ACID ROCK DRAINAGE IN THE UPPER SNAKE RIVER:
THE PRESENCE OF HEAVY METALS IN A MINERALIZED WATERSHED

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Overview

The coupled environmental impact of acid rock and acid mine drainage is a problem facing countless waterways across the Rocky Mountains. Here we examine the Snake River watershed, located near the former mining boomtown of Montezuma. Over the three decades, researchers for numerous government agencies, the Institute of Arctic and Alpine Research, and graduate students at the University of Colorado have closely monitored changes here in water chemistry and heavy metal contamination present in its contributing streams, resulting from both over a hundred and fifty years of mining activities and the natural weathering of pyrite-laden rock.

The purpose of this project, funded in large part by an Undergraduate Research Opportunity Grant, is to test the dissolved metals present in the upper Snake River, an undisturbed portion of the reach that is naturally acidified and loaded from both surface and subsurface flow. Augmenting this data are field measurements of stream flow, pH, and total dissolved solids collected at a one-week interval between September 22nd and 28th, 2012. The follow-up lab analysis of samples was performed by the Laboratory for Environmental and Geologic Studies using Inductively Coupled Plasma Mass Spectrometry to determine concentrations of Aluminum, Cadmium, Copper, Iron, Manganese, Sulfate and Zinc present at 15 sites distributed among the Upper Snake; the headwaters, 3 main tributaries and their conflux, and the confluence downstream with the pristine Deer Creek. Certain sites were chose due to availability of water chemistry data going back over 30 years, with others chosen because of their reflection of similar climate conditions at the time of sampling. By choosing sites which have been heavily studied and measured over a large temporal scale, it is therefore possible to correlate these new results with pre-existing data to draw new conclusion regarding the presence of heavy metals in the upper Snake River as to whether these levels have increased, further enrichment is occurring, and how these change in relation to drivers such as climate.

Chapter 1
Background

The Snake River is located west of the Continental Divide in the Rocky Mountains of central Colorado. A long history of hardrock mining in the region and its location in the Colorado mineral belt, which supports natural weathering processes, is respectively responsible for the problem of Acid Mine Drainage and Acid Rock Drainage in the Snake River. The parent material from which these mountains were formed contains high concentrations of the mineral Pyrite. It is often called "fools gold" for it's shiny resemblance to the real thing and the similar depositional features. But an interesting thing happens when water flows over this mineral. Ferrous iron, sulfate, and sulfuric acid are created through a redox reaction when water and oxygen interact. Bacteria can contribute by catalyzing the reaction, speeding up the rate in which the water becomes acidified. As these acidic waters move through a watershed, in the process coming into contact with other minerals and exposed rocks, they dissolve and mobilize more heavy metals like iron, aluminum, copper, cadmium, iron, and zinc. The following equation shows the reaction where Fe is oxidized and O_2 is reduced, which creates as a byproduct ferrous iron, sulfuric acid, and reduces the pH of the water.

$$2\ FeS_2 + 7\ O_2 + 2\ HO_2 \rightarrow 2\ Fe^{2+}\ \ 4\ SO_4^{2-} + 4\ H^+$$

This ferrous iron can now be further oxidized into ferric iron by extremephilic bacteria.

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

These heavy metals can also precipitate out when this acidic water is neutralized with more pristine waters, which are then deposited on the rocks and streambed material of a river. Visually, it looks as if the rocks and river bottom itself have been painted with metals, be it the chalky silver sheen of aluminum or the red rusting of iron, with continued exposure to air furthering these processes. Due to the decreased solubility of certain metals from rising pH conditions, here we see how ferric iron precipitates out of water as ferric hydroxide to coat the streambed.

$$4\ Fe^{3+} + 12\ H_2O \rightarrow 4\ Fe(OH)_2 + 12\ H^+$$

As more ferric iron is rendered into the stream, it also accelerates the oxidation of other pyrite-bearing minerals from which the water may contact. This highlights a significant increase in hydrogen ions and more sulfuric acid to which pH will further decrease, acting to further the dissolving of metals.

$$FeS_2 + 14\ Fe^{3+} + H_2O \rightarrow 12\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

In the case of the Snake River, the problem of reduced pH and metal-enrichment is worsened further by later tributaries such as Peru Creek that are themselves laden with metals because of mine drainage. Where metals such as iron and aluminum precipitate out when pH conditions normalize, others such as zinc remained dissolved in the water column and present a serious challenge in maintaining water quality downstream.

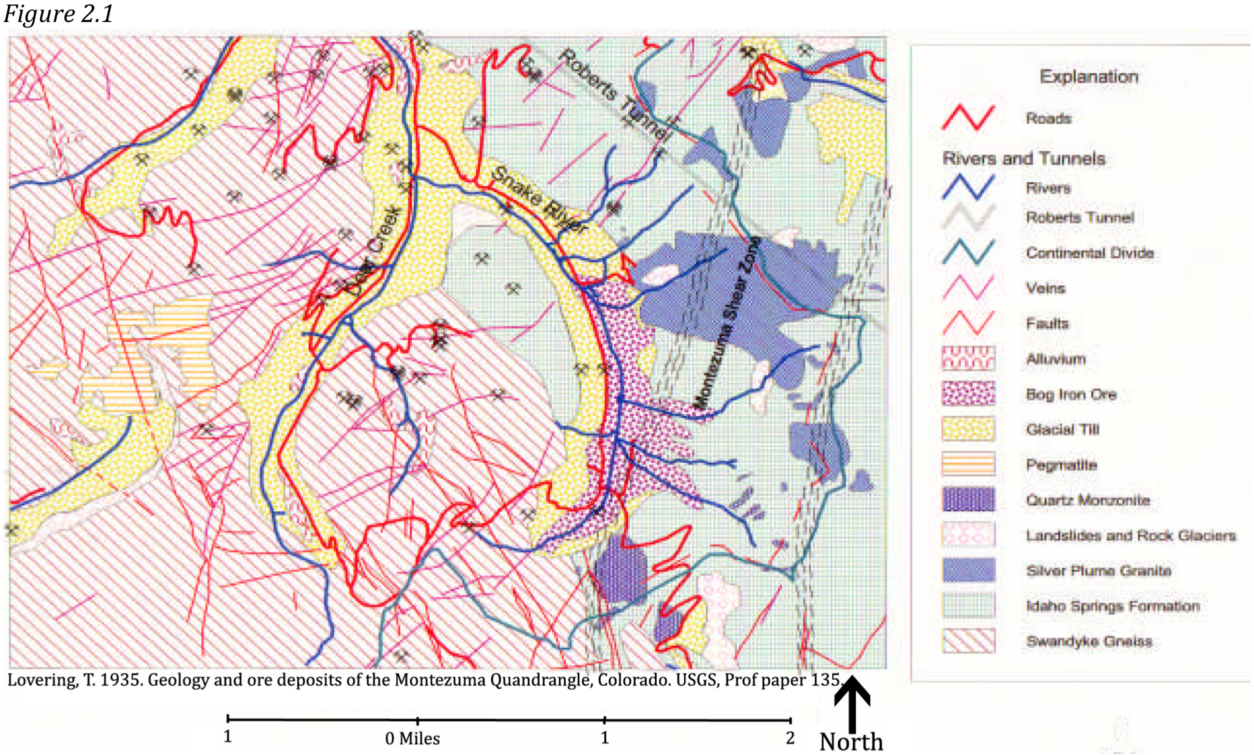
Although the Snake River along its contributing creeks and streams, have levels of metals that seriously affect stream ecology and biotic life, the nature of its sourcing being both due to natural weathering and the legacy of mining in the area makes it difficult to address. Some of these metal concentrations well exceed limits of toxicity set by the state and mandated federally through the Clean Water Act, particularly zinc, however it's important to note that they present a minor health risk for people. The Snake River is only 15 miles long and flows into the larger Blue River, later discharging into the Dillon Reservoir. And even though this reservoir serves as a source of drinking water for Denver, this water becomes so highly diluted and neutralized from other water sources downstream as well as groundwater contribution, that it poses no serious threats to human health. Taking this into account, along with the high projected costs of mine site cleanup, and the metal enrichment already taking place naturally in the upper Snake, has kept it a low priority for state and federal cleanup efforts even though it represents one of the most contaminated watersheds in the state. Because even if millions of dollars are spent on addressing even a priority site such as the Pennsylvanian Mine, natural metal loading will still be taking place and may according yield marginal results. In this regard, it may never be possible for certain parts of the Snake River to become compliant with clear water standards set by the EPA.

The Snake River currently cannot support a self-sustaining fish population due to the concentrations of metals proven toxic to aquatic life. The Colorado Department of Wildlife stocks this river periodically, to maintain the indigenous populations, however this is a losing battle due to the coupled impact of Acid Rock Drainage and Acid Mine Drainage on water quality. In an effort to better understand these influences on water quality by ARD and AMD, the Snake River Task Force was founded. This highlights a partnership between stakeholders, Colorado Department of Public Health and Environment, EPA, Keystone Ski Resort, the Blue River Watershed Group, and conservation groups such as Trout Unlimited whom also have experience with abandoned mine cleanups. The focus has centered on understanding the factors that influence water quality, as improvement proves difficult due to murky issues regarding liability as outlined in the Clean Water Act, high costs, and prior failed attempts at mitigation by the Colorado Division of Minerals and Geology in the 1980s. It's important to again note that even serious reductions in AMD only represent part of the problem; as to date there are no remediation strategies for ARD. Therefore, it is possible that the Snake River will never meet the water quality criteria necessary to support fish and a rich aquatic biota.

Chapter 2
Site Description

This particular project, adapted from a previous study completed in 1998 by a partnership between Institute for Arctic and Alpine Research and United States Geological Society, focuses on a 4.55 square mile upper portion of the Snake River that serves as the headwaters for the catchment. Along the valley floor is largely bog iron ore, with portions of glacial till on the western slope and further down the reach (north). Sedimentary rock known as the Idaho Springs Formation is the predominant material from which the surrounding mountains are composed, however there are small deposits of Quartz Monzonite at the southern most portion of the valley. Silver Plume Granite deposits are also present on the eastern slope, roughly half way down the valley.

Figure 2.1



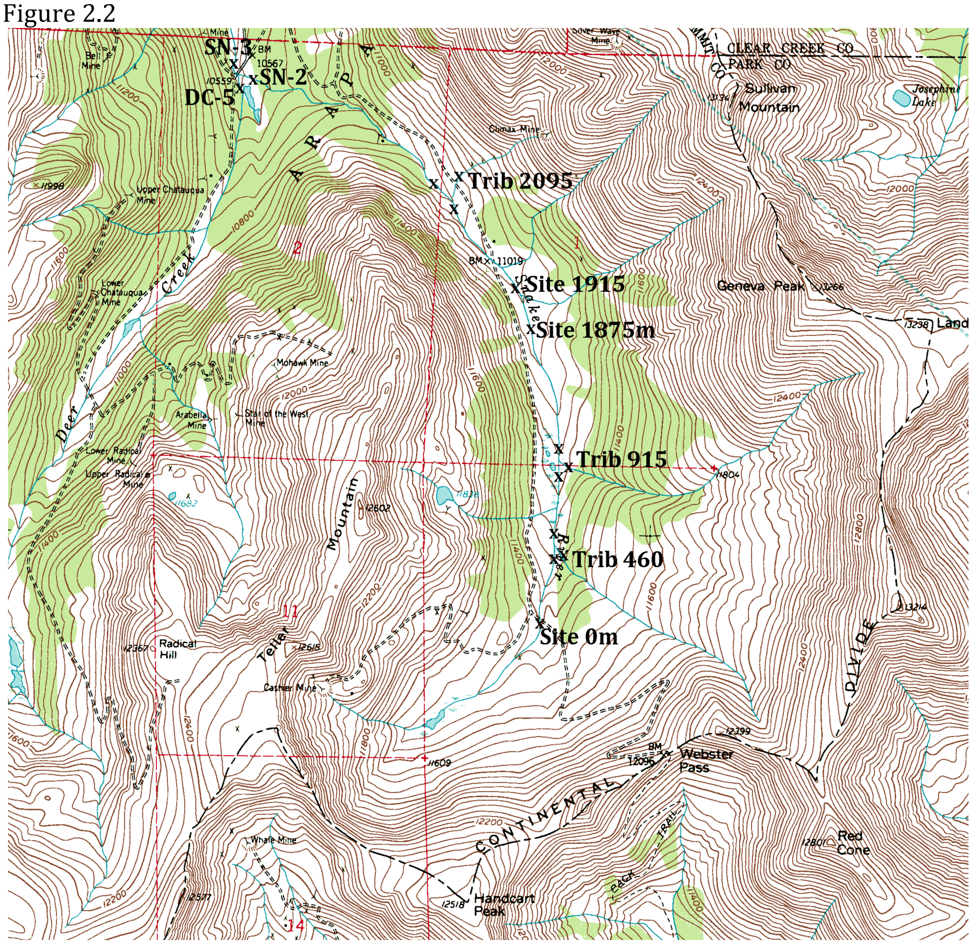
Lovering, T. 1935. Geology and ore deposits of the Montezuma Quandrangle, Colorado. USGS, Prof paper 135.

Study Sites

There are 6 tributaries of the upper Snake River, however only 3 were flowing beyond a trickle during the time of sampling. This was due to warm temperatures in March, which facilitate an early spring melt, and the above-average snowpack quickly disappearing to leave only 19% of average on May 1st. These conditions and the summer drought to follow were greatly similar to those to the 2002 diel sampling study performed by Laura Belanger. Due to this, her previously evaluated sites, which were also based off the earlier study (Boyer et al, 1999), were chosen for this project to help correlate results with pre-existing data sets in periods of reduced flow. Measurements for pH, TDS, and temperature were collected at each site as well, in some cases at a temporal interval of one week to highlight any change in stream chemistry. Stream discharge was also measured via pygmy meter at multiple spatial and temporal intervals, to indicate any changes in flow or possible addition contributions by lateral inflow (groundwater).

At each site, samples were taken from both the Snake River and tributaries 10 meters above the conflux as well as 25 meters below the mixing zone. This was the protocol outlined in previous studies and such distance is necessary to maintain that samples not influenced by overlap of hyporheic zones. An additional samples was also taken from the headwaters (0m) help establish baseline loading and pH of the Upper Snake as well as interval sites 1875m and 1935m to coincide with previously collected data. Further downstream, at the confluence of the Snake River and Deer Creek, each stream was sampled as well as the conflux to better understand how a pristine stream serves to alter the water chemistry and precipitation of metals.

