

AN ASSESSMENT OF THE EFFECTS OF ELEVATION AND ASPECT ON FLUX
OF AIRBORNE POLLUTION AND WATER QUALITY IN AN ALPINE CRITICAL-
ZONE: SAN JUAN MOUNTAINS, COLORADO, USA

A Dissertation

by

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ABSTRACT

The local, highly mineralized geology, along with years of mining and improper disposal of the tailings and acid-mine drainage have degraded the quality of surface water within the San Juan Mountains, specifically, the area between the towns of Silverton and Ridgway, CO. This area is a fragile ecosystem with inputs ranging from local geologic baseflow and mining to atmospheric flux (AF) of contaminants. Thus, significant questions arise: Does elevation or aspect affect the AF of pollutants, and is AF a potential source of water quality degradation in this study area?

It is assumed AF occurs on the slopes, as well as in streams, lakes, and ponds, which can be transported to nearby surface waters, further degrading them. Atmospheric deposition data were collected for aluminum, iron, manganese, nitrate, phosphate, and sulfate. Water chemistry data were collected for the same constituents as the atmospheric deposition, with the addition of temperature, dissolved oxygen, pH, and specific conductance. Samples were collected on a five-day sampling regime, over a three-week period, during a two-year period. Water quality samples were collected in-stream adjacent to the deposition-sample collectors. Collection sites were located on opposite sides of Red Mountain, at five elevations on each side, providing two different aspects.

Significant AF differences were detected between elevations for NO_3 and SO_4 on the northern aspect examined; however, no significant differences were found for AF on the southern aspect or between aspects. In regard to the water quality results, differences

were detected between multiple elevations for all constituents examined, except PO_4 , on both aspects; no differences were detected between aspects for the in-situ or the lab-analyzed water-quality constituents. No runoff occurred during this study; therefore, no conclusion regarding the impact of AF on water quality could be made. Additionally, environmental stochastic modeling was performed to examine how AF may have affected water quality if runoff had occurred. Based on these calculations and the assumptions upon which they were based, it was determined that the atmospheric flux of NO_3 , PO_4 , and Fe may be sufficient to affect the surface water quality in this study area if runoff had occurred.

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NOMENCLATURE

Al	Aluminum
DO	Dissolved Oxygen
Fe	Iron
m	Meters
mg	Milligram
Mn	Manganese
NO ₃	Nitrate
PO ₄	Phosphate
SO ₄	Sulfate
Sp. Cond.	Specific Conductance
T	Temperature
TF	Total Flux
TL	Total Load
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

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CHAPTER I

INTRODUCTION

Introduction

For decades people have been trying to better understand how we affect the physical world around us. Simple acts such as driving vehicles and buying a new computer have farther reaching impacts than we like to imagine. Studies have shown automobile exhaust and the constituents it introduces into the atmosphere can travel across state and country lines eventually depositing, and potentially causing harm, far from its origin (Lawrence, Painter, Landry, & Neff, 2010; Neff et al., 2008). Mining of metals for electronics and jewelry can have lasting impacts on the local environment, especially waterways (Burbank & Luedke, 2008; Macklin, Hudson-Edwards, & Dawson, 1997; Razo, Carrizales, Castro, Díaz-Barriga, & Monroy, 2004). Depending on the destination, this harm may be mitigated with dilution and distance, or unfortunately, it may be compounding the problems being experienced by an already stressed environment. One stressed environment lies within the San Juan Mountains of southwestern Colorado. These mountain, along with the entire mountain range dividing the western United States, fall within the path of the westerly trade winds, which are known to carry particulate and gaseous constituents from the west coast and as far away as Asia (Lawrence et al., 2010; Neff et al., 2008). With air-pollution on the rise and the growing need to preserve our fresh-water resources, it makes sense to study them in conjunction.

This dissertation was based in the San Juan Mountains near the towns of Ouray and Silverton. Atmospheric flux and stream water samples were collected for a period of three weeks in August, 2015. The research trip, equipment, and follow-up sample analysis was supported by myself and committee members.

Though the length of sample collection was short, sample sites were established, methods were tested, and conclusions were drawn from the results. I hope future research will expand upon these methods and results to garner a more complete picture of the effects of elevation and aspect on atmospheric flux and water quality in the San Juan Mountains.

Problem Statement and Objectives

This dissertation examines two major questions: how is atmospheric flux for a variety of constituents affected by elevation and aspect and how does in-stream water quality, for the same constituents, compare between elevation and aspect.

The objectives of this dissertation were to evaluate the role of elevation and aspect on the atmospheric flux of aluminum (Al), iron (Fe), manganese (Mn), nitrate (NO₃), phosphate (PO₄), and sulfate (SO₄) within the study area and to assess whether the atmospheric flux has significant effects on the surface water quality within the study area.

CHAPTER II

AN ASSESSMENT OF THE EFFECTS OF ELEVATION AND ASPECT ON THE FLUX OF AIRBORNE POLLUTANTS IN AN ALPINE CRITICAL-ZONE ECOSYSTEM: SAN JUAN MOUNTAINS, COLORADO, USA

Synopsis

Studies from around the world have shown atmospheric transport and deposition affect high elevation ecosystems. One such fragile ecosystem with inputs ranging from local mining to atmospheric transport and deposition is the San Juan Mountains of southwestern Colorado. This research addressed the question: does elevation or aspect affect the atmospheric flux of nitrate (NO_3), phosphate (PO_4), sulfate (SO_4), aluminum (Al), manganese (Mn), or iron (Fe) in the San Juan Mountains? I found elevation affects the flux of SO_4 and NO_3 ; however, none of the examined constituents were significantly different between opposing aspects. The second objective of this study was to determine if the atmospheric flux of NO_3 , PO_4 , SO_4 , Al, Mn, or Fe were potentially affecting surface water quality in the San Juans. It was determined that no precipitation runoff occurred during the study period, therefore, the flux (mass of a constituent per unit area per time) of these constituent was unlikely affecting surface water quality during this study.

Introduction

The long-range air-borne transport and deposition of pollutants have been documented at the global scale (Gouin, Mackay, Jones, Harner, & Meijer, 2004). Global-circulation patterns move air in consistent patterns all over the world. Particles, volatilized and solid, will drop out of the atmosphere, at some point. Deposition occurs through precipitation, dry deposition, vegetation interception, and cloud-vapor deposition (Burrows et al., 2009; Simeonov, Kalina, Tsakovski, & Puxbaum, 2003). The long-range transport of substances is monitored throughout the world; however, the contaminants examined vary between studies as do the elevations examined, and the methods used. Multiple studies are based in remote places to reduce the bias of local pollution sources (Gouin et al., 2004). A prime example of remote regions plagued by long-distance transport of pollutants is the Arctic regions (Gouin et al., 2004).

When global air currents reach the Arctic regions where the air is colder and has a higher density, some compounds have a high affinity for deposition and a low affinity for re-volatilization, making the polar regions atmospheric pollution sinks (Gouin et al., 2004; Kirchner et al., 2009). Evidence exists that besides the polar regions, areas of high elevation may also act as sinks for pollution deposition, specifically, mountainous regions (Kirchner et al., 2009; Semeena & Lammel, 2005).

Mountain ranges around the world are all susceptible to deposition of air-borne pollutants. A site-specific relationship between elevation and pollution deposition has been established, especially within mountainous regions of Europe and limitedly in the Eastern United States (Balestrini, Galli, & Tartari, 2000; Gouin et al., 2004; Kirchner et

al., 2009; NADP, 2014; Sickles Ii & Grimm, 2003; Simeonov et al., 2003; Xu et al., 2011). The Rocky Mountains of the western United States are no exception. Whereas the methods used in world-wide studies may be useful for designing new studies, it would be inappropriate to directly compare the deposition patterns detected in Europe to the mountains of the United States.

The Rocky Mountains, in the western United States, differ from other mountain ranges in the United States and throughout the world in a variety of ways, including the north-south trend and other factors which differ between continents such as weather patterns, pollution sources, vegetation species, and simply that different latitudes affect the way air-borne pollutants will be transported and be deposited. The Rocky Mountains, which include the San Juans, fall in the direct path of the westerly trade winds (Lawrence et al., 2010; Neff et al., 2008; Painter et al., 2007).

The San Juan Mountains, located in southwestern Colorado, USA, is a major mountain range, which is part of the Rocky Mountains. The San Juans encompasses ~32,000 km², which is 12% of the State of Colorado, and the range has numerous peaks that rise over 4,000 m in elevation (Painter et al., 2007; Southwest, 2016). As a high elevation ecosystem, the San Juan Mountains are a fragile component of what has recently been termed the critical zone (Giardino & Houser, 2015; NRC, 2001). This fragile ecosystem is susceptible to a variety of contamination pathways besides within as well regionally and globally (Lawrence et al., 2010). Locally, particles are derived from natural mineralization and mine tailings (Brodin, Helmig, & Oltmans, 2010; Sickles Ii & Grimm, 2003; Simeonov et al., 2003).

Two important components likely to affect the deposition of air-borne pollutants appear to be elevation and aspect. Alpine ecosystems are open systems; therefore, the effects of air pollution deposition may be adding to or compounding the impacts to this ecosystem caused by the historic and current mining activity. Air pollution has been increasing for many years, making atmospheric transport and deposition an important worldwide issue (Beiras et al., 2012; D. A. Burns, 2004). With air pollution on the rise world-wide and changing weather patterns associated with climate change, this region could be at greater risk than ever before of being impacted by atmospheric deposition (Barry & Chorley, 2009; Foley et al., 2005).

In the United States the National Atmospheric Deposition Program (NADP) compiles precipitation amounts and chemistry data, deposition data for select constituents, and compiles isopleth maps showing deposition patterns (NADP, 2014). The NADP has been operating since 1978, monitoring the precipitation chemistry in the Nation through a cooperative network of government agencies, educational institutions, non-governmental agencies (NGOs), and even some private companies (NADP, 2014). In addition to NADP monitoring in the Rocky Mountains, two previous studies in the San Juans have examined the atmospheric deposition of a variety of constituents, primarily metals, to the alpine system.

Lawrence et al. published a study in 2010 which took place in the San Juan Mountains that examined the dust deposition and biogeochemical flux of twenty-seven major, minor, and trace elements (Lawrence et al., 2010). The sample collection for this study took place in the winter and spring seasons from 2004-2008 and the study area was

a large clearing (elevation: ~3,500 m) north of the town of Silverton, CO (Lawrence et al., 2010). The results of this study found the size distribution and geochemical makeup of the dust deposited likely originated from regional (not local) sources, especially the arid and semi-arid regions of the Southwestern United States and possibly from as far as Asia (Lawrence et al., 2010).

The second study which examined atmospheric deposition within the San Juan Mountains was a master's thesis from Texas A&M University, which examined oligotrophic fens for the presence of atmospherically deposited lead (Pb). Oligotrophic lakes and wetlands (such as fens) are only open to atmospheric inputs because of the topographic position which does not allow for the input of surface drainage. This study found the timing of levels of lead in the fen sediments corresponded with the use and discontinuation of leaded gasoline (McClenning, 2012). If oligotrophic fens in the San Juans have been receptive to long-range transport and flux of Pb, how might they have been affected by the transport and deposition of other constituents? This study asks: does a difference exist in the atmospheric flux of aluminum (Al), iron (Fe), manganese (Mn), nitrate (NO₃), phosphate (PO₄), or sulfate (SO₄) at various elevations or opposing aspects in the San Juan Mountains? This study is defining atmospheric deposition as the concentration (mass/volume) of a measured constituent within a deposition sample. Flux is the amount (mass) of a measured constituent deposited per unit area of deposition per unit time.

The objective of this research is to evaluate the role of elevation and aspect on the atmospheric flux of aluminum (Al), iron (Fe), manganese (Mn), nitrate (NO₃),

phosphate (PO₄), and sulfate (SO₄) for this alpine area. Although this study examines atmospheric flux, it is important to acknowledge that the surface water in some areas of the San Juans is highly contaminated. Therefore, the second objective of this paper is to assess whether the atmospheric flux which occurred may have significant effects on the surface water quality. To address these objectives, this study examines three hypotheses:

H₁: Elevation has a significant effect on the atmospheric flux of SO₄, NO₃, PO₄, Al, Mn, or Fe.

H_{a1}: Elevation has no significant effect on the atmospheric flux of SO₄, NO₃, PO₄, Al, Mn, or Fe.

H₂: Aspect has a significant effect on atmospheric flux of SO₄, NO₃, PO₄, Al, Mn, or Fe.

H_{a2}: Aspect has no significant effect on the atmospheric flux of SO₄, NO₃, PO₄, Al, Mn, or Fe.

