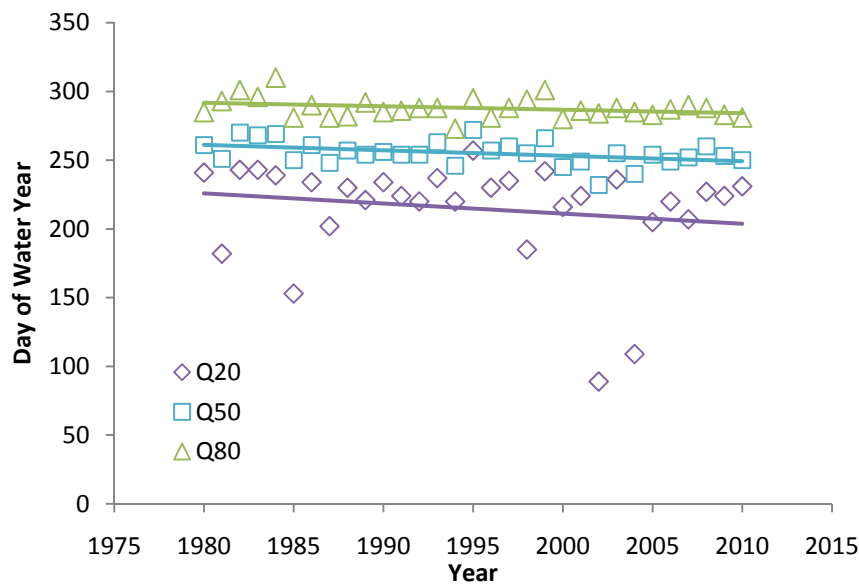
According to streamflow records from the southeastern portion of the Snake River watershed, Q20 (the onset of snowmelt) has advanced by 1.5 days per decade over the past 50 years. The snowmelt peak, Q50, has advanced by 3.9 days per decade and the end of the snowmelt pulse, Q80, has advanced 3.0 days per decade over the past 30 years. The weakness of the trend in Q20 since 1970 (6.3 days per decade;  $p = 0.43$ ) may be due to the large variation in the onset of snowmelt timing, particularly associated with the drought and warm air temperatures in the 2002 water year. This disparity of several days between the change of the onset and end of the snowmelt pulse might be attributed to many factors, including 1) earlier season warming, which causes melt to begin earlier and spring precipitation to come in the form of rain rather than

**Table 3.3.3** Trends in streamflow timing at the Montezuma Gage. The slope of the regression line is given with significance in parentheses.

	Advancement of Streamflow (days per decade)		
	Q20	Q50	Q80
1956-2010	1.5 (0.06)	1.1 (0.10)	-
1979-2010	6.3 (0.43)	3.9 (0.03)	3.0 (0.06)

snow and 2) increased maximum SWE in some locations which result in longer melt times.

However, an analysis of maximum annual flow in the Snake River does not indicate any significant change in annual flow over the time period considered in these analyses. Clow (2010) found that Q80 did not shift as much or as significantly in the state of Colorado as in the rest of the Western US and hypothesizes that this was due to an increased influence of spring and summer rain.



**Figure 3.3.6** The Snake River at Montezuma has shown statistically significant advancement of the onset and peak of the spring snowmelt pulse over the past 30 years.

Other analyses of peak streamflow and snowmelt timing in Colorado and the Southern Rocky Mountains have found similar results. Regonda et al. (2005) did not find significant advancement of snowmelt timing in high-elevation basins such as the Colorado Rockies using linear regression analysis. However, Clow (2010) found far fewer significant trends in snowmelt timing and streamflow using regression analysis than when he used the regional Kendall test. However, much like the present analysis, Clow (2010) found more significant streamflow trends than SNOTEL SWE trends. Whereas previous studies using regression analysis found few if any significant trends (Regonda et al. 2005), Clow (2010) found that snowmelt and streamflow

timing had advanced approximately 5 days per decade on average – similar to the average value determined in this study using linear regression.

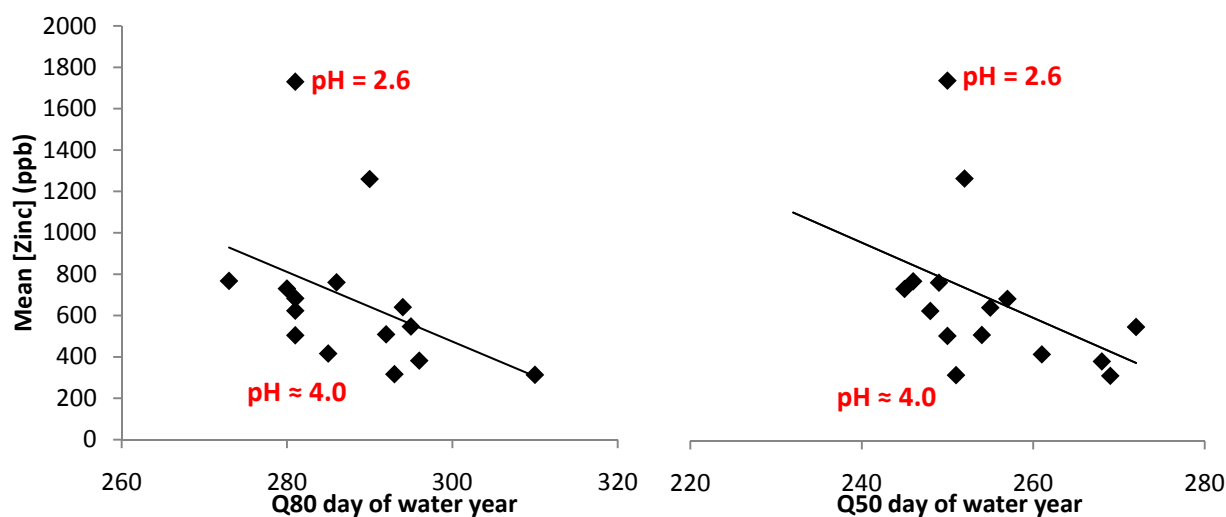
### 3.3.3 Stream Chemistry and Climate-Induced Hydrologic Changes

Results of this analysis show that the concentrations of some solutes are weakly correlated with streamflow timing, consistent with the hypothesis that earlier streamflow timing may result in increased low-flow dissolved metals concentrations (Table 3.3.4). Specifically, zinc, copper, and aluminum concentrations are consistently related to Q50 and Q80 streamflow ( $p < 0.10$ ). The stronger relationships with Q50 and Q80 compared with Q20 make sense in light of the hypothesis that earlier termination of snowmelt results in the acceleration of ARD due to a change in groundwater. These metals are also the three that are expected to be the least reactive at low pH so in that sense it is likely that if they were mobilized in greater amounts during years of earlier snowmelt and accelerated weathering, that they might be still in solution as much as several kilometers downstream of their source.

**Table 3.3.4** Relations between streamflow timing and metals concentrations. The slope of the linear regression is given with significance in parentheses. Negative relations indicate a correlation between earlier stream flow and increased solute concentrations. Units represent the mean change in zinc concentration ( $\mu\text{g L}^{-1}$ ) per day of advancement in streamflow.

Stream Chemistry Relations (mean September values, 1980-2010)			
Solute	Q20 Streamflow $\mu\text{g L}^{-1}\text{day}^{-1}$	Q50 Streamflow $\mu\text{g L}^{-1}\text{day}^{-1}$	Q80 Streamflow $\mu\text{g L}^{-1}\text{day}^{-1}$
Zn	-0.76 (0.76)	-15.1 (0.09)	-18.1 (0.07)
Cu	-0.05 (0.42)	-0.40 (0.05)	-0.44 (0.07)
Al	-9.74 (0.59)	-113 (0.09)	-135 (0.07)
Mn	-1.14 (0.82)	-27.0 (0.14)	-33.6 (0.11)
SO <sub>4</sub>	-0.10 (0.86)	-1.46 (0.28)	-1.76 (0.14)
Cd	+0.01 (0.74)	-0.052 (0.47)	-0.05 (0.61)
Fe	+0.28 (0.93)	-7.76 (0.52)	-7.35 (0.60)

Significant negative trends in metal concentrations do exist in the Upper Snake River, where increases in zinc concentration may be largely explained by advances in peak and conclusion of snowmelt runoff discharge at both Q50 and Q80 ( $p = 0.09$  and  $0.07$ , respectively; Figure 3.3.6). A negative trend also exists between metals and Q20, although this relation is not statistically significant. The greater significance of solute concentrations correlations with Q50 and Q80 compared to Q20 is consistent throughout the dataset (Table: 3.3.6).



**Figure 3.3.7** In the Upper Snake River, low-flow dissolved zinc concentrations appear to be correlated with changes in the timing of Q50 ( $p < 0.09$ ) and Q80 ( $p < 0.07$ ). Earlier peak flows and earlier completion of snowmelt may contribute to observed increases in zinc concentrations. The pH was measured at or near 4.0 throughout the 1980s and 90s; pH of 2.6 was measured in September 2011.

Although trends in snowmelt timing were not as significant as those in streamflow timing, statistical analyses were performed to examine the potential for an explanatory relationship between snowmelt parameters and changes in stream chemistry. The results of these analyses are presented in Table 3.3.5.

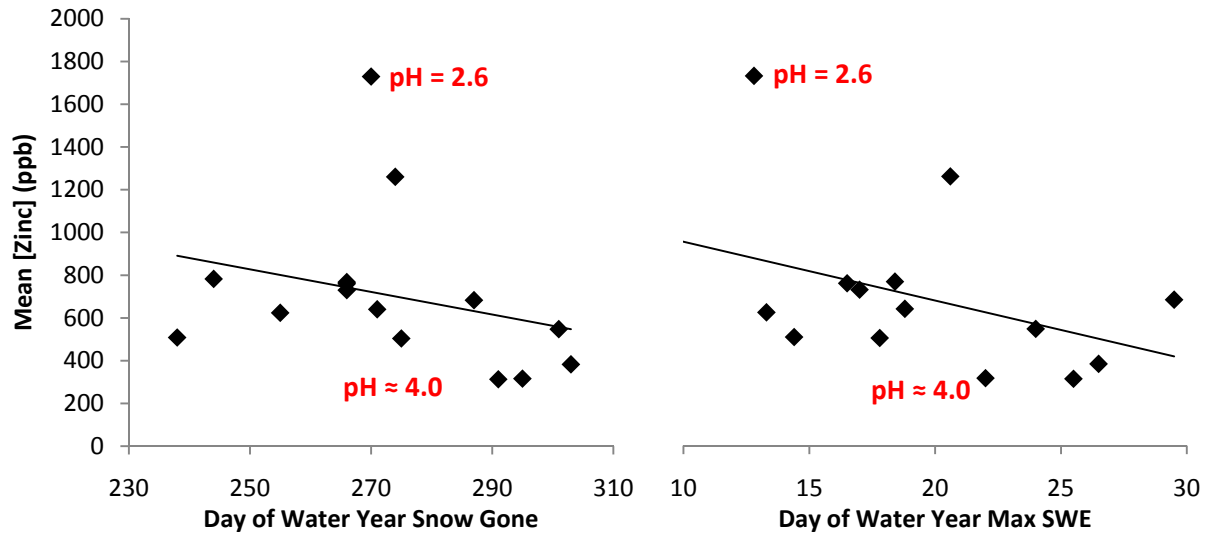
There are two outliers in each of the graphs in Figures 3.3.6 and 3.3.7. These represent the mean zinc concentrations from the two most recent sampling events, when the trend has increased exponentially. They are also the two highest values for dissolved zinc and correlate

with the lowest pH measurements known to have been taken from the Upper Snake River (as low as 2.6 in September 2010). Prior to these two years, the statistical relationship of zinc concentrations with both streamflow and snowmelt was much stronger and statistically significant ( $p < 0.05$ ). This suggests that perhaps the same mechanism that has driven the pH so low has caused the dramatic recent increase in zinc concentrations in the Upper Snake River. This hypothesis is addressed further in the discussion and conclusions to Chapter 4.

**Table 3.3.5** Relationship between snowmelt timing and solute concentrations. The slope of the regression line is given with significance in parentheses. Negative relations indicate a correlation between earlier snow accumulation and/or melt and increased solute concentrations.

Stream Chemistry Relations (mean September values, 1980-2010)					
Solute	Day of Max SWE		Snow Gone		Max SWE
	% chg/day	µg L-1/day	% chg/day	µg L-1/day	µg L-1/inch
Zn		-6.70 (0.24)		-5.30 (0.32)	-27.5 (0.12)
SO <sub>4</sub>		-5.12 (0.17)		-0.43 (0.47)	-0.18 (0.92)

SNOTEL data from the Grizzly SNOTEL site were compared with solute concentrations in the Upper Snake River. A weak correlation exists between an increase in low-flow dissolved zinc concentrations and earlier maximum accumulation, earlier snowpack depletion, and maximum SWE (Figure 3.3.8). It is of note that all trends are negative regardless of their significance, consistent with the idea that there may be a relation between the increase in low-flow solute concentrations and climate-driven hydrologic change.



**Figure 3.3.8** Correlations between mean September dissolved zinc concentrations in the Upper Snake River with day of maximum accumulation, earlier snowmelt completion, and values of maximum SWE at the Grizzly SNOTEL site. The pH was measured at or near 4.0 throughout the 1980s and 90s; pH of 2.6 was measured in September 2011.

Overall, solute concentrations yielded somewhat stronger correlations with the streamflow observations than with the SNOTEL data. While streamflow measurements are not an exact measurement of snowmelt, they have the advantage of providing information that represents an entire region; conversely, SNOTEL data provide accurate, high resolution information about one location. However, SNOTEL data must be extrapolated to estimate snow accumulation and melt for an entire region. One possible lesson from this analysis is that proximity of the gage or SNOTEL site to a stream chemistry sampling site may be an important factor due to the significant spatial heterogeneity of snowfall and snowmelt in mountain regions. This may be especially true if the source of the increased metals is distributed throughout the Upper Snake River valley. Nonetheless, without strongly significant relationships and longer-term data records, it may also be the case that a different mechanism is driving the changes in solute concentration.

However, there are several conceptualizations of changing groundwater conditions and interactions between surface water and groundwater in regions of ARD that can explain the



results of this analysis. Acidity and metals concentrations in streams – the result of ARD – have been found to gradually increase during prolonged dry periods (Nordstrom 2009, Maest et al., 2004). Therefore, it follows that earlier snowmelt and a longer low-flow period would likely increase the zinc concentrations in a stream. Nordstrom (2009) extrapolated that warming spring temperatures and changes in climate that result in earlier snowmelt would lengthen the dry period even more, increasing the concentrations of soluble salts in the groundwater and their prevalence in the unsaturated zone. This would be the result of a lower groundwater table and greater exposure of subsurface material to oxygen, and therefore weathering conditions.

Other literature suggests that the relationship between annual snowmelt and groundwater flows might be on a longer scale than previously thought. Cowie (2010) used  $\delta^{18}\text{O}$  values in precipitation and stream waters to describe residence times of alpine groundwater systems and determined a residence time of 1.12 years. The mechanism of this relationship is described by Liu et al. (2004). Average residence times of greater than one year suggest that hydrogeological impacts may occur on a time-scale greater than the few months between the completion of snowmelt and the September stream chemistry data presented here. Still, it is most probable that the accelerated ARD occurs in the shallow groundwater and the unsaturated zone, where oxygen is present, and that this oxygenated zone is larger as the water table lowers in late summer.

Still, research has suggested that the highest proportion of annual snowmelt to flow in the stream may occur during the hydrograph recession, before low flow conditions (Cowie 2010). This indicates that the baseflow of a stream is made predominantly of deeper groundwater with longer flowpaths and greater residence times. It may still be the case, however, that increasing solute loads from the shallow, oxygenated groundwater are high enough to cause the dramatic changes in water chemistry described above. Detailed modeling of groundwater geochemistry is

needed to help further understand any impacts of climate-driven hydrologic change on stream chemistry.

### 3.4 CONCLUSIONS

Dissolved solute concentrations during the low-flow period have increased significantly over the past three decades in the Upper Snake River with the increase accelerating since the early 2000s. The five-fold increase in zinc concentrations is of particular concern because due to the conservative nature of its solubility, zinc will remain at elevated levels much farther downstream than the other dissolved metals. Measured zinc concentrations exceeding  $1700 \mu\text{g L}^{-1}$  in 2010 have increased at an average rate of  $35.7 \mu\text{g L}^{-1}\text{year}^{-1}$  over the past 30 years ( $p < 0.001$ ), with a more accelerate rate of increase over the past decade. Concurrent increasing trends in dissolved zinc and sulfate over the study period indicate that water quality changes are driven primarily by accelerated chemical weathering in the watershed. However, over the past decade, dissolved zinc concentrations have increased faster than sulfate suggesting that some portion of the increases zinc and other metals may be derived from a different source.

Day of maximum accumulation and snowmelt have both advanced significantly by 5 to 15 days over the past three decades at both SNOTEL sites used in this analysis. Results of the streamflow analysis also support the contention that snowmelt is occurring earlier in the Rocky Mountains than it was 30 years ago. The Snake River flowing at the Montezuma gage has shown statistically significant advances (between 1-5 days per decade) in the onset and conclusion of the spring snowmelt pulse over both the intervals of the past 30 and past 50 years. Metals concentrations are correlated with streamflow timing. In particular, dissolved concentrations of zinc, copper, and aluminum are strongly correlated with the peak and conclusion of snowmelt. These and other solutes are also weakly correlated with snowmelt accumulation and depletion

data from SNOTEL sites. These data are consistent with the hypothesis that earlier snowmelt timing may result in increased low-flow dissolved metals concentrations. Therefore, increases in zinc concentration are largely explained by advances in snowmelt. Earlier snowmelt may be driving watershed-scale changes in stream chemistry due to shifts in the phases of Liu et al.'s (2004) conceptual model. With snowmelt initiated earlier, water penetrates into oxygenated subsurface material earlier in the year, likely resulting in an earlier initialization of weathering. Similarly, weathering may be accelerated further when the snow is melted and more oxygen can penetrate into the subsurface. Because snowmelt has occurred earlier, however, groundwater tables are likely to be lower by September than in later snowmelt years resulting in a lower water table and more subsurface material available to weathering conditions for the first time. As the hydrograph peak recedes and low-flow conditions set in, this groundwater becomes the primary source of streamwater. However, if this lower pH water follows more vertical, longer flowpaths to the stream, some of the effects of this accelerated weathering may not be seen on annual time scales.

These data do not clarify the potential role of the severe drought event in 2002, which may have impacted watershed-scale hydrology, contributing to the accelerated increase in dissolved metals concentrations measured in the stream. It remains a viable possibility that the accelerated increase in metals concentrations observed during the past several years began with the 2002 drought.

## **Chapter 4**

### **TRACER INJECTION STUDY**

#### **4.1 BACKGROUND**

Two field investigations were performed to help delineate the factors associated with metals loading into the Upper Snake River. The first was a preliminary synoptic study along the length of the Upper Snake River. The second was an intensive tracer injection study conducted in September 2010 in a tributary of interest identified for elevated metal loading based on previous studies and a preliminary synoptic study.

##### ***4.1.2 Purpose***

The questions addressed in this study were: What is the loading of metals from the tributary of interest into the Upper Snake River during low flow conditions? Which areas of the catchment are weathering or transporting contaminants to the river? To what degree are these solutes from surface erosion or leaching from precipitation and groundwater flow? Are there point sources such as previously unidentified mine waste piles that are contributing significant contamination? To answer these questions, field and analytical data from surface water were collected from the Upper Snake River and its tributary of interest during low flow conditions of October 2009 and September 2010.