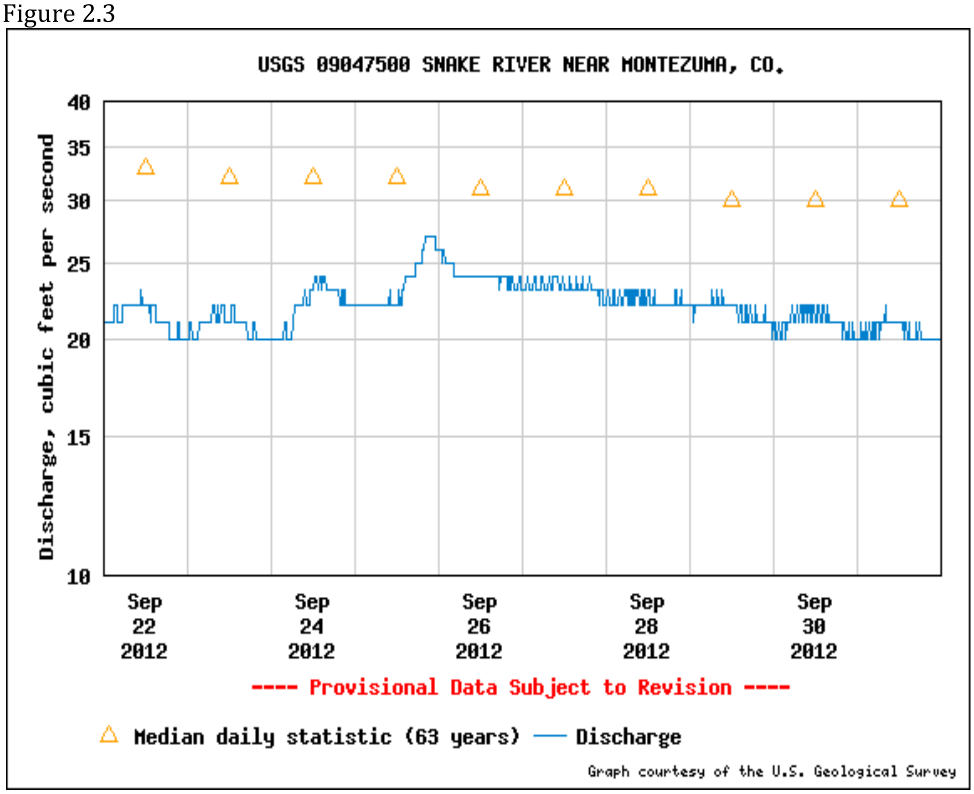
Figure 2.2



USGS Topographic Map, Montezuma Quadrangle, 1:24000

Late September was chosen as the best time for sampling, as according to 30 years of USGS stream flow data, this is a period of lowest flow and least contributions of "new" water. In 2012, further exacerbating this was an early snowpack melt and dry summer that reduced flows of the Snake River to near-record lows. During times of sampling, the USGS gauge station near Keystone showed relative similar levels discharge on between days (9/22 and 9/29) and also highlight that flows are well below median daily values over the last 63 years of collection. Using pygmy meter measurements of discharge below the Snake River and Deer Creek, it was possible to correlate these measurements for accuracy with its estimated 20% contribution to the gauge at Keystone (Boyer et al, 1999).

Figure 2.3



<u>Methods</u>

Sample collection will be done according to the Colorado Department of Public Health and Environments methodologies and standards for testing surface water (CDPHE, 2001) as well as EPA Method 200.8. Samples were collected in 60ml HDPE plastic containers, with a sample volume of no more than 50ml. Prior to collection, each container was first be bathed overnight in a 3% mixture of above reagent-grade nitric acid in ultra-pure deionized water, followed by two flushes of ultra-pure deionized water after of which they will be left to dry. During collection, samples will be acquired through 60ml syringes, with .45 um nylon filters to prevent colloidal or eigencolloids contamination. After collection, samples will be labeled with their respective pH, total dissolved solids, and then acidified with trace-metal-grade nitric acid to a value near or less than 1.5 for laboratory analysis. A field blank was prepared using ultra-pure deionized water, also acidified to the same value, to quantify any further possible contamination from containers or acids used. Samples will then be delivered to the Laboratory for Environmental and Geological Studies for ICP-MS (metals) and IC (sulfate) analysis.

In-site measurements of pH and total dissolved solids were obtained using Eutech instruments that were calibrated twice daily, and rinsed between sampling. Interval measurements of one week were also made to indicate any significant changes in stream chemistry. Discharge measurements were also made using a USGS Pygmy Meter (model 6205) at the Snake River and Deer Creek confluence on September 22nd and 29th, and at select points of the Upper Snake on September 29th.

Included in the results/analysis section is historical data from the Boyer diel study completed in July of 1998, particularly because sites for this project were chosen from here to allow for corollary comparison. Due to the low-flow conditions observed prior to this project, certain sites were omitted because of a lack of measureable discharge. More recent studies (Belanger, 2001. Crouch, 2009), which took place during times of similar climate conditions and flow, further focused on certain tributaries of upper Snake River as significant sources of metal loading. Accordingly, discharge measurements were taken at select points above and below site (trib) 2095, a previously identified major source of enrichment, to provide insight into concentration and subsequent dilution of solute metals in terms of mass balance. However, due to changing lateral inflow of groundwater at this site and only a single discharge measurement these mass loads were highly inaccurate when compared to concentrations observed with ICP-MS analysis. Due to more accurate discharge measurements which were corollary at 20% of that recorded by the USGS gauge station at Keystone, mass loads were instead calculated for sites SN-2 and SN-3, which lie above and below the confluence with Deer Creek. The following equation was used for calculating actual mass metal loads per unit time (sec) at a particular site

$$M_x = Q_x C_x$$

This equation was used to estimate mass loads using known values for discharge and concentrations of metals above the sites of confluence, and was also rearranged algebraically to solve for estimated concentrations above the confluence using observed concentrations from below.

$$\frac{(C_{above}Q_{above}) + (C_{trib}Q_{trib})}{Q_{below}} = C_{below}$$

<u>Schedule</u>

• 9/22: Collect initial pH, TDS, and discharge measurements, as well samples from select sites.

- 9/29: Collect primary samples from 13 sites, as well as auxiliary measurements of pH, TDS, and discharge to quantify any change in stream flow or chemistry from previous week.

- 9/30: acidify samples, catalog data, and deliver samples to LEGS

- 10/13: Collect secondary pH and TDS measurements from select sites

Chapter 3
Literature Review

The purpose of this project is to better understand the metals present in the contributing streams of the Snake River. Through the testing of 4 sites within the Upper Snake, collecting samples at the confluences of contributing streams and their respective tributaries, concentrations and sources of metal loading can be evaluated. In particular, where smaller streams conflux with one another and how their heavy metal concentrations change relative to water volume (discharge). By also collecting field measurements of pH, TDS, and temperature at time of sampling, it can be further understood how water chemistry changes throughout this upper portion of the river and which tributaries are most influential. It is through the establishment of these baseline levels of metal loading present at the headwaters of the Snake River that a standard of water quality can be created in which to evaluate other sources of contamination such as acid mine drainage, which also has a significant role in this watershed.

The compounding of acid rock drainage with acid mine drainage has served to make the problem of water quality much worse for areas such as the Snake River watershed. This is certainly the case for other places located in the Colorado mineral, the town of Silverton for example. Here both processes are also serving to exacerbate the levels of metals that are discharging into streams, and as a result 3 out of 4 indigenous fish species have disappeared from portions of the Upper Animas River. To a lesser degree, this is also the case with the Snake River and the coupled worsening of water quality due to these two factors. However, because ground waters here percolate through bedrock rich in conservative elements and multiple high-order streams such as the North Forks and Deer Creek are relatively pristine, acid drainage tend to be neutralized and diluted further down the catchment.

Long-term data sets of precipitation, temperature, river discharge at many sites throughout the Colorado Rockies show decreasing trends in summer flows (Rood et al, 2008) which correlate to other, more recent findings which highlight a snowpack that is melting 2-3 weeks earlier (Clow, D. 2010). Using snow water equivalent measurements from SNOTEL sites nearest to the Snake River, a trend was shown between advancement of peak stream flow by an earlier melt season and rising metal concentrations in summer months (Todd et al, 2012). A 30-year water chemistry data set from the upper Snake River further show that fluctuations from 100-400% of baseline are occurring during these low-flow months. However, these increases cannot simply be explained by shifting snowmelt timing, nor by decreased dilution from reduced discharge. It has been postulated that increasing temperatures observed in the Rockies over the last few decades could affect the rates of oxidation of sulfide minerals, but there is uncertainly that this can account for such drastic increases in metals. The coupled influence of all these factors, including their relation to dropping water tables due to reduced recharge of groundwaters as well as how more exposed rock due to reduced snow cover and duration also increases rates of weathering, all explicitly linked and appear to be driven by changes in climate.

Between 2001 and 2005, a study was done to deduce the quality of groundwater prior to mining at an active site near Red River, New Mexico. An unmined catchment nearby was also evaluated to provide an analogous idea as to the groundwater composition. It was discovered that two types of water are dominant here, which related to their overlying geology and location. The headwaters of the Red River are fed by springs that are buffered by conservative elements such as carbonate, which kept groundwater pH around 7.5-8.5. At middle and lower portions of the Red River, it was found that the water chemistry was vastly different and altered by acid drainage and mineralized water discharging into these lower reaches both above and alongside the mine site. Similar to the Snake River, these acid mineralized waters were formed from debris created by weathering and rapid erosion of pyrite-bearing minerals. Also observed at the site was how rainstorms had large impacts and alterations on the water chemistry of the Red River. This was further confirmed by later analysis of BLM historical data between 1982-1985. The increase in discharge in the spring due to snowmelt served to dilute solutes present in the river, with their concentration continually rising through the dry season until the next snowmelt. If a lackluster snowpack occurred, and no definitive peak in spring discharge, these concentrations continued to rise. Rainstorms in the summer served to slightly dilute these mineralized water, but more importantly it was observed that heavy rains actually reversed this trend to create an drastic increase in metal concentrations such as zinc and a profound drop in pH from roughly 7.8 to 3.8. Here we see a flushing effect from a extreme rainfall event, with materials effloresced from evaporation due to prolonged drought being washed into the river. Another interesting observation was that the highest levels of metals and sulfate in the Red River were when an intense rainstorm occurred in the valley, where no mining activities are taking place. This highlights that natural acid rock drainage can serve to alter water quality just as severely, if not more, than acid mine drainage. This becomes an important acknowledgement when we look to understand water quality in areas with both high amount of exposed sulfate-bearing minerals and have undergone mining actives, as well as how changes in precipitation frequency and intensity can serve to alter it.

In the context of these previously mentioned examples of ARD and AMD in differing areas across the US, the aforementioned author of the study, D. Kirk Nordstrom, translated these processes within the context of available long-term climate data and hydrologic change. Particularly troubling was that in 2009 the western US has experienced an increase in average temperatures that is upwards of 70% higher than that of the global average. These changes were analyzed in relation to such influencing factors as the Pacific Decadal Oscillation (PDO), El Nino Southern Oscillation (ENSO), North American Monsoon (NAM), and global warming. Though these all act on differing scales, where as ENSO serves to alter weather patterns for a few years and PDO acts on many more, these together can serve to compound the effects of climate change, or help reduce the effects of each other. Careful examination of climate records dating from 1948-2000 in the Sierra Nevada, Rocky, and the Pacific Northwest mountains showed a quickening of snowmelt streamflow timing by 1-4 weeks (Dettinger et al, 1995). This shift in snowmelt has serious consequences in terms of acid rock and mine drainage for the following reasons; it extends the summer dry period, increases the rates of evaporation that leave more residual effloresced salts and also the time in which they may accumulate. It also important to note that in terms of global warming, warmer temperate have the potential to decrease rainfall frequency and increase the intensity of rains when they do occur. This again has large, looming implications in the terms of water quality as it relates to AMD/ARD. As was demonstrated in the data, intense storms had to tendency to reverse the trend of metal concentration dilution to instead flush high and higher levels in catchments. Therefore, greater shifts in climate, whether due to natural or anthropomorphic causes, has the potential to further mobilize acid rock drainage and worsen its effects by increasing the frequency of these flush-out events. Though not specifically mentioned in this study, recent work have highlighted that a decreasing snowpack, whether due to climate change or not, can further the problem of acid rock drainage because it leave more exposed, mineral-laden rock to be weathered by less frequent, more intense rainfall events.

The impact of acid rock and mine drainage on the water quality of the Snake River watershed has led to numerous studies to quantify sources of metal loading and there respective amounts over the last 30 years. In 2001, a grant from the EPA and National Science Foundation supported an 11-month University of Colorado/INSTAAR project to assess this. Across numerous sites in the watershed, sampling was done during periods of high flow (Spring) and low flow (Summer/Fall), in order to observe how heavy metal concentrations changed seasonally. It was observed that at most study sites, many of which are shared with this study, that these concentrations were at their highest during the summer and continually decreased as snowmelt contributed to stream flows. . Flow-up studies in 2010 evaluated groundwater contributions and subsurface metal loading through tracer analysis in the Upper Snake and more recent research has focused on interpreting long-term data from this area to establish trends in metal loading in relation to influences such as climate change (Crouch, 2011).

The most recent study, done in partnership by the USGS, EPA, and INSTAAR, evaluated the increases in metal concentrations in the Snake River utilizing the entire 30 years of available water chemistry records, particularly the influence that climate change may be playing to exacerbating the decrease in water quality. Correlating these large increases in metals with long-term climate, snowpack, and observed hydrologic measurements, a trend can be established between warmer temperatures, decreased stream flow, and earlier shifts in spring melt as having major influence on this. Because the study focused analysis of large temporal and spatial records, as well as combining previous research on changes in Colorado climate (Clow, 2007) utilizing similarly comprehensive data, there are valid concerns on how anthropomorphic influences are altering water chemistry and metal concentrations in high alpine streams. Accordingly, as it is estimated that some form of acid rock or acid mine drainage affects over 40% of the headwaters in the Colorado rivers and streams (Forhardt, 2003), there serious implications as to how this may play out in the future. If the trends indicative of this research are indeed correct, then climate change and its influence on the hydrology of the Rocky Mountains are indeed cause for concern. Decreasing water quality serves to not just disrupt biotic communities, disturb delicate stream ecosystems, and endanger indigenous aquatic species, but also its later utilization in terms of recreation, drinking water sourcing, and other human use

The inherent variability of factors that drive our climate can serve to exacerbate or reduce the impacts of acid rock drainage, but the problem will not simply go away. The shown variability in metal concentrations has serious implications for both water quality and the ecology of the Snake River. The natural metal-enrichment occurring in the Upper Snake already makes this portion of the stream all but inhabitable for aquatic life, with only a few species of benthic invertebrates able to survive in such extreme conditions. Flushing events similar to those documented in New Mexico by Nordstrom are quite possible here, if not inevitable in years of earlier snowmelt and prolonged summer drought. Instances of mass fish kills have already been observed after large flood events in the watershed, as sediments and precipitates are washed from primary sources of contamination, such as the Pennsylvania Mine, into Peru Creek which confluences with the Snake River (Berwyn, 2007). There remain portions of the Snake River and Peru Creek that cannot support self-sustaining fish population, and rely of stock efforts by state wildlife officials to maintain their presence. Zinc concentrations also remain well above clean-water standards until the North Forks acts is diluted these waters further down the reach.