H₃: Significant precipitation runoff occurred, which could introduce atmospherically fluxed constituents into the local surface streams.

H_{a3}: Significant runoff did not occur, which could introduce atmospherically fluxed constituents into the local surface streams.

SO₄, NO₃, PO₄, Al, Mn, and Fe were selected for examination for multiple reasons: 1) the metals and sulfate are present locally in the San Juans in the lithology and surface waters, 2) NO₃ and PO₄ are known surface water contaminants which are closely

monitored in many fragile ecosystems, and 3) all six constituents are documented as being capable of long-range atmospheric transport and deposition.

Study Area

The study area for this research is located within the San Juan Mountains in southwestern Colorado, between the towns of Ridgway and Silverton (Figure 1). The aspects of two watersheds of interest trend in opposite directions. These watersheds are the Uncompaghre River and the Animas River watersheds. The Uncompaghre River flows through the towns of Ouray and Ridgway within Ouray County and the Animas River flows through the town of Silverton within San Juan County.

Five sample locations on each side of Red Mountain Pass were established. Sample collectors were deployed along four streams: Red Mountain Creek and the Uncompaghre River within the Uncompaghre watershed and Mineral Creek and the Animas River within the Animas watershed (Figure 1). On the north-facing (Ouray) side, the five sample locations were at ~3,379, 2,982, 2,937, 2,338, and 2,134 m above sea level; on the south-facing (Silverton) side, the five sample locations were at ~3,359, 3,083, 3,071, 2,839, and 2,804 m above sea level.

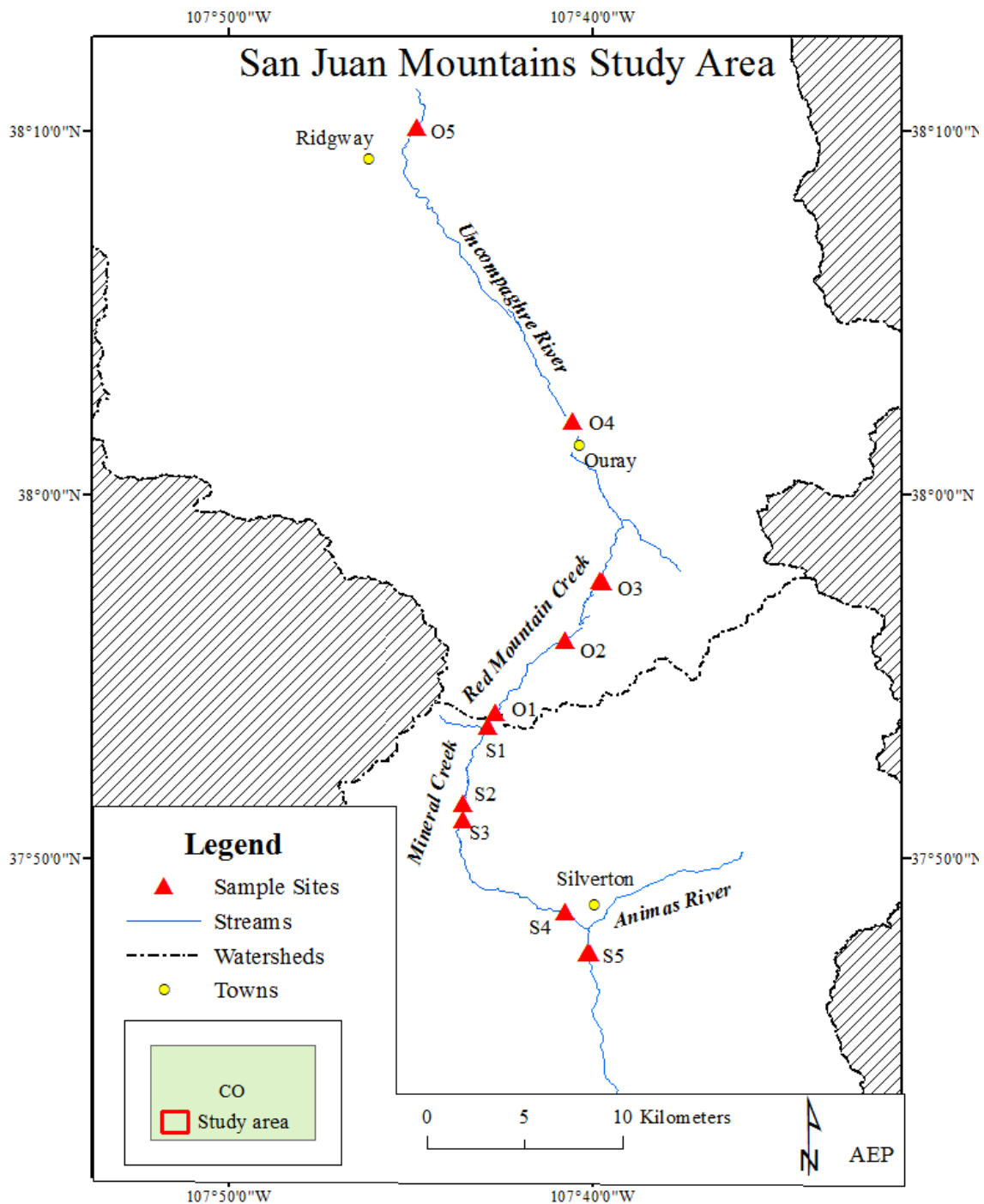


Figure 1. The study area is comprised of two watersheds between two aspects in Southwestern Colorado. Five sample sites were selected along Red Mountain Creek and the Uncompaghere River on the Ouray side of the mountain and along Mineral Creek and the Animas River on the Silverton side.

To understand the role the local environment plays in providing particles (pollutants), the geology of the area must be considered. The San Juan Mountains were an active volcanic area until the Pleistocene, when the volcanic activity ended (Blair, 1996b). The major formations present today (from youngest/highest elevation to oldest/lowest elevation) within the study area are the Burns Formation (Tuff-Breccia), the San Juan Formation (Tuff-Breccia), the Uncompaghre Formation (Quartzite and slate), the Cuttler Formation (Permian Red Beds), and the Hermosa Formation (Limestone) (Blair, 1996a, 1996b; Cross & Larsen, 1935). During the Pleistocene, the San Juans are thought to have been glaciated at least fifteen times (Blair, 1996b; Lipman, Steven, Luedke, & Burbank, 1978; Sinnock, 1981). The most recent major glaciation occurred approximately 18,000 years ago (Blair, 1996b).

The processes that have been operational in the area over a long time period have resulted in steep slopes, U-shaped valleys, and many glacial moraines of various ages (Blair, 1996b). Elevation in the study area ranges from ~2,000 to 3,400 m above sea level. The peaks within the study area have been eroded to create slopes with high surface roughness. Vegetation distribution along these slopes has also helped to increase surface roughness. Whereas the San Juan Mountains enhance adiabatic processes, the high surface roughness creates a variety of microclimate conditions.

The climate of the San Juan Mountains is a Dfb Koppen-type climate (Kottek, Grieser, Beck, Rudolf, & Rubel, 2006). The San Juans have a typical northern hemisphere cycle of the winter months having the lowest temperatures (average low winter temperature is -18.8°C) and the summer months being warmest (average high

summer temperature is 22.8°C) (County, 2015). Most of the precipitation within this study area occurs in the winter as snowfall; however, July and August are the wettest months with averages of approximately 7.6 cm of rainfall (County, 2015) (Figures 2 and 3). The local weather during this study was cool and rainy at the beginning of the sixteen-day sample period and became slightly warmer and dryer for the latter portion of the research (Figures 4 and 5). These differing weather patterns likely affected land-atmosphere interactions including atmospheric flux, dry and through precipitation.

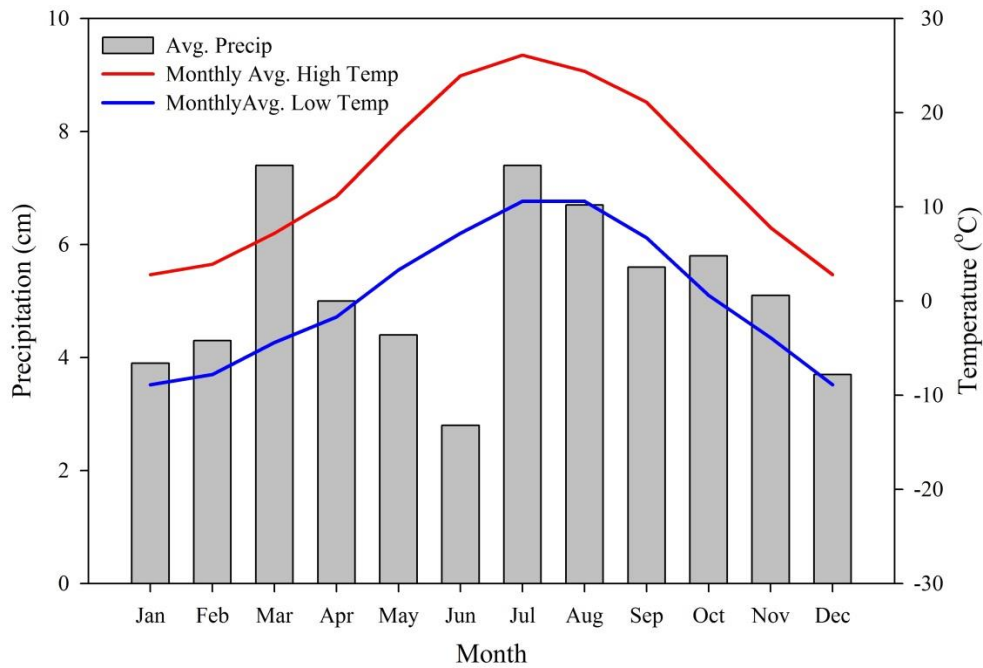


Figure 2. The average monthly weather (precipitation and temperature) records for Ridgway from 1981-2010 show July to be the wettest and warmest month.

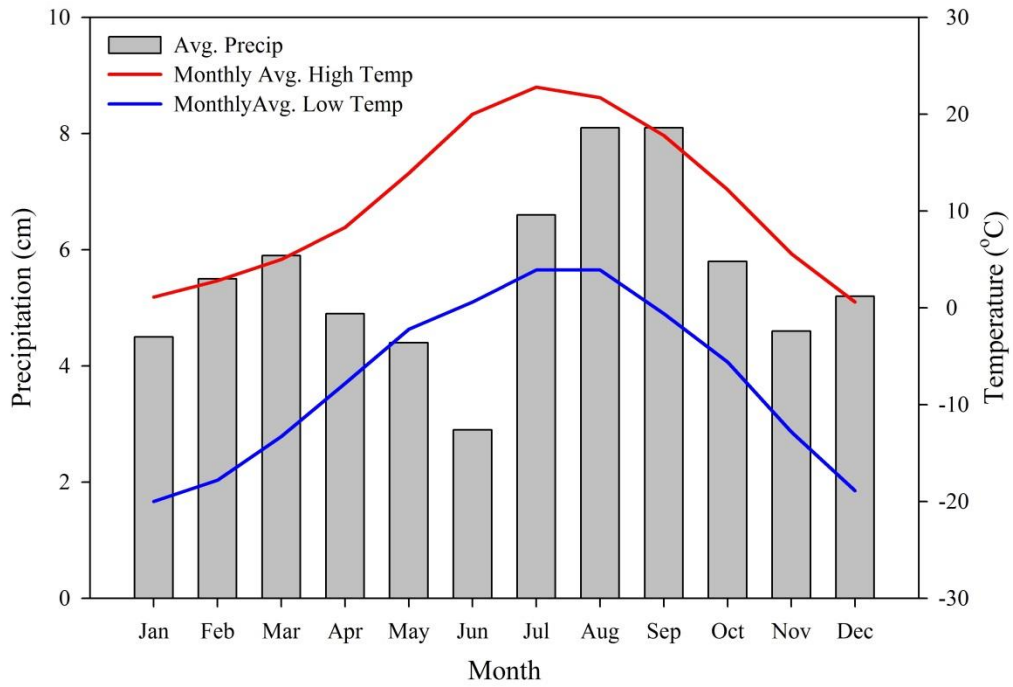


Figure 3. The average monthly weather (precipitation and temperature) records for Silverton from 1981-2010 show August to be the wettest month July to be the warmest month.