If surface water samples from the tributary of interest identify a discrete rather than distributed source of metals loading, the cause of increasing metals concentrations in the stream may be the result of either previously underestimated inputs from historic mining activities, increased anthropogenic activity, or a local change in groundwater flow. Identification of metal loads from distributed sources may indicate that the increase in metals concentrations is the

result of watershed-scale hydrologic change such as lowering of the groundwater table as the result of earlier snowmelt due to climate change.

#### ***4.1.2 Previous Studies***

For her 2002 Masters thesis, Laura Belanger conducted a diel study in the Upper Snake River in which she measured stream chemistry along the main stem of the stream and in its 3 largest tributaries, one of which is the tributary of interest focused on in this study. She found that, in July 1998, the tributary of interest and the lateral inflows through the bog iron-ore both were significant sources of dissolved metals to the Upper Snake River. The tributary of interest contributed approximately two-thirds of the solute loads to the stream, although it only increased the in-stream concentration from  $107 \mu\text{g L}^{-1}$  to  $135 \mu\text{g L}^{-1}$  (Belanger 2002). She calculated that the discharge of the tributary of interest to be  $0.031 \text{ m}^3 \text{ s}^{-1}$  and that it carried a zinc load of  $130 \mu\text{g s}^{-1}$  (measured zinc concentration during the study was  $307 \mu\text{g L}^{-1}$ ).

In October 2009, I designed and conducted a field study with two classmates, Alison Ling and Patrick Robinson, for our Applied Stream Ecology course. The primary goal was to investigate spatial trends in dissolved metals and related water quality parameters including pH, conductivity, hardness, anion concentrations, and dissolved organics at low flow. Changes in in-stream zinc concentrations were found to be inversely related to pH, consistent with the hypothesis that zinc is sourced from sulfate mineral weathering. Large contributions of metals and ions from two tributaries on the northeastern side of the catchment, one of which was the tributary of interest, were found to be an order of magnitude higher than in the main stream. Zinc was measured at 16,617 ppb in the tributary of interest below which the concentration in the main channel of the Upper Snake River more than doubled from 354 ppb to 744 ppb. This tributary, and the one just downstream of it (with a concentration of 5,668 ppb), also showed

high conductivity, high sulfate concentrations, and low pH. Although the Upper Snake River is generally considered to be a natural acid rock drainage stream, several small mine tailings piles were observed in the tributary, opening up the question of previously unknown historic mining impacts on water quality in the Upper Snake River (Figure 4.1.1).



**Figure 4.1.1** (A) View up the portion of the Upper Snake River valley studied during October 2009, (B) and (C) small tailings piles observed on the northeastern portion of the watershed

## 4.2 FIELD METHODS

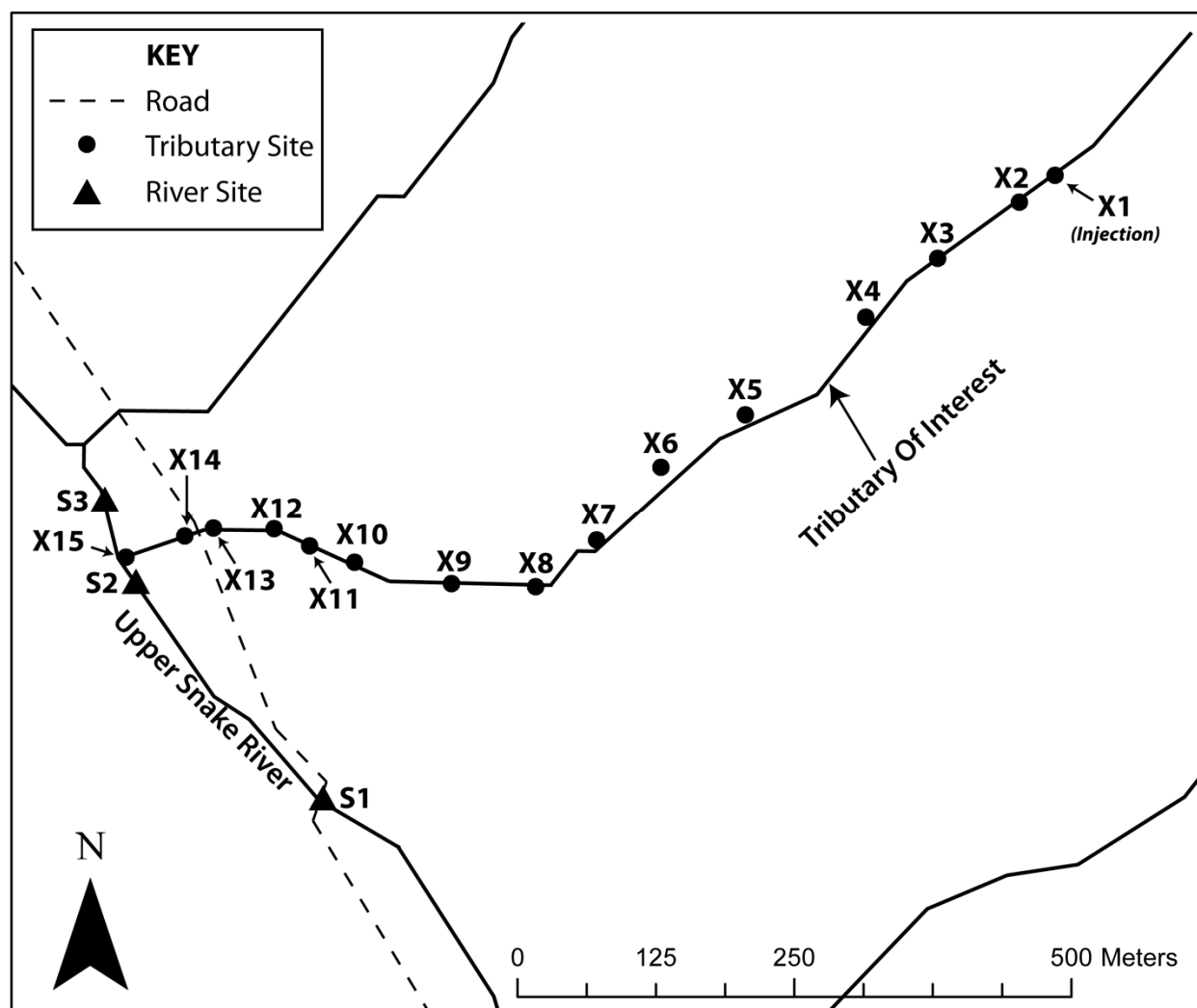
The tracer study was conducted on a small, perennial tributary (the tributary of interest) to the Upper Snake River. The headwaters of the tributary are located on a steep, rocky hillslope above treeline on the northeastern side of the Upper Snake River valley at 3620 m above sea level (Figure 4.2.2). The tributary runs for 1,054 meters to its mouth, located at an elevation of 3,308 meters above sea level, approximately 2,000 meters upstream of the confluence of the Upper Snake River and Deer Creek.



**Figure 4.2.1** Sampling at site X3, approximately 160 meters downstream of the injection site. Here, the tributary of interest is steep, exposed, and runs over bedrock with some visible inflow seeps on either side on the channel.

### 4.2.1 Reconnaissance 2010

Field reconnaissance was performed in July 2010 to choose sampling sites on the tributary of interest. Locations were marked with a GPS based on changes in topography and visible inflows. Only one surface channel inflow was observed in July and it was dry by the study in September. Several inflow seeps were observed along the stream channel. Detailed site descriptions are given in Table 4.2.1. Latitude and Longitude coordinates are included in Appendix D.



**Figure 4.2.2** This map shows the sites sampled during the September 2010 tracer injection study. All sites were sampled for metals analysis during the plateau. Samples for  $\text{Cl}^-$  tracer analysis were collected every 5-15 minutes at the odd-numbered sites (see Appendix D).

**Table 4.2.1** Site descriptions from July 2010 field reconnaissance of the tributary of interest. These sites were used in the September 2010 field study.

Site	Stream distance from injection (m)	Elevation (m)	Slope above (degrees)	Streambed Precipitates	Notes/Observations
X0	-5	3609		Dry, clear	Above spring inflow
X1	0	3608		Clear	Meadow, very rocky
X2	66	3582	23.1	Dark red stain	Meadow, very rocky
X3	164	3549	19.8	Dark red	Steep and exposed; bedrock
X4	252	3525	15.9	Dark red	Steep and exposed; bedrock
X5	405	3461	24.6	Orange-red	Stream widens, rocky
X6	498	3438	14.3	Orange	Stream narrows, grassy banks
X7	590	3410	17.7	Orange	Stream narrows, grassy banks
X8	661	3396	11.5	Orange	Into forest
X9	737	3385	8.2	Orange	Into forest
X10	829	3365	12.6	Orange	Several shallow channels
X12	909	3355	7.2	Orange	Several shallow channels
X13	963	3347	8.5	Orange	Single channel
X14	990	3343	8.4	Orange	Channel widens below road
X15	1054	3338	4.5	Muddy, dark	In meadow immediately above inflow to Upper Snake River
S1	n/a	3357		Orange-red	Main stem of stream
S2	n/a	3340		Orange-red	Main stem above tributary
S3	1110	3334		Orange-red	Main stem 50m below trib.

The entire length of the tributary is relatively straight. Most of the morphological variation between reaches is due to substrate, which varies from bedrock (at sites X3-X4) to large gravel (sites X1-X2 and X5-X10) to sand and gravel (sites X12-X15). The stream reaches also vary in the degree and color of metal hydroxides precipitated on the bed. Images of the stream bed at each reach are presented in Figure 4.2.3.





**Figure 4.2.3** Photos of selected stream sampling sites along the tributary of interest.



#### ***4.2.2 Tracer Injection September 2010***

The injection site of the tracer experiment was located at the spring from which the tributary emerges. A 240,000 mg/L NaCl conservative tracer solution was injected at a rate of approximately 150 mL/min using a Geopump 2 peristaltic pump powered by three 12v/6amp batteries chained in parallel in order to maintain a constant voltage. The injection lasted 4.75 hours from 10:15 to 15:00 mountain time during which downstream conductivity measurements were made to track the NaCl pulse and to ensure that the tracer reached plateau concentrations. Although the pump rate was measured at regular intervals to maintain a consistent rate, once during the 6-hour injection the NaCl pump rate was measured as high as 168mL/min but was lowered back to 150mL/min and stayed more consistent (at 11:50 am, 95 minutes into the experiment time). The pump rate did, however, continue to increase slowly for the remainder of the injection (see Appendix D).



**Figure 4.2.4** Pump set up at site X1 (left) and filtering synoptic stream chemistry samples at site X9 (right).

During the rising and falling limbs of the tracer study, water samples (for  $\text{Cl}^-$  analysis) were collected in 5-minute intervals. During the plateau phase, tracer samples were collected at 15 minute intervals. Sample bottles were triple-rinsed with sample water and filled directly from

the stream. Water samples for anion analysis were stored in 100-200 mL plastic bottles until laboratory analysis.

Stream chemistry water samples were collected and conductivity and pH measurements were taken at fifteen sites along the tributary (X1-X15) and three sites along the Upper Snake River (S1-S3). Water from surface sampling locations was collected synoptically and simultaneously (within one minute) at 1400 and 1500 hours mountain time. Several teams collected all samples during this limited time frame. Total and dissolved samples for metal analysis were collected at each location. All metals samples were collected in triple-rinsed gallon milk jugs, and samples for dissolved metals analysis were filtered using 0.45  $\mu\text{m}$  cellulose acetate membrane filters with hand filter pumps. All samples were stored in plastic bottles and those for metals analysis were preserved with nitric acid later that day.

#### **4.3 ANALYTICAL METHODS**

Chloride has been established as a conservative tracer - more reliable than sodium - in acidic environments such as the waters of the Upper Snake River (Bencala et al. 1990). For this reason, chloride was used as the tracer despite the background concentrations, which were measured and subtracted during analysis. In anticipation of the background levels of  $\text{Cl}^-$ ,  $\text{NaCl}$  load was injected such that it would increase the  $\text{Cl}^-$  concentration in the stream by an order of magnitude at the most downstream sampling location.

##### ***4.3.1 Laboratory Analysis***

Unacidified samples collected during the rising and falling limbs of the tracer injection were filtered in the lab with 0.45 micron syringe filters and analyzed for  $\text{Cl}^-$  and  $\text{SO}_4$  using Ion Chromatography (Dionex ICS-2000). To address the inherent challenges of analyzing acidic, metal-enriched samples, the Ion Chromatograph (IC) was fitted with Dionex InGuard Na

cartridges (P/N 074036) to remove metals from each sample prior to analysis. Because samples were diluted due to the high  $\text{Cl}^-$  concentrations and the potential damage that the metals could cause the columns of the IC, relatively low concentrations of  $\text{Cl}^-$  were present in the samples when they were run. As a result of the presence of the InGuard Na cartridge, this may have introduced some error into the lowest concentration samples due to some complexation with or release of  $\text{Cl}^-$  ions from the Na in the cartridge (Dionex 2009). Based on the use of standards, duplicates, and blanks periodically throughout each run of the IC, this minor error is not believed to have significantly affected the results. To ensure data quality, one undiluted sample was run for each site during the plateau and this result was used to calculate downstream dilution effects and changes in discharge (Section 4.3.2). Use of the InGuard Na cartridge created large error in results for nitrate and sulfate which prevented the use of these data.

Filtered and acidified stream chemistry samples collected during the plateau of the tracer injection were analyzed for dissolved metals (Al, Ba, Fe, Mn, Sr, Zn, Ti, Be, Cu, V, Cr, Co, Mo, Sb, As, Cd, Pb, Ni, Se, Ag, Tl) at the USEPA Region 8 laboratory in Golden, Colorado. Samples were analyzed for dissolved metals using an ICP-MS (method EPA 200.8). Descriptions of these samples are presented in Appendix D.

#### ***4.3.2 Data Processing***

Discharge was calculated by using plateau  $\text{Cl}^-$  concentrations in the following equation (Kimball 1997):

$$Q_s = (C_i * Q_i) / (C_B - C_A) \quad (4.3.1)$$

where  $Q_s$  (L/s) is the stream discharge,  $Q_i$  (L/s) is the rate of injection into the stream,  $C_i$  (mg/L) is the  $\text{Cl}^-$  concentration of the injection solution,  $C_A$  (mg/L) is the  $\text{Cl}^-$  concentration of the stream water upstream of the injection, and  $C_B$  (mg/L) is the  $\text{Cl}^-$  concentration downstream of the

injection. Because  $\text{Cl}^-$  plateau concentrations varied, values used to calculate discharge were taken from the same place on the curve – just after the pump was lowered back to a known rate of 150 mL/min.

These discharge measurements were used to determine solute loads into the tributary of interest at each point where a synoptic water sample was collected (all sampling sites). Loads for the mass of solute per time at various locations along the tributary were calculated by the following equation (Kimball et al. 2002):

$$M_x = Q_x C_x \quad (4.3.2)$$

where  $M_x$  (mg/s) is the load at that point in the tributary,  $Q_x$  (L/s) is the estimate of tributary discharge (Equation 4.3.1), and  $C_x$  (mg/L) is the concentration of the solute in the tributary.

Because no surface flows (just several small shallow groundwater seeps) were large enough to be sampled, no inflow concentrations were directly measured. Therefore, the increases in solute loads from groundwater inflow along each stream reach were calculated using the following equation (Kimball et al. 2002):

$$M_t = Q_b C_b - Q_a C_a \quad (4.3.3)$$

where  $M_t$  (mg/s) is the total load of that solute along the stream reach  $Q_b$  (L/s) is the discharge at the downstream end of the reach,  $C_b$  (mg/L) is the solute concentration measured upstream of the reach,  $Q_a$  (L/s) is the discharge upstream of the inflows, and  $C_a$  (mg/L) is the solute concentration measured at the upstream end of the reach. The total additional loading represents the loading from subsurface seeps and groundwater inputs.

Total solute load for the tributary was calculated by adding all of the positive lateral inflow values along the separate reaches. Dividing each positive lateral inflow load by the total cumulative load (at site X15) quantifies the percent of the total load contributed by groundwater

over each reach. This allows a quantitative assessment of which of these reaches are the greatest sources of the metal and other solute loads contributed to the Upper Snake River.

#### **4.3.3 Modeling with OTIS and OTIS-P**

Data obtained during the tracer experiment were also used to characterize hydrologic properties with the One-dimensional Transport with Inflow and Storage (OTIS) solute transport model (Runkel 1998). OTIS enables determination of stream cross-sectional area and velocity, and uses the shape of the rising and falling limbs of the  $\text{Cl}^-$  concentrations to provide quantitative information about the hydrologic properties of residence times in the hyporheic zone of each stream segment. In the current study, the stream channel is sufficiently straight and narrow such that transient storage other than that associated with the hyporheic zone is considered negligible.

To use OTIS, model inputs must first be established including the upstream boundary condition (USBC), which can be created with data from the injection site. However, because in this study the pump rate was unsteady, concentrations measured at the first sampling site were used as the upstream boundary condition. This approach allowed for more accurate estimates of changes in downstream solute concentrations. Discharge at the USBC (X3) was calculated using Equation 4.3.1. The unit (per meter) lateral inflow between each site was calculated using Equation 4.3.2. Lateral inflow concentrations of  $\text{Cl}^-$  were assumed to be 1.2 mg/L along the entire stream, a value representative of background  $\text{Cl}^-$  concentrations measured throughout the stream system.

OTIS was first used to estimate  $\text{Cl}^-$  plateau concentrations, main channel cross-sectional area,  $A$ , and the dispersion coefficient,  $D$ . In these initial runs, the exchange coefficient was ignored ( $\alpha = 0$ ) in order to facilitate a more accurate estimate of  $A$ , which was adjusted for each site until the simulated time of the rising limb visually matched timing of the rising limb from

collected data. Decreasing  $A$  caused the simulated stream velocity to increase (because discharge was known) and moved the arrival of the rising limb to an earlier time, while increasing  $A$  modeled a slower stream velocity and moved the breakthrough curve to a later time. The parameters established in these initial OTIS runs were then applied in OTIS-P to optimize the parameters for all sites, now including  $\alpha$  and the cross-sectional area of the storage zone,  $A_s$ . All measured inputs to OTIS-P remained the same as those used in OTIS. The exchange coefficient,  $\alpha$ , was initially set at 0 for all parameters but was allowed to vary with the model for all reaches except the first. Modeling  $\alpha$  for the first reach yielded results several orders of magnitude outside of the range of values found in the literature for similar streams. To optimize the results for all parameters, OTIS-P was rerun with the output parameters and this process was repeated several times. Results of several OTIS-P runs yielded very high dispersion values. These values were suspect because they did not simulate the tail of the breakthrough curve accurately. Most likely, because the large variation in the pump rate was measured at different 15-minute intervals for each site, the OTIS-P simulation placed too much emphasis accurately simulating the plateau phase of the breakthrough curve. Because there is no way to have the model emphasize the tail over the scatter in the plateau data, work with OTIS-P was abandoned and OTIS was used for the final parameter estimations.