Chapter 4
Results

Field Observations:

In an effort to provide a better understanding as to the steady-state of water chemistry of the upper Snake River, measurements and sampling were done at a one week time series. In addition to water sampling, also collected were discharge, pH, total dissolved solids measurements were taken throughout the reach as well as the downstream confluence with Deer Creek. All were collected with 2 hours of the previous week, and many within 1 hour so that any diurnal fluctuations were minimized.

The headwaters of the Snake, marked as Site 0, showed the highest pH measurements recorded as well as the lowest total dissolved solids. This provided a suitable baseline level and a basis of comparison for observations further down the reach.

Site 450, above tributary 460, showed slightly more acidic conditions, but only marginal increases in conductivity. Slight precipitation of iron was visually present, and water temperatures here were near identical to the previous site and suggest no additional subsurface inputs. The tributary itself, however, had the 2nd lowest measurements of pH and 2nd highest levels of conductivity recorded. Visually reinforcing this was an entire streambed coasted in iron, and this continued for at least 10 meters below its confluence with the Snake. After of which, at Site 485, we see a rebound of pH and dissolved solud to near levels prior to the conflux.

Site 900, tributary 915, and the confluence at 940 showed a near identical levels of tds, pH, and temperature which continued for a further 1000 meters, as corroborated by readings at sites 1875 and 1935. Iron precipitation was still present through this section, although still relatively minor.

Previous research suggested from tracer experiments that site 2095 had additional groundwater inputs (Crouch, 2011), this was also evident in measurements by significant decreases in water temperature and conductivity from a point above the road (a2095) to 25m below (2095b). Differences in pH were also observed, with dilution by groundwater seeming increasing this as well as reducing the amount of solids dissolved in solution. Accordingly, iron precipitates were highly visible in the streambed of tributary 2095. Upon mixing with the Snake River (2120), reduction of these acidic waters occurred and total dissolved solids decreased here as well. Discharge measurements were taken here on 9/29 show how high concentrations with relatively low volume were further diluted by the dominant Snake River flow.

Further downstream, above the confluence with Deer Creek, the conductivity of the Snake River had increased as well as slight uptick in pH. Iron precipitates were also visually present here. Upon mixing with Deer Creek, a radical change in pH and conductivity occurred. This is likely due to the pristine sourcing of Deer Creek, combined with its high pH and extremely low total dissolved solid. Immediately noticeable at this conflux is a color gradient of orange (iron) and white (aluminum) precipitates. Further downstream, at sample site SN-3, pH increased and conductivity remained at over double that which was present in Deer Creek. The chalky silver coating on the streambed here suggested that aluminum was now the predominant precipitant, with any remaining metals present in solution to likely remain insensitive to low pH conditions. Metal mass balance calculations will be possible with icp-ms results and discharge measurements to confirm this

Field Data:

pH & TDS

September 22nd

Site	pH	TDS	temp ©
1875	3.56	200	9.2deg
1935	3.57	200	9.3deg
2085	3.46	200	13deg
a2095	2.93	1020	8.6deg
b2095	3.36	530	5deg
2120	3.52	240	12.1deg

September 29th

Site	pH	TDS	temp ©
0	4.34	110	9.5deg
450	3.73	140	9.4deg
460	3.18	450	9.3deg
485	3.66	160	9.7deg
900	3.56	200	7.8deg
915	3.58	200	5.2deg
940	3.58	200	7.7deg
1875	3.55	210	3.2deg
1935	3.56	210	
2085	3.55	210	5.2deg
2095a	3.02	1100	3.1deg
2095b			
2120	3.55	240	6.0deg
Snake River abv Deer	3.65	310	7.2deg
Deer Creek	7.75	60	7.3deg
Snake River below Conf	4.83	140	

Figure 4.1

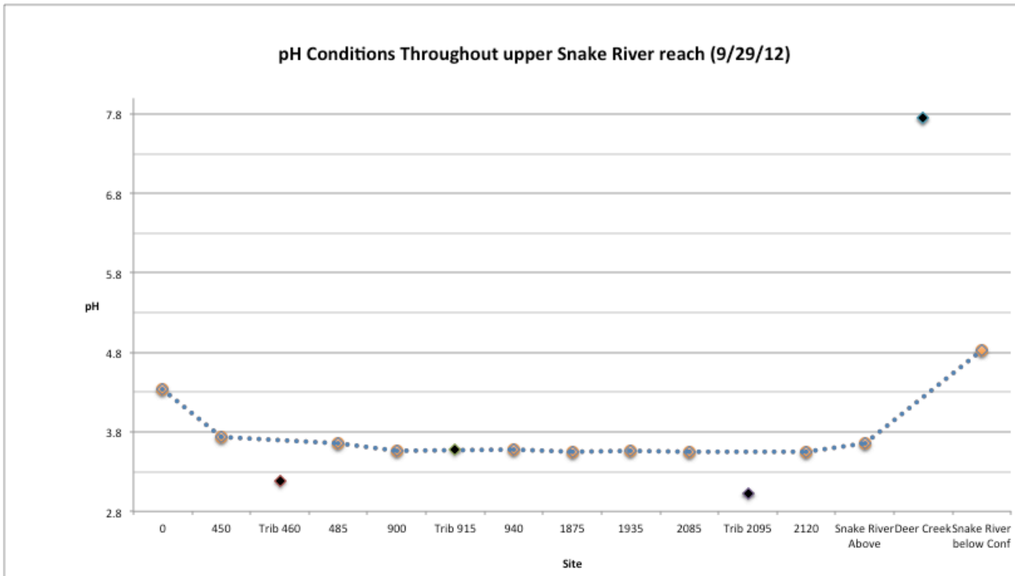
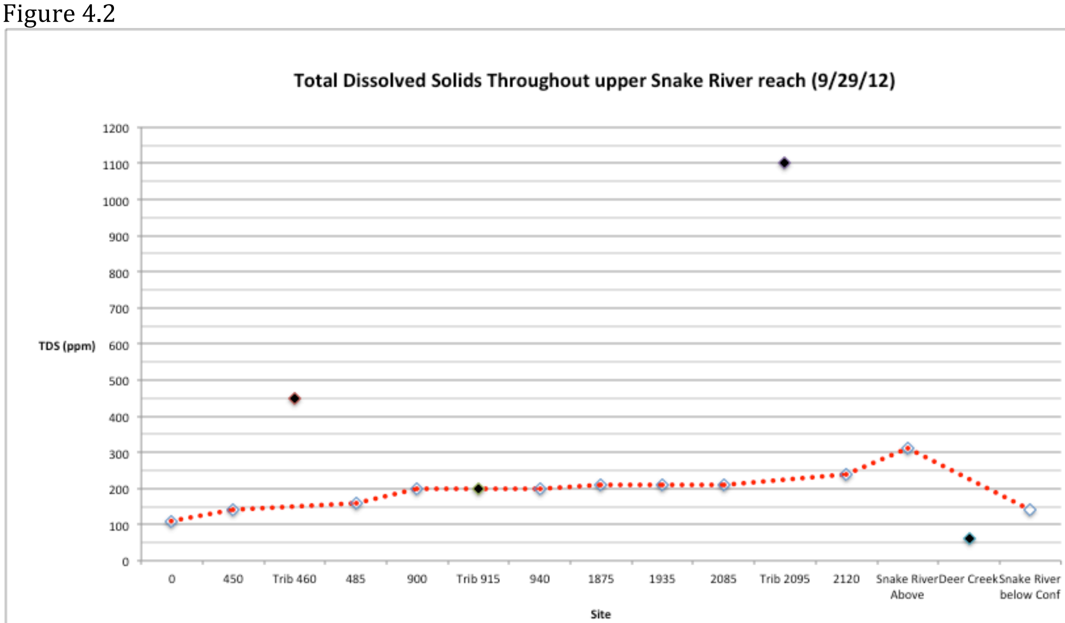


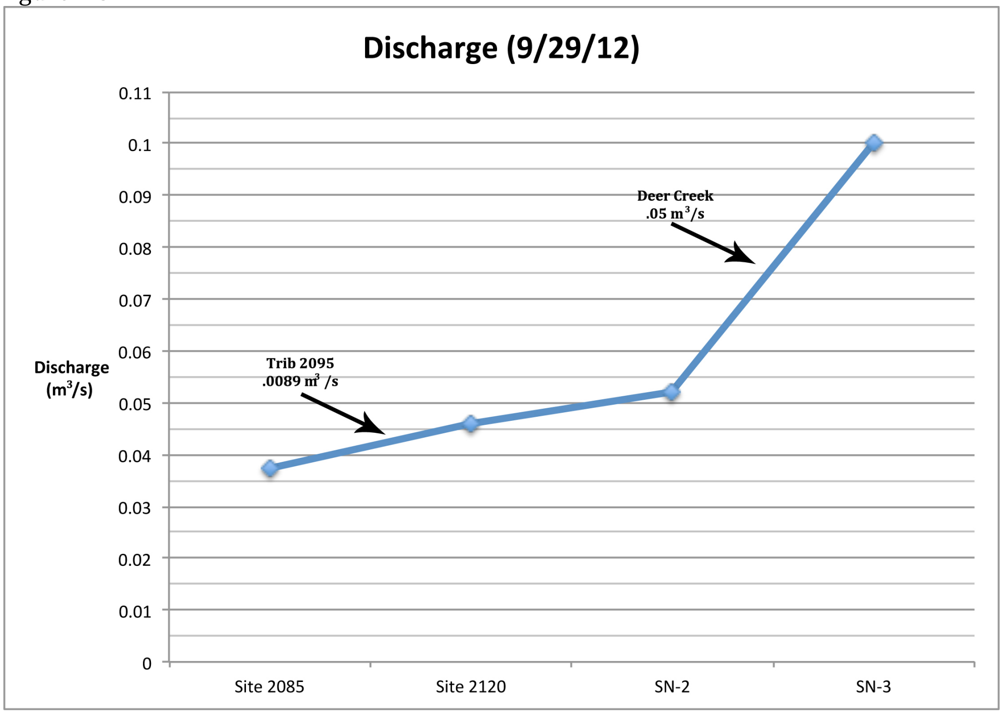
Figure 4.2



Discharge

9/29/12 3:00								
SN-3								
width	depth	revolutions	time	width	area	RPS	V (m/s)	discharge
5								
4.8	0.06	58	40	0.2	0.012	1.45	0.43396814	0.005207618
4.6	0.06	53	40	0.2	0.012	1.325	0.3973769	0.004768523
4.4	0.08	34	40	0.2	0.016	0.85	0.25833019	0.004133283
4.2	0.08	49	40	0.2	0.016	1.225	0.36810391	0.005889663
4	0.06	81	40	0.2	0.012	2.025	0.60228785	0.007227454
3.8	0.12	67	40	0.2	0.024	1.675	0.49983238	0.011995977
3.6	0.08	68	40	0.2	0.016	1.7	0.50715062	0.00811441
3.4	0.12	77	40	0.2	0.024	1.925	0.57301486	0.013752357
3.2	0.1	79	40	0.2	0.02	1.975	0.58765135	0.011753027
3	0.1	70	40	0.2	0.02	1.75	0.52178712	0.010435742
2.8	0.08	79	40	0.2	0.016	1.975	0.58765135	0.009402422
2.6	0.06	44	40	0.2	0.012	1.1	0.33151267	0.003978152
2.4	0.02	38	40	0.2	0.004	0.95	0.28760318	0.001150413
2.2	0.02	26	40	0.2	0.004	0.65	0.19978421	0.000799137
2	0.04	20	40	0.2	0.008	0.5	0.15587472	0.001246998
1.8	0.02	20	40	0.15	0.003	0.5	0.15587472	0.000467624
1.7								
							total (m^3/s)	0.100322799
9/29/12 3:15								
SN-2								
	depth	revolutions	time	width	area	RPS	V (m/s)	discharge
4.8								
4.7	0.06	31	40	0.15	0.009	0.775	0.23637545	0.002127379
4.5	0.04	12	40	0.2	0.008	0.3	0.09732874	0.00077863
4.3	0	0	40	0.2	0	0	0.00950976	0
4.1	0.02	26	40	0.2	0.004	0.65	0.19978421	0.000799137
3.9	0.04	24	40	0.2	0.008	0.6	0.18514771	0.001481182
3.7	0.02	26	40	0.2	0.004	0.65	0.19978421	0.000799137
3.5	0.07	15	40	0.2	0.014	0.375	0.11928348	0.001669969
3.3	0.1	15	40	0.2	0.02	0.375	0.11928348	0.00238567
3.1	0.06	16	40	0.2	0.012	0.4	0.12660173	0.001519221
2.9	0.18	11	40	0.2	0.036	0.275	0.09001049	0.003240378
2.7	0.32	20	40	0.2	0.064	0.5	0.15587472	0.009975982
2.5	0.32	30	40	0.2	0.064	0.75	0.2290572	0.014659661
2.3	0.32	8	40	0.2	0.064	0.2	0.06805574	0.004355568
2.1	0.28	10	40	0.2	0.056	0.25	0.08269224	0.004630765
1.9	0.2	9	40	0.2	0.04	0.225	0.07537399	0.00301496
1.7	0.08	5	40	0.2	0.016	0.125	0.046101	0.000737616
1.5								
							total (m^3/s)	0.052175253
9/29/12 3:30								
deer creek								
0	depth	revolutions	time	width	area	RPS	V (m/s)	discharge
0.5	0.13	30	40	0.375	0.04875	0.75	0.2290572	0.011166539
0.75	0.14	33	40	0.25	0.035	0.825	0.25101194	0.008785418
1	0.16	2	45	0.25	0.04	0.04444444	0.02251998	0.000900799
1.25	0.16	4	40	0.25	0.04	0.1	0.03878275	0.00155131
1.5	0.185	25	41	0.25	0.04625	0.6097561	0.18800361	0.008695167
1.75	0.21	0		0.25	0.0525			0
2	0.2	0		0.175	0.035			0
2.1	0.125	19	41	0.1	0.0125	0.46341463	0.14516509	0.001814564
2.2	0.11	55	41	0.1	0.011	1.34146341	0.40219624	0.004424159
2.3	0.12	59	41	0.1	0.012	1.43902439	0.43075525	0.005169063
2.4	0.12	46	41	0.125	0.015	1.12195122	0.33793845	0.005069077
2.55	0.11	25	41	0.15	0.0165	0.6097561	0.18800361	0.00310206
2.7	0.085	0		0.175	0.014875			
2.9								
							total (m^3/s)	0.050678155