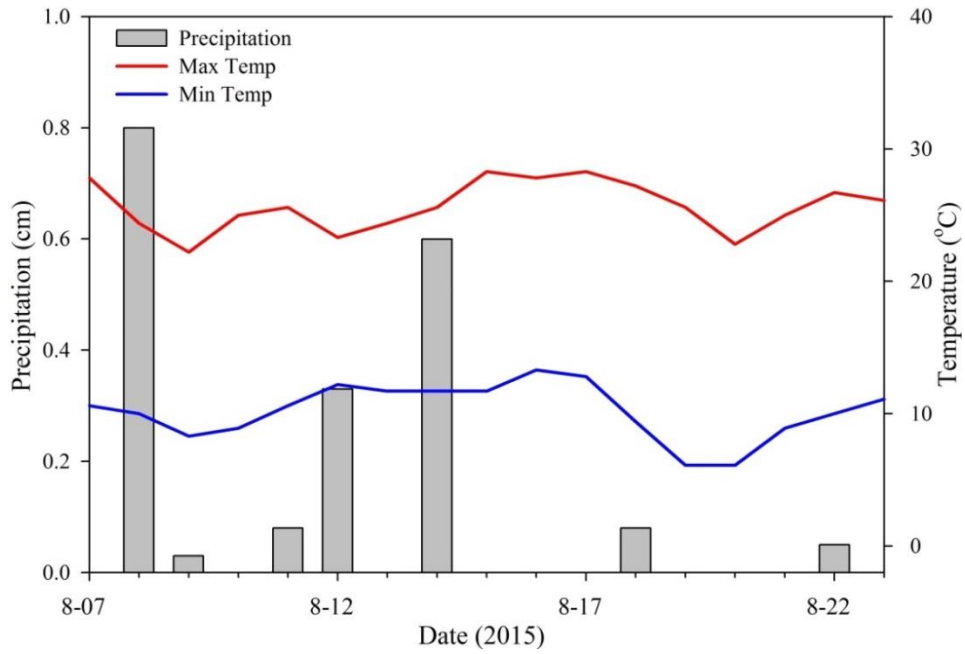


Figure 4. The weather (temperature and precipitation) of Ouray varied daily during the study period of this dissertation.

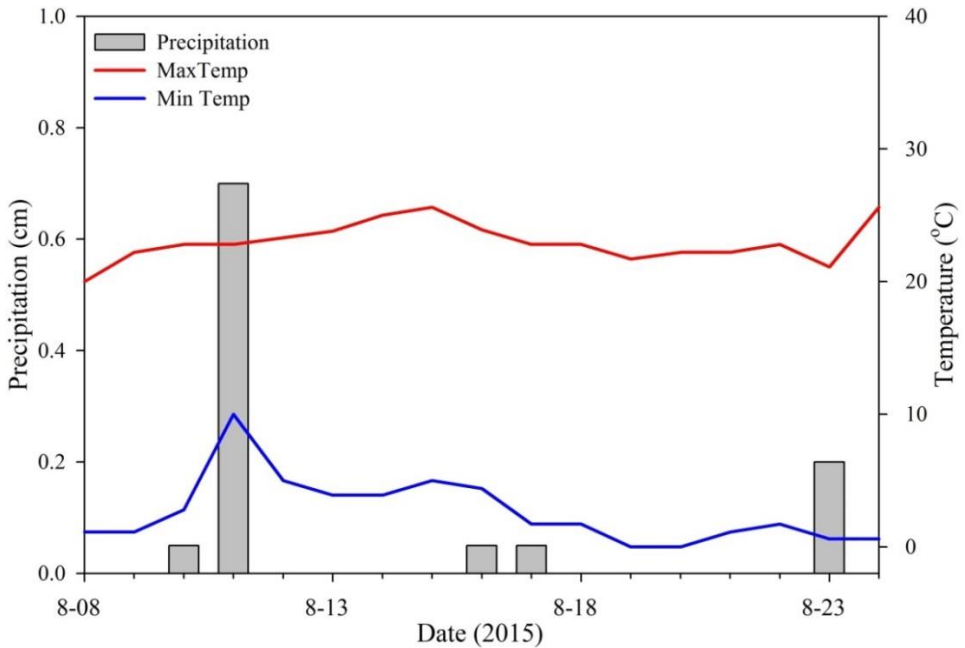


Figure 5. The weather (temperature and precipitation) of Silverton varied daily during the study period of this dissertation.

Methodology

The objective of this study is to determine the effects of elevation and aspect on the atmospheric flux of sulfate (SO₄), nitrate (NO₃), phosphate (PO₄), aluminum (Al), manganese (Mn), and iron (Fe) for this area of the San Juan Mountains. Atmospheric-flux samples were collected for SO₄, NO₃, PO₄, Al, Mn, and Fe at each of the five sample sites along the Red Mountain Creek/Uncompaghre River and Mineral Creek/Animas River. Composite wet-and-dry deposition samples were collected from each sample location every five days.

The deposition-collector design was based on a paper by Azimi et al. (2003) and was constructed of 1.2 m section of PVC pipe with a funnel-bottle collection apparatus attached at the top along with a rain gauge (Figure 6) (Azimi, Ludwig, Thévenot, & Colin, 2003).

Total deposition samples collected dust and precipitation falling into the funnel and was washed into the attached 250 ml Nalgene® bottle. The deposition samples were collected every five days and stored in fifty-ml centrifuge tubes prior to analysis. All samples were preserved using hydrochloric acid within twelve hours of collection.



Figure 6. The deposition collector was constructed of PVC pipe with a funnel attached through the top of a 250 milliliter Nalgene sample bottle. A piece of 12.7 mm PVC was attached to the top of the collector to which a rain gauge was attached for precipitation quantification.

The atmospherically deposited samples were analyzed for SO_4 , NO_3 , PO_4 , Al, Mn, and Fe. The metals were measured using an inductively coupled plasma mass spectrometer (ICP-MS). The anions were measured using an Ion Chromatograph.

Fifteen ml of each deposition sample was extracted for constituent analysis. Each remaining sample was filtered onto a sterile membrane filter (0.45 μm pore size). Each filter was weighed prior to filtering samples and then dried and re-weighed. The difference between the pre- and post-filtering mass was the amount of particulate deposition per unit volume filtered. This particulate mass was normalized to the original

fifty-ml sample by dividing the mass by the volume sampled and then multiplying by fifty, the original volume collected over the interior area of the funnel over the five-day collection period.

Atmospheric flux was determined using equation 1:

$$\text{Equation 1: } X = \left[\frac{\text{Conc} * \text{Particulate mass}}{\text{area}} \right] / \text{time}$$

where X is atmospheric flux, “Conc” is the constituent concentration (ICP-MS and Ion Chromatograph results), “Particulate mass” is the normalized mass of the atmospherically deposited samples, “area” is the interior surface area of the collection funnel (238.55 cm²), and “time” is the deposition collection time (five days).

Hypothesis H₁ states elevation has an effect on the rate and volume of the deposition of Al, Fe, Mn, NO₃, PO₄. Hypothesis H₂ states aspect has an effect on the rate and volume of the atmospheric flux of Al, Fe, Mn, NO₃, PO₄, and SO₄. To evaluate the first hypothesis, the atmospheric flux results from each location were compared to each other using an analysis of variance (ANOVA) to determine if significant differences exist between any of the five elevations on each aspect. If differences were detected, a multiple comparison test (Tukey’s) was used to determine which elevations are significantly different from the other elevations for each constituent. To evaluate the second hypotheses, the means of the atmospheric deposition data associated with each

aspect were compared to each other using an analysis of variance. Because only two aspects were being examined, if a significant difference was detected, no post-hoc analysis was necessary. In any case where the data were not normally distributed, that is not meeting the assumptions of ANOVA, the non-parametric Kruskal-Wallis test was employed, followed by the Tukey's post hoc when necessary.

To evaluate whether atmospherically deposited materials were entering surface streams during this study, it was necessary to calculate the runoff within the watershed during the study. Runoff was calculated using the Natural Resources Conservation Service (NRCS) curve-number procedure (eq. 2).

$$\text{Equation 2: } Q = \frac{(P-0.2S)^2}{P+0.8S}$$

This procedure quantifies runoff (Q) as precipitation (P) less the infiltration and surface storage (S) (eq. 2).

The S variable in the NRCS equation is a parameter which utilizes the curve number (CN), which is based on soil type and land cover (eq. 3) (Ward & Trimble, 2003). Soil types and land cover were extracted from soil and landuse GIS data layers produced by the National Land Cover Database (Homer et al., 2007) and the NRCS Web Soil Survey (Nrcs, 2009). The soils within the study area were all assigned to soil class D, meaning that they have high runoff potential because the soils are predominantly thin or bare surfaces with steep slopes (Ward & Trimble, 2003).

$$\text{Equation 3: } S = \frac{1000}{CN} - 10$$

Precipitation data consisted of five-day composite rainfall measurements collected in conjunction with the atmospheric deposition and water quality samples and daily precipitation records acquired from USClimateData.com for five cities (Gunnison, Telluride, Montrose, Ridgway, and Silverton) within or just outside the study area (USClimateData, 2016) (Figure 7). To utilize the greatest number of measurement locations for precipitation as possible, the daily precipitation records were summed per a five-day collection period parallel to the study-site precipitation measurements.

Dividing the watersheds into sub-basin watersheds was necessary to determine the drainage area affecting each sample site should runoff occur. To delineate the sub-basins, first, a ten-meter digital elevation model of Colorado was masked slightly larger than the study area to improve analysis run time. The contributing watersheds for each sample site were delineated using the Flow Direction[®], Flow Accumulation[®], Snap Pour Points[®], and Watershed[®] tools within ArcMap[®]. The sample sites were used as pour points (i.e., lowest elevation of a drainage basin). The resulting watershed layer was in a raster format, so it was converted to a vector (polygon) format for the analysis (figure 8).

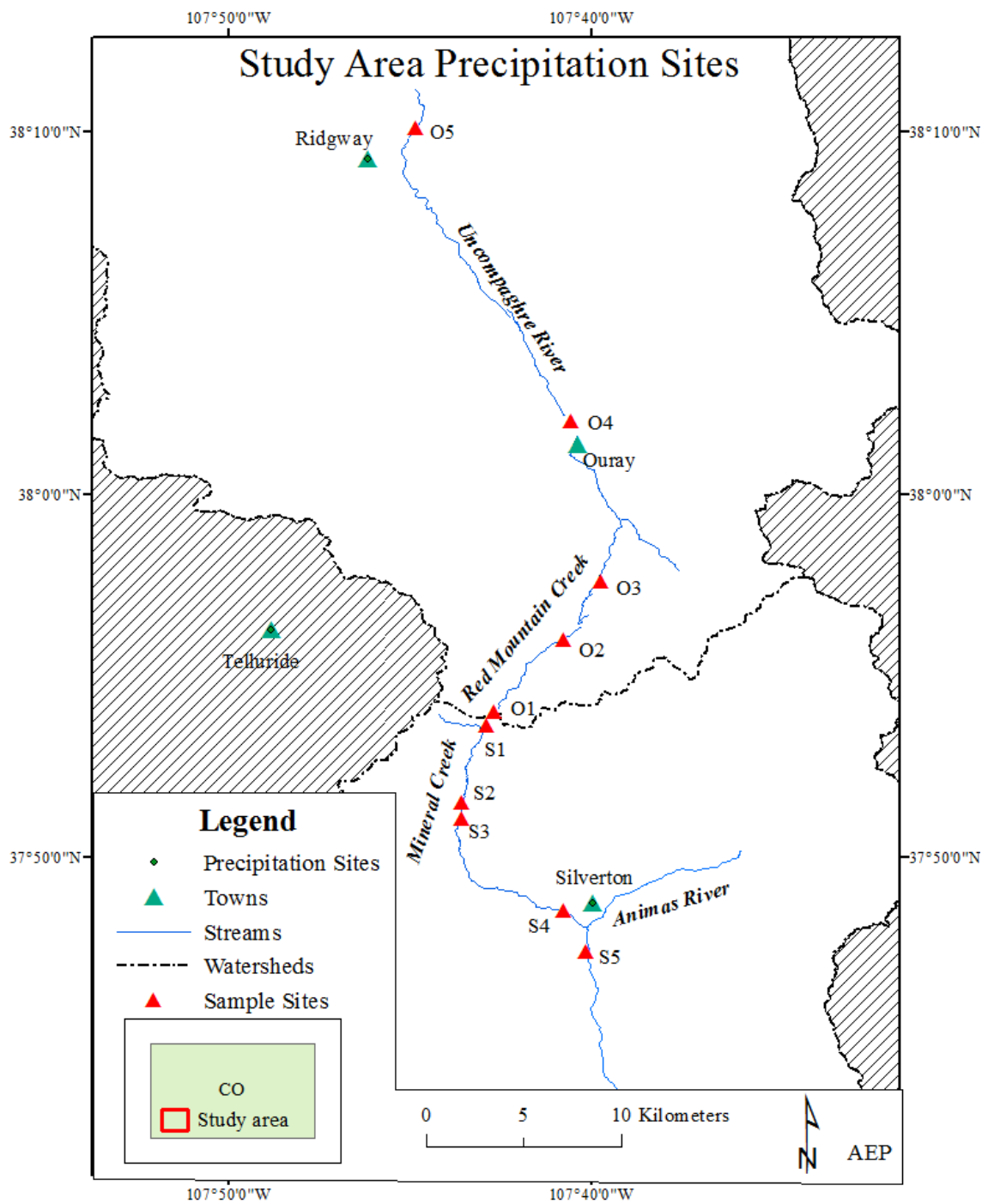


Figure 7. Precipitation information was collected from rain gauges at the sample sites and three additional weather sites located within and slightly outside the study area.