Because of the difficulty of simulating several reaches at once, while incorporating large storage effects, hydrologic parameters were calculated on an individual reach basis using OTIS. Once parameter values for each reach were established, they were combined in OTIS and, working from the highest reach to the lowest, adjusted for the best visual fit. During the final round of model runs in OTIS, estimates of  $D$  known for similar first-order mountain stream were used. A value of  $0.5 \text{ m}^2/\text{s}$  was used for the reaches with rough, rocky beds (above X7, X9, and

X13) and a value of  $0.2 \text{ m}^2/\text{s}$ , was used for reaches above X5 and X15 which have wider, smoother flow. To confirm a close fit between the observed and modeled data sets, linear regressions were run comparing the values at each site.

#### **4.4. RESULTS**

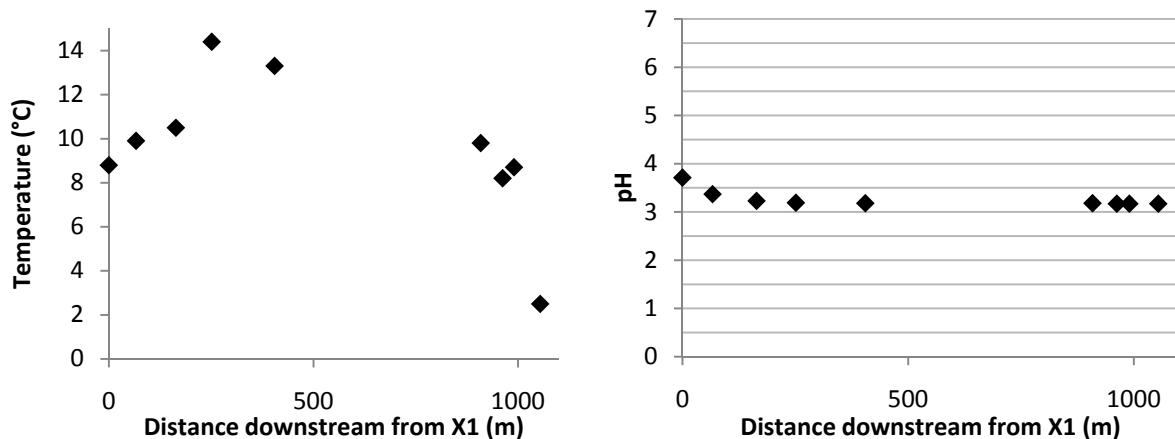
##### ***4.4.1 Field Observations***

At the time of the tracer experiment on September 11, 2010, the location of the tributary spring was approximately 50 meters below where the stream was observed to emerge earlier during the July field reconnaissance. This change suggests that in September the groundwater table was lower than it had been earlier in the summer. During the morning, freezing air temperatures overnight gave way to sunny weather with  $13^\circ\text{C}$  air temperature. Ice on the edges of the tributary between the injection site and site X5 melted throughout the morning and was completely gone by 12:00. No ice was present on lower reaches of the tributary at the start of the tracer injection. One dry tributary was observed immediately above site X2.

##### ***4.4.2 Temperature and pH***

Stream water temperature and pH were measured longitudinally at sites X1 – X5 and X10 – X15 (Figure 4.4.1 A and B). Temperature and pH data are not available for sites X6 – X9 because an additional probe was not working in the field that day. Due to rough terrain, it was not feasible to move another thermometer and pH probe to these middle sites.

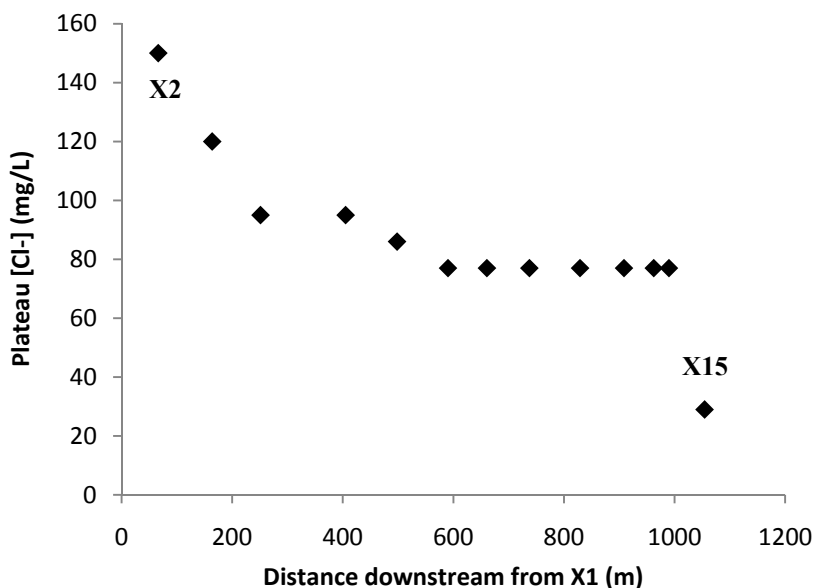




**Figure 4.4.1** Measurements of downstream temperature and pH taken concurrently with stream chemistry samples during the plateau phase of the investigation at 14:00.

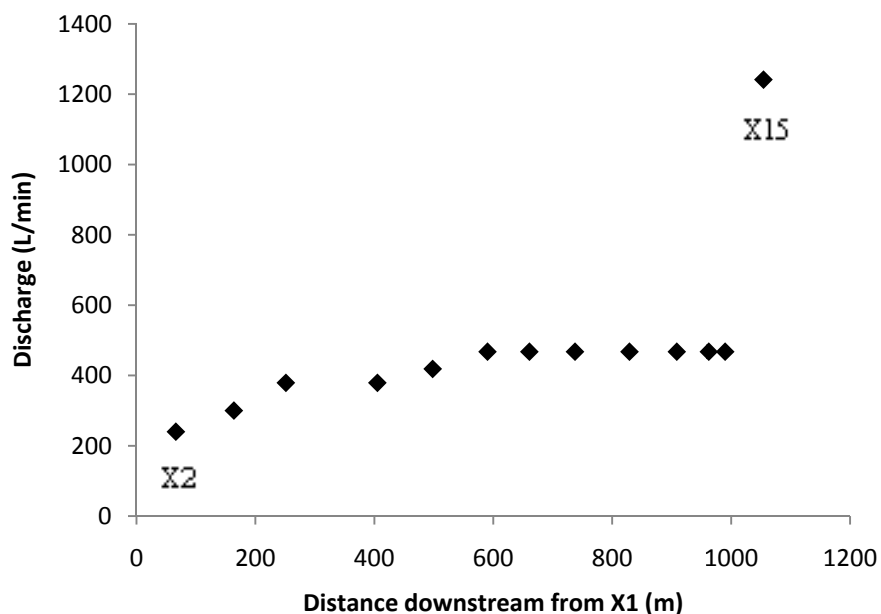
#### 4.4.3. Tracer Breakthrough Curves: discharge and velocity

Dilution data were acquired from the plateau tracer concentrations (Figure 4.4.2). A plot of these data shows that the  $\text{Cl}^-$  concentrations were diluted as the tracer moved downstream. Tracer dilution is caused by increases in stream discharge. Dramatic dilution occurs above site X5 and again between sites X14 and X15. Tracer concentrations were constant between sites X6 and X14.



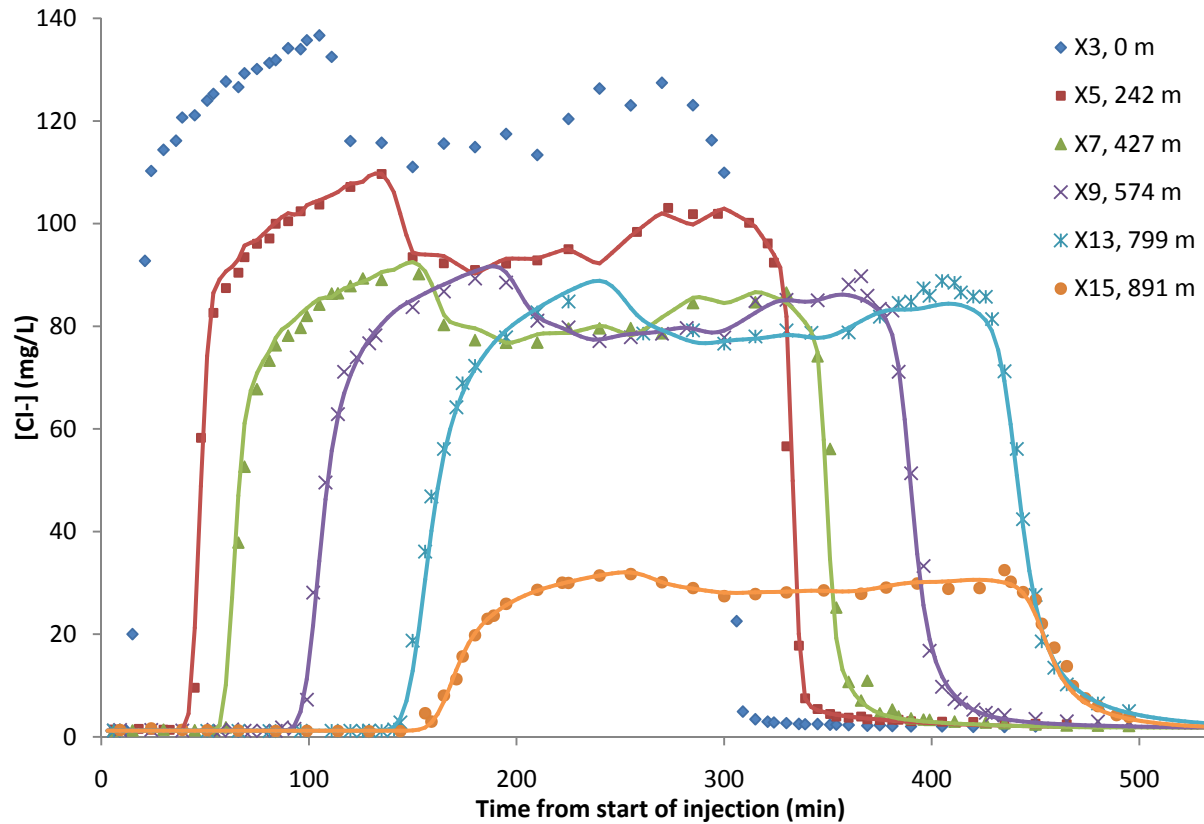
**Figure 4.4.2.** Plateau tracer concentrations measured at sites X2-X15 (no site X11) along the tributary show large dilution effects above site X5 and again below site X14.

Using the principle of conservation of mass, precise estimates of discharge were made using the downstream  $\text{Cl}^-$  concentrations. Calculated discharge for all sites is shown in Figure 4.4.3. Flows increase steadily from the injection point to site X5 and then remain constant until after site X14, located at the top of the meadow and location of bog-iron ore. The most significant increase in discharge occurs in these last 60 meters of the tributary as it flows through the meadow before flowing into the Upper Snake River. These increases in discharge appear to be the result of groundwater inflow through the hyporheic zone, with the exception of a seep that were observed in the upper reaches of the tributary (above site X4).



**Figure 4.4.3** Calculated discharge at sites X2-X15 (there is no site X11) along the tributary show large increases in discharge above site X5 and again below site X14.

Breakthrough curves were created for  $\text{Cl}^-$  concentrations at each of six stream sites where regular tracer samples were collected (Figure 4.4.4).



**Figure 4.4.4** Breakthrough curves of tracer data for six measured sites. Measured  $\text{Cl}^-$  concentrations are represented by individual symbols and the modeled curves are shown as solid lines.

The breakthrough curves show the travel time of the tracer to each reach. These data are used to calculate the average velocity over each stream reach (Table 4.4.1).

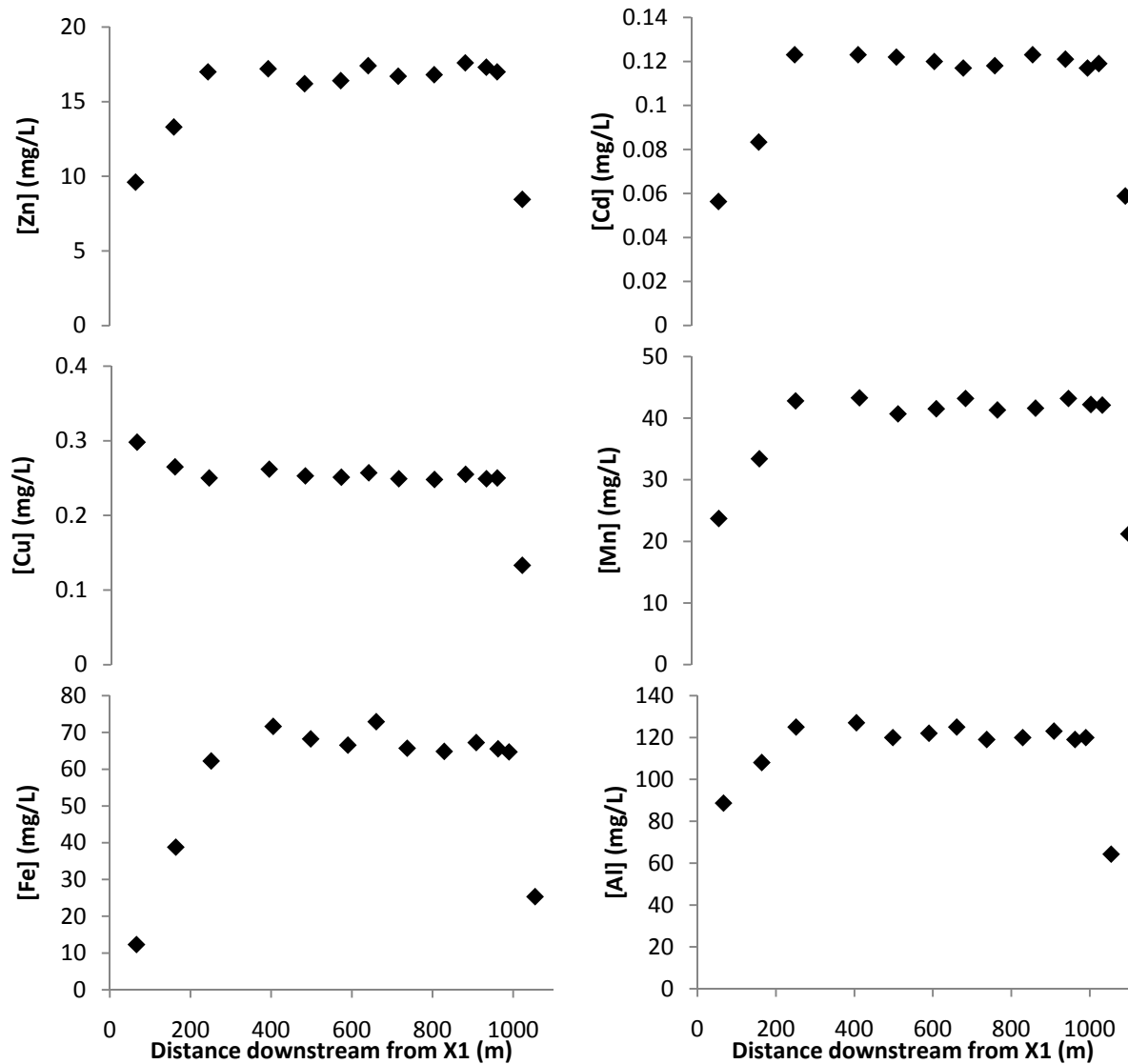
**Table 4.4.1** Travel times and stream velocities measured from the first rise in  $\text{Cl}^-$  concentrations indicating that the tracer had reached the sampling site (samples taken at 5-minute intervals).

Reach (meters from injection)	Travel time (min)	Stream velocity (m/s)
X5, 405	45	0.15
X7, 590	65	0.15
X9, 737	100	0.12
X13, 963	145	0.11
X15, 1054	155	0.11

The breakthrough curves also show that the reaches above sites X7, X9, and X13 have similar tracer concentrations and therefore similar discharges, suggesting no net inflow over this stretch of the tributary. Similarly, changes in discharge over the first and last reaches are also apparent. As would be expected, the downstream curves have broader tails, a reflection of the cumulative nature of flow out of storage in the hyporheic zone from upstream reaches.

#### ***4.4.4 Metals Concentrations***

Longitudinal changes in metals concentrations were plotted for the six metals of interest at all 13 stream chemistry sampling sites, X2-X15 (Figure 4.4.5). These results show that in-stream metals concentrations increase sharply over the first approximately 400 meters downstream of the injection site and generally level off between sites X5 and X14 before decreasing again through the final reach. Copper is the most obvious outlier from this trend; copper concentrations decrease slightly over the first 400 meters before leveling off along with the rest of the metals. Downstream trends in iron concentrations also differ from most metals. Iron concentrations increase more substantially over the first few reaches than do the other metals. However, iron concentration also decrease somewhat over the middle reaches (sites X5-X14) when concentrations of other metals remain fairly constant.



**Figure 4.4.5** Downstream changes in metals concentrations measured during the tracer plateau.

Inflow concentrations were considered for the reaches that had significant inflow discharge. Limited inflows (and in some cases minor outflows) were measured between sites X5-X14 so these sites were not included in this analysis. Inflow concentrations were much higher between sites X2-X4 than in the final reach between sites X1-X15 (Table 4.4.2).

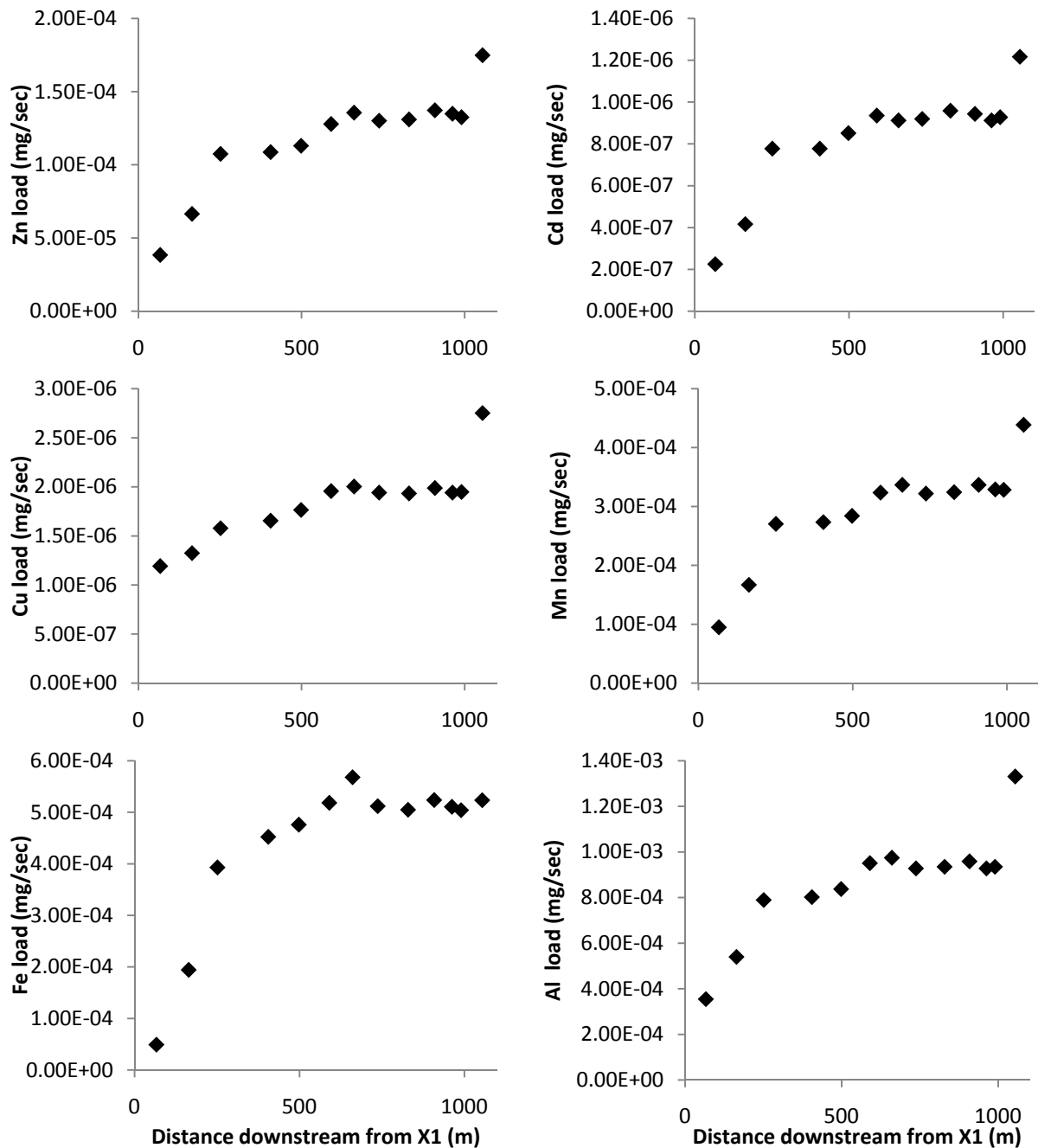
**Table 4.4.2** Inflow concentrations for the highest reaches and lowest reach, for which inflows were significant enough to effect stream chemistry.