Figure 4.3



ICP-MS & IC Results

			ICP-MS				
	9/22/12						
	Aluminum	Cadmium	Copper	Iron	Magnanese	Lead	Zinc
	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb
Site 1875	8245	2.08	32.19	2123	1000	0.96	439
Site 1935	8173	2.20	33.41	2133	1014	1.04	456
Site 2085	9082	2.48	36.16	2380	1188	1.59	521
Trib 2095	42943	31.76	76.52	14872	12149	1.32	4880
Site 2120	12097	5.12	37.12	2640	2167	1.44	904
SN-2	13372	8.56	48.68	1317	3131	1.70	1585
SN-3	7810	5.13	23.64	601	1945	0.84	924
DC-5	6.9	below detect	2.92	147	20	0.14	51
	9/29/12						
	Aluminum	Cadmium	Copper	Iron	Magnanese	Lead	Zinc
	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb	ug/L ppb
Site 0m	1344	0.41	1.31	2549	392	1.16	119
Site 450	2812	0.81	1.32	3182	422	0.95	204
Trib 460	23904	5.45	24.61	24037	2414	1.04	1082
Site 485	5178	1.20	3.60	4493	590	1.03	264
Site 900	7192	1.63	5.42	5757	807	0.94	344
Trib 915	6877	3.33	117.98	7553	1302	0.27	759
Site 940	6927	2.04	34.65	5739	910	0.75	439
Site 1875	7863	2.04	32.74	2119	1017	0.96	429
Site 1935	8019	2.03	31.28	2360	1104	1.01	463
Site 2085	8507	2.24	30.11	2263	1155	1.13	494
Trib 2095	43622	33.97	70.75	17376	12398	0.62	5141
Site 2120	11251	4.91	32.68	2876	2124	1.01	876
SN-2	12963	8.11	36.93	1316	3024	1.51	1474
SN-3	8101	4.74	23.55	1112	1871	1.10	792
DC-5	6.5	below detect	0.29	188	27	0.16	37

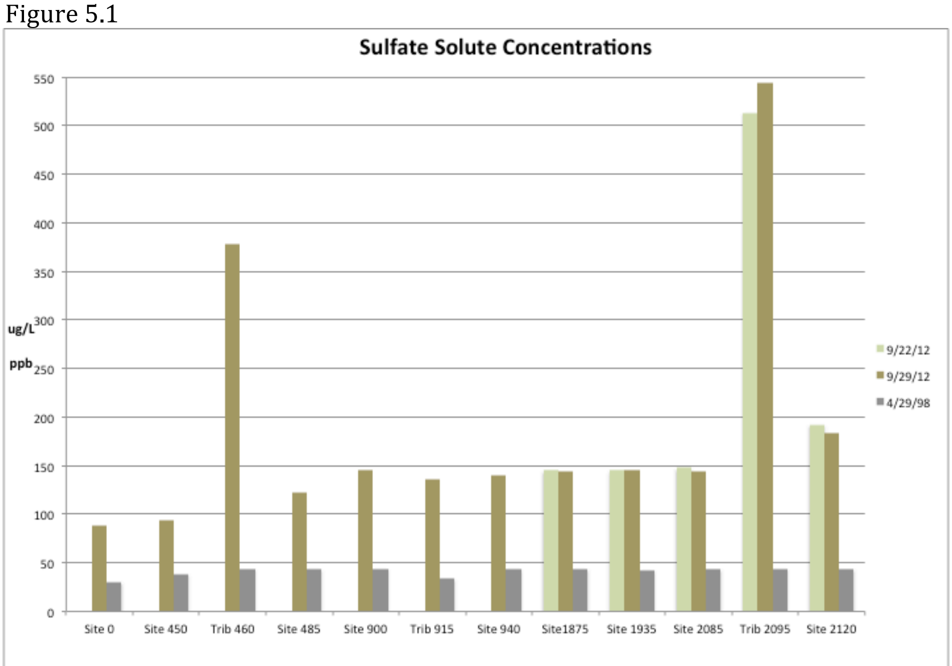
	IC	
	9/22/12	9/29/12
Site 0		88.9
Site 450		94.3
Trib 460		378.0
Site 485		123.0
Site 900		145.8
Trib 915		135.9
Site 940		139.4
Site1875	145.1	143.7
Site 1935	145.3	146.0
Site 2085	147.6	144.6
Trib 2095	513.1	544.0
Site 2120	192.3	182.9
SN-2	203.4	206.3
SN-3	128.8	133.3
DC-5	23.6	25.5

Chapter 5
Analysis

Sulfate

The presence of sulfate as a byproduct of the weathering reaction of pyrite serves as an important proxy for determining flow source. Samples were analyzed by LEGS using Ion Chromatography, providing concentrations present in solute. In evaluating the data, its clearly evident the sourcing of sulfate in the upper Snake River. Tributaries 460 and 2095, which both had extremely high levels of dissolved metals, show a similar trend in sulfate concentrations. This is indicative of a weathering as well as contact with mineralized material as the water percolates through the subsurface. Water temperatures well below what was observed upstream of these tributaries further hint that lateral inflow was making significant contributions. Of additional interest is how high these concentrations are above that which was measured in 1998, although the higher mean discharge values of July are much greater than those of September. This would hint that as inputs of "new" water decrease, and snowmelt tapers off, sulfate solute concentrations rise to the corresponding lack of dilution occurring.

Figure 5.1

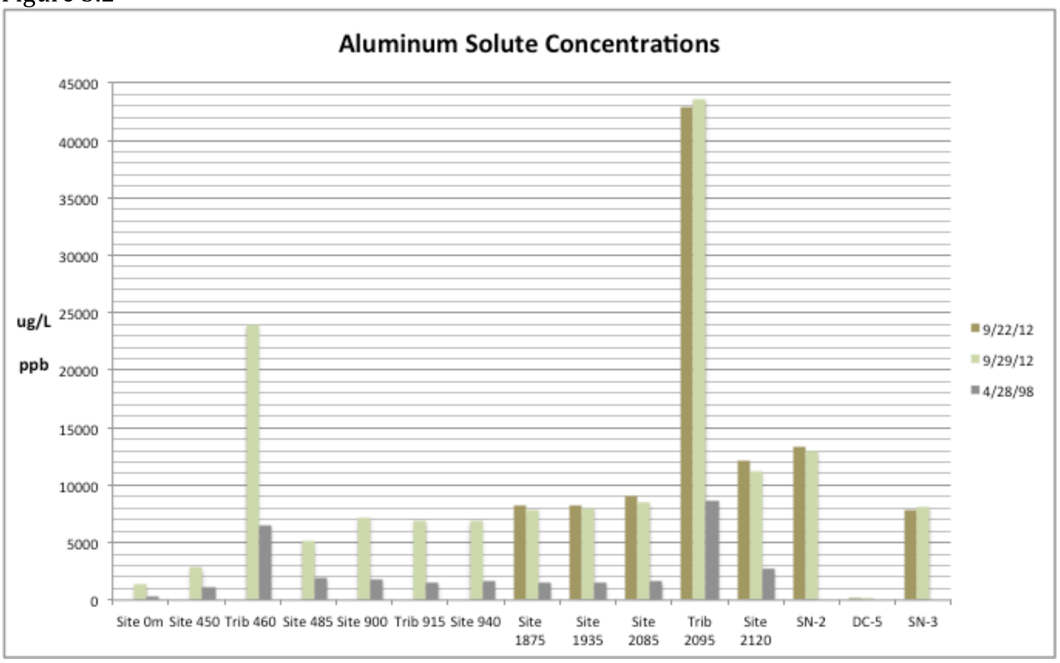


As previously detailed, the reaction in which sulfate is generated also creates hydrogen ions. With this is established a clear relation between changes in pH, the rendering anions, and the subsequent dissolving/mobilization of metals. Here we see a statistically significant (r^2>95%) trend between observed pH and measured sulfate concentrations for both sampling days. As similar levels were observed at sites tested a week apart, this process would appear relatively intransigent.

Aluminum

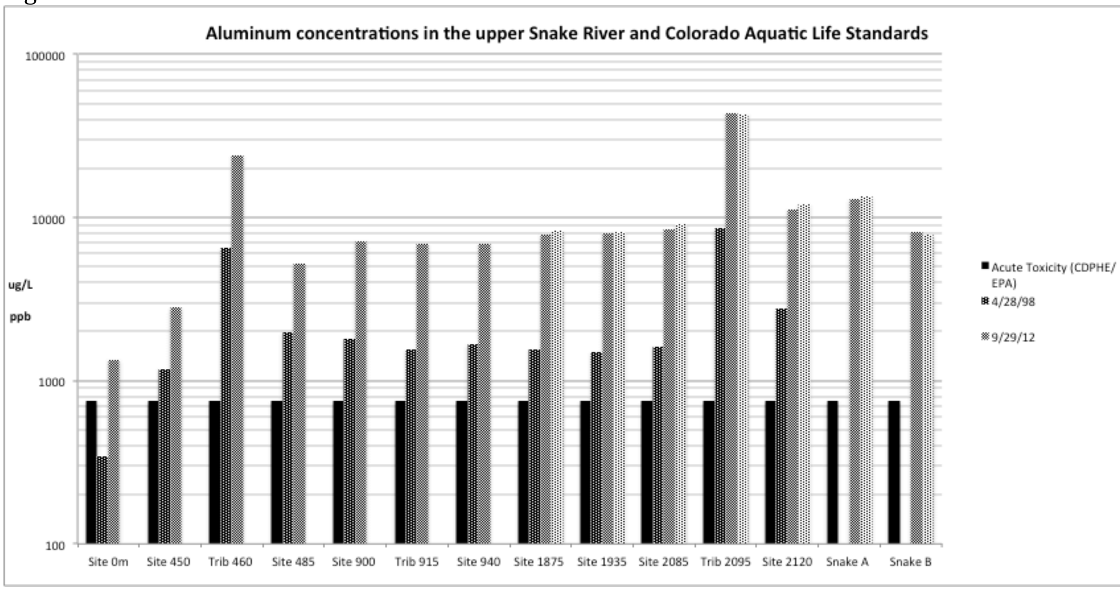
As aluminum is a metal that is sensitive in terms of solubility to pH, we expect to see high concentrations which correlate to observations of low pH along the upper Snake River. Tributary 460, which had high amounts of sulfate present, showed significant levels of dissolved aluminum. At least a four-fold increase from that recorded in 1998, though again this does not account for differences in discharge that would serve to reduce these concentrations through dilution.

Figure 5.2



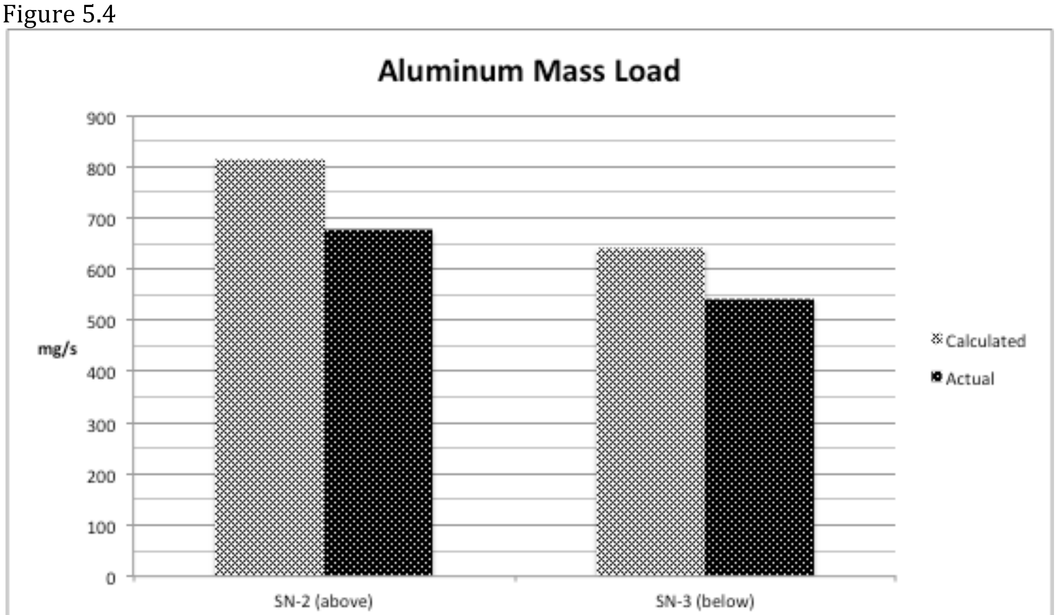
Assuming an average water hardness value of 41 mg/L (Boyer et al, 1999) to calculate CDPHE Aquatic Life Standards, it is very clear just how high these aluminum concentrations are in comparison. The logarithmic scaling highlights a difference by nearly 2 orders of magnitude at its highest levels. It also infers how these levels change relative to observed pH. Particularly, how pristine inflows such as Deer Creek make drastic reductions in dissolved concentrations of aluminum. Although these levels remain still remain high enough to be acutely toxic to most aquatic species.

Figure 5.3



But if these concentrations are falling with the neutralizing effect of high pH, pristine waters beyond the amount of dilution occurring then what explains the significant mass reductions? Using discharge measurements and known concentrations from lab analysis we are able to calculate a mass balance to help explain this. Through a mass load calculation outlined in the methods section, we can empirically solve for the unknown mass load after the confluence of the Snake River with Deer Creek and additionally compare this with the actual observed concentration. As we see here, taking into account the dilution occurring by Deer Creek inflow, a significant reduction in dissolved aluminum mass is occurring. This can be attributed to its precipitation from solute due to the rise in pH that makes such high levels no longer soluble. This is also visually evident in this portion of the reach below the confluence, as chalky silver residue coats the streambed.