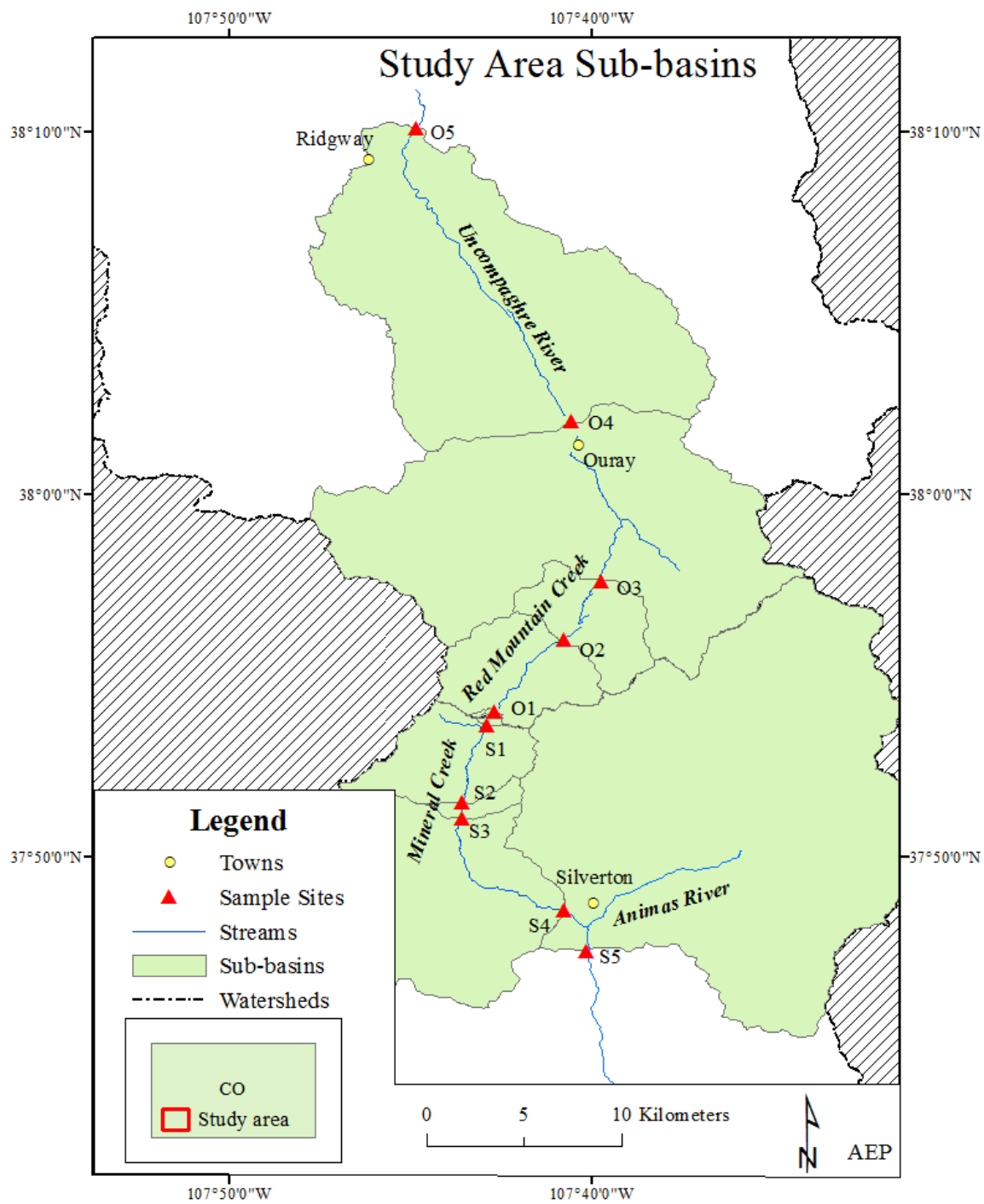


Figure 8. Sub-basins delineated for each sample site using ArcMap®.

The method for interpolating the precipitation throughout the watersheds using a Thiessen-polygon approach was adapted from gis4geomorphology.com[®] (Figure 9) (Cooley, 2015). Thiessen polygons were constructed within ArcMap[®] using the Create Thiessen Polygons[®] tool to interpolate the precipitation measured during the study period. To determine the total precipitation that fell on the watershed during each five-day collection, the Thiessen polygons had to be intersected with the watersheds of the study area and the precipitation weighted by the area of each watershed to intersect with each Thiessen location polygon (Figure 10).

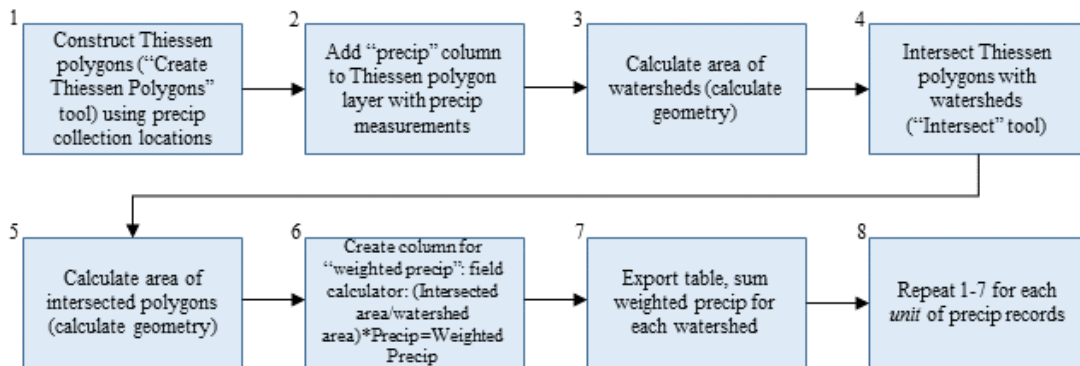


Figure 9. Seven steps taken within ArcMap[®] to construct Thiessen Polygons and calculate runoff within the watersheds of interest during the study period.

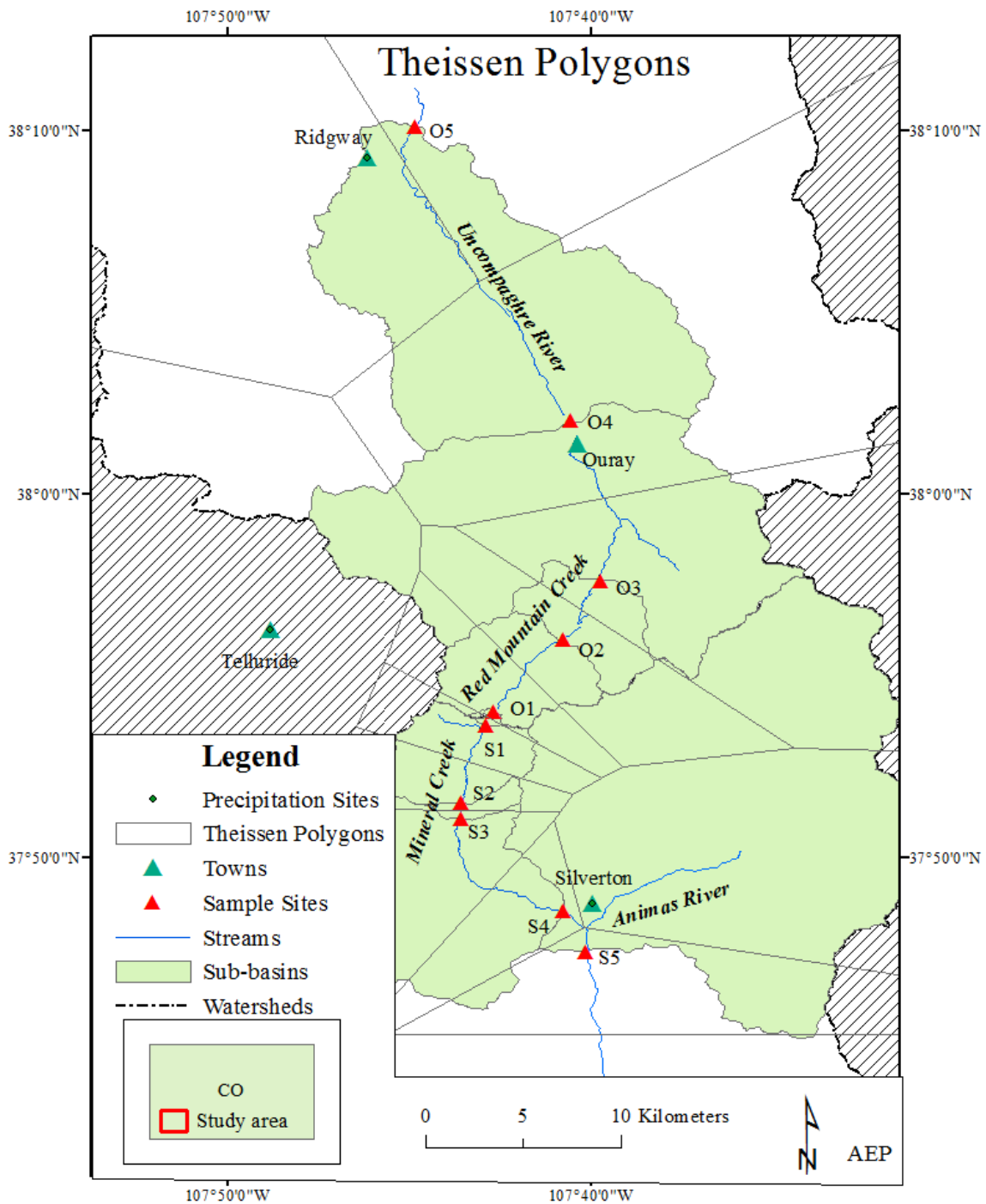


Figure 10. The Thiessen Polygon and Watershed layers were intersected so the distribution of precipitation from each Thiessen polygon within each watershed could be determined.

Runoff was calculated within ArcMap[®] by adding columns for CN, precipitation (determined through the Thiessen polygon method), S, and runoff to the attribute tables of the land use raster. S was calculated using equation 3 with the “Field Calculator” within the attribute table. Runoff was then calculated using equation 2 using the “Field Calculator”. Runoff values of <2.54 mm were considered negligible because it was assumed that is unlikely this runoff would be able to reach a stream before infiltration had occurred. In the case where the five-day precipitation total produced runoff, the highest single-daily precipitation measurement (one of the four cities), which influenced the watershed where runoff supposedly occurred, was used to calculate potential runoff for that day only. In these cases, the runoff potential was <2.54 mm. Therefore, the assumption was made that no runoff occurred during the sample collection during this study.

Results and Discussion

The results of this study are presented in the order of elevation and then aspect. These results and discussion are followed by a comparison of the results from this study to the results of similar studies which examined the same constituents examined here.

The results are presented as bar charts with error bars representing standard deviation. The statistically significant differences determined by the Tukey’s HSD test are represented using letters (i.e., “a”, “b”, “c”), to denote the group to which a result belongs. These groups could also be represented using symbols or numbers, this notation is simply a personal choice, to distinguish the various statistical groups. If a

result cannot be distinguished statistically from more than one group, it is assigned the “letters” of both groups. Figure 11 is an illustration of this denotation of statistical groups. In this example, samples 1 and 3 are statistically different from each other (sample 3 being significantly higher than 1) and therefore belong to different groups: “a” and “b”. Sample 4 is significantly higher than all three other samples and belongs to its own group: “c”. The sample 2 falls between samples 1 and 3 and could not be statistically distinguished from either group, therefore, this is denoted by assigning it the letters (“a” and “b”) of both groups (Figure 11).