Reach	Length of Reach (m)	Average Inflow Concentration (mg L <sup>-1</sup> m <sup>-1</sup> )					
		Zn	Cd	Cu	Mn	Fe	Al
X2-X3	98	28	0.19	0.13	72	150	190
X3-X4	87	31	0.27	0.19	79	150	190
X14-X15	64	3.3	0.022	0.062	8.6	1.5	31

Inflow concentrations above X4 readily increased both the concentration and load of metals in the tributary. Although inflow concentrations in the lowest reach were lower than the tributary concentrations, they were large enough to substantially increase the overall metals load from upstream sites (Figure 4.4.6, Table 4.4.3).

#### **4.4.5 Metals Mass Loads**

Longitudinal profiles were created to illustrate downstream changes in metal loads for the six metals of interest at all 13 stream chemistry sampling sites, X2-X15 (Figure 4.4.6). These results show that in-stream metals loads increase sharply over the first approximately 400 meters downstream of the injection site and generally level off between sites X5 and X14 before sharply increasing through the final reach (X14-X15). Copper exhibits a trend that differs from the other metals; copper loads increase steadily over the entire first 600 meters, until X7. Also an outlier from the norm, iron load increases sharply over the first 300 meters then increases at a lower rate until its maximum load at X7, after which load drops slightly and remains constant all the way to the inflow to the Upper Snake River. Although concentrations of all metals (with the exception of iron) decrease through the meadow between sites X14 and X15, loads of all these metals (again, with the exception of iron), increase substantially over this final reach.



**Figure 4.4.6** Downstream changes in metals loads estimated from samples taken during the tracer plateau.

In the October 2009 study, more than 50% of the zinc load present below the inflow came from the tributary of interest (and lateral inflows within approximately 50 m of the tributary). In September 2010, the proportion of the metal metal load contributed by this tributary was much

smaller, at approximately 20%. However, in both studies, the zinc concentration were approximately the same, suggesting that the difference is likely to be the change in flow of the Upper Snake River between September and October.

To further quantify the downstream changes in metals loads, percent total loading per reach was calculated for each reach (Table 4.4.2). Bold values are the large values for each dissolved metal load, representing at least 50% of the inflow of the total load for each metal.

**Table 4.4.3** Percent total loading per reach for six metals of interest. Bold values indicate the source of 2-3 reaches which supply for than half of the loading to the tributary.

Site	Reach end (m)	Percent Total Load					
		Zn	Cd	Cu	Mn	Fe	Al
X2	66	<b>22.0</b>	<b>18.5</b>	<b>43.3</b>	<b>21.6</b>	9.4	<b>26.7</b>
X3	164	16.1	15.7	4.8	<b>16.5</b>	<b>27.7</b>	13.9
X4	251	<b>23.4</b>	<b>29.6</b>	9.2	<b>23.6</b>	<b>38.0</b>	18.8
X5	405	0.7	0.0	2.8	0.7	11.3	0.9
X6	498	2.5	6.1	4.0	2.4	4.5	2.6
X7	590	8.4	6.9	6.9	9.0	8.1	8.5
X8	661	4.5	-1.9	1.7	3.0	9.5	1.8
X9	737	-3.1	0.6	-2.3	-3.4	-10.7	-3.5
X10	829	0.4	3.2	-0.3	0.5	-1.3	0.6
X12	909	3.6	-1.3	2.0	2.8	3.6	1.8
X13	963	-1.3	-2.6	-1.7	-1.8	-2.5	-2.3
X14	990	-1.3	1.3	0.3	-0.2	-1.2	0.6
X15	1054	<b>24.2</b>	<b>23.8</b>	<b>29.2</b>	<b>25.2</b>	3.7	<b>29.7</b>

The majority of the loading comes from high, steep, rocky reaches above tree line as well as from the meadow at the lowest reach of the tributary. Apart from iron, for which load inputs from the meadow are negligible (3.7% of the total), the greatest metal loads generally come from the meadow, which is a relatively short reach of just 65 meters. Therefore the greatest metal inflow loads are through this lowest reach. High metal inflow loads also occur at the highest reaches of the stream. This is especially true for copper, for which 57% of the total load is



present in the stream before site X5. Dissolved iron loads increase most substantially between reaches X2 and X4; low dissolved iron loads are present before X3. After X7, more significant decreases in iron load (a total of 15% loss) occur through the midreaches of the stream than for any other metal. For all metals, any inflow load contributions between sites X4 and X14 are very diffuse as in-stream processes seem to dominate in this region where loading values generally vary between -0.5% and 0.5% per reach.

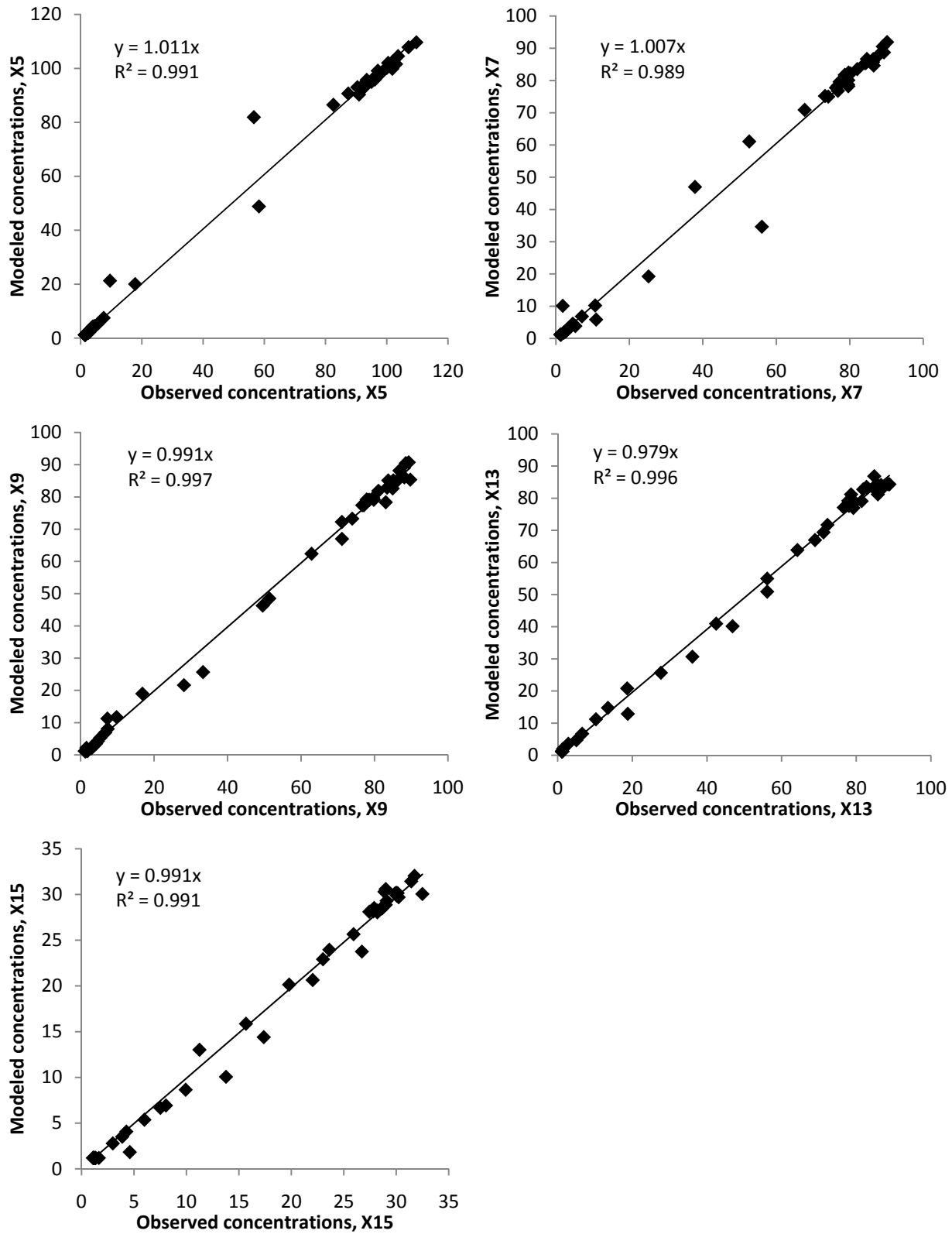
#### 4.4.6. Hyporheic Exchange

Final estimated model parameters for each reach are presented in Table 4.4.4. These values were manually adjusted in OTIS until the best visual fit to the tail of the falling limb was found.

**Table 4.4.4** Estimated parameters for each reach. Dispersion was set based on values for other steep, first-order mountain streams.

Reach	Lateral Inflow ( $\text{m}^3 \text{ sec}^{-1} \text{ meter}^{-1}$ )	Dispersion, $D$	channel area, $A$ ( $\text{m}^3$ )	hyporheic area, $A_s$ ( $\text{m}^2$ )	Exchange coefficient, $\alpha$
X5, 405	4.90E-06	0.02	0.041	0.0019	1.70E-05
X7, 590	6.20E-06	0.05	0.029	0.0045	5.00E-04
X9, 737	0.00E+00	0.05	0.120	0.0055	8.00E-05
X13, 963	5.00E-07	0.05	0.101	0.0065	4.00E-05
X15, 1054	1.50E-04	0.02	0.110	0.0200	2.00E-04

When OTIS-P yielded dispersion values that differed by two orders of magnitude, OTIS was used instead so that parameters could be manually estimated by trial and error, allowing a good fit with the tail rather than trying to fit all inconsistencies in the pump which, with 15 minute sampling intervals for the measured data, were unable to be accurately interpolated between by the model. R-squared values for the fit of the modeled to measured values are presented in Figure 4.4.7. These graphs show better than 99% fit for all relationships.



**Figure 4.4.7** Parameter estimates were manually adjusted to produce an acceptable match between modeled and measured tracer concentrations for all 5 reaches. A fit of measured concentrations vs those modeled in OTIS show a very good fit ( $R^2 = 0.99$ ).

The effect that parameters assigned to surrounding reaches have on a given reach is known as inter-reach sensitivity (Goosef et al. 2005). This effect was problematic in the transition from X13 – X15 as a result of greatly different parameter values in the lowest reach (through the meadow) compared to values above. As a result, the print value for X13 was moved upstream 1 meter to allow the model to achieve a good fit. All output locations are therefore 1 meter upstream of their measured locations.

After the first large inputs of solutes between the injection site and X4, the large input values at X7 and X15 are correlated with a one order of magnitude increase in the exchange coefficient,  $\alpha$ . The largest influx of metal loads along the stream reach – at the lowest reach through the meadow – is also correlated with a one-order of magnitude increase in the size of the storage area, assumed to be almost entirely representative of hyporheic storage since no significant potential in-stream storage areas (ie. pool-riffle structures) were observed along the length of the stream.

It appears that most of the variation from the 1:1 line is in the middle section, which represents the plateau. This result is good for two reasons: First, it supports the explanation that a good fit was difficult to find using OTIS-P because of the large variation in the plateau due to the unsteady pump rate. Second, the purpose of this modeling analysis was primarily to determine the degree of hyporheic zone storage and exchange between the channel and this transient storage zone. Therefore it is most important that the model simulate the measured values during the tail portion of the breakthrough curve.

In order to better understand the influence that storage in the hyporheic zone has on solute concentrations in this stream system, the ratio of storage zone to main channel cross-section area ( $A_s/A$ ) was used (Harvey et al. 2003). A ratio of  $A_s/A > 1$  means that the storage

zone area is greater than the main channel for that reach. All five reaches have  $A_s/A$  ratios that are between 0.5-0.18, indicating this tributary to the Upper Snake River has a relatively small hyporheic zone (Table 4.4.4). While this ratio does not include the rate of exchange (and therefore travel time) through the storage zone, we can look qualitatively at the values of  $\alpha$  to better understand the system. The value of alpha for reach five (X13-X15) is the highest by an order of magnitude, indicating that it is this final reach through the meadow that has the largest hyporheic zone, and likely also the greatest exchange rate.

Alpha is a useful quantitative tool for understanding relative storage and exchange, but it does not represent a physical property of the stream.  $A_s/A$  better represents the stream by providing information about the relative physical sizes of the hyporheic zones of different stream reaches, but does not provide information that is directly relevant for understanding reactions and stream chemistry, for which we are interested in the temporal rather than spatial characteristics of the hyporheic zone. Runkel (2002) developed a metric to better understand the temporal transport within the transient storage area.  $F_{med}$  quantifies the portion of the median travel time resulting from storage in the hyporheic zone, shown in Equation 4.3.4 (Runkel, 2002, Wong 2006).

$$F_{med} \cong (1 - e^{-L(\alpha/u)}) \frac{A_s}{A+A_s} \quad 4.3.4$$

where  $L$  represents the average reach length, set to 200 m (Runkel 2002) and  $u$  represents the advective velocity ( $Q/A$ ). Table 4.4.5 shows the values of  $A_s/A$  and  $F_{med}$  calculated from estimated parameters.

**Table 4.4.5.** Values of  $A_s/A$  and  $F_{med}$  calculated from estimated parameters.

Reach	Discharge, $Q$ (m <sup>3</sup> /sec)	Advective velocity, $u$ (m/s)	$A_s/A$	$F_{med}$
X5, 405	6.3E-3	0.15	0.04634	0.043323
X7, 590	7.8E-3	0.27	0.15517	0.092626
X9, 737	7.8E-3	0.07	0.04583	0.034264
X13, 963	7.8E-3	0.08	0.06436	0.054516
X15, 1054	2.1E-2	0.18	0.18182	0.124486

The values of  $F_{med}$  show that the travel time through the hyporheic zone is fairly constant between 3-9% through most of the tributary but changes substantially through the meadow. The lower value of  $F_{med}$  through the meadow indicates that transient storage accounts for 12% of the travel time in this reach, indicating an increase in the relative time that a water molecule has to interact and react with constituents in the hyporheic zone. The median time that a water molecule spends in reach X7 was also about two-fold higher than along the rest of the tributary. Along this same reach, metals concentrations increased more than they did through other reaches.

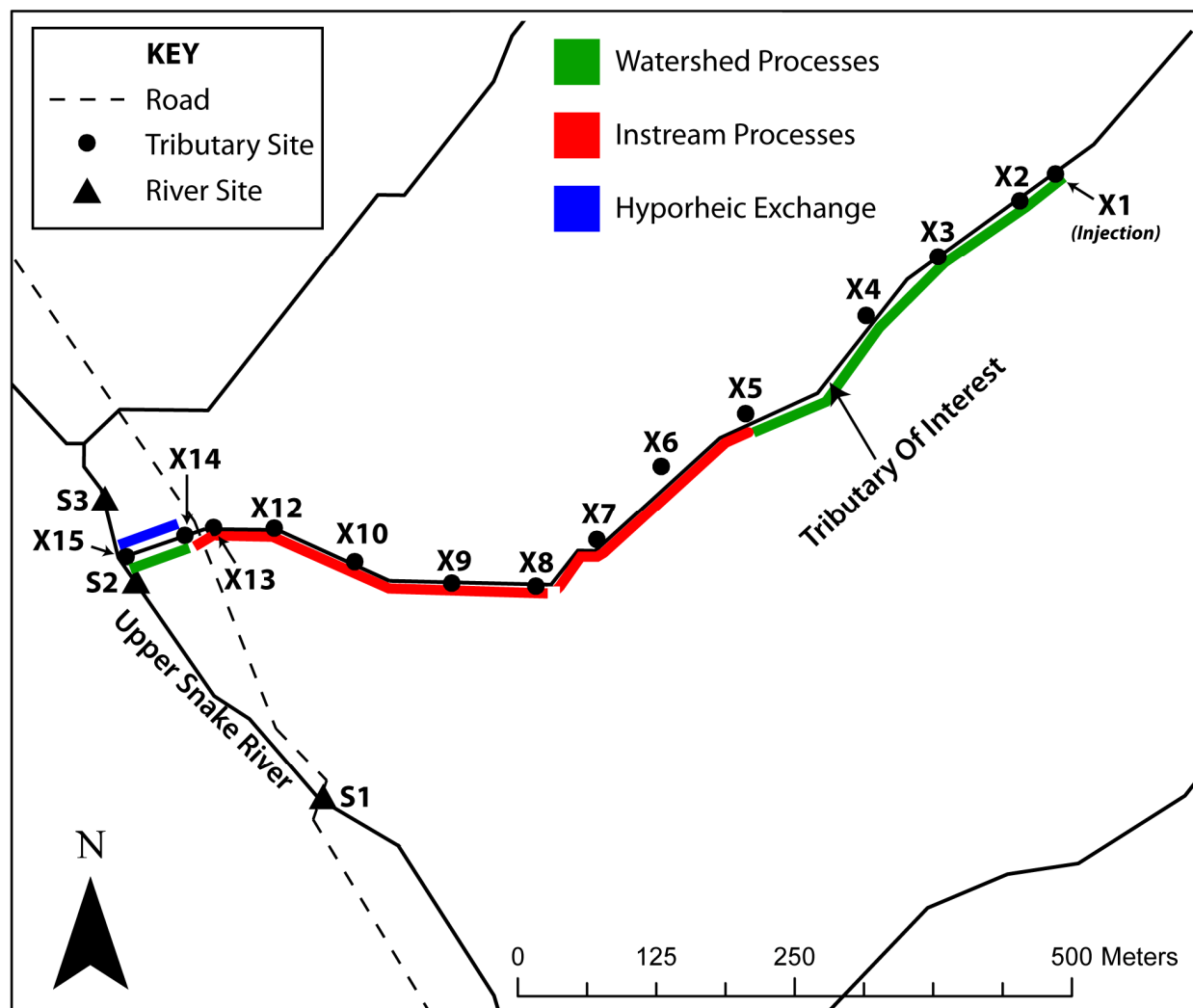
#### 4.5 DISCUSSION

The source of the tributary spring was lower in September than it had been in July. This may indicate that groundwater flow feeding the tributary in early summer was largely a product of snowmelt. This evidence supports the hypothesis that as snow melted, much of it recharged the shallow groundwater table and/or followed a relatively short path through the unsaturated zone to the tributary. If this is the case, it makes sense that the groundwater table (and therefore the spring supplying the tributary) was lower in September than in July, exposing more material to oxygen. Moreover, a small channel inflow to the tributary at site X2 was observed to be flowing in July and was dry in September. These observations that groundwater flow is sensitive

to snowmelt provide some evidence supporting the hypothesis that climate-driven changes in the snowmelt timing and quantity could affect stream chemistry by exposing more subsurface material to weathering. As snowmelt occurs earlier, groundwater may be lowered further by September, exposing new material to oxygen for the first time and resulting in greater ARD. Further analysis could be performed to determine if the residence times of the groundwater are longer at the end of the summer compared to earlier in the year during snowmelt runoff. By this method, the relative contribution of snowmelt and groundwater flow to the stream can be determined.