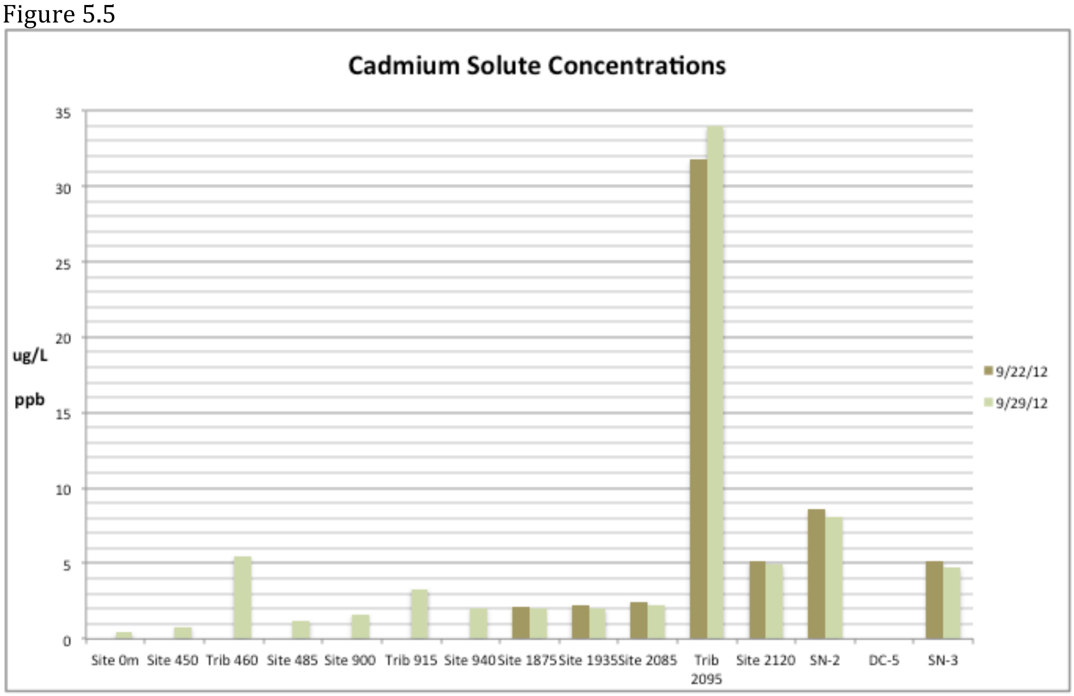
Figure 5.4



Cadmium

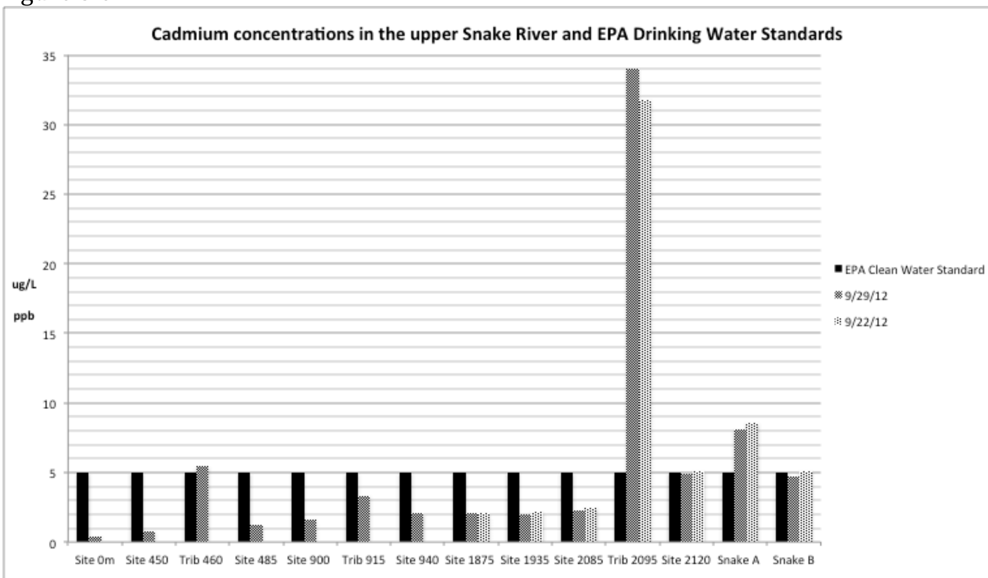
Cadmium is an extremely toxic metal that is often found in zinc ores. Concentration levels of cadmium observed in upper Snake River were relatively low throughout the headwaters, with notable increases in tributaries and below their conflux. The concentrations observed below Trib 940 until Site 2086(m) seemed governed by in-stream processes and chemistry. However, Trib 2095 exhibited a concentration almost 10 times above the proceeding. When compared to Trib 460, which has similar pH/TDS characteristics and trends in metal concentrations, this was still exceedingly high. The differing geology of this tributary is perhaps responsible for the increased loading observed, with granite being the predominate material in which (low pH) groundwater would contact and hence dissolve.

Figure 5.5



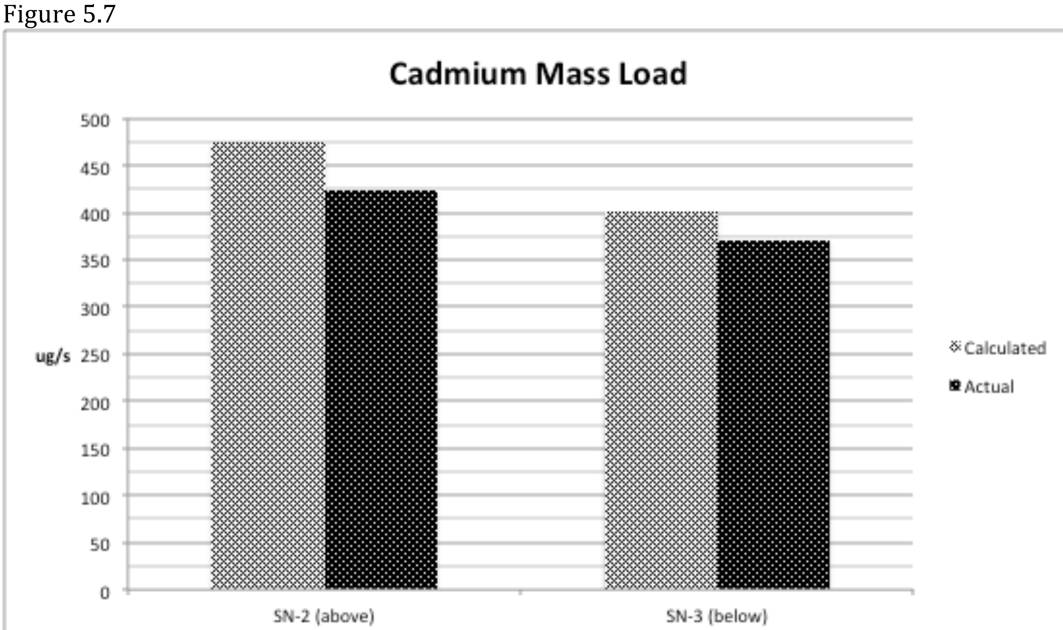
There is an overall lack of definitive information regarding the toxicity of cadmium in terms of an Aquatic Life Standard (EPA, 2001), as there is no testing method known to accurate express this. However, it is regulated list as a primary contaminant for EPA Clean Water Standards as they pertain to drinking water. Regardless of water hardness, the maximum level allowed is 5 ppb or 5 ug/L. In the graph below we see that much of the upper Snake is well below this amount with only a slight exceedence at Trib 460. Although further downstream we see that Trib 2095 is well above this amount, but 25m below the conflux these levels are highly diluted and these levels fall very near to the standard again. Between Site 2120 and SN-2 further enrichment is occurring, perhaps due to the river flowing through a noted iron bog, but again these levels fall below 5 ppm just after the conflux with the pristine waters of Deer Creek.

Figure 5.6



From the calculated and actual mass loads above and below the confluence with Deer, there are slight differences that would indicate precipitation is occurring. But it's important to note that due to the variability between calculated loads versus actual, this amount could be well less than the 100 ug/s observed.

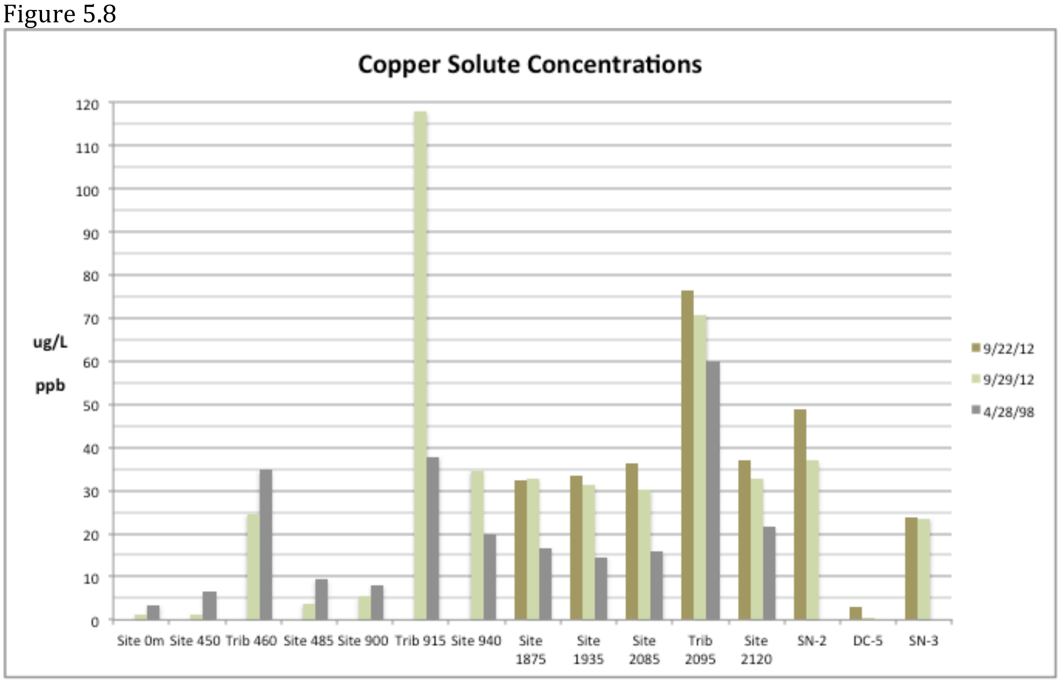
Figure 5.7



Copper

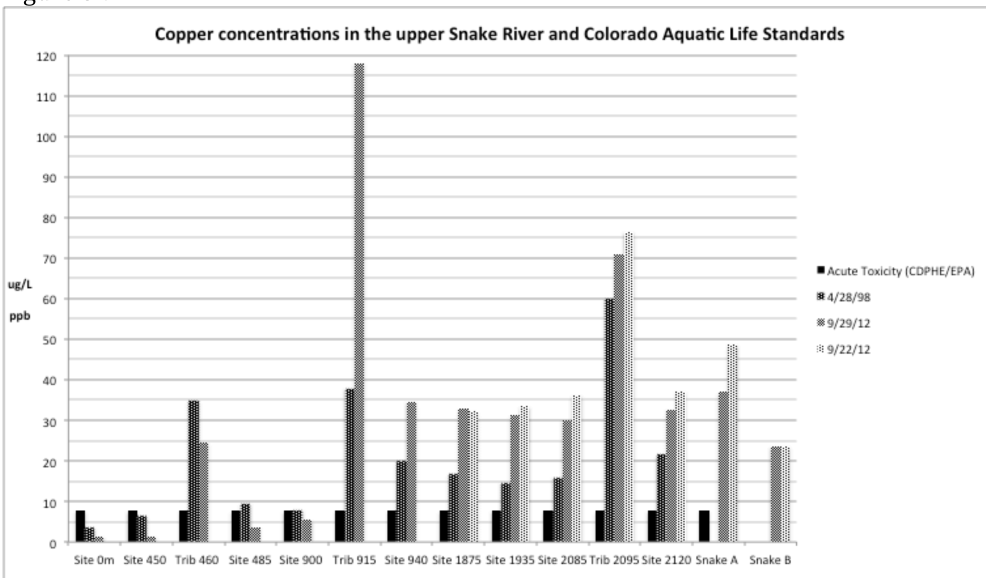
Concentrations of copper observed through the upper Snake River show a much differing distribution than other heavy metals. Though Trib 460 and 2095 exhibit spikes in concentration, this are levels not much higher than historical measurements from 1998 which could again be explained by differences in water inputs, discharge, or dilution. Particularly interesting is that Trib 915, which showed almost no elevated metal concentrations above stream baselines across the panel, is the highest concentration. This tributary shared nearly identical physical characteristics with the Snake River in terms of pH, TDS, and temperature, so this is a peculiar result. This is also indicative of surface, in-stream loading of metals as there is no indicators of lateral inflow or seepage that are presence at other tributaries.

Figure 5.8



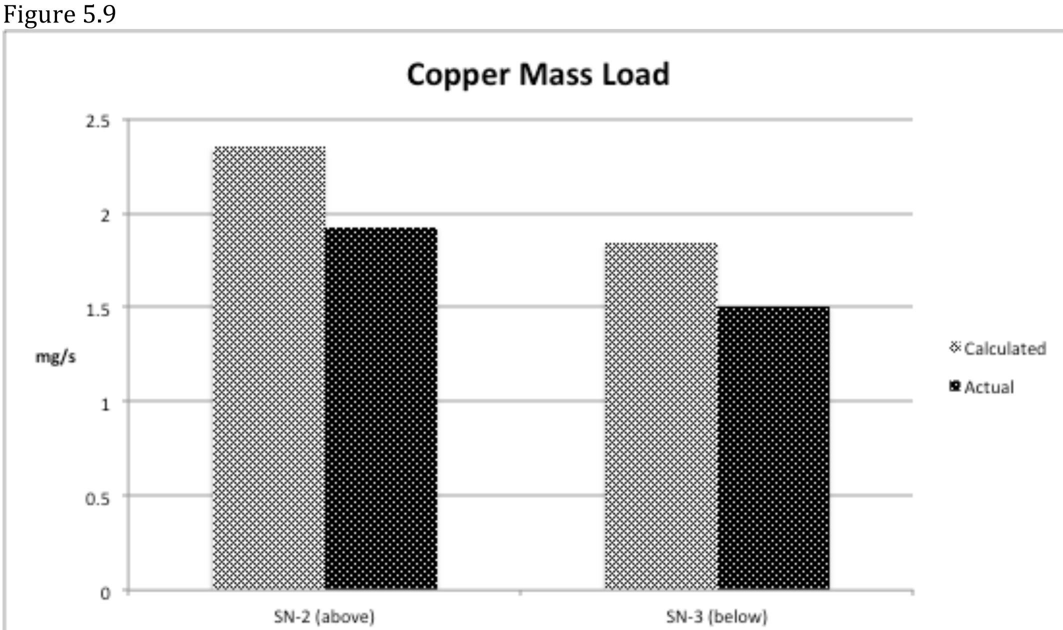
Again using an average water hardness value of 41 mg/L (Boyer et al, 1999) to calculate CDPHE Aquatic Life Standards for copper, we see that concentrations observed above Trib 915 are actually lower than historical data. This is the only metal to exhibit this trend, and further supports the idea that in-stream processes are the primary enrichment source. As periods of lowest flow and least water inputs such as September show a inverse relationship with the levels measured in July of 1998. Trib 2095, a primary loading source of other metals, here shows only slightly increase above 1998 data. Of further concern is how elevated copper levels remain through the remainder of the reach, exceeding acute toxicity levels even below the confluence with Deer Creek.

Figure 5.9



From computing the mass loads, there is evidence of precipitation occurring. Though we again see a variation between calculated and actual measurement, so the amount is likely well less than the .8 mg/s.