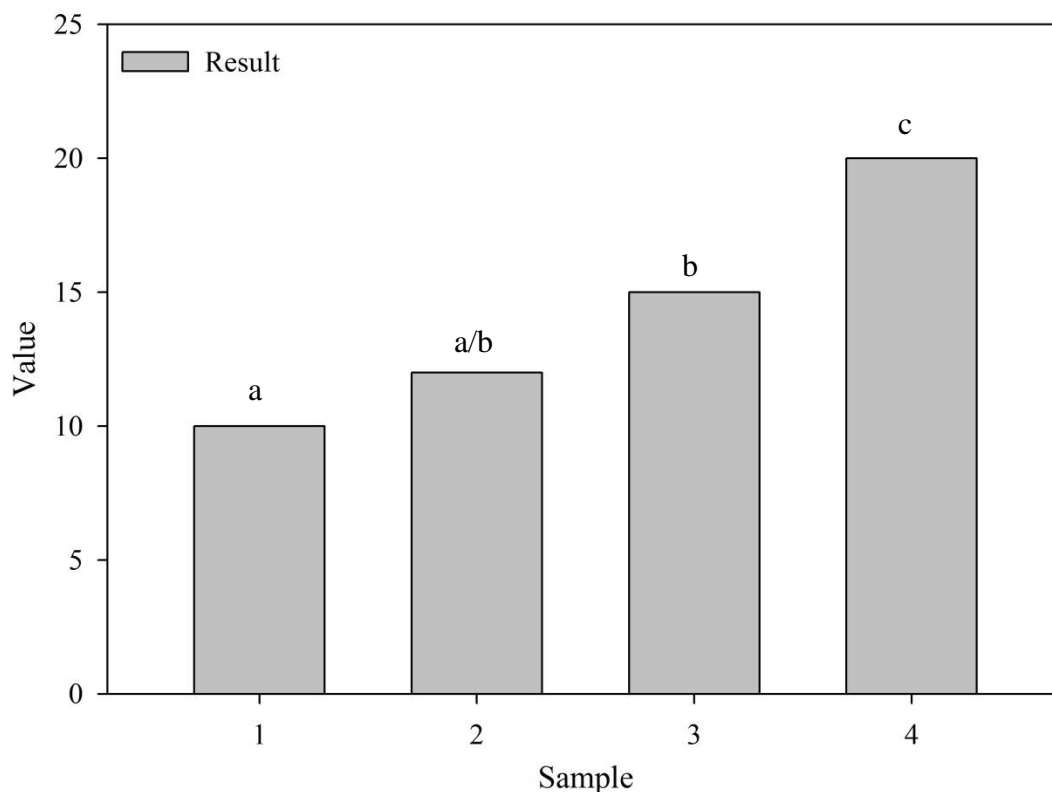


Figure 11. This example figure illustrates how significant differences are denoted based on Tukey's HSD results. Sample 1, denoted by the letter "a" is one statistical group. Samples 3 and 4 are both significantly larger than sample 1 and are denoted using different letters ("b" and "c") from "a". The sample 2 result falls between samples 1 and 3 and cannot be statistically distinguished from either, therefore, it is denoted as belonging to both groups and assigned the notation of both groups ("a" and "b").

Elevation

The first hypothesis examined was whether elevation affected the rate and volume (flux) of atmospherically deposited constituents between two aspects. On the north-facing aspect (i.e., Ouray side), elevation did have a significant effect on the deposition of multiple measured constituents (Figure 12). The fluxes of constituents measured increase by varying amounts with elevation, though significant differences

were only detected for SO₄ and NO₃. Fluxes of SO₄ and NO₃ both decrease slightly (1.4E-5 and 4.4E-5 ug/cm²*day⁻¹ respectively compared to 2.7E-5 and 7.6E-5 ug/cm²*day⁻¹ respectively at site O2) at site O1 (the highest elevation sampled). Site O1 (for SO₄ and NO₃) are belong statistically to groups “a” and “b” with O2 being the only elevation to belong solely to group “a” and sites O3, O4, and O5 belonging solely to group “b” for SO₄, whereas NO₃ belongs statistically to groups “a” and “b”.

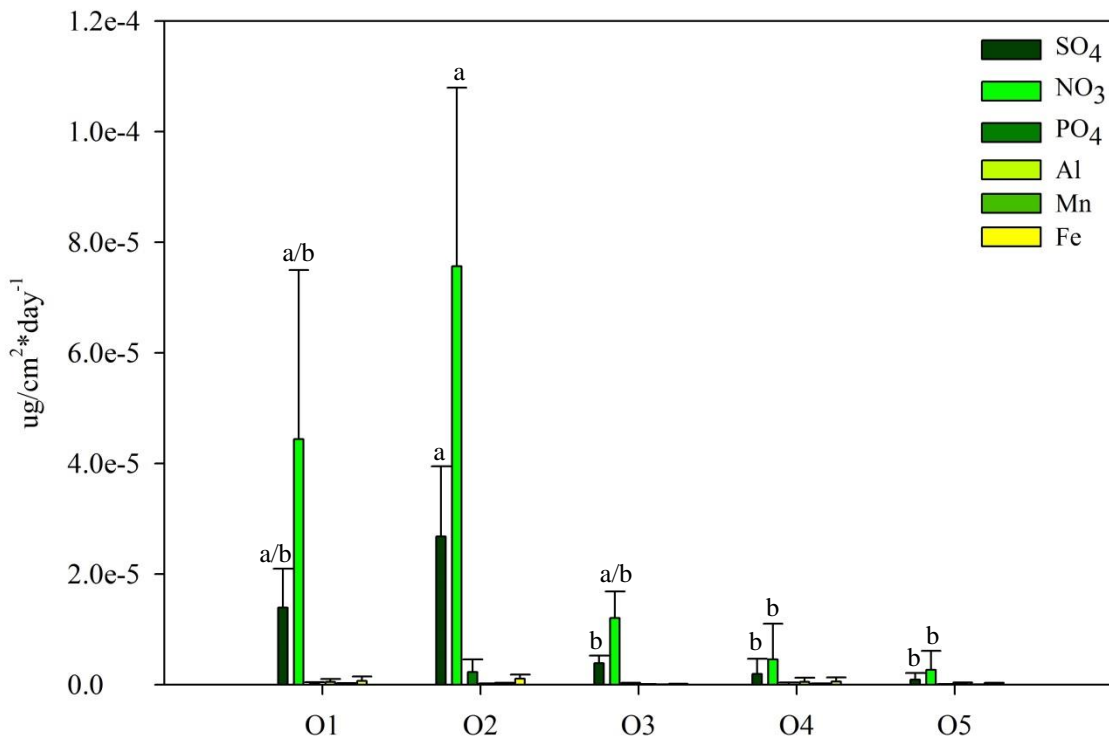


Figure 12. North-facing aspect elevation atmospheric flux means (n=3; ± SD) for sulfate (SO₄), Nitrate (NO₃), Phosphate (PO₄), aluminum (Al), manganese (Mn), and iron (Fe). The letters denote to which statistical group a site belongs by constituent.

Differences were detected between elevations as shown above. Thus, hypothesis H₁, which states elevation has a significant effect on the atmospheric flux of one or more

constituents, is accepted for the constituents where statistical differences were detected (SO_4 and NO_3). Hypothesis H_{a1} , which states no significant difference existed in the atmospheric flux of these constituents with elevation, is accepted for the remaining constituents, for which no statistical relationship with elevation was detected (PO_4 , Al, Mn, and Fe).

On the south-facing aspect (i.e., Silverton side), elevation did not have a significant effect on the atmospheric flux of any of the measured constituents (Figure 13). Therefore, the alternative hypothesis 1 (H_{a1}) for all constituents measured at the five elevations on the south-facing aspect is accepted.

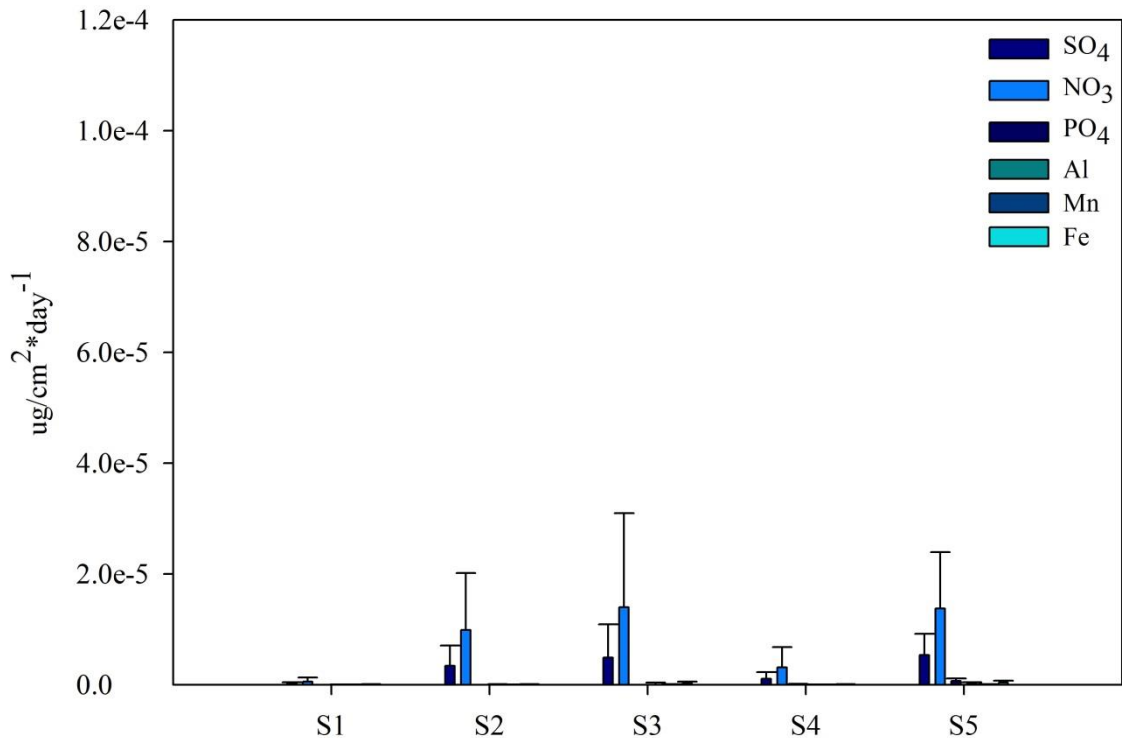


Figure 13. South-facing elevation atmospheric flux means ($n=3$; \pm SD) for sulfate (SO_4), nitrate (NO_3), phosphate (PO_4), aluminum (Al), manganese (Mn), and iron (Fe). No significant differences were detected between elevations.

Sulfate in the atmosphere generally comes from automobile exhaust, coal-fired power plants, and sea salt and crustal sources (He et al., 2014; Udisti et al., 2016). Any or all of these sources, especially local soil/lithologic sources, may have contributed to the SO₄ detected in the atmospheric flux samples.

The long-range transport and deposition of NO₃ and PO₄ have both been linked primarily with agricultural activity (Allen et al., 2010; Anderson & Downing, 2006). Other sources of NO₃ to the atmosphere include sewage/manure, wastewater treatment operations, confined animal feeding operations (CAFOs), and industry (Brahney, Mahowald, Ward, Ballantyne, & Neff, 2015; Liu, Wang, Michalski, Xia, & Liu, 2013). Much of the NO₃ in the atmosphere likely originated as ammonia (NH₃), which oxidized to NO₃. Major sources of NH₃ (thereby, NO₃) include agriculture, animal-husbandry operations, and vehicle exhaust (Behera, Sharma, Aneja, & Balasubramanian, 2013). Additional sources of PO₄ to the atmosphere, besides agriculture, include anthropogenic and natural wildfires and to a lesser extent, industry and mining operations (Brahney et al., 2015).

Metals are typically introduced to the atmosphere through automobile exhaust, industrial smoke stacks, and crustal-dust mobilization (R. Duce, Unni, Ray, Prospero, & Merrill, 1980; R. A. Duce & Tindale, 1991; Pacyna & Pacyna, 2001; Tian et al., 2015). Because the study area has extensive deposits of metal ore bodies, which have been mined for over 100 years, it is possible some of the metal flux measured in this study are from local lithologic sources, including mining activity and abandoned tailing ponds. Other studies conducted in this same region of the San Juan Mountains, however, have

measured a variety of metals, including Al, Fe, and Mn, which were attached to dust particles from the deserts of the southwestern United States (Lawrence et al., 2010; McClenning, 2012).

Though no significant differences between elevations were detected for any of the constituents studied, some variations between elevations are noteworthy for certain constituents, such as SO₄ and NO₃. This lack of significant difference may be the result of large standard deviations (as high as 1.7E-5, for a sample mean of 1.4E-5) between samples. More research and a larger sample set may show significant differences in atmospheric flux between elevations on the south-facing aspect as were detected on the north-facing aspect.