It is also significant that the groundwater outflow is just above the most upstream location of any visible metal hydroxide precipitates on the streambed. Below this, a dark red precipitate was observed that is present (and becomes a lighter orange color) in the downstream direction. This could indicate that seasonal flow above this site is ephemeral, that the pH is well below 3.5 such that all metals remain in solution, or that low metals concentrations are present when the water flows out of the spring. Further understanding of these observations may elucidate the roles of in-stream and watershed processes. The pH of the water flowing out of the spring immediately above the tracer injection site was observed to have values greater than 3.5, suggesting that iron should precipitate out of solution at this location. However, metals may not immediately begin to precipitate out, but instead may take ten or more meters of in-stream flow to have enough time to form oxides in the newly exposed conditions. Water quality analysis suggests that metals concentrations do not change in the first approximately 100 meters downstream of the spring. Data for Zn, Cd, Cu, Mn, and Al show that approximately 20-30% of the total metals load along the tributary is in the water when it emerges from the spring. This inflow of metal-rich groundwater continues downstream for 300 meters from the injection site,

suggesting that watershed processes dominate the stream chemistry and solute loads along the first 300 meters of the tributary above site X4 (Figure 4.5.1). A slight increase in metals also occurs at site X7.



**Figure 4.5.1.** Results of the tracer study and observations made along the study sites suggest that watershed processes dominate stream chemistry at the highest reaches of the tributary where lateral inflows are high, that instream processes dominate along the midreaches where there is little or no inflow and outflow, and that watershed processes and hyporheic exchange both play important roles in the stream chemistry of the tributary as it flows through the meadow along the final reach through the meadow and bog iron ore.

Because there is essentially no inflow in the tributary between 300 m and nearly 1000 m downstream, the primary observed change in water quality over the next section of the tributary (until site X14) is the increase in dissolved iron concentration that takes place before site X7 at

approximately 650 meters downstream. In-stream iron chemistry is complex because it is also affected by photochemistry, which has been shown to generate significant diel fluctuations in in-stream concentrations. Although samples were taken simultaneously along the entire tributary, this increase in iron concentrations may be the result of photochemistry fluctuations due to the effects of solar shading. The tributary does not enter full forest canopy until near site X7, where iron concentrations cease to increase. Such photoreduction of iron hydroxides on the streambed is well documented (McKnight et al. 1988 and 2001, McKnight and Bencala 1989, Runkel et al. 1996).

Although watershed processes were most likely the main control along the first 300 meters of the tributary, water chemistry is chiefly controlled by in-stream processes through the middle 600 meters, in which stream chemistry seems to be dominated by iron photochemistry. When watershed processes dominate the solute concentrations, there is a substantial increase in discharge due to groundwater inflow. In the case of this tributary, those inflows also introduce high metals loads, increasing the total mass loading in the tributary. Along the final reach, watershed processes and hyporheic mixing together control the solute concentrations in the tributary. Transient storage accounted for the largest percent of the median travel time in this lowest reach, supporting the conclusion that much of these increase in solute load through the meadow results from an increase in the relative time that a water molecule has to interact and react with constituents in the hyporheic zone. The median time that a water molecule spends in reach X7 was also slightly higher than along the rest of the tributary, a reach along which metal loads increase more quickly than along most of the mid-reaches of the tributary.

Previous studies have noted significant spatial and temporal changes in metals contamination in the Upper Snake River watershed (Belanger 2002). In her July study, Belanger



(2002) found that both tributaries and lateral inflows are significant sources of solutes to the Upper Snake River. However, due to varying exposure to rock, soils, and other solutes, lateral flows provided more of the metals loading to the Upper Snake River. Belanger (2002) found inflow concentrations for Zn, Al, Mn, and Cu, to be  $0.003 \text{ mg L}^{-1}$ ,  $0.045 \text{ mg L}^{-1}$ ,  $0.007 \text{ mg L}^{-1}$ , and  $0.109 \text{ mg L}^{-1}$ , respectively. These values are all several orders of magnitude smaller than the inflows measured to the tributary during the current low flow study. The lateral inflow to the reach the Upper Snake River through the part of the meadow that includes the tributary was calculated to be  $6.3\text{E-}4 \text{ m}^3 \text{ s}^{-1}$ , comparable to the inflow rate of  $1.5\text{E-}4 \text{ m}^3 \text{ s}^{-1}$  measured in the current study.

Belanger's (2002) finding that lateral inflows had a large contribution to the total solute load is consistent with the findings of the current study. High lateral flows into the tributary in the 60-m before flow into the Upper Snake River are likely to correspond to high lateral inflow rates into the main stem of the stream through the same meadow. Although groundwater inflows are high and have a large effect on the solute concentration of the stream, the tributary of interest is also a significant contributor of metal loads. The tributary of interest was found to contribute approximately half of the zinc load to the Upper Snake River in October 2009 and nearly 20% in September 2010. This difference suggests that flow in the Upper Snake River may have been less in October 2009 than in September 2010. These very large increases in load resulting from such a small tributary indicate that much can be learned about the source of the increasing metals from the closer study of this tributary presented in this analysis.

In the final stream reach, the source of ARD was very high inflow rates that brought a dramatic increase in metals loads. These loads may be the result of two processes. The first processes potentially working on the final stream reach is the inflow of groundwater due to the

sudden and dramatic change in topography from a steep slope to a low slope at the bottom of the valley. Much of this groundwater is likely to have followed a very long flow path and may have much longer residence times than the water inflow in the first 300-m reach of the tributary (Liu 2002). The second process is a more complex relationship between hyporheic exchange and the bog-iron ore present in the meadow through the bottom of the valley along the Upper Snake River. Hyporheic exchange was higher through the final stream reach than anywhere else along the tributary. With accelerated chemical weathering upstream, the pH of the tributary water through the bog-iron may be lower than it was 30 years ago. If this is the case, the bog which was once a sink for many metals may now be a greater source. This hypothesis is supported by the OTIS modeling results, which indicate that the exchange of water through the hyporheic zone along the final reach of the tributary is substantially higher than any other reach of the tributary. This means that water molecules spend more time in the hyporheic zone of this reach compared with the other reaches, increasing their opportunity to interact with the reactive environments such as subsurface sediments and colloids of the bog-iron.

The pH-dependence of trace metal sorption was investigated by Runkel et al. (1999). This study describes changes in copper concentrations during a pH-modification experiment in an ARD stream. The pH was experimentally elevated, causing dissolved copper concentrations to sorb to iron oxides on the stream bed as well as suspended iron colloids. The result was a decrease in copper solute concentrations during that time which recovered to their original concentrations with a return to ambient pH. This same process of trace metal desorption from iron oxides, as well as trace metal complexation with organic matter in the bog and meadow, may be driving the increases in metals concentrations in the Snake River Watershed over the longer term. This explanation is consistent with the increasing concentrations of zinc and other

solutes in the Upper Snake River (Chapter 3), and the exponential increase in metals concentrations that has occurred over the last decade, replacing a strong, linear trend observed to have occurred since the 1980s.

August et al. (2002) investigated a natural wetland receiving AMD with high metals concentrations and extensive iron oxide deposits. They found seasonal variability of metals transport such that the wetland acted as a net sink in the summer and then a net source of metals in the winter. Zinc loading to the stream through the wetland decreased by an average of 65% from June to October. Because precipitation of zinc oxides could not have occurred at the low pH present in the wetland, they hypothesized that the loss was due to precipitation of zinc sulfide and sorption to iron oxides and/or complexation with organic matter. Release of zinc and other metals in the winter may have been the result of seasonal change in flowpaths through the wetland or decreases in microbial activity. The current study differs from August (2002) because that wetland site was below a mine and therefore had less than 100 years of metal precipitates accumulated in it. The Upper Snake River bog-iron ore has likely experienced iron hydroxide deposition (and associated trace metal sorption) for thousands of years. As a result it has perhaps reached a quasi-equilibrium of metals accumulation, at least during some seasons (August 2002). Results of the current study suggest that perhaps this quasi-equilibrium has been shifted by upstream increases in weathering and a subsequent decrease in pH. The meadow and bog-iron ore are no longer acting as a sink for trace metals but rather have become a source, at least during seasonal low flow.

#### **4.6 CONCLUSIONS**

At low flow in the Upper Snake River watershed (September and October) up to 50% of low-flow metals loads come from a tributary on the northeastern slope of the catchment. Along

the length of this tributary, discharge increases downstream and inflows bring increased metals loads. Inflow concentrations were highest at the uppermost reaches, but lower concentrations through the meadow immediately above the confluence with the Upper Snake River were compensated for by very high relative discharges. Therefore metals loads increased most substantially through the last 60 meters of the tributary as it flows through the meadow and bog iron ore before flowing into the Upper Snake River.

Results of this tracer study indicate that the drivers of stream chemistry vary along the reach. High discharges and inflow concentrations along the uppermost reaches are indicative of these groundwater inflows – and therefore watershed processes – dominating stream chemistry. For some solutes, the majority of the load is already present in the tributary in the upper reaches, suggesting that this has historically been the source of much of the ARD. Neither discharge nor solute load for most constituents varied substantially through the middle reaches of the tributary, indicating that changes in stream chemistry were driven predominately by in-stream processes.

Although solute concentrations decrease through the meadow, solute loads increase substantially over this final reach in which watershed processes and hyporheic mixing together control the solute concentrations in the tributary. Inflow of groundwater with the change in topography at the valley floor is likely to contribute more reacted groundwater. Through the hyporheic zone in the meadow, a water molecule has more time to react with subsurface sediments and colloids of the bog-iron. Together, these two processes help to explain not only the source of the increases in solute concentrations observed over the past 30 years, but also lend a potential explanation to the exponential increase in zinc concentrations in the past decade replacing the more linear trend observed since 1980 (Chapter 3). With accelerated chemical weathering upstream, the pH of the tributary water through the bog-iron may be lower than it

was 30 years ago. If indeed a threshold pH has been reached, the meadow and bog-iron ore are no longer acting as a sink for trace metals but rather have become a source, at least during seasonal low flow.

This explanation for the changing water chemistry of the tributary is sufficient to explain the increases in solute concentrations observed in the Upper Snake River. Observations made over the course of the current study suggest that in the Upper Snake watershed the groundwater table is substantially lower in the fall than during and immediately following the completion of snowmelt. This may suggest that by September and October the groundwater flow into the stream is no longer primarily constituted of that year's snowmelt. More intensive study of groundwater levels is necessary to better understand surface water and groundwater interactions in this watershed but results of this study are consistent with the idea that earlier snowmelt results in a lower groundwater table in late summer, exposing sulfite-containing rocks to weathering for the first time. This would result in an increased rate of ARD production in the watershed.

These observations that groundwater flow is sensitive to snowmelt support the hypothesis that climate-driven changes in the snowmelt timing and quantity could affect stream chemistry by exposing more subsurface material to weathering (Chapter 3). Similar processes may be driving water quality changes throughout the watershed and further analysis may be important for further understanding of this interesting, significant, and policy-relevant change in water quality (Chapter 5).

## Chapter 5

### IMPLICATIONS FOR REMEDIATION

#### *Colorado mining history and remediation policies*

Although Colorado mining began in the mid-nineteenth century, the most severe acid mine drainage (AMD) impacts have occurred as a result of mining during and after World War II. At this time, a resurgence of mining activity brought the new technology of lode mining, in which mine shafts were built to carry out the minerals and tailings were dumped on nearby hill slopes and in river valleys. Because AMD reactions are self-propagating and will not end until available pyrite is completely weathered away, streams cannot naturally recover from the adverse conditions associated with AMD on timescales that are relevant to human societies. In Colorado today, as much as 1,600 miles of streams are affected by AMD (Durkin & Hermann 1994, Todd et al. 2003) and therefore the state has been the focus of many abandoned mine remediation efforts.

Both mine adits and tailings piles can be sources of AMD. Modern mitigation technologies have been developed to help remediate abandoned mine areas and mitigate impacts to polluted streams (Gaikwad and Gupta 2008, Kalin et al. 2006, Johnson and Hallberg 2005). AMD can be controlled by removing tailing piles from direct contact with streams or by capping them (with concrete, for example) as a barrier to pyrite oxidation. Additionally, flow paths can be redirected away from exposure to AMD waste piles and mine adits. Chemical treatments such as the addition of limestone can increase the pH of streams, decreasing the solubility of metals. Similarly, detention ponds with reactive barrier walls can be constructed to collect metal precipitates. Natural and artificial wetlands can be used to remove metals from AMD

contaminated water (Sheoran and Sheoran 2006, Mays et al. 2001).

These remediation techniques can carry a very high price tag due to both high initial capital costs and continued maintenance. In the early 1990s, it was estimated that \$32.7 to \$71.5 billion will be necessary to clean up sources of AMD in the United States (Mineral Policy Center 1993). Under current laws, cleanup of AMD sources is guided by the federal Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, aka Superfund) and the Clean Water Act, which mandate that responsible parties fund remediation. Superfund establishes criteria for considering and selecting sites for remediation, and risk assessment procedures determine the methods for quantifying related risks as well as probabilities of harm that exist before and after remediation. However, responsible parties no longer exist in many cases because many of the mines have been out of operation for a century or more. Good Samaritan laws have been established to facilitate the cleanup of watersheds affected by AMD by encouraging the efforts of non-labile parties who are willing to voluntarily clean up some of these sites. However, these laws do not protect Good Samaritans from civil lawsuits and therefore have not been applied in Colorado since a 1993 case was brought against a clean-up effort in California. The financial penalty under the Clean Water Act is up to \$32,500 per day for exceedances of water quality standards. Would-be Good Samaritans therefore have abandoned their clean-up efforts because they cannot risk this long-term financial liability.

Because these legal restrictions apply only to point-sources of AMD such as mine adits, clean-up efforts of tailings piles throughout Colorado remain active. Therefore, although some of the most significant contributors to stream degradation in Colorado cannot be remediated at this time without significant legal and financial risks, there are still many sources of AMD that can, including tailings piles throughout the state.

### ***Research Implications***

A watershed-based approach is often used to identify sources of AMD before remediation is implemented. Streams are chosen for remediation based in part on the hydrologic and chemical processes that drive water quality. These hydrologic processes include hyporheic exchange and in-stream dispersion. Because these stream conditions change with season, weather, daily temperature and light fluctuations, quantifying individual hydrologic processes can be very difficult. As the current research shows, it is also important to consider larger-scale watershed processes. Effective remediation must consider how much contaminant loading comes from various sources in the watershed as well as seasonal and annual trends in stream chemistry.

Colorado water quality standards are based on the designated use of a water body. The four classifications of water bodies are for aquatic life, recreation, drinking water supply, and agriculture. Water quality criteria are developed for each of these classifications for regulation by the federal Clean Water Act and the State of Colorado Water Quality Control Act, determined by the Colorado Department of Public Health and Environment (CDPHE 1999). State water quality standards are assigned for each of the state's 7 major river basins. Water quality standards are applied to individual stream segments for which a single classification has also been assigned. Classifications may represent multiple uses.



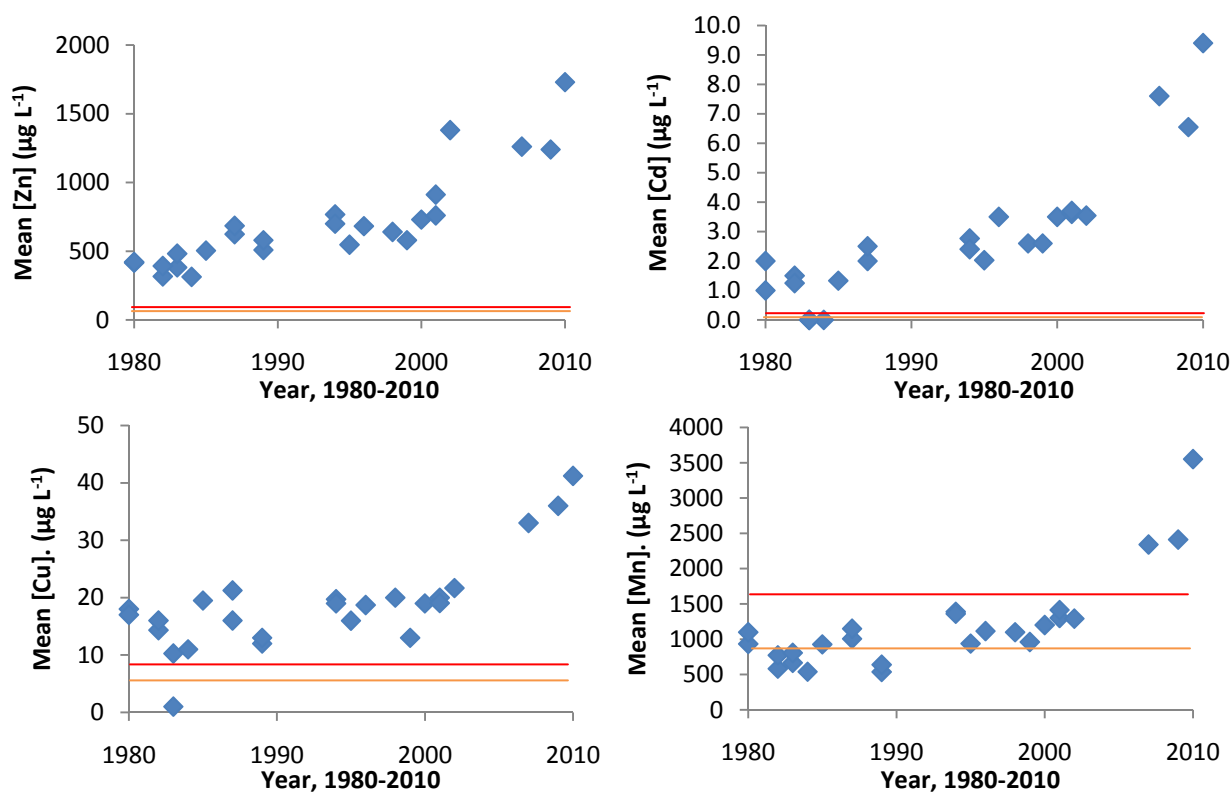
**Table 5.1** State of Colorado Aquatic Life Standards applied to the Snake River (CDPHE 1999). Toxicity levels are based upon a hardness of 41.0  $\text{mg L}^{-1}$ .