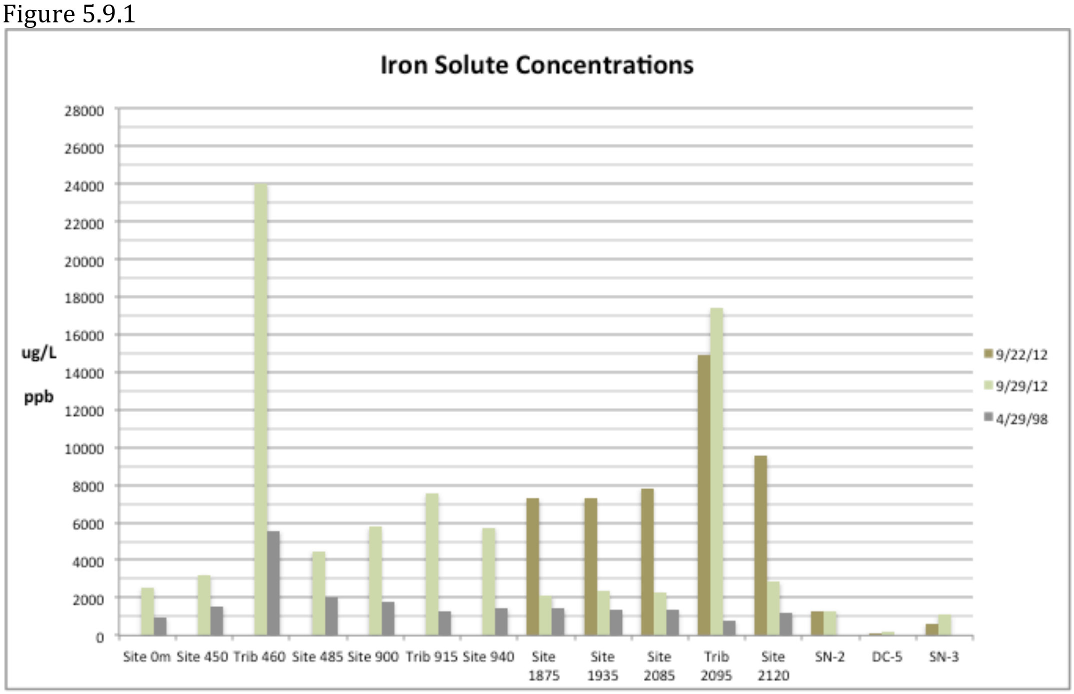
Figure 5.9



Iron

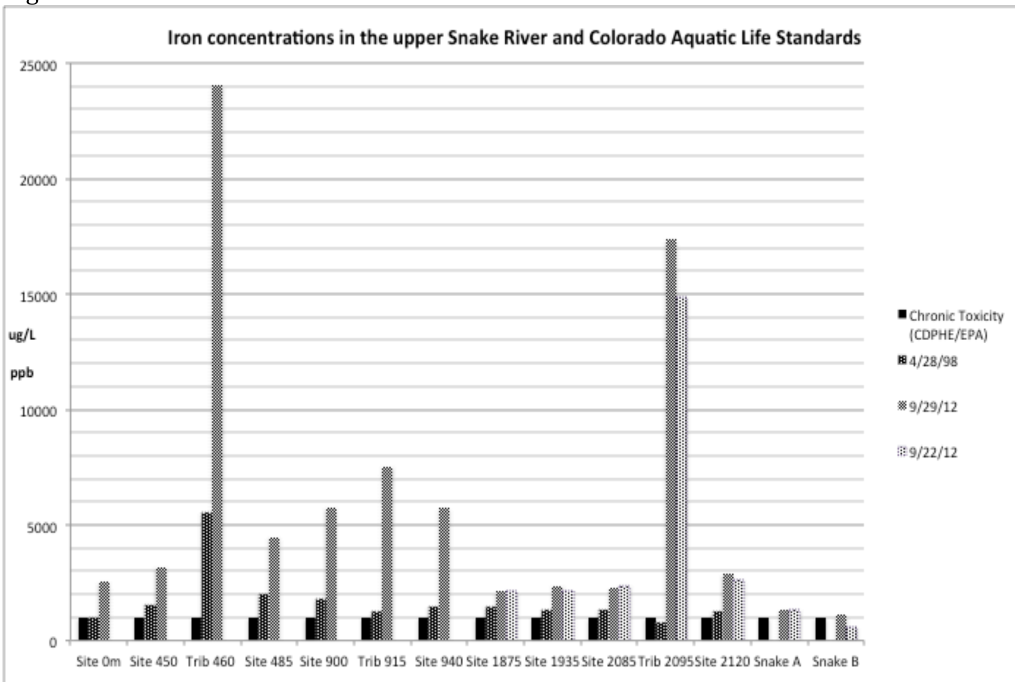
As iron is implicit in the creation of acid rock drainage, we can draw similar conclusions to its concentration as proxy for pyrite weathering. Throughout the upper Snake River, it appears that iron concentrations are well above historical data. This can be also possibly explained by periods of decreased flow such as September having less water inputs to dilute, but because 2012 had a premature snowmelt this could have additionally exposed more (pyrite-laden) rock sooner than normal and therefore increasing the weathering rates of weathering. Trib 460 shows an extremely high level of dissolved iron, much higher than that observed elsewhere, which was very evident visually with a redish rust coating the streambed of both the entire tributary and 25m downstream of the confluence where the sample was collected. The peaks in concentrations at Trib 460 and 2095 are similar to those of aluminum, although significant variations between 9/22 and 9/29 support the inherent variability of iron concentrations due to photochemical influence at different times of day or uv conditions. (Bencala et al, 1988). Therefore any conclusion regarding these concentrations when such fluctuations are present in the data are highly dubious.

Figure 5.9.1



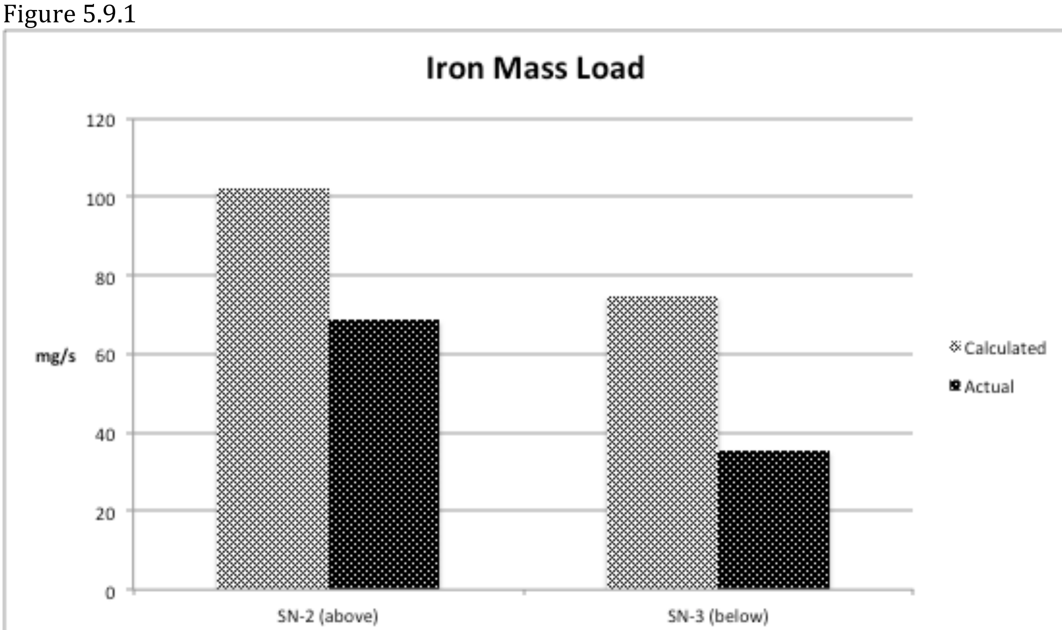
Iron is a difficult metal to evaluate against CDPHE Aquatic Life Standards due to its influence on water hardness and how it is calculated. But using the average water hardness value of 41 mg/L for the upper Snake River(Boyer et al, 1999) it is still possible to make a basic comparison that for most of the reach concentrations of iron exceeded the 1000ppb (ug/L) standard. However, as similarly observed with aluminum, the solubility of iron is particularly influenced by low pH.

Figure 5.9.9



The largest discrepancy in mass loads between calculated and observed concentrations for all metals evaluated was that of iron. The aforementioned dependence of iron solubility on pH is well demonstrated here by the near 50% reduction in mass load after the pristine inflow of Deer Creek. Although this subsequent loss of mass from the water column as precipitate could have been eventually been remobilized by photochemical reactions that render ferrous iron back into its ferric state, which also helps explain the variation and sources of error between calculated and actual loads.

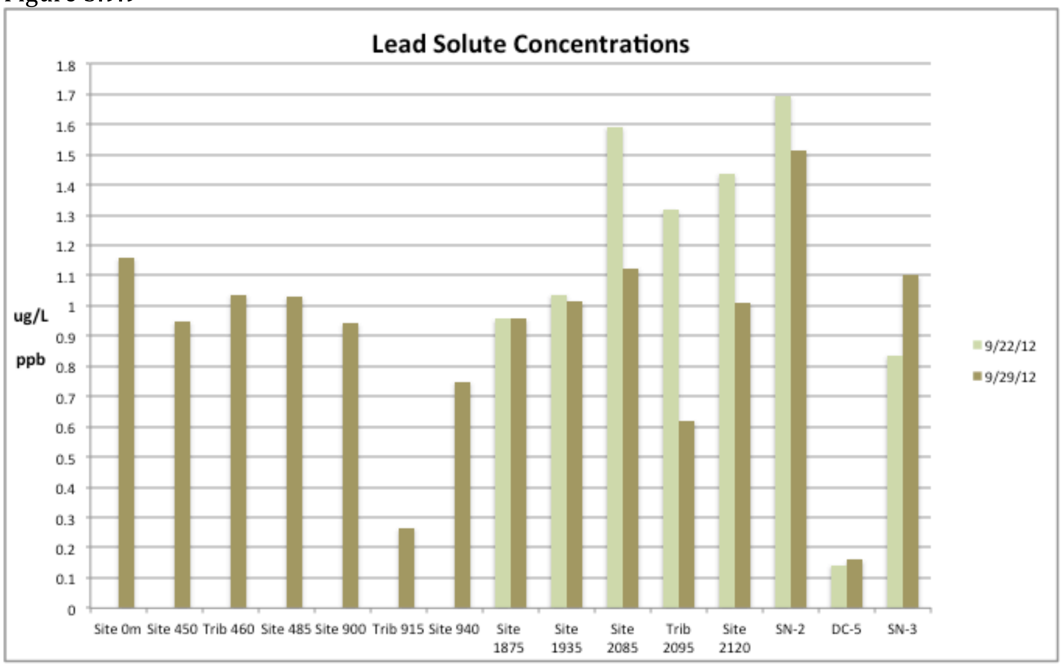
Figure 5.9.1



Lead

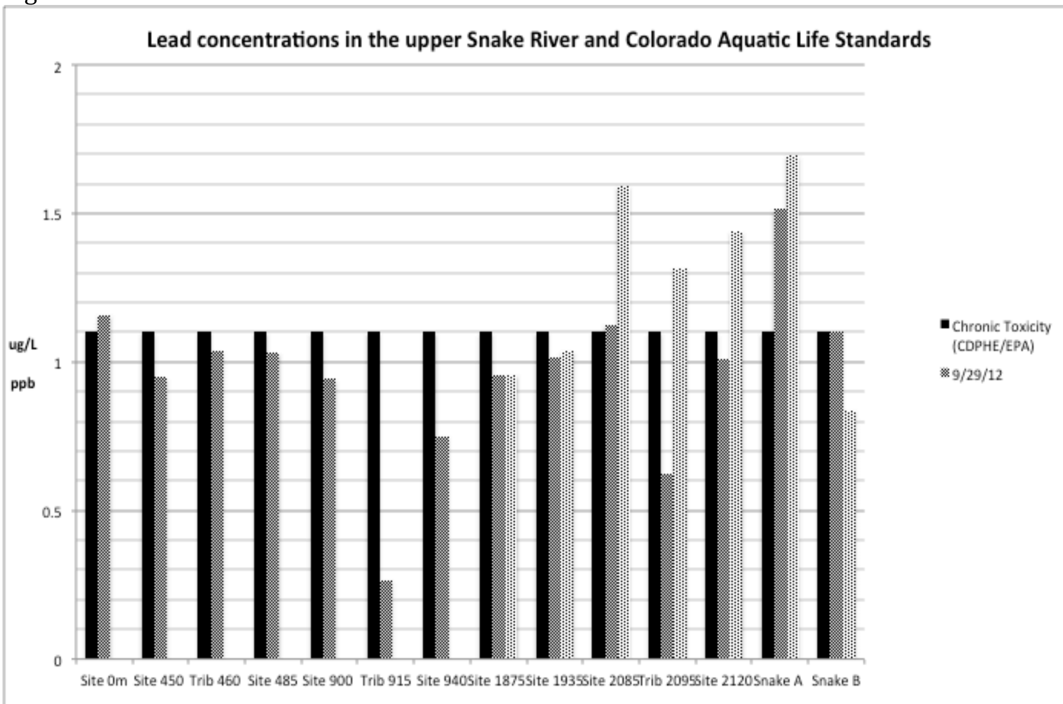
Of all the metals evaluated for this project, lead showed one of the most stable concentrations observed throughout the reach. It did not provide any great flux or excessive enrichment, but did exhibit significant fluctuation in measurements between 9/22 and 9/29 at certain cites.

Figure 5.9.9



Lead concentrations remained below CDPHE Aquatic Life Standards for nearly the entire reach, only spiking at Trib 2095 and remaining only slightly above the standard until after the conflux with Deer Creek. No mass loads were calculated due to the relatively small concentrations and high inherent sources of error due to data variability. Lead is perhaps the least harmful metal present in the upper Snake River in terms of concentration in relation to discharge, even though it has a low threshold for toxicity.