Aspect

A comparison of the flux of each constituent between the north and south-facing aspects suggests that the south-facing side appears to receive overall less atmospheric flux of the measured constituents the north-facing aspect. The difference in flux between aspects may be explained by the general wind patterns in this region. The westerly winds blow from the western side of the San Juan Mountains and flow through this region by first passing over the north-facing (Ouray) aspect and then down the south-facing (Silverton) side (Lawrence et al., 2010; Neff et al., 2008; Painter et al., 2007). As the air mass moves over the north-facing aspect, wind speeds slow because of surface roughness, boundary layer turbulence occurs, and the atmosphere thins and cools with increased elevation (Alford, 1985; Barry, 2012). As a result of these processes, I

think the air mass deposited much of the particulate matter it carried on the Ouray side which resulted in a reduced load available for deposition on the Silverton aspect. The lack of particulate mass in the atmosphere available for deposition on the Silverton aspect may also explain the reduced variability of fluxes apparent between elevations on the Silverton side as compared to the variations detected between the Ouray sample sites (Figures 12 and 13).

No significant differences were detected for any measured constituents between aspects (Figure 14). Because no significant differences between aspects were detected, the hypothesis H_{2a} , which states aspect does not significantly affect the atmospheric flux of the six constituents of interest during this study, is accepted.

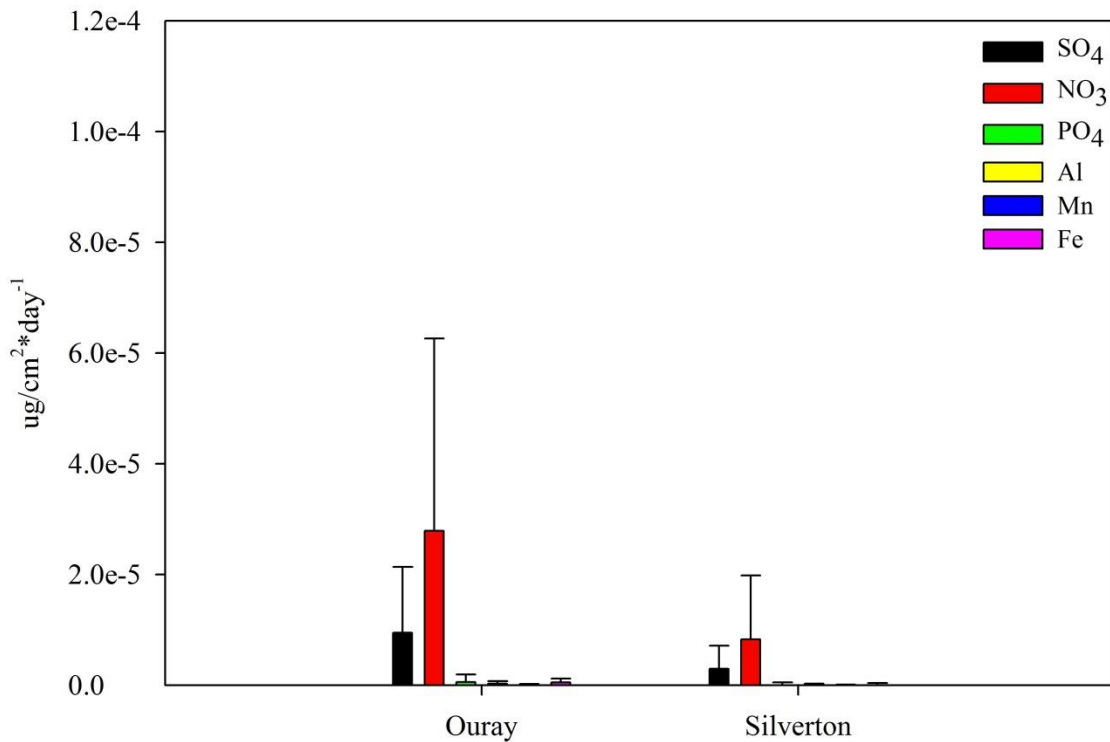


Figure 14: North and south-facing aspect atmospheric flux means (n=15; ± SD) by aspect for sulfate (SO₄), Nitrate (NO₃), Phosphate (PO₄), aluminum (Al), manganese (Mn), and iron (Fe).

Even though no significant differences were observed between the aspects for any of the six constituents, the fluxes on the north side are higher than those on the south aspect for all constituents (9.5E-6, 2.8E-5, 5.6E-7, 2.8E-7, 8.5E-8, and 5.0E-7 compared to 3.0E-6, 8.3E-6, 1.5E-7, 1.0E-7, 2.7E-8, and 2.5E-7 for SO₄, NO₃, PO₄, Al, Mn, and Fe respectively). This consistency between constituents suggests that a consistent driver affected the atmospheric flux in this system.

One reason that no statistical differences might have been detected between aspects was because of the limited sample size and duration of the sampling program.

The standard deviation bars present show a wider range of constituent measurements occurs, especially for Al on the north-facing (Ouray) aspect, than would be preferred for this type of comparison. Additional sampling would likely strengthen the robustness of this dataset by increasing the n-size, for confirming or denying the lack of difference between aspects for atmospheric flux of these constituents.

Comparisons with Similar Studies

Many comparable studies have been conducted around the world and within the Rocky Mountains of CO. Many of these studies examined a greater array of constituents than were examined in this study. The topic of atmospheric deposition has been extensively studied and is important. The following discussion presents the various studies of an individual constituent. The first constituent presented is NO₃.

The deposition of sulfate within the United States has been well studied, especially in the 1990s and early 21st century (Ingersoll et al., 2008; Kester, Baron, & Turk, 2003; Liu et al., 2013; Michalski, Böhlke, & Thiemens, 2004; Nanus, Campbell, Ingersoll, Clow, & Mast, 2003). The mean atmospheric SO₄ deposition for the study area of this research ranges between 1.6 and 4 kg/ha yr⁻¹ (0.04-0.11 ug/cm² day⁻¹) (Ingersoll et al., 2008; Kester et al., 2003; Nanus et al., 2003). From my study, I determined the range of SO₄ deposition was 6.23E-6 ug/cm² day⁻¹ (figure #). Many possible reasons exist that my results are so much lower than other prior studies, including difference in methods, length of study, and difference of season sampled.

A review paper by Burns (2003) estimates the annual total-N deposition within the Rocky Mountains was between 2-7 kg/hectare yr⁻¹ (0.06-0.19 ug/cm² day⁻¹) (D. A. Burns, 2003). Within my study area, I measured a mean NO₃ flux of 1.81E-5 ug/cm² day⁻¹ (Figure 14). Again, some possible reasons my results were lower than the NO₃ fluxes measured in other studies include differences in collection and analyses methods, duration of study, and difference of season sampled.

Phosphate deposition within the United State (specifically CO) is less well studied than NO₃ and SO₄. A thesis from Kansas State University, however, examined the effect of season on wet and dry deposition on various constituents at Niwot Ridge, CO (also in the Rocky Mountains), including PO₄ (Oldani, 2014). Oldani measured a mean PO₄ deposition between two years, 2012 and 2013, to be approximately 0.112 kg ha⁻¹yr⁻¹ (0.003 ug/cm² day⁻¹) (Oldani, 2014). Comparatively, I measured a mean PO₄ flux of 3.55E-7 ug/cm² day⁻¹ (figure 13). For the case of PO₄, whereas my results are lower than those found by Oldani, both studies found the flux of PO₄ to be very low. Oldani's collection methods and medium were different from mine, and she was reporting a two-year average rate of flux. It is possible her average contains large individual flux events which I was unable to capture during my comparatively short study duration.

Many studies and books document the atmospheric transport and deposition of aluminum (Mayer, 1983; Prospero, Nees, & Uematsu, 1987). I was only able to locate one research paper, by Lawrence et al., however, which through the course of examining the atmospheric deposition of various constituents to the San Juan Mountains, included

Al, Fe, and Mn in their analysis (Lawrence et al., 2010). Lawrence et al. found a mean Al, Fe, and Mn concentrations (as part of a bulk deposited dust sample) of 59.45 mg/g, 23.37 mg/g, and 0.53 mg/g, respectively. The deposition surface area for these samples was 0.5 m² and samples were collected twenty-four to forty-eight hours after a “dust event”, therefore, the results have the units of mg/g*0.5 m² (Lawrence et al., 2010). Lawrence et al. then scaled their measurements up to a mean estimated deposition per year using their results; the mean estimated Al, Fe, and Mn for this study were 386.4, 151.92, and 3.45 mg/m² yr⁻¹, respectively (0.11, 0.04, and 0.0009 ug/cm² day⁻¹, respectively) (Lawrence et al., 2010). For comparison, my mean Al, Fe and Mn fluxes for this dissertation were 1.93E-7, 3.29E-7, and 5.59E-8 ug/cm² day⁻¹, respectively. A key reason my results are lower than those found by Lawrence et al. is likely their collection method. Lawrence et al. collected snow samples after what he described as “dust events”; therefore, these authors may have found higher fluxes of metals because they specifically targeted large flux events (Lawrence et al., 2010).

For all six parameters measured, my results are lower than has been found in other studies. These differences may be attributed to a variety of factors including differences in sample collection, duration of study, and difference in season. Also, each author of these other studies collected samples according to different frameworks. Another difference in sample collection between my study and others I have found is the use by multiple researchers of acid to wash the deposition collection surface to collect all deposited material. For my sample collection, the funnels which were the deposition collection surface were washed with DI water and then the sample was acidified for

storage. It would be interesting to collect atmospheric flux samples for a much longer period of time than I was able, to possibly detect seasonal or even annual differences of atmospheric flux between elevations or aspects.

Summary and Conclusions

As a summary, the San Juan Mountains are a unique and varied critical zone ecosystem where environmental issues unfortunately abound. This study examined how this study area between the cities of Ridgway and Silverton, CO (Figure 1) may be affected by the introduction of atmospherically fluxed contaminants. Six constituents were examined (SO_4 , NO_3 , PO_4 , Al, Mn, and Fe) across ten sample sites separated between two aspects. Between elevations, significant differences were detected for two constituents: SO_4 and NO_3 (Figure 12). Interestingly, no significant differences were detected between the two aspects included in this study area (Figure 14).

Precipitation was measured throughout the study and additional weather data was downloaded post sample collection from nearby weather stations. Runoff calculations were performed, but it was determined no runoff was likely to have occurred during the study period. Therefore, the conclusion was reached that although atmospheric flux did occur for all six constituents of interest it is unlikely this input source was affecting surface water quality during this study.

The differences between the results of this study and those of other similar studies likely have a variety of sources. The weather patterns between seasons, locations, and even daily and weekly occurrences likely all contributed to my

measurements being lower than those of other studies. Also, differences in equipment and methods used are definitely accountable for some of the differences. For example, Anderson et al. specifically measured “dust events”. I was sampling ambient conditions and did not target any specific weather or atmospheric events. Also, there was a distinct lack of precipitation during this study, which took place during a drought period; atmospheric deposition is typically higher during precipitation events as this moisture captures particles from the atmosphere at a faster rate than natural fallout tends to occur (Gunawardena, Egodawatta, Ayoko, & Goonetilleke, 2013; Lynam, Dvonch, Hall, Morishita, & Barres, 2014; Zhu et al., 2015).

Therefore, although the lack of precipitation, and runoff, during the sample period meant I cannot make assumptions about the direct effects of atmospheric flux in this study to the local surface water systems, I think this study was a success. The atmospheric deposition collector and methods of my and Dr. John R. Giardino’s design was found to successfully collect and store atmospherically deposited material over the course of several days until it could be collected. The sample analysis performed then had the precision necessary to detect statistically significant differences between elevations, one of the hypotheses being examined. The simple, yet effective, design allowed this instrument to be simple to construct onsite and deconstruct for transport as well as its negligible local installation disturbance makes them ideal for future studies of this kind.

Therefore, the conclusions of this study are:

1. Differences in concentrations of the flux of SO_4 and NO_3 at different elevations suggest elevation affects the atmospheric flux of these constituents more than the other constituents examined (PO_4 , Al, Mn, and Fe).
2. No significant runoff occurred during the study period, so atmospheric flux was likely not significantly affecting surface water quality.
3. The atmospheric deposition collector designed for this study was a successful design for addressing the question: can significant differences between atmospheric fluxes be detected between elevations.