Metal	Chronic Toxicity Level ( $\mu\text{g L}^{-1}$ )	Acute Toxicity Level ( $\mu\text{g L}^{-1}$ )
Al	87	750
Cu	5.5	7.67
Fe	1000	Not designated
Pb	1.1	22.7
Mn	900	1566
Zn	49.8	55.0

Dissolved metals concentrations in the Upper Snake River were evaluated in the context of the Aquatic Life Standards applied to the Snake River watershed (CDPHE 1999). Toxicity levels are based upon a hardness of 41.0  $\text{mg L}^{-1}$  (as a proxy for carbonate alkalinity), a reasonable or somewhat high hardness value for the Upper Snake River during low flow conditions. With hardness lower than 41.0  $\text{mg L}^{-1}$ , the water quality standards would be lower due to the increased toxicity of dissolved metals at lower hardness. Measured September and October hardness values in the Upper Snake River have varied between 27 and 73  $\text{mg L}^{-1}$  over the past 30 years; the median of these values is approximately the value used in CDPHE standards. It is also worthy of note that these aquatic life standards do not take into account the additional effects of the metal oxide deposition on the stream bed. In the Upper Snake River and additionally downstream along the main stem of the Snake River, iron and aluminum oxides compound the impacts of toxic levels of many metals, severely hindering periphyton growth and therefore also inhibiting the health of populations at higher trophic levels.

Of the dissolved metals for which the Snake River is listed on the State's EPA 303(d) list, all were well above both the acute and chronic toxicity standards (Figure 5.1), including lead at

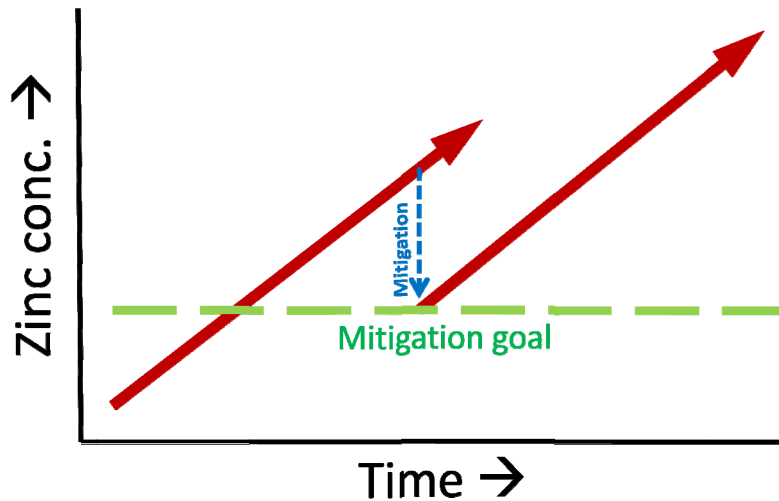
1.5 ug/L. These exceedances suggest that aquatic biota in the Upper Snake River are incapable of surviving in the Upper Snake River likely remain severely stressed well downstream.



**Figure 5.1** Dissolved September and October metals concentrations in the Upper Snake River. State of Colorado Aquatic Life Standards for acute toxicity (red lines) and chronic toxicity (orange lines) are marked on the map.

Iron and aluminum have very active stream chemistry due to diel fluctuations and precipitation/dilution reactions near the pH of the Upper Snake River, where they generally remain dissolved in solution. However, downstream of the confluence with Deer Creek, where the pH is raised, aluminum and iron form precipitates, greatly decreasing dissolved metals concentrations (but, notably, still stressing the stream ecosystem by restricting growth on the streambed). Nevertheless, Al and Fe concentrations in the Upper Snake River were well above State of Colorado Aquatic Life Standards in 2010. Aluminum was measured at 11,700 ug/L and iron at 1970 ug/L (total concentration was 2140 ug/L).

Greater understanding of metal concentrations and trends in natural stream biogeochemistry may be a pre-requisite for establishing mitigation criteria at abandoned mines (Figure 5.2). In the Snake River watershed, for example, the largest tributary to the Snake River (Peru Creek) is contaminated with acidic and metal rich runoff from the Pennsylvania Mine. The Pennsylvania Mine site, which is believed to be the primary source of anthropogenic contamination in the watershed, has both an adit with extensive mine workings and large tailings piles. Several remediation attempts at the mine site have either been inadequate or have been stifled by Good Samaritan liability concerns associated with the Clean Water Act. When these liability concerns are figured out and remediation again progresses at this site, there may be issues associated with increased natural background concentrations. These concentrations may come from both the Upper Snake River and watershed effects throughout other drainages, including those upstream of the mine. A frequently stated goal of Pennsylvania Mine remediation is to improve downstream ecosystems to a level such that fish populations can be self-sustaining. Currently, the town of Keystone restocks fish populations each year to encourage fishermen to fish in the region. If background metals concentrations continue to increase such that they cause downstream reaches of the Snake River to be unable to sustain healthy ecosystems and robust fish populations, this may disincentivize or deprioritize mitigation efforts in the watershed by making clean-up goals harder to meet in the short term and impossible to maintain in the longer term.



**Figure 5.2** If background metals concentrations are increasing due to widespread hydrologic change, then a greater understanding may be a pre-requisite for establishing mitigation criteria at abandoned mine sites in that region.

A tangible implication of this study is support for the contention that there are limits to wetland remediation after some type of sorption threshold is reached, often as the result of reduced pH. In order to remediate mine drainage at a lower cost than traditional methods, wetland treatment systems have been employed to sorb heavy metals, removing them from the water column and concentrating them in sedimentary deposits (Sheoran and Sheoran 2006). August (2001) found that shifts in biotic growth and pH in a natural Rocky Mountain wetland yielded seasonal changes in the role of the wetland as a source or sink for heavy metals in mine drainage. Others have found similar limitations to wetland remediation of AMD (Nyquist and Greger 2009, Kalin 2006).

A more positive implication of the current study is that removal of tailings piles and metal-rich sediments from streams would likely remain an effective mitigation strategy. Presence of these materials in streams greatly increases their exposure to water and oxygen, which initiate the ARD reactions.

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## APPENDICES

### APPENDIX A: Archived sample collection and analysis

Samples used in the investigation of the long-term changes in the Upper Snake River were collected during the late summer and fall months of years between 1980 and 2010, during low-flow conditions. All samples were collected from the Upper Snake River just above its confluence with Deer Creek. Samples included in this analysis were collected between July and December of those years. Some water samples had been previously analyzed for metals and some samples (including some that had not yet been analyzed) had been in storage since their collection and were available for (re)analysis. Samples in storage at INSTAAR were sorted and catalogued during the fall of 2009. Table A.1 presents these samples, their collection dates, any known sample treatment, and if the sample had been previously analyzed. All sample bottles appeared to be in good condition and there was no obvious evidence of leaks on the bottles or the cardboard boxes that they were in.

Samples from 1980 - 1995 were collected under the supervision of Diane McKnight at the USGS. At the end of 1996 these samples were moved to the Institute of Arctic and Alpine Research (INSTAAR) at the University of Colorado, Boulder, as part of an agreement with the USGS. Results of the analysis of samples taken between 1980 and 1990 were published by INSTAAR under the authority of the USGS (Boyer et al. 1999). These 1980 - 1990 samples were not available for reanalysis. Samples from 1996 were collected by Paul Brooks (Table A.1; Heuer et al. 1999) and analyzed for stream chemistry parameters that did not include metals. Samples from 1993-1996 have been stored in the same place at INSTAAR since 1996 and were therefore available for analysis; samples from 1993-1995 were not known to have been

previously analyzed. Samples collected between 1996 and 2005 were collected by University of Colorado graduate students under the supervision of Diane McKnight as part of research studies and efforts to designate portions of the watershed for mitigation. Most recently, sampling specifically for this investigation was conducted in October 2009 and September 2010.

**Table A.1** Upper Snake River samples (site ID: SN2 or SAD) catalogued from INSTAAR, fall 2009. No information about sample treatment was labeled on most of the samples; when available, it is listed parenthetically. All samples were analyzed in Jan 2011 for total metals except for those known to have been filtered, which were run for dissolved metals.

Sample Year	# of samples	Sample description	Previous Analysis?
1993	1	July 14	No
1994	6	Sept. 21, Sept 22 (2), Oct. 18, Nov. 22, Nov. 23	No
1995	18	July 6 (2), July 12 (2), July 17 (2), July 25 (2), Aug. 4 (2), Aug 16 (filtered un-acidified), Aug 22 (2), Sept. 6 (2), Sept. 9 (filtered un-acidified), Sept 21 (2)	No
1996	3	July 3 (2), Sept. 9	Yes
2001	3	Oct. 7 (raw), Nov. 4 (raw), Dec. 8 (raw)	Yes
2002	4	July 9 (raw), July 21 (raw), Aug. 1 (raw), Sept 21 (raw)	Yes
2009	2	Oct. 12 (2, filtered acidified; raw acidified)	Yes
2010	2	Sept 11 (2, filtered acidified; raw acidified)	No

All of the samples in Table A.1 were analyzed in February 2010. While the trend had been previously described for the months of September and October, samples from July, August, November, and December were also reanalyzed to help establish any trend between earlier peak snowmelt and changing metals concentrations (i.e. if higher solute concentrations occurred earlier in years with earlier snowmelt, and if this trend could be seen as early as July).

Available water samples collected from the Upper Snake River between the years of 1993-2010 were analyzed at the USEPA Region 8 laboratory in Golden, Colorado. Samples were analyzed for total or dissolved metals using an ICP (method EPA 200.7) and ICP-MS (method

EPA 200.8). Descriptions of these samples are presented in Appendix A. A total of 39 samples were analyzed for dissolved for total metals (depending on what was known about the field treatment of the samples). Because for some of the samples it was not recorded on the sample bottle whether or not the samples had been filtered in the field at the time of their collection, these samples and the ones labeled “raw” or “total” were run for total metals (see chain of custody, Figures A.1a,b,c). Only those known to have been filtered were run as dissolved metals samples. At the lab, samples were first checked for preservative and if the pH was greater than 2.0 were treated with nitric acid and held for at least 16 hours before being processed in order to ensure that all of the metals were dissolved in solution.

Stream chemistry data from samples collected from 1980-1990 were combined with data from the (re)analysis of samples collected between 1993 and 2010 to better characterize the timing of the trend (see Appendix B).

Region 8 Laboratory  
16194 W. 45th Drive  
Golden, CO 80403  
Fax: 303-312-7800

PROJECT NAME:		LSR #:		ANALYSIS		COMMENTS	
SAMPLER(S):		DATE:		PRESERVATIVE		NUMBER OF CONTAINERS	
Name:		Signature:		Matrix		BOTTLE ID.	
Name:		Signature:		Matrix		BOTTLE ID.	
STATION ID.	STATION DESCRIPTION + NOTES	DATE	TIME				
SNZ		7/14/93					
SNZ		11/23/94					
SNZ		11/23/94					
SNZ		10/18/94					
SNZ		9/22/94					
SNZ		9/22/94					
SNZ		9/21/94					
SNZ		9/21/95					
SNZ		9/21/95					
SNZ		9/16/95					
SNZ		8/22/95					
SNZ		8/22/95					
SNZ		8/14/95					
SNZ		8/14/95					
SNZ		7/25/95					
SNZ		7/25/95					
SNZ		7/12/95					
SNZ		7/12/95					
SNZ		7/6/95					

1. Requisitioned By: Gene M Cul Date/Time: 1/13/11

2. Received By: Gene M Cul Date/Time: 1/13/11

3. Requisitioned By: Gene M Cul Date/Time: 1-13-11 10:30

3. Received By: Gene M Cul Date/Time: 3/30/11

Comments: UNO7 APPROX TO ALL SAMPLES WITH PH > 2 AT LABS 1-13-11 12:00

LAB ID: 1101002-01

BOTTLE ID: 02

BOTTLE ID: 03

BOTTLE ID: 04

BOTTLE ID: 05

BOTTLE ID: 06

BOTTLE ID: 07

BOTTLE ID: 08

BOTTLE ID: 09

BOTTLE ID: 10

BOTTLE ID: 11

BOTTLE ID: 12

BOTTLE ID: 13

BOTTLE ID: 14

BOTTLE ID: 15

BOTTLE ID: 16

BOTTLE ID: 17

BOTTLE ID: 18

BOTTLE ID: 19

PRESERVATIVES: 1. HNO<sub>3</sub>, 2. H<sub>2</sub>PO<sub>4</sub>, 3. H<sub>2</sub>SO<sub>4</sub>, 4. HCl

6. Ice, 7. Dry Ice, 8. NaOH, 9. Other

Matrix: W. Water, S. Soil, Sed. Sediment, Bio. Bio. Tissue, O. Other

Shaded Areas = Lab use only

Cooler Temperature =

Figure A.1a. Chain of custody for 2011 EPA (re)analysis

PROJECT NAME:		LSR #:	
Snake R Historical Samples		1101-002	
SAMPLER(S):		DATE:	
Name:		DATE:	
STATION ID.		TIME	
STATION DESCRIPTION + NOTES		DATE	
SNZ		7/16/95	
SNZ		7/17/95	
SNZ		7/17/95	
SNZ		9/9/96	
SNZ		9/9/96	
SNZ		8/16/96	
SNZ		7/3/96	
SNZ		7/3/96	
SNZ		12/8/01	
SNZ		11/4/01	
SNZ		10/7/01	
SNZ		9/21/02	
SNZ		8/11/02	
SNZ		7/12/02	
SNZ		7/9/02	
SNZ		10/11/05	
SNZ		10/11/05	
SNZ		4/12/10	
SNZ		4/12/10	
1-Relinquished By:		2-Relinquished By:	
Date/Time		Date/Time	
11/3/11		11/3/11	
1-Received By:		2-Received By:	
Date/Time		Date/Time	
PRESERVATIVES		MATRIX	
1-HNO <sub>3</sub>	2-H <sub>2</sub> SO <sub>4</sub>	3-H <sub>2</sub> SO <sub>4</sub>	4-HCl
5-Na <sub>2</sub> SO <sub>4</sub>	6-Ice	7-Dry Ice	8-NaOH
9-Other			
PRELIMINARY ANALYSIS		ANALYSIS	
NUMBER OF CONTAINERS		NUMBER OF CONTAINERS	
BOTTLE ID.		LAB ID.	
		1101002-21	
		22	
		27	
		74	
		25	
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## APPENDIX B: Evaluation of sample reanalysis

Because this analysis examines a 30-year record of water sample data that were analyzed on different instruments in several different laboratories, this appendix addresses the possibility of internal processing biases from previous analysis of archived water samples. In order to attain results that accurately represent water chemistry in the Upper Snake River over the past three decades, available archived samples from this record were all rerun on the same instrument in the EPA Region 8 laboratory in Golden, Colorado.

Results of the EPA analysis of SN2 samples (above the confluence of Deer Creek with the Snake River) revealed some values for metals concentrations that seemed inconsistent with the original analysis and others that were comparable to the initial results. Table B.1 shows results from three representative metals as well as estimated hardness values for the six samples for which there exists data from previous analyses. Water samples from six sampling dates had been previously analyzed and thus data existed from the initial analysis of these samples, which occurred within standard holding times (6 months for metals samples). These samples were from 1996, 2001 (2), 2002 (2), and 2009.

**Table B.1** Results for years for which data exists for the archived samples

	Mg+Ca (mg/L)		Cu (µg/L)		Zn (µg/L)		Mn (µg/L)	
	initial	EPA 2011	initial	EPA 2011	initial	EPA 2011	initial	EPA 2011
8/16/1996	12.3	12.99	-	16.5	-	537	-	887
12/8/2001	63.4	-	22.1	22.2	869.2	1050	1388.6	1560
11/4/2001	62.5	-	19.4	22.1	1006.8	1330	1589.5	1950
9/21/2002	63.8	-	21.7	38.8	782.4	1380	1291.7	2280
8/1/2002	64.6	-	20.1	28.8	872.2	1270	1444.4	1920
2009	24.81	24.36	31.13	36	1151	1240	2348	2340



The results of the 1996 and 2009 sample analyses were similar to the initial analysis. The results from the 2001 and 2002 indicate a discrepancy of greater than 20% from the initial analysis (Table B.2).

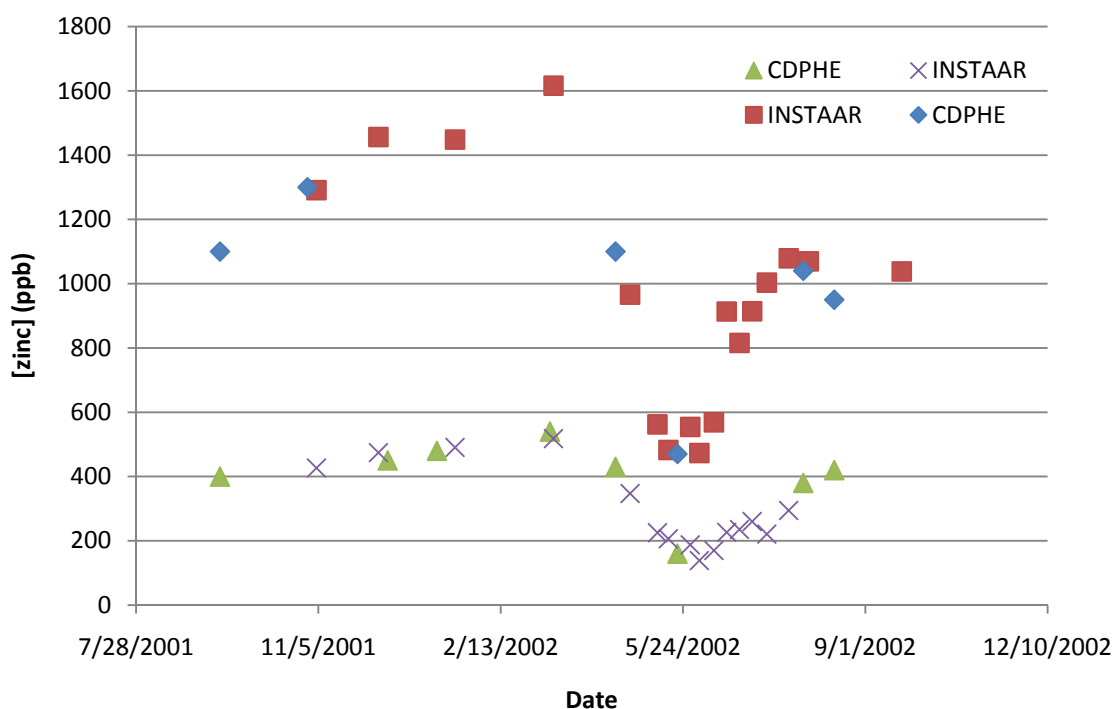
**Table B.2** Results from 1996 and 2009 samples are similar to their initial analysis in those respective years. Samples from 2001 and 2002 differed by greater than 20% from their initial analysis in 2001/2002.