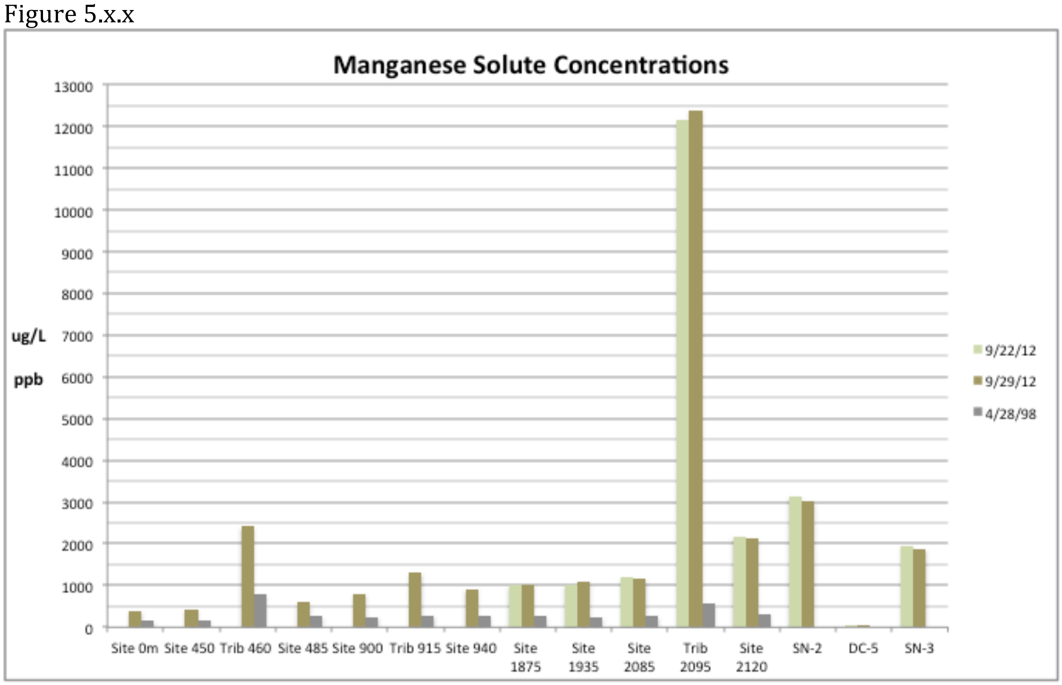
Figure 5.9.x



Manganese

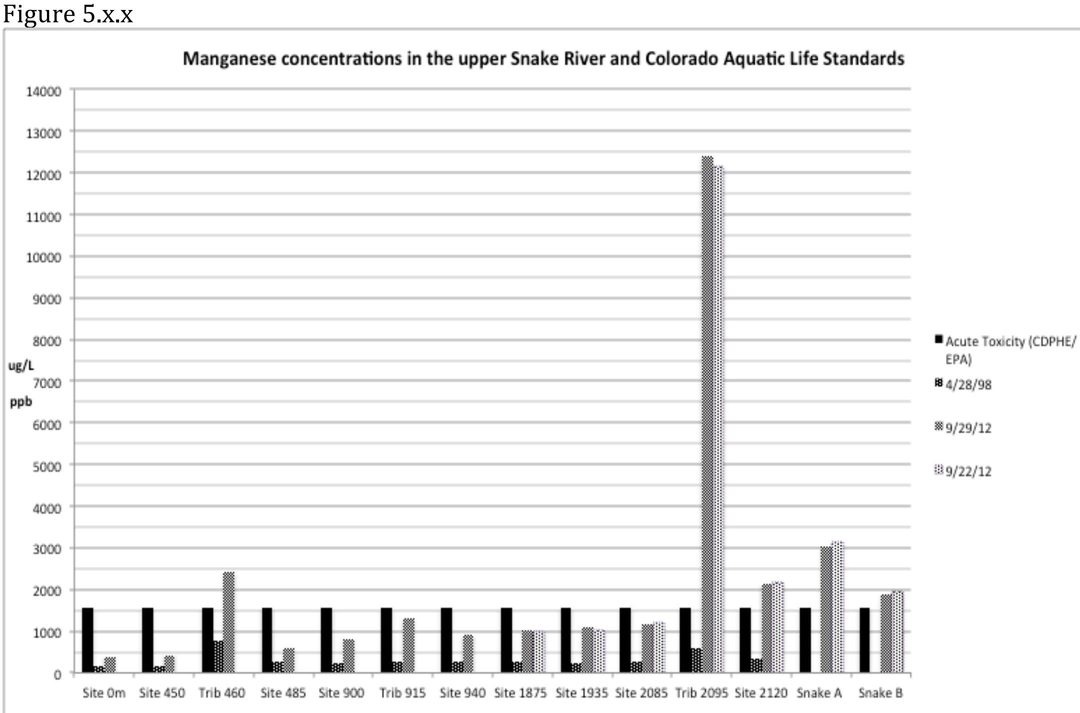
Manganese did not display much variation in the data along the upper Snake. Tributaries were the peak concentrations observed, particularly at 2095 which was 12x above baseline. This proved well above historical data levels, which is likely due to low flow conditions reducing dilution.

Figure 5.x.x



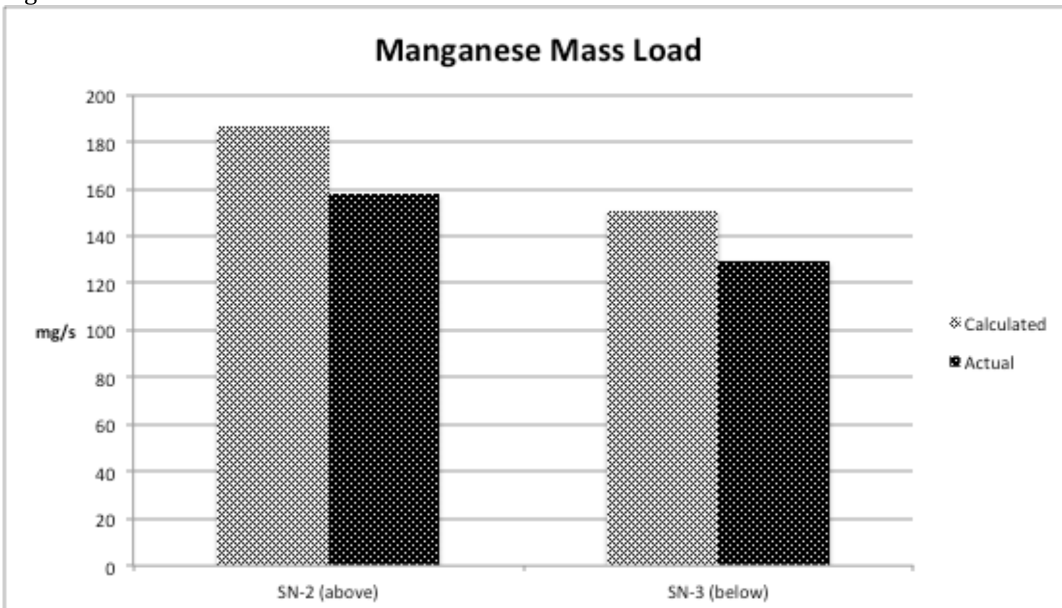
Manganese is difficult to evaluate against CDPHE Aquatic Life Standards due to its abundance as a mineral and taking into account how water hardness affects toxicity levels. By using water hardness value of 41 mg/L for the upper Snake River(Boyer et al, 1999) the acute to toxicity standard of manganese is 1556 ug/L. These levels are exceeded in the below Trib 2095 and remain so after the confluence with Deer Creek, though only slighty.

Figure 5.x.x



Manganese showed very similar calculated and actual concentrations in terms of mass load. It indicates that precipitation could be occurring, however it is also possible that uptake with sulfate to render magnesium sulfate could help explain this decrease.

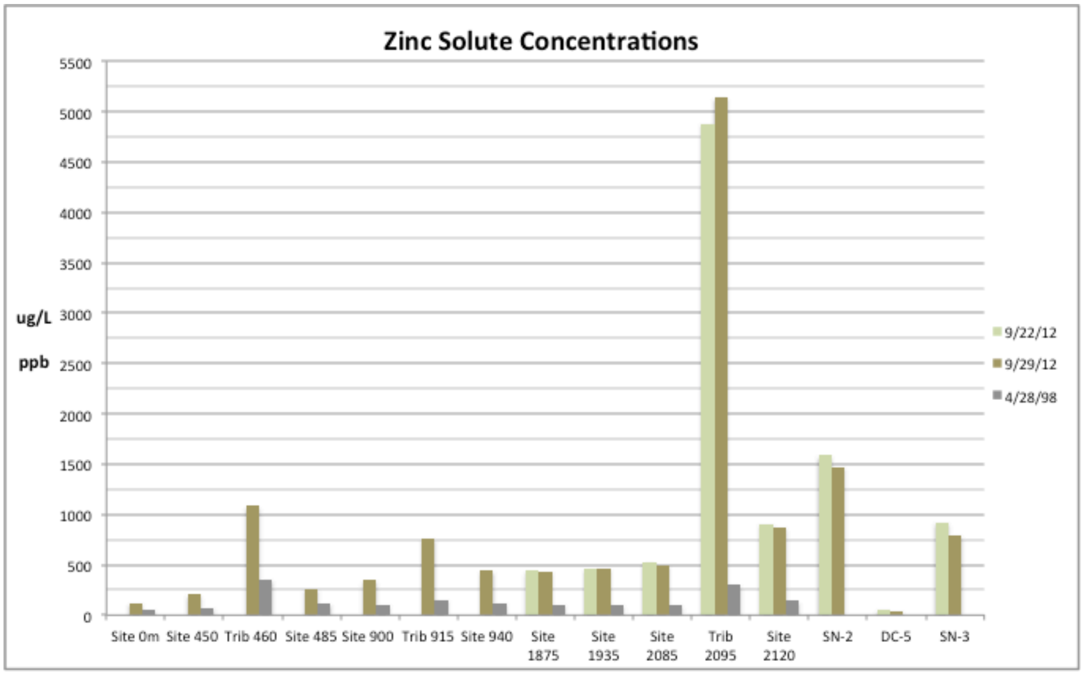
Figure 5.x.x



Zinc

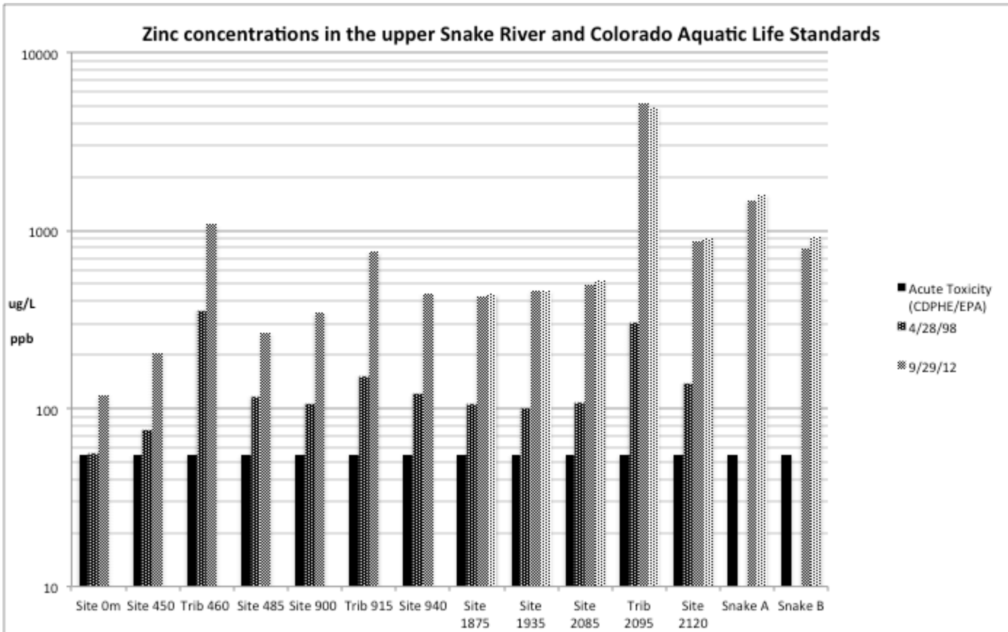
The levels of zinc measured throughout the upper Snake River are extremely high and present a particular hazard in such high concentrations due to its intransigence to pH. Tributaries seemed to be a primary source, even in those such as Trib 915 which hinted at water chemistry dominated by surface flows. Concentrations observed at Trib 2095 were a full order of magnitude over levels above stream baseline, which results in a doubling of in-stream amount after its confluence with the upper Snake. Another 50% increase occurred between Site 2120 and SN-2, a trend similarly observed with copper and also perhaps due to flow through more mineralized material.

Figure 5.x.x



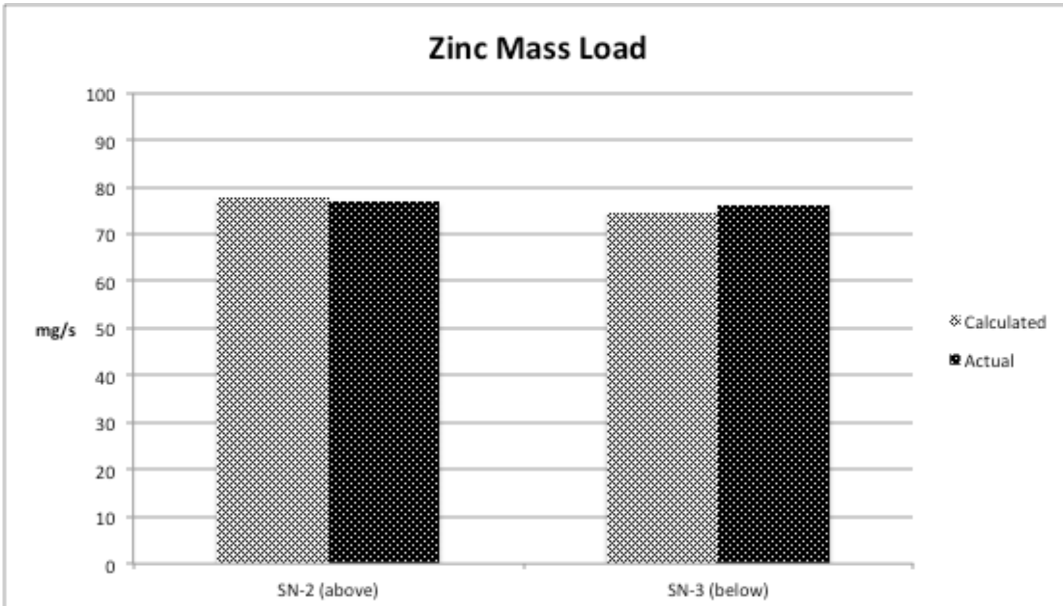
The necessary logarithmic scaling of measurements throughout the upper Snake River makes obvious the exceedingly high concentration of zinc present. Again using the 41 mg/L water hardness average (Boyer et al, 1999), we further see that zinc concentrations exceed acute toxicity levels for aquatic life by at least a full order of magnitude at each site in the reach. For Tib 2095 this proves to be a conservative estimate, as the observed concentrations amount to two orders of magnitude beyond this standard. This nearly doubles the in-stream concentration below its confluence with the Snake. Accordingly, zinc is a metal of serious concern and a primary limitation in the stream in terms of biotic life. As zinc also demonstrates insensitivity to changes in pH in terms of solubility, this metal is being transported further downstream that any others observed, underlining its threat well below the sampling area of this project.

Figure 5.x.x



Here we seen the intransigence of zinc to pH conditions demonstrated in the mass loads calculated and observed at site SN-2 and SN-3. Of particular interest are how these amounts are nearly identical, inferring that almost no precipitation is occurring and this metal load is remaining in solute well after the additional pristine inflow of Deer Creek. This well exemplifies the dangers surrounding the presence of zinc in the water column, especially when accounting for its exceedence of toxicity standards. It also serves to explain why fish stocking is necessary to maintain fish populations, as zinc loading at the headwaters of the upper Snake is implicit in making the stream environment largely uninhabitable.