CHAPTER III

AN ASSESSMENT OF THE EFFECTS OF ELEVATION AND ASPECT ON WATER QUALITY IN THE ALPINE CRITICAL ZONE OF THE SAN JUAN MOUNTAINS, COLORADO, USA

Synopsis

Surface water-quality issues are prevalent world-wide. An ecosystem, which is no exception, occurs in the San Juan Mountains of Southwestern Colorado. Over 100 years of mining and careless disposal of tailings has resulted in extensive degradation of water-quality of Red Mountain Creek, the Uncompaghre River, Mineral Creek, and the Animas River. As a result of the diverse terrain of this alpine ecosystem, important questions arise: does the concentration of sulfate (SO_4), nitrate (NO_3), phosphate (PO_4), aluminum (Al), manganese (Mn), iron (Fe), temperature (T), pH, dissolved oxygen (DO), or specific conductance (Sp. Cond) in surface streams vary with elevation or aspect? Over the course of fifteen days, three stream grab samples were collected, one every five days, from nine sample sites to assess the effects of elevation and aspect on the concentrations of SO_4 , NO_3 , PO_4 , Al, Mn, and Fe as well as in-situ T, pH, DO, and Sp. Cond. In this study I found differences in surface-water quality associated with elevation to include SO_4 , Mn, T, pH, DO, and Sp. Cond. No significant differences associated with aspect were detected for the examined constituents.

Introduction

The effects of mining activity on a landscape can be far reaching and severe. Poor mining practices can result in polluted soils and water bodies (i.e., surface and groundwater) (Leenaers, Okx, & Burrough, 1990; Runnells, Shepherd, & Angino, 1992). This is especially true in the San Juan Mountains.

The San Juan Mountains are a major mountain range in southwestern Colorado (CO) in the United States. The San Juans lie to the west of the major trend of the Rocky Mountains and encompass ~32,000 km², which is 12% of the land area of CO. Eighteen peaks over 4,000 meters in elevation are present in the San Juan Mountains (Painter et al., 2007; Southwest, 2016). The San Juan Mountains are well-known for the extensive mining, which occurred from late 1800s to present day, as well as the beautiful scenery (Henderson, 1926; Ransome & Cross, 1901).

Years of mining, and careless disposal of the tailings and acid-mine drainage, have affected the quality of surface water in the San Juan Mountains (Litt, 2014; Runnells et al., 1992). But, mining may not be the only factor however, that significantly contributes to the quality of surface water in this high elevation ecosystem. Whereas this paper focusses on the correlation of elevation and aspect on water quality, the overall study focusses on how the atmospheric flux of a variety of constituents which occur within the San Juan Mountains is affected by elevation and aspect and whether this flux could be affecting surface water quality within the San Juans. Deposition of atmospheric pollutants is affected by elevation more than the aspect of particular slopes for the area of the San Juan Mountains examined in this study (Price, 2015).

The only major studies focusing on surface-water-quality of the San Juan Mountains in the past fifty years have been U.S. Geological Survey reports addressing mining, water-quality, and remediation efforts. Most research in this area has been conducted in the Animas watershed, but some select studies and U.S. Geological Survey Professional Papers are based in the Uncompaghre watershed, specifically Red Mountain Creek (Kimball, Runkel, Walton-Day, & Bencala, 2002; Mast, Verplanck, Wright, & Bove, 2007; Runkel, Kimball, Walton-Day, & Verplanck, 2007; von Guerard et al., 2007).

Litt (2014), in an unpublished master's thesis, examined the effects of the remediation of mine tailings on the surface water-quality of Red Mountain Creek (Litt, 2014). Litt found that the water-quality downstream of the remediated tailings was not significantly different from reaches of Red Mountain Creek upstream of the tailings. Litt's study specifically focused on metals present in the stream and focused only on Red Mountain Creek downstream from the Idarado Mine.

The objective of the current study is to explain if and how water quality varies with elevation or aspect within the San Juan Mountains of Colorado for metal and non-metal parameters. To address this objective, this research examines two hypotheses:

H₁: A significant difference exists in water quality of streams along an elevation gradient for temperature (T), dissolved oxygen (DO), pH, specific conductance (Sp. Cond), sulfate (SO₄), nitrate (NO₃), phosphate (PO₄), aluminum (Al), manganese (Mn), or iron (Fe).

H_{a1}: No significant difference exists in water quality of streams along an elevation gradient for T, DO, pH, Sp. Cond, SO₄, NO₃, PO₄, Al, Mn, or Fe.

H₂: A significant difference exists in water quality of streams between two opposing aspects for T, DO, pH, Sp. Cond, SO₄, NO₃, PO₄, Al, Mn, or Fe.

H_{a2}: No significant difference in water quality of streams between two opposing aspects for T, DO, pH, Sp. Cond, SO₄, NO₃, PO₄, Al, Mn, or Fe.

Study Area

The research study area is located in the San Juan Mountains in southwestern Colorado, between the towns of Ridgway and Silverton (Figure 15). The San Juan Mountains were an active volcanic area until the Pleistocene, when the volcanic activity ended (Blair, 1996b). The mountains in this area consist of multiple calderas (Lipman et al., 1978; Sinnock, 1981). Around the same time the volcanic activity ended, during the Pleistocene, the San Juans are thought to have been glaciated at least fifteen times (Blair, 1996b; Lipman et al., 1978; Sinnock, 1981). The most recent major glaciation occurred ~18,000 years ago, and some small glaciers still exist in the San Juans today (Blair, 1996b). The presence of glaciers, both past and present, is fundamental to the current geomorphic shape of the San Juan Mountains.

Erosion has resulted in steep slopes with high surface roughness as a result of the geomorphic processes and various vegetation covers. Many of the slopes in the area are above tree line as well as being relatively steep. These two parameters create high-runoff potential for the watersheds in the San Juan Mountains. This study focuses on

four streams within two watersheds. All streams within the study area may be affected by the deposition and runoff of atmospheric deposition of aerosols (Price, 2015).

The study area consists of igneous, sedimentary, and metamorphic rocks ranging from limestone, dolomite, shale, sandstone, conglomerate/breccia, mudstone, tuff, to porphyritic granodiorite (Burbank & Luedke, 2008). Contact metamorphism and hydrothermal alterations are the primary source of the metal-based ore bodies in this region, which have been extensively mined (Burbank & Luedke, 2008; Neubert, Kurtz, Bove, & Sares, 2011). Around 6-10 million years ago (Ma) metal-rich hydrothermal fluids invaded the numerous faults and fractures depositing economically viable quantities of metallic minerals (Neubert et al., 2011). The locations of the sample sites within the study area are associated with multiple geologic formations: sites O1 and S1 are associated with the Burns Formation (Tuff-Breccia), sites O2, S2, and S3 are associated with the San Juan Formation (Tuff-Breccia), sites O3, and S4 are associated with the Uncompaghre Formation (Quartzite and Slate), and sites O4 and O5 are located within the Hermosa Formation (Limestone) (Figure 16) (Blair, 1996a, 1996b; Cross & Larsen, 1935). The Cuttler Formation, also shown in Figure 16, is composed of Permian Red Beds (Blair, 1996b).

The two primary formations within this study area which are economically mineralized and have been heavily mined are the Burns and San Juan formations. Mining activity has primarily been for gold and silver but other metals mined in this area include copper and lead. These ore bearing formations, as well as the abandoned mine portals and tailings ponds all contribute to the surface water quality Red Mountain Creek

and Mineral Creek, headwater streams within the Uncompaghre and Animas River watersheds respectively.

Along with the local geology, local soils play a crucial role in surface water quality. As surface runoff seeps atop and through soil, the chemistry may change through interactions with the minerals and organic matter which makeup soil. Also, within streams, the soil and mud along the bottom of the streambed may trap or release ions under certain conditions. For example, PO_4 tends to accumulate in aluminum or iron rich soils under aerobic conditions; however, if the waterbody becomes anaerobic, the stored PO_4 is released (Jin, He, Kirumba, Hassan, & Li, 2013; Lu et al., 2013; Smil, 2000). The soils within this study area which the sample sites intersect primarily include alluvium and till soils with parent materials consisting of andesite, rhyolite, breccia, sandstone, and limestone (CASoilResource; Nrcs, 2009).

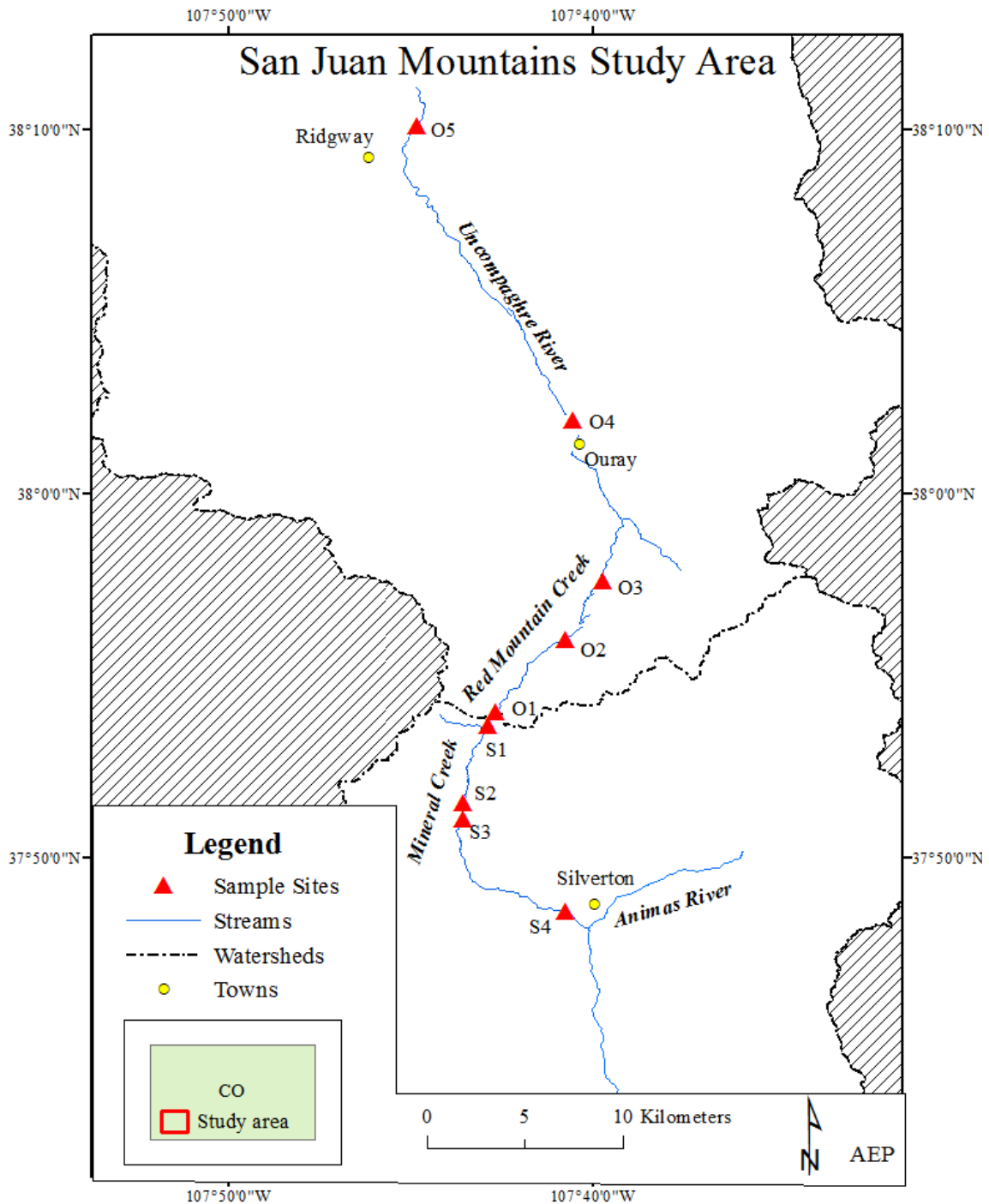


Figure 15. The study area is two watersheds on two opposing aspects in Southwestern Colorado. Five sample sites were selected along Red Mountain Creek and the Uncompaghere River on the Ouray side of the mountain and along Mineral Creek on the Silverton side.