	Percent Difference			
	Mg+Ca	Cu	Zn	Mn
8/16/1996	5	n/a	n/a	n/a
11/4/2001	n/a	14	32	23
12/8/2001	n/a	1	21	12
8/1/2002	n/a	43	46	33
9/21/2002	n/a	79	76	77
2009	-2	16	8	0

### ***2001 and 2002 Samples***

Percent changes from the initial analysis were increases of 21% to 79% for the 2001 and 2002 samples. It is likely that the samples from 2001 and 2002 that were reanalyzed were not the exact same samples initially run. Although they were from the same location and were collected on the same date, they may be different bottles that were treated differently upon sample collection in the field. Data from the 2001 sampling and analysis suggest that filtered samples were run. The only samples re-run in 2011 were marked as “totals” indicating that they were raw (unfiltered) samples. This difference suggests that these changes that were of the large magnitude observed upon the second analysis were due to dissolution of particulate oxides collected in the sample. However, this explanation may not be plausible depending on environmental and stream chemistry conditions.

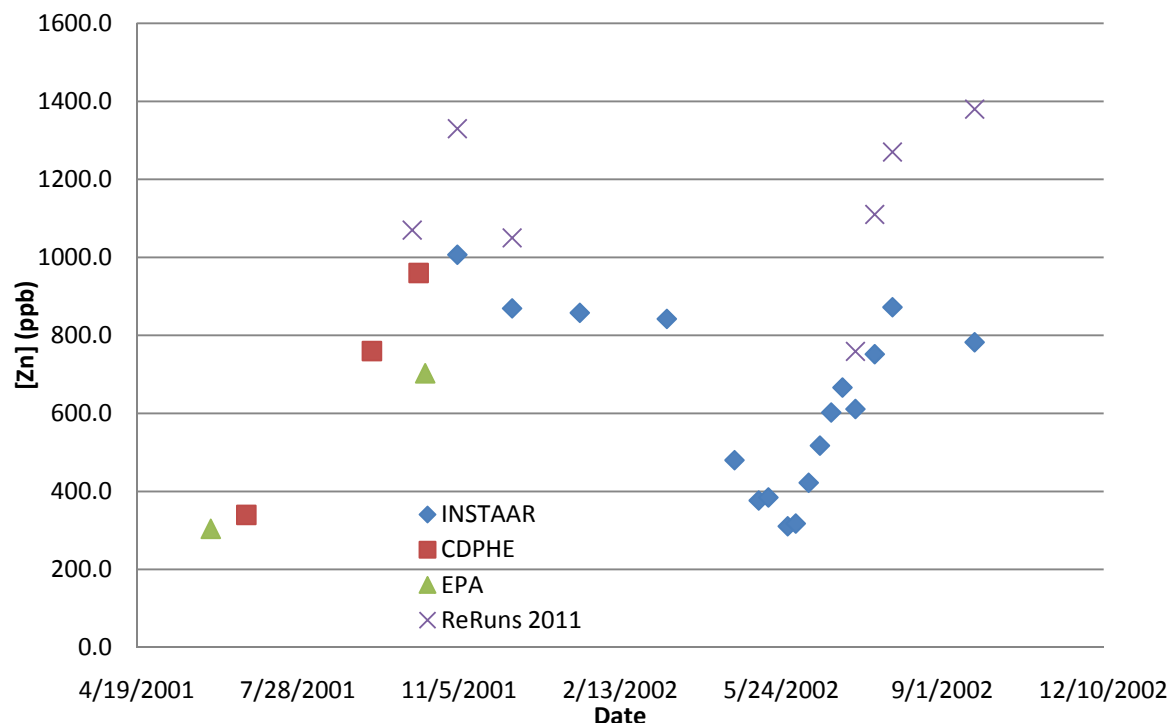
To further investigate the discrepancies between results of the initial and 2011 analyses and determine which better represent the true concentrations of metals in the Upper Snake River, results were compared with those from other sampling sources and laboratories (Figures B.1 and B.2).



**Figure B.1.** Dissolved zinc measured from water samples collected at the town of Montezuma (green triangles and violet x's) on the Snake River and on Peru Creek (red squares and blue diamonds). Results indicate that laboratory results from INSTAAR are very similar (within 10%) of the results from the CDPHE laboratory.

The EPA and the Colorado Department of Public Health and the Environment (CDPHE) collect water samples throughout the Snake River watershed (Figure B.1), including from the Upper Snake River site (Figure B.2). Results from 2001/2002 are not significantly different for data produced by INSTAAR or samples analyzed from similar dates by CDPHE. This suggests that laboratory analysis from 2001/2002 was sound and that no substantial methodological or human errors contributed to the discrepancy in the results. However, because the data from the Upper Snake River were not used in this comparison, uncertainty remains in whether or not those

samples and the laboratory results were processed in the same way. To resolve this, an attempt was made to compare the samples from the Upper Snake River to other available data from different laboratories but the results of this analysis were inconclusive due to the few coincident dates on which samples were taken (Figure B.2). Therefore, since the same person analyzed all of these samples in the same lab, it is most likely that all 2001/2002 analyses are accurate.



**Figure B.2.** Comparison of water sample results taken from the Upper Snake River and analyzed in different laboratories. In only one case does a 2011 EPA ReRun or INSTAAR sample overlap with a CDPHE or EPA sample and therefore no conclusions can be made.

The results of these comparisons do not necessarily rule out the explanation that the specific samples analyzed in 2011 were from unfiltered sample bottles, with different field treatment than those analyzed in 2001/2002.

Finally, these samples were run at INSTAAR's KIOWA laboratory for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to help determine if the discrepancy in the results was due to evaporation (and concentration of solutes) over the past decade or some other source of error (Table B.3).

**Table B.3** Comparison of calcium and magnesium concentrations measured in 2001/2002 and reanalysis in May 2011. Results indicate substantial differences in the two Mg analyses, suggesting that evaporation may also have contributed to the discrepancy between the two analyses.

Sample date	Initial analysis		2011 Reanalysis	
	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)
11/4/01	12.7	7.46	13.7	8.6
12/8/01	12.7	7.39	13.7	8.1
8/1/02	13.5	7.48	14.5	9.6
9/21/02	13.1	7.53	14.9	12.3

The values for Ca<sup>2+</sup> and Mg<sup>2+</sup> would be expected to be unaffected by any field treatments because they are predominantly in solution. Results of the calcium analysis are consistent with the explanation that the samples were not filtered in the field. However, the results of the magnesium analysis are consistent with the explanation that some evaporation occurred over the past 9-10 years. In both cases, this analysis suggests that the data from the initial 2001/2002 analysis are more accurate.

In order to limit the uncertainty from the explanation of these discrepancies, future work could include analysis of other samples taken at this same time for Ca<sup>2+</sup> and Mg<sup>2+</sup>, because the reanalysis by EPA in 2011 did not include these constituents.

#### ***1994, 1995, and 1996 Samples***

Samples from 1996 had not been previously analyzed for metals but there were data from the analysis of anions and other cations. Because the 1996 bottles were thoroughly marked, they were known to have been filtered and therefore were run for dissolved metals. As a result, there are Ca<sup>2+</sup> and Mg<sup>2+</sup> data for the initial analysis and the 2011 EPA analysis. These data are similar for both analyses (a 5% change), suggesting that there was no significant evaporation from the bottle. Therefore the metals data from the 2011 EPA analysis of the 1996 samples provide

valuable new data for the trend analysis. These new data add information about metals concentrations in the Upper Snake River during the mid-1990s, a period for which there was previously no available data.

### ***2009 Samples***

Results of the reanalysis of the 2009 samples differ by -2% to 14% for different analytes. The range of the percent change around zero suggests that there was no significant change in the sample bottle but that rather the source of the change is due to different labs and analysis techniques. The 2011 EPA reanalysis should be used because data produced by the federal laboratory should be of the highest quality due to stringent laboratory protocols including quality assurance and quality control procedures. The integrity of the samples is not believed to have been degraded with time.

### ***Conclusions***

Available information suggests that data used for the analysis of the trend in stream chemistry for this thesis were from the EPA 2011 reanalysis for all reanalyzed samples apart from the 2001/2002 data. Due to the uncertainty in the collection/treatment or degradation of the 2001/2002, and the absence of evidence that the initial analysis is questionable, the data from the initial 2001/2002 analysis are used in the body of this thesis (Chapter 3, Table C.2). Notably, the conceptual conclusions of this thesis do not change, regardless of which data are used to represent water quality in 2001/2002. The consequence of this uncertainty is an inability to get nearer to a resolution of the question of the potential role of the 2002 drought period in triggering the accelerated increase in solute concentrations observed since 2002.

# APPENDIX C: Metals trend data from the Upper Snake River (above Deer Creek), 1980-2010

**Table C.1 SN2 Metals Data from EPA 2011 (re)analysis. All values given as µg/L**

	1993							1994							1995													
Sample Date	7/14	9/21	9/22	9/22	10/18	11/23	11/23	7/6	7/6	7/12	7/12	7/17	7/17	7/25	7/25	7/25	8/4	8/4	8/22	8/22	9/6	9/6	9/21	9/21				
Analysis	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total	Total				
Zinc	321	722	797	782	700	817	874	244	254	233	228	235	238	331	289	289	346	338	404	395	502	669	512	504				
Vanadium	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0				
Titanium	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0				
Thallium	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.3	<0.3	<0.3	<0.3	<0.3	0.4	<0.3	<0.3				
Strontium	46.5	90.1	93.7	92.9	91.5	98.7	107	36.1	37.6	34.2	34.2	34.4	35.7	45.3	40.4	40.4	47.3	45.2	55.1	53.6	62.6	82.8	67.8	67				
Sodium																												
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5				
Selenium	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0				
Potassium																												
Nickel	9.7	23.2	23.7	23.4	24	25.8	26.7	7.5	7.6	6.4	6.4	6.6	6.8	9.2	7.9	7.9	9.9	9.3	12.4	12.3	15.5	20.1	16.2	16.2				
Molybdenum	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0				
Manganese	422	1350	1420	1400	1360	1390	1500	377	391	305	296	309	317	445	391	391	487	477	655	639	821	1090	926	917				
Lead	1.1	1.8	2.2	1.9	1.6	2.3	2	1.1	1.1	1.1	1.2	1.1	1.2	1.1	1	1	1.1	1.1	1.2	1.2	1.6	2	1.1	1.2				
Iron	716	654	905	663	749	725	619	328	524	294	404	295	334	385	511	511	275	698	282	306	614	267	977	440				
Copper	10.5	21.1	19.1	18.9	19	21.3	21.8	8.2	8.5	9.3	8.3	9.2	9.3	11.2	9.2	9.2	10.9	10.9	13.2	13	16.8	21.3	12.8	13				
Cobalt	4.4	13.5	13.4	13.3	13.8	13.3	13.7	4.1	4	3.3	3.3	3.3	3.5	4.5	4.1	4.1	5.2	5.1	6.7	6.9	8.3	10.8	9	9.1				
Chromium	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0				
Calcium																												
Cadmium	1.2	2.6	2.9	2.8	2.4	2.9	3	0.8	0.8	0.8	0.8	0.8	0.8	1.2	1	1	1.2	1.2	1.4	1.4	1.9	2.6	1.8	1.8				
Beryllium	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0				
Barium	25.9	30.9	31	30.2	29.3	27.9	30.6	20.6	21.3	22.2	21.2	23.2	23.4	27.5	23.6	23.6	26.1	25.7	29.1	27.6	29.8	38.8	27.9	26.9				
Arsenic	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0				
Antimony	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0				
Aluminum	1870	5690	5870	5840	6070	6140	6570	1700	1730	1380	1340	1330	1350	1890	1670	2020	1950	2530	2460	3090	4120	3890	3800					

Sample Date	1996					2001			2002				2009		2010	
	7/3	7/3	8/16	9/9	9/9	10/7	11/4	12/8	7/9	7/21	8/1	9/21	10/11	10/11	9/12	9/12
Analysis	Total	Total	Dissolved*	Total	Total	Total	Total	Total	Total	Total	Total	Total	Dissolved*	Total	Dissolved*	Total
Zinc	261	329	537	659	706	1070	1330	1050	759	1110	1270	1380	1240	1260	1560	1730
Vanadium	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Titanium	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Thallium	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Strontium	37.7	41.4	66.7	73.8	76.6	96.9	104	104	90.4	119	131	158	107	107	103	106
Sodium			2590										3740		3820	
Silver	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Selenium	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1
Potassium			<1000										1110		<1000	
Nickel	7.2	7.9	16.7	19.7	19.6	27.4	30.2	28.4	21.7	31.1	35.1	41.6	35.9	35.1	46.8	47.3
Molybdenum	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Manganese	352	381	887	1090	1140	1690	1950	1560	1170	1680	1920	2280	2340	2410	3280	3550
Lead	<1.0	1.6	1.3	1.5	2.9	1.6	2	1.8	1.7	2.8	2.9	2.9	1.2	1.2	1.5	1.6
Iron	432	622	715	581	700	748	767	783	734	810	625	1230	1160	1010	1970	2140
Copper	7.8	10.8	16.5	16.1	21.3	28.1	22.1	22.2	18.3	27.9	28.8	38.8	36	36	39.5	41.2
Cobalt	3.4	3.9	8.8	11	11.3	15.9	17.3	15.1	12.1	17.3	18.7	24.8	18.7	19.5	25.5	28.2
Chromium	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Calcium			8350										14600		14600	
Cadmium	0.9	3.9	2	2.3	4.7	4.7	5.5	4.1	3	4.4	5.3	5.7	6.5	6.6	8.9	9.4
Beryllium	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1	<1.0
Barium	21	167	27.1	26.9	157	30.8	28.5	27.6	28.5	31.6	34.2	41.6	29	29.2	29.8	30.9
Arsenic	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Antimony	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Aluminum	1420	1630	3490	4090	4250	6810	7410	6700	5120	7050	7710	10100	9090	9070	11700	12100

\*Designations of "total" vs "dissolved" refer to the analysis procedure not the phase of the constituent. Only bottles known to have been filtered in the field (Appendix A) were run as dissolved samples.

Table C.2: Metals data used to describe trend at site SN2 (Snake River above Deer Creek) in the Upper Snake River, 1980-2010

Date	Data source	Zn (µg/L)	Cd (µg/L)	Cu (µg/L)	Mn (µg/L)	SO <sub>4</sub> (µg/L)
9/late/1957	Theobald, 1963	350				
10/23/1979	Boyer et al., 1999	441		21	1031	80.647
9/18/1980	Boyer et al., 1999	416	1	18	933	70.651
10/21/1980	Boyer et al., 1999	421	2	17	1098	80.677
9/4/1982	Boyer et al., 1999	296	2	16	694	54.01
9/12/1982	Boyer et al., 1999	299	2	12	595	62.65
9/19/1982	Boyer et al., 1999	303	1	439	439	54.96
9/26/1982	Boyer et al., 1999	366	1	605	605	62.78
10/3/1982	Boyer et al., 1999	422	1	15	701	70.57
10/10/1982	Boyer et al., 1999	378	2	16	685	69.93
10/18/1982	Boyer et al., 1999	394	1	16	855	71.39
10/25/1982	Boyer et al., 1999	375	1	16	854	72.36
9/7/1983	Boyer et al., 1999	338	0	0	571	52.1
9/15/1983	Boyer et al., 1999	414	0	3	663	57.8
9/22/1983	Boyer et al., 1999	378	0	0	680	59.8
9/29/1983	Boyer et al., 1999	399	0	1	749	62.8
10/5/1983	Boyer et al., 1999	403	0	3	810	68.7
10/12/1983	Boyer et al., 1999	455	0	15	754	64
10/19/1983	Boyer et al., 1999	399	0	10	756	69.1
10/26/1983	Boyer et al., 1999	668	0	13	905	74.6
9/7/1984	Boyer et al., 1999	307	0	11	523	46.8
9/10/1984	Boyer et al., 1999	319	0	11	557	48.7
9/3/1985	Boyer et al., 1999	527	1	13	962	
9/14/1985	Boyer et al., 1999	481	2	26	893	
9/1/1987	Boyer et al., 1999	576	1	4	905	84.856
9/8/1987	Boyer et al., 1999			29		88.268
9/16/1987	Boyer et al., 1999			27		87.834
9/23/1987	Boyer et al., 1999					98.349
9/30/1987	Boyer et al., 1999	671	2	25	1105	95.6
10/10/1987	Boyer et al., 1999	706	1	12	1128	
10/20/1987	Boyer et al., 1999	662	4	20	1168	

Date	Data source	Zn (µg/L)	Cd (µg/L)	Cu (µg/L)	Mn (µg/L)	SO <sub>4</sub> (µg/L)
9/10/1989	Boyer et al., 1999	482		12	491	
9/19/1989	Boyer et al., 1999					88.547
9/26/1989	Boyer et al., 1999	535		12	581	
10/15/1989	Boyer et al., 1999	604		12	644	
10/16/1989	Boyer et al., 1999	556		14	634	99.485
9/21/1994	Current Study	722	2.6	21.1	1350	
9/22/1994	Current Study	782	2.8	18.9	1400	
9/22/1994	Current Study	797	2.9	19.1	1420	
10/18/1994	Current Study	700	2.4	19	1360	
9/6/1995	Current Study	502	1.9	16.8	821	
9/6/1995	Current Study	669	2.6	21.3	1090	
9/21/1995	Current Study	504	1.8	12.8	917	
9/21/1995	Current Study	512	1.8	13	926	
9/9/1996	Current Study	659	2.3	16.1	1090	
9/9/1996	Current Study	706	4.7	21.3	1140	
9/24/1998	CDPHE	640	2.6	20	1100	82
10/12/1999	CDPHE	580	2.6	13	960	73
9/28/2000	CDPHE	730	3.5	19	1200	100
9/12/2001	Todd, 2005	760	3.6	20	1300	97
10/7/2001	Todd, 2005	1070				
10/11/2001	Todd, 2005	960	4.2	21	1600	120
10/15/2001	Todd, 2005	703	3.2	17.1	1230	
9/21/2002	Todd, 2005	782.39	3.54	21.67	1291.75	
9/26/2007	US EPA	1260	7.6	33	2340	137
9/23/2008	US EPA					152
10/11/2009	Current Study	1240	6.6	36	2410	
9/12/2010	Current Study	1730	9.4	41.2	3550	

## APPENDIX D: Tracer study data, tributary of interest to Upper Snake River, Sept. 11, 2010

**Table D.1a:** Field Site Descriptions

Tributary sites				
Site	Latitude	Longitude	Elevation (m)	Distance from injection (m)
X1	39.56030	-105.83652	3608	0
X2	39.55983	-105.83688	3582	66.35587766
X3	39.55943	-105.83782	3549	163.8600442
X4	39.55895	-105.83857	3525	251.2790559
X5	39.55815	-105.83982	3461	405.2141071
X6	39.55772	-105.84070	3438	498.17434
X7	39.55712	-105.84137	3410	590.3404732
X8	39.55673	-105.84200	3396	660.77584
X9	39.55675	-105.84288	3385	737.4984892
X10	39.55692	-105.84390	3365	829.1278317
X12	39.55718	-105.84475	3355	908.6590205
X13	39.55713	-105.84537	3347	962.5066064
X14	39.55712	-105.84568	3343	989.9595771
X15	39.55689	-105.84637	3338	1054.383896

**Table D.1b:** Field Site Descriptions

Upper Snake River sites			
Site	Latitude	Longitude	Elevation (m)
S3	39.55736	-105.84659	3334
S2	39.55667	-105.84624	3340
S1	39.55496	-105.84428	3357

**Table D.2a:** Injection Pump Notes

**GOALS:**

1.3 mg/L Initial Cl level  
 3.25 mg/L Initial NaCl level  
 32.5 mg/L Tracer Concentration