Figure 5.x.x



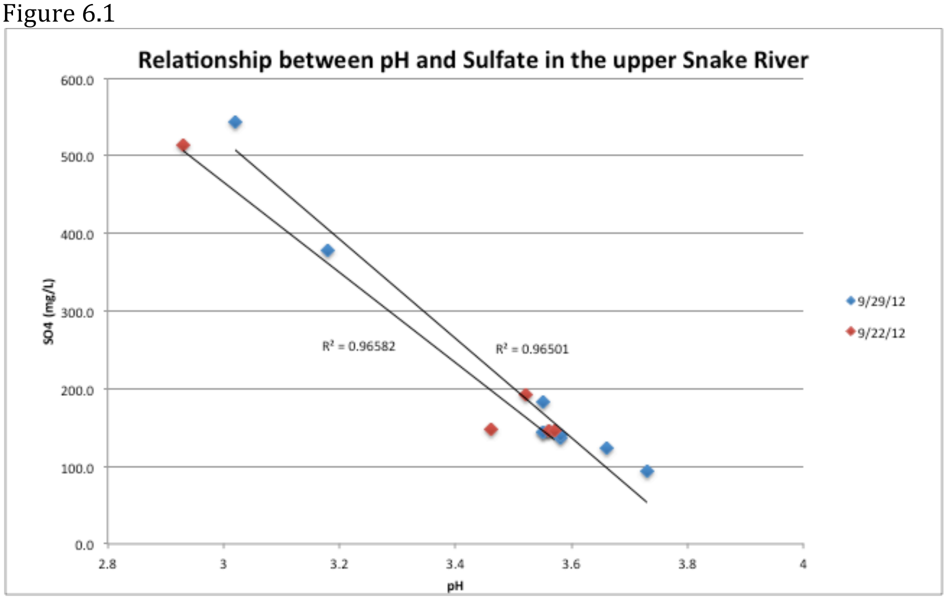
Zinc Mass Load
mg/s
100
90
80
70
60
50
40
30
20
10
0
SN-2 (above)
SN-3 (below)
Calculated
Actual

Chapter 6
Conclusions

<u>Sulfate</u>

When comparing collected field observations of pH to levels of sulfate observed in samples, a relationship was indicated between increasing concentrations of sulfate and reductions in pH. Both sampling days showed this trend, with high r^2 values indicating significant correlation.

Figure 6.1



As the presence of sulfate as a proxy for pyrite weathering and the rendering of hydrogen ions, this provides additional insight into stream chemistry and dominant processes of metal enrichment occurring. Tributary 915, for example, demonstrated levels of sulfate (and pH conditions) slightly below the Snake River above its confluence, indicating groundwater sourcing. The observed lower temperature of this inflow further supports this hypothesis. Other tributaries with high concentrations of sulfate also had corresponding levels of iron, which is implicit in the weathering of pyrite-bearing minerals. However, a statistically valid correlation could not be established between iron and sulfate concentrations. This is could be due to fluctuations in observed iron between 9/22 and 9/29 due to photochemical reactions and precipitate processes.

All sampled sites did show sulfate concentrations well above historical data, but it is difficult to say exactly what is the cause. It could reflect increased weathering, higher discharge values of the Upper Snake during mid-summer months, or decreased groundwater contributions due to falling water tables from reduced recharge. More recent data would provide greater insight into these changes, allowing for more conclusive comparison.

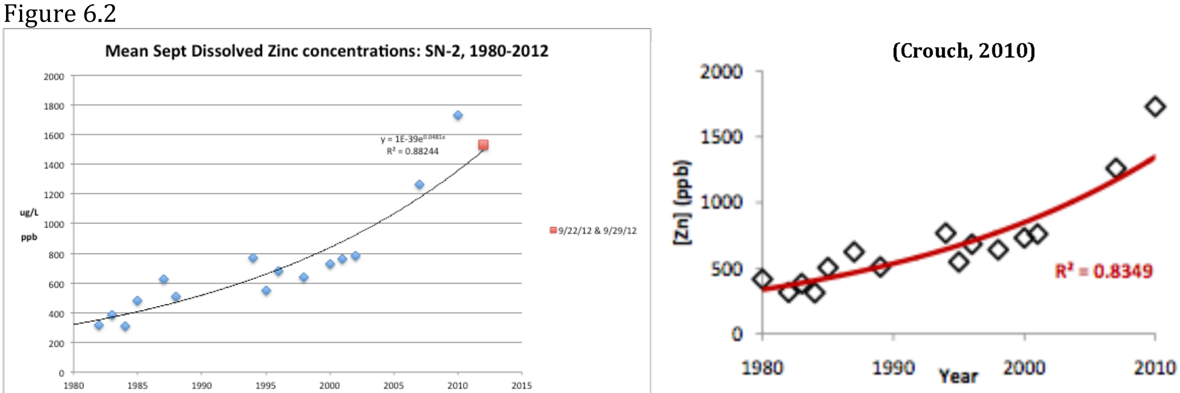
<u>Metals</u>

Metal concentrations did not unilaterally increase when compared to historical data. In the case of copper, the upper portions of the reach had significantly lower levels. For the reductions of copper observed at Trib 460, there were massive increases in other metal concentrations such as aluminum and iron. High sulfate concentrations further indicate this is due to weathering byproducts. Trib 916, on the other hand, showed relatively smaller increases in these metals and drastic increases in copper. As this tributary shows water chemistry characteristic close to those observed in the Snake, and temperature well below baseline, this suggests lateral inflow become the dominant source of water and helps explain the rise in copper concentrations. Since Trib 460 is at a higher elevation, a decreasing water table could have also possibly reduced groundwater contributions to this particular stream. This is supported by the decrease in copper as well as a rise in metals that are more soluble at low pH and also indicative weathering processes. Increased concentration of copper at Trib 2095, a stream with high contributions of lateral inflow as demonstrated in tracer testing by Caitlin Crouch and evident in observed low water temperatures on sampling days, provides additional evidence of copper as indicative of groundwater.

Despite metals such as aluminum and iron observed at extremely high concentrations throughout the upper Snake, these levels were reduced drastically upon the confluence with the pristine waters of Deer Creek. Zinc, on the otherhand, also having similarly high concentrations, remained in solute even after the confluence. This was demonstrated in the mass loads, highlighting both the intransigence of zinc towards pH changes in terms of solubility and the threat it presents to water quality further downstream.

The concentrations of zinc observed at SN-2 were high and well above average, though less than those taken in 2010. However, when the averaged data from 9/22 and 9/29 was added to the existing available record, a higher statistical correlation value resulted. This provides greater confidence in the findings of previous research that indicated an exponential increase of zinc concentration in the upper Snake River is occurring.

Figure 6.2



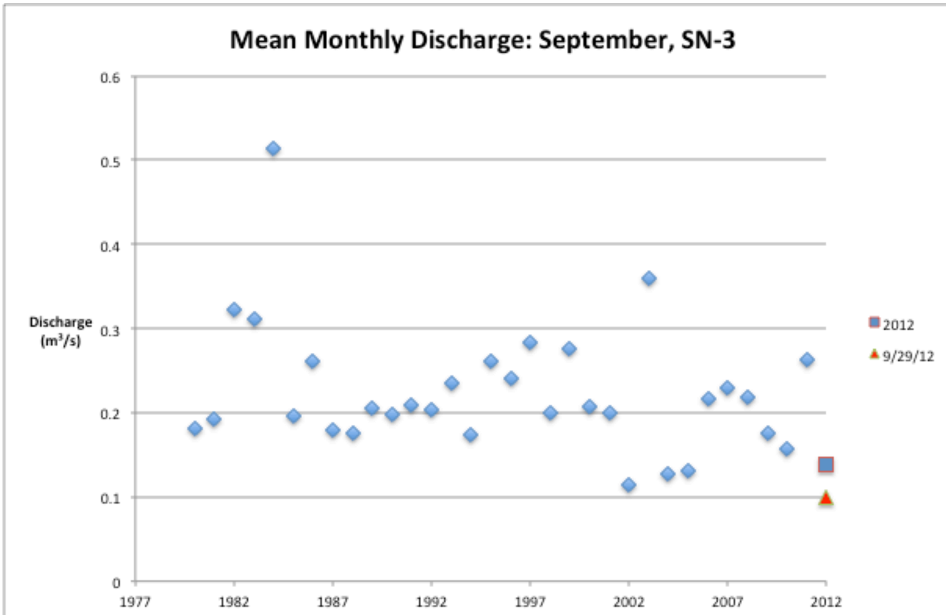
Conditions

Snake River discharge observed on 9/22 and 9/29 were nearly 40% lower than average over the 63 years of available data. If trends in early snowmelt continue, coupled with increased warming in the Rocky Mountains and reductions in summer precipitation due to climate change, these flows may become further become the norm. Water table levels will drop accordingly, as they did in 2002, and in the process exposing more mineralized material to both weathering and oxidation. The transition from a linear to an exponential increase in zinc concentration observed appeared to be related to these periods of reduced flow, indicating for the future a potential for even greater metal-enrichment in the upper Snake. As this river later confluences with Peru Creek, an AMD-impacted stream, this problem will only be enhanced.

As evident in observation from this project and those previous, groundwater contributions play a significant role in changing concentrations of certain metals. As recharge is reduced, in turn reducing the water table, some tributaries may become further dominated by ARD inflows. Massive increases in sulfate, aluminum, iron, zinc in certain tributaries are already evidence of this, especially when compared against historical data. Greater reductions in stream pH will also play in role in rendering waters more soluble to metals and enhancing their transport downstream further.

When observations from 2012 at Site SN-3 are included with the long-term monthly means from September, the frequency of anomalously low flow years appears to be increasing. If such trends continue, metal concentrations may exceed even exponential increases. The corresponding reductions in pristine inflows that currently serve to dilute these concentrations and neutralized low pH conditions will only serve to compound this. As a result, environments downstream that are currently marginal for aquatic life will become acutely. This presents a unique challenge to resource managers and stakeholders who must maintain access to clean waters, as does the presence of the Snake River on the EPA 303(d) Impaired Waters list. Without the implementation of remediation strategies, currently hampered by outdated provisions of the Clean Water Act, the presence of metals in the Snake River will also remain “in perpetuity”.

Figure 6.3



<u>Presence of Rare Earth Metals</u>

Thanks to the diligent work of Fred in the Laboratory for Environmental and Geologic Studies, the results of ICP-MS analysis showed extremely high levels of rare earth metals in Trib 2095. Here the concentrations of Samarium , Neodymium , Uranium, Lanthanum, Gadolinium, Dysprosium, Erbium, Praseodymium, and Terbium were over an order of magnitude of those observed elsewhere in the reach. Considering the extremely low flows of this tributary, this is quite surprising. This site also did not correspond with any know surveyed ore or mineral deposits in the area which would explain such high levels, making their occurrence all the more peculiar. As such rare earth metals are just as their name implies, the presence of them into a low-flow, high alpine stream is a topic that merits greater research. Tracer and isotope testing could possibly provide additional insight, as well as continued sampling of Trib to determine if these levels are rising.

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Appendix

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 souce	Zn (µg/L)	Cd (µg/L)	Cu (µg/L)	Mn (µg/L)	SO_4 (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	54.96
9/26/1982	*Boyer et al., 1999*	366	1	15	605	62.78
10/3/1982	*Boyer et al., 1999*	422	1	16	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	
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	

USGS Gauge Station 09047500:SNAKE RIVER NEAR MONTEZUMA, CO.

YEAR	Monthly mean in cfs (Calculation Period: 1980-09-01 -> 2011-09-30) Period-of-record for statistical calculation restricted by user											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1980									32.1	22.5	18.4	15
1981	12.8	10.6	10	20.1	57.6	141.3	64.7	39.4	34	25.4	21.9	14.4
1982	12	12.3	13	15.2	54.6	307	233	102.7	57	40.8	25.7	22.5
1983	15.2	14.4	13	13.8	36.1	344.3	242.3	93.5	55	31.7	25.2	22
1984	16.7	15	12.9	14.2	136.8	348.3	242.9	176.7	90.7	66.9	39.5	25.9
1985	18	15.2	14.9	34.4	130.1	292.2	105	57.8	34.7	31.9	21.7	17.5
1986	12.3	11.7	12.7	22.8	109	362.1	195.3	72.5	46.1	32.5	24.8	18.6
1987	17	16	14.5	26.9	144.5	216.8	78.8	52.6	31.7	19.4	17.2	18.5
1988	10.8	10.3	12.6	22	101.1	320.1	115.1	51.8	31	27.7	19.8	16.3
1989	12.5	10.7	11.8	28	137.5	228.5	120.2	63.1	36.2	25.6	18.2	15.5
1990	12.1	9.74	12	17	65.7	296.6	113.3	45.6	35.1	30.1	20.5	19.1
1991	14.6	12.8	11.8	12.5	109.7	261.5	93.9	53.1	37.1	25.6	14.7	12.2
1992	11.5	9.84	8.83	16.8	146.5	184.8	92.9	48.2	36	23.7	20.2	17.7
1993	11.8	9.88	9.93	12	112.9	352.4	207.7	63.4	41.7	29.4	17.6	14.6
1994	11.2	10	9.75	19.5	148.1	226.7	57.1	33.4	30.8	23.4	15.9	15
1995	11.5	9.4	9.39	11.1	28.7	441.7	384.9	110.8	46	26.9	20.1	21.3
1996	15.3	14.7	12.2	22.4	203.5	438.6	181.2	55.8	42.4	37.1	25.5	18.4
1997	16	16.4	17	20.4	124.8	519.8	200.2	104.4	50	35.5	27.3	20.1
1998	16.6	13.5	12.4	18.1	91	181.1	123.2	60.5	35.2	30.1	20.4	14.2
1999	11.8	9.22	10.2	14.8	78	364.6	200.8	119.8	48.9	33.5	21.5	14.8
2000	12.3	11	11.5	23.5	184.5	210.9	77.5	42.1	36.6	25.7	21.1	19.1
2001	16.6	13.9	11	18.1	166.8	240.6	120.3	51	35.2	26.5	18.6	16
2002	15.9	13.3	12.1	19.5	52.1	55.8	29	22.9	20.1	22.9	17.7	16
2003	16	14.6	13.1	18.1	174	359.7	138.3	67.6	63.5	30.6	25.9	20.9
2004	15.8	11	17.4	24.8	86.5	99	58.2	30	22.6	23	20.1	19.2
2005	17.1	13.8	12.4	16.3	104.5	201.1	91.4	44.1	23.3	23.8		
2006				29.2	184	259.9	121	70.3	38.2	32.1		
2007				19.7	168.4	267.5	116.8	85.5	40.5	27.9		
2008				16.9	90.6	312	157.1	65.6	38.6	28.8		
2009				15.7	162.6	275.3	137.4	53	31.1	22.1	19	
2010				15.9	114.2	314.4	69.2	70.5	27.8	25.2	30.3	
2011				15.6	45.1	504.7	436.5	98.3	46.6			
2012 monthly Discharge	14	12	12	19	114	288	149	68	40	29	22	18