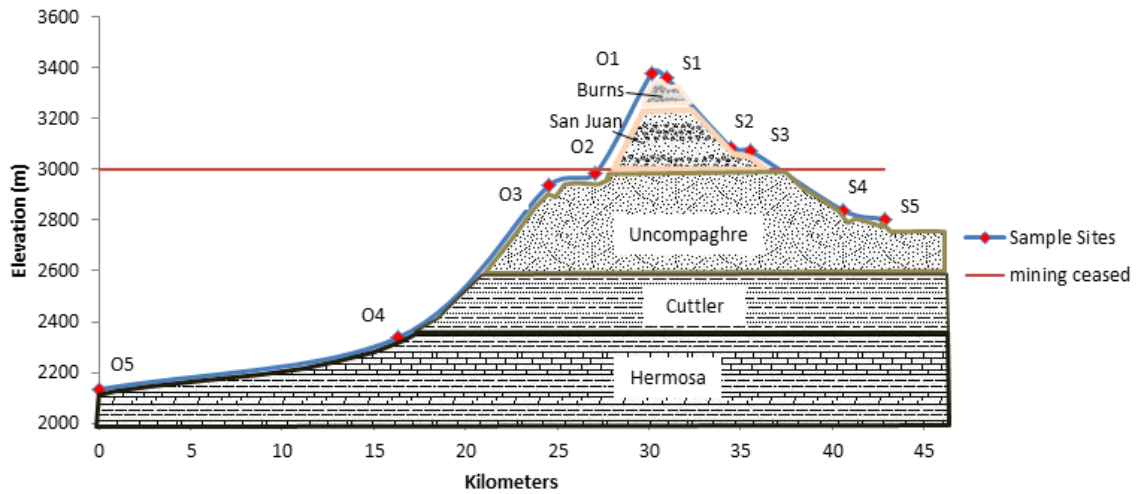


Figure 16. The sample sites within the study area intersect five major geologic formations.

This study area of the San Juan Mountains is known as the Red Mountains; this name comes from the red coloration of the bare peaks in this area. The red color of these peaks is a product of the weathering of iron rich minerals (e.g., pyrite (FeS_2)). The oxidation reaction of FeS_2 and water (H_2O) produces ferric Fe (Fe^{2+}), SO_4 , and free H^+ in the local surface waters (Neubert et al., 2011). This H^+ is responsible for the normal pH of Red Mountain Creek range between 2 and 5 on the pH scale (Neubert et al., 2011).

The climate in this region of the San Juan Mountains is a Dfb Koppen-type climate (Kottek et al., 2006). The San Juans have a typical cycle of winter months having the lowest temperatures (average low temperature for winter in San Juan County is $\sim -18.8^\circ\text{C}$), and the summer months have the highest temperatures (average high temperature of San Juan County for summer is $\sim 22.8^\circ\text{C}$) (County, 2015). July and

August are considered the wettest months with averages of approximately 7.5 cm of rainfall (County, 2015; USClimateData, 2016).

The two watersheds that serve as the basis for this study are the Uncompaghre River and the Animas River watersheds, respectively (Figure 15). Water samples and atmospheric deposition samples were collected along Red Mountain Creek, the Uncompaghre River, Mineral Creek, and the Animas River. Ten sample locations were established. On the Northern aspect, five sample locations were established at ~3,379, 2,982, 2,937, 2,338, and 2,134 meters above sea level, respectively; on the southern aspect, sample locations were at 3,359, 3,083, 3,071, and 2,839 meters above sea level, respectively. On the southern aspect, only four water-quality sample locations were used because a breach of the Gold King Mine sent over three-million gallons of mine wastewater into Cement Creek, a tributary of the Animas River (Schlanger, 2015). Thus, the lowest elevation site on the south side was closed to access and compromised.

Methodology

To evaluate if and how the concentrations of aluminum (Al), iron (Fe), manganese (Mn), nitrate (NO₃), phosphate (PO₄), and sulfate (SO₄), as well as four *in-situ* water-quality parameters (T, pH, DO, and Sp. Cond.) vary with elevation or aspect, water samples were collected from the streams at nine locations of different elevations between two aspects once every five days. Grab samples were collected using triple-rinsed plastic sample bottles (500 ml) and stored in fifty-milliliter (ml) centrifuge tubes until analysis. A portion of each sample collected was filtered through 0.45 um syringe

filters. All samples were preserved using hydrochloric acid within twelve hours of collection.

The concentrations of the metals were measured using an inductively coupled plasma mass spectrometer (ICP-MS). The anions were measured using an Ion Chromatograph; for the anion analysis, only the filtered samples were evaluated. Stream *in-situ* measurements were taken concurrent with each grab sample collection using a handheld YSI Professional Plus[®] series multi-probe sonde. Discharge of the stream was determined at the point and time of each grab sample using width, depth, and velocity measurements. Width was measured using a tape measure, depth was determined using the depth rod on the flow meter, and velocity was determined with a USGS Type AA[®] velocity meter, which allowed for discharge to be determined for each site (Figures 17 and 18). Discharge for sites O4 and O5 were acquired from USGS gauging stations (USGS, 2016a, 2016b).

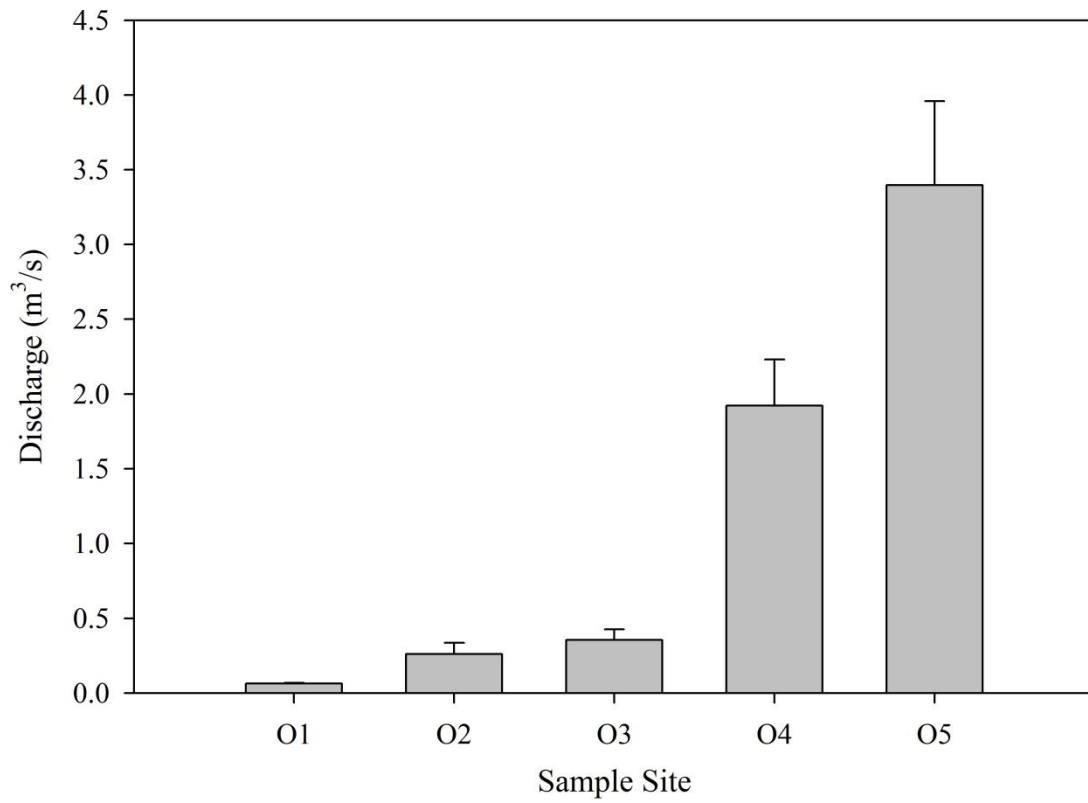


Figure 17. Mean discharge ($n=3\pm SD$) of the northern aspect (Ouray) sample sites.

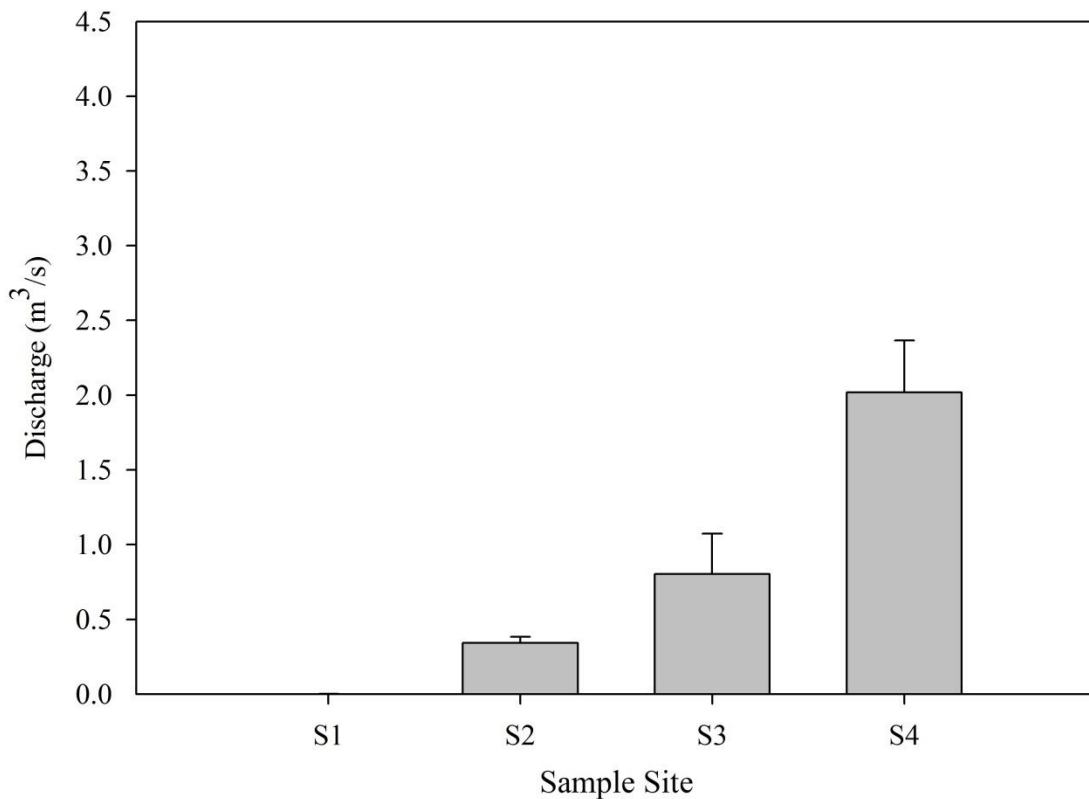


Figure 18. Mean discharge ($n=3\pm SD$) of the southern aspect (Silverton) sample sites.

Hypotheses H_1 and H_2 state a significant difference occurs in the water quality of streams along an elevation gradient or between opposing aspects for T, DO, pH, Sp. Cond, SO_4 , NO_3 , PO_4 , Al, Mn, or Fe. To evaluate H_1 , the water quality results from each location were compared using analysis of variance (ANOVA) to determine if significant differences occurred between any of the five elevations to test the hypotheses that no significant differences exist in the rate of deposition or water quality for any constituent in relation to elevation. If differences were detected, a multiple comparison test (Tukey's) was used to determine which elevations were significantly different from the other elevations for each constituent. To evaluate H_2 , the means of the stream-water-

quality data associated with each aspect were compared using an analysis of variance. Because only two aspects were being examined, if a significant difference was detected, no post-hoc analysis was necessary. In any case if the data were not normally distributed, that is, not meeting the assumptions of ANOVA, the non-parametric Kruskal-Wallis test was employed, followed by the Tukey's post hoc, when necessary.

The second objective of this study was to examine if and how atmospheric deposition affects surface water quality within the study area. However, limited precipitation resulted in no runoff during this study, therefore it is unlikely the water quality results measured were affected by the atmospheric flux measured concurrent with surface water quality.

Follow-up calculations were performed however, to determine what amount of each constituent measured during this study may have reached a stream had runoff occurred and to determine what amount of flux for each constituent would be necessary to impact the surface water quality within the study area. These calculations were performed within Microsoft Excel[®] and were based on certain assumptions.

The assumptions used for the first calculation (what mass of each constituent would be available to runoff into the local surface water) were: the measured flux (mass/area/time) was applied to the entire sub-basin in which it was measured (i.e., the measured fluxes from site O1 was applied to the area of sub-basin O1) and that all fluxed constituent was available for contribution, through runoff, to the local stream. The assumptions associated with the second follow-up calculation, how much flux (mass/area/time) would be necessary to impact the surface water quality, was that it

would require a minimum of 10% of the total in-stream total load to have originated as flux to be considered a significant contribution (i.e., if a site contained a mean NO₃ load of 20 mg, a total atmospheric flux of 2 mg or more across the sub-basin would be necessary to be considered a significant contributor to surface water quality). Total load within a stream is calculated as the concentration measured multiplied by the discharge of the stream (Equation 4) (Garrett, 2012; Jones et al., 2001). Stream total load was used for this comparison because a sample site under the influence of a larger sub-basin would be more heavily impacted by surface runoff and the constituents it