**CALCULATING LOAD:**

20 L/s Qs  
 32.5 mg/L Cb  
 3.25 mg/L Co  
 585 mg/s Tracer Load  
 21600 seconds Inj. time  
 12636000 mg Mass required 12.636 kg 28 lbs  
 200000 mg/L Ci  
 0.002925 L/s Qi  
 63.18 L Vol 6 hours



**Table D.2** Estimated injection Rates. Pump was turned on at 10:20 and off at 15:00. A single pump-rate measurement was made at 12:00 and the pump was turned back town

<b>Time (min)</b>	<b>Rate (mL/min)</b>	<b>Time (min)</b>	<b>Rate (mL/min)</b>
5	150	150	150
10	151	155	150
15	152	160	150.3
20	153	165	150.6
25	154	170	150.9
30	155	175	151.2
35	156	180	151.5
40	157	185	151.8
45	158	190	152.1
50	159	195	152.4
55	160	200	152.7
60	161	205	153
65	162	210	153.3
70	163	215	153.6
75	164	220	153.9
80	165	225	154.2
85	166	230	154.5
90	167	235	154.8
95	168	240	155.1
100	150	245	155.4
105	150	250	155.7
110	150	255	156
115	150	260	156.3
120	150	265	156.6
125	150	270	156.9
130	150	275	157.2
135	150	280	157.5
140	150	285	157.8
145	150		

**Table D.3** Temperature and pH along the tributary of interest. Measured with synoptic metals samples at 15:00

site	pH	Temp (deg. Celcius)
X1	3.71	8.8
X2	3.37	9.9
X3	3.23	10.5
X4	3.19	14.4
X5	3.18	13.3
X6	•	•
X7	•	•
X8	•	•
X9	•	•
X10	•	•
X11	3.18	9.8
X12	3.17	8.2
X13	3.17	8.7
X14	3.17	2.5
X15	3.38	2

Table D.4 Cl<sup>-</sup> tracer data, tributary to the Upper Snake River, Sept. 11, 2010

X3		X5		X7		X9		X13		X15	
Time	[Cl <sup>-</sup> ] (mg/L)	Time	[Cl <sup>-</sup> ] (mg/L)	Time	[Cl <sup>-</sup> ] (mg/L)	Time	[Cl <sup>-</sup> ] (mg/L)	Time	[Cl <sup>-</sup> ] (mg/L)	Time	[Cl <sup>-</sup> ] (mg/L)
5	1.20	5	1.20	5	1.20	5	1.20	50	1.19	5	
7	1.20	6	1.75	7	1.21	8	1.44	65	1.18	8	1.33
11	1.20	7	1.42	15	1.26	9	1.33	80	1.16	25	1.66
16	20.00	19	1.56	30	1.41	23	1.37	95	1.17	38	1.36
21	92.73	24	1.39	45	1.28	38	1.25	110	1.17	50	1.30
22	103.51	29	1.40	55	1.32	53	1.36	120	1.21	66	1.24
24	110.26	34	1.37	60	1.83	58	1.21	125	1.15	85	1.15
30	114.37	39	1.42	65	37.85	63	1.48	130	1.21	100	1.18
35	116.13	44	9.56	70	52.62	68	1.17	135	1.20	115	1.14
40	120.67	49	58.27	75	67.74	73	1.18	140	1.42	130	1.09
45	121.11	55	82.59	80	73.27	78	1.22	145	2.85	145	1.13
50	123.97	60	87.43	85	76.27	83	1.18	150	18.77	155	4.61
55	125.29	65	90.43	90	78.15	88	1.88	155	36.08	159	2.99
60	127.68	70	93.45	95	79.66	93	1.55	160	46.84	165	8.05
65	126.60	75	96.08	100	82.02	98	7.27	165	56.12	170	11.25
70	129.27	80	97.10	105	84.19	103	28.11	170	64.21	175	15.67
75	130.12	85	99.98	110	86.35	108	49.56	175	68.93	180	19.80
80	131.30	90	100.45	115	86.42	113	62.86	180	72.27	185	23.01
85	131.85	95	102.39	120	87.80	118	71.15	195	77.87	189	23.62
90	134.17	105	103.69	125	89.32	123	73.94	210	82.74	195	25.93
95	133.97	120	107.14	135	89.02	128	76.67	225	84.81	210	28.66
100	135.73	135	109.67	152	90.15	133	78.24	260	78.58	223	30.04
105	136.65	150	93.44	165	80.23	150	83.74	285	79.20	225	30.00
110	132.49	165	92.28	180	77.26	165	86.79	300	76.63	240	31.44
120	116.10	180	90.95	195	76.77	180	89.32	315	78.03	254	31.73
135	115.74	195	92.22	210	76.81	195	88.53	330	79.16	270	30.14
150	111.02	210	92.82	226	79.56	210	81.07	342	78.75	285	29.00
165	115.58	225	94.99	240	79.59	225	79.81	360	78.81	300	27.43
180	114.88	259	98.37	255	79.61	240	77.10	375	81.84	316	27.83
195	117.45	274	103.06	270	78.61	255	77.86	385	84.53	330	28.16
210	113.37	286	101.84	286	84.50	270	78.57	390	84.78	347	28.56
225	120.37	298	101.91	315	84.65	283	79.64	395	87.41	366	27.90
240	126.30	312	100.16	330	86.53	300	77.84	400	85.92	379	29.09
255	123.03	320	96.14	345	74.14	315	84.94	405	88.85	394	29.89
270	127.42	325	92.38	350	56.07	330	85.17	410	88.50	409	28.87
286	123.06	330	56.61	355	25.20	345	85.07	415	86.61	424	29.00
295	116.23	335	17.78	360	10.69	360	88.13	420	85.77	434	32.49
300	109.92	340	7.51	365	7.08	365	89.73	425	85.76	439	30.23
305	22.53	345	5.44	370	10.95	370	85.93	430	81.42	444	28.20
310	4.92	350	4.46	375	4.59	375	83.43	435	71.21	449	26.72
315	3.42	355	3.96	380	5.29	380	83.06	440	56.12	454	22.04
320	2.96	360	3.74	385	3.95	385	71.12	445	42.44	459	17.38
325	2.81	365	3.95	390	3.57	390	51.37	450	27.64	464	13.78
330	2.69	370	3.44	395	3.37	395	33.30	455	18.60	469	9.93
335	2.52	375	3.28	400	3.31	400	16.80	460	13.45	474	7.52
340	2.48	380	3.33	410	2.96	405	9.74	465	10.23	479	6.00
345	2.49	385	3.32	425	2.77	410	7.35	480	6.55	489	4.27
350	2.35	390	3.04	435	2.66	415	6.68	495	5.00	494	3.89
355	2.38	405	2.97	450	2.41	420	5.29	•	•	•	•
360	2.30	420	2.88	465	2.21	425	4.70	•	•	•	•
370	2.17	435	2.70	480	2.17	430	4.31	•	•	•	•
375	2.26	450	2.55	495	2.12	435	4.20	•	•	•	•
380	2.11	465	2.45	•	•	450	3.47	•	•	•	•
390	2.04	•	•	•	•	465	3.01	•	•	•	•
405	2.04	•	•	•	•	480	2.98	•	•	•	•
420	1.95	•	•	•	•	495	2.88	•	•	•	•
435	1.92	•	•	•	•	•	•	•	•	•	•
450	2.03	•	•	•	•	•	•	•	•	•	•

Figure D.1 Chain of Custody for Sept. 11, 2010 tracer study metals samples

RETURNING 54 50ml PLASTIC TUBES CONTAINING THE DISCREGATES FOR  
US ENVIRONMENTAL PROTECTION AGENCY REGION 8 - Chain Of Custody

Region 8 Laboratory  
16194 W. 45th Drive  
Golden, CO 80403  
Fax: 303-312-7800

3-30-11

PROJECT NAME:		LSR #:		ANALYSIS		NUMBER OF CONTAINERS		Comments	
Snake R. Historical Samples		1101-002		100ml dissolved					
SAMPLER(S):		Date:		PRESERVATIVE		MATRIX		BOTTLE ID.	
Name:		Date:		DATE		TIME		LAB ID.	
Signature:	Signature:	9/11/10	15:00	1	M			1101002-38	
		9/11/10	15:00	1				38	
		9/11/10	15:00	1				40	
		9/11/10	15:00	1				41	
		9/11/10	15:00	1				42	
		9/11/10	15:00	1				43	
		9/11/10	15:00	1				44	
		9/11/10	15:00	1				45	
		9/11/10	15:00	1				46	
		9/11/10	15:00	1				47	
		9/11/10	15:00	1				48	
		9/11/10	15:00	1				49	
		9/11/10	15:00	1				50	
		9/11/10	15:00	1				51	
		9/11/10	15:00	1				52	
		9/11/10	15:00	1				53	
		9/11/10	15:00	1				54	
		9/11/10	15:00	1				55	
		9/12/10	11:00	1				56	
		9/12/10	11:00	1				57	
		9/12/10	11:00	1				58	
		9/12/10	11:00	1				59	
		9/12/10	11:00	1				60	
		9/12/10	11:00	1				61	
		9/12/10	11:00	1				62	
		9/12/10	11:00	1				63	
		9/12/10	11:00	1				64	
		9/12/10	11:00	1				65	
		9/12/10	11:00	1				66	
		9/12/10	11:00	1				67	
		9/12/10	11:00	1				68	
		9/12/10	11:00	1				69	
		9/12/10	11:00	1				70	
		9/12/10	11:00	1				71	
		9/12/10	11:00	1				72	
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		9/12/10	11:00	1				75	
		9/12/10	11:00	1				76	
		9/12/10	11:00	1				77	
		9/12/10	11:00	1				78	
		9/12/10	11:00	1				79	
		9/12/10	11:00	1				80	
		9/12/10	11:00	1				81	
		9/12/10	11:00	1				82	
		9/12/10	11:00	1				83	
		9/12/10	11:00	1				84	
		9/12/10	11:00	1				85	
		9/12/10	11:00	1				86	
		9/12/10	11:00	1				87	
		9/12/10	11:00	1				88	
		9/12/10	11:00	1				89	
		9/12/10	11:00	1				90	
		9/12/10	11:00	1				91	
		9/12/10	11:00	1				92	
		9/12/10	11:00	1				93	
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		9/12/10	11:00	1				95	
		9/12/10	11:00	1				96	
		9/12/10	11:00	1				97	
		9/12/10	11:00	1				98	
		9/12/10	11:00	1				99	
		9/12/10	11:00	1				100	
		9/12/10	11:00	1				101	
		9/12/10	11:00	1				102	
		9/12/10	11:00	1				103	
		9/12/10	11:00	1				104	
		9/12/10	11:00	1				105	
		9/12/10	11:00	1				106	
		9/12/10	11:00	1				107	
		9/12/10	11:00	1				108	
		9/12/10	11:00	1				109	
		9/12/10	11:00	1				110	
		9/12/10	11:00	1				111	
		9/12/10	11:00	1				112	
		9/12/10	11:00	1				113	
		9/12/10	11:00	1				114	
		9/12/10	11:00	1				115	
		9/12/10	11:00	1				116	
		9/12/10	11:00	1				117	
		9/12/10	11:00	1				118	
		9/12/10	11:00	1				119	
		9/12/10	11:00	1				120	
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		9/12/10	11:00	1				122	
		9/12/10	11:00	1				123	
		9/12/10	11:00	1				124	
		9/12/10	11:00	1				125	
		9/12/10	11:00	1				126	
		9/12/10	11:00	1				127	
		9/12/10	11:00	1				128	
		9/12/10	11:00	1				129	
		9/12/10	11:00	1				130	
		9/12/10	11:00	1				131	
		9/12/10	11:00	1				132	
		9/12/10	11:00	1				133	
		9/12/10	11:00	1				134	
		9/12/10	11:00	1				135	
		9/12/10	11:00	1				136	
		9/12/10	11:00	1				137	
		9/12/10	11:00	1				138	
		9/12/10	11:00	1				139	
		9/12/10	11:00	1				140	
		9/12/10	11:00	1				141	
		9/12/10	11:00	1				142	
		9/12/10	11:00	1				143	
		9/12/10	11:00	1				144	
		9/12/10	11:00	1				145	
		9/12/10	11:00	1				146	
		9/12/10	11:00	1				147	
		9/12/10	11:00	1				148	
		9/12/10	11:00	1				149	
		9/12/10	11:00	1				150	
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		9/12/10	11:00	1				155	
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		9/12/10	11:00	1				158	
		9/12/10	11:00	1				159	
		9/12/10	11:00	1				160	
		9/12/10	11:00	1				161	
		9/12/10	11:00	1				162	
		9/12/10	11:00	1				163	
		9/12/10	11:00	1				164	
		9/12/10	11:00	1				165	
		9/12/10	11:00	1				166	
		9/12/10	11:00	1				167	
		9/12/10	11:00	1				168	
		9/12/10	11:00	1				169	
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		9/12/10	11:00	1				171	
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		9/12/10	11:00	1				174	
		9/12/10	11:00	1				175	
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		9/12/10	11:00	1				177	
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		9/12/10	11:00	1				185	
		9/12/10	11:00	1				186	
		9/12/10	11:00	1				187	
		9/12/10	11:00	1				188	
		9/12/10	11:00	1				189	
		9/12/10	11:00	1				190	
		9/12/10	11:00	1				191	
		9/12/10	11:00	1				192	

Table D.5 Metals data from Sept. 11, 2011 tracer study on tributary of interest (to the Upper Snake River)

Site	Zinc	Vanadium	Titanium	Thallium	Strontium	Silver	Selenium	Nickel	Molybdenum	Manganese	Lead
S1	368	<10.0	<10.0	<0.3	70.5	<0.5	<1.0	24.1	<5.0	894	<1.0
S2	393	<10.0	<10.0	<0.3	68.7	<0.5	<1.0	24.0	<5.0	931	1.0
S3	455	<10.0	<10.0	<0.3	69.2	<0.5	<1.0	25.8	<5.0	1120	<1.0
X01	6390	<10.0	<10.0	<0.3	59.2	<0.5	5.5	243	8.4	16600	<1.0
X02	9600	<10.0	<10.0	<0.3	63.4	<0.5	5.7	297	7.6	23700	<1.0
X03	13300	<10.0	<10.0	<0.3	69.9	<0.5	7.2	384	8.2	33400	<1.0
X04	17000	<10.0	<10.0	<0.3	73.2	<0.5	8.7	429	10.0	42800	<1.0
X05	17200	<10.0	14.3	<0.3	75.5	<0.5	8.8	427	9.9	43300	<1.0
X06	16200	<10.0	<10.0	<0.3	71.8	<0.5	7.9	413	9.3	40700	<1.0
X07	16400	<10.0	<10.0	<0.3	76.0	<0.5	8.9	417	9.4	41500	<1.0
X08	17400	<10.0	<10.0	<0.3	78.4	<0.5	8.6	419	10.2	43200	<1.0
X09	16700	<10.0	<10.0	<0.3	74.3	<0.5	9.0	418	9.6	41300	<1.0
X10	16800	<10.0	<10.0	<0.3	76.3	<0.5	8.8	422	10.3	41600	<1.0
X11	16500	<10.0	<10.0	<0.3	75.5	<0.5	8.8	419	9.5	41300	<1.0
X12	17600	<10.0	<10.0	<0.3	78.3	<0.5	8.8	419	9.6	43200	<1.0
X13	17300	<10.0	<10.0	<0.3	75.7	<0.5	8.5	415	10.3	42200	<1.0
X14	17000	<10.0	<10.0	<0.3	76.7	<0.5	8.3	416	10.6	42100	<1.0
X15	8450	<10.0	<10.0	<0.3	85.8	<0.5	4.7	223	8.1	21200	<1.0

Site	Iron	Copper	Cobalt	Chromium	Cadmium	Beryllium	Barium	Arsenic	Antimony	Aluminum
S1	2300	27.9	15.9	<5.0	1.5	<1.0	34.9	<4.0	<1.0	6120
S2	2230	32.0	16.0	<5.0	1.6	<1.0	36.6	<4.0	<1.0	6080
S3	2200	32.4	16.9	<5.0	2.1	<1.0	34.9	<4.0	<1.0	6600
X01	1640	298	167	<5.0	45.5	3.5	33.2	<4.0	<1.0	72600
X02	12300	298	214	7.3	56.3	4.5	22.3	<4.0	<1.0	88700
X03	38800	265	264	8.1	83.3	5.3	17.5	<4.0	<1.0	108000
X04	62200	250	325	8.8	123	6.9	14.5	<4.0	<1.0	125000
X05	71600	262	326	8.9	123	7.2	15.7	<4.0	<1.0	127000
X06	68200	253	307	8.4	122	7.0	13.3	<4.0	<1.0	120000
X07	66500	251	314	8.5	120	7.2	14.4	<4.0	<1.0	122000
X08	72900	257	322	8.5	117	7.2	14.4	<4.0	<1.0	125000
X09	65700	249	313	8.4	118	7.0	13.9	<4.0	<1.0	119000
X10	64800	248	309	8.1	123	6.9	14.2	<4.0	<1.0	120000
X11	63900	247	309	8.0	118	7.0	14.0	<4.0	<1.0	119000
X12	67200	255	317	8.0	121	7.2	14.5	<4.0	<1.0	123000
X13	65500	249	318	8.9	117	7.0	14.6	<4.0	<1.0	119000
X14	64700	250	314	8.9	119	7.0	15.4	<4.0	<1.0	120000
X15	25300	133	163	<5.0	58.8	3.7	19.1	<4.0	<1.0	64300

**Table D.6** In-stream metals mass-loads along the tributary of interest

<b>Site</b>	<b>Zn load (mg/sec)</b>	<b>Cd load (mg/sec)</b>	<b>Cu load (mg/sec)</b>	<b>Mn load (mg/sec)</b>	<b>Al load (mg/sec)</b>	<b>Fe load (mg/sec)</b>
X02	3.84E-05	2.25E-07	1.19E-06	9.48E-05	3.55E-04	4.92E-05
X03	6.65E-05	4.17E-07	1.33E-06	1.67E-04	5.40E-04	1.94E-04
X04	1.07E-04	7.77E-07	1.58E-06	2.70E-04	7.89E-04	3.93E-04
X05	1.09E-04	7.77E-07	1.65E-06	2.73E-04	8.02E-04	4.52E-04
X06	1.13E-04	8.51E-07	1.77E-06	2.84E-04	8.37E-04	4.76E-04
X07	1.28E-04	9.35E-07	1.96E-06	3.23E-04	9.51E-04	5.18E-04
X08	1.36E-04	9.12E-07	2.00E-06	3.37E-04	9.74E-04	5.68E-04
X09	1.30E-04	9.19E-07	1.94E-06	3.22E-04	9.27E-04	5.12E-04
X10	1.31E-04	9.58E-07	1.93E-06	3.24E-04	9.35E-04	5.05E-04
X12	1.37E-04	9.43E-07	1.99E-06	3.37E-04	9.58E-04	5.24E-04
X13	1.35E-04	9.12E-07	1.94E-06	3.29E-04	9.27E-04	5.10E-04
X14	1.32E-04	9.27E-07	1.95E-06	3.28E-04	9.35E-04	5.04E-04
X15	1.75E-04	1.22E-06	2.75E-06	4.39E-04	1.33E-03	5.23E-04
S3	1.05E-03	4.84E-06	7.47E-05	2.58E-03	1.52E-02	5.07E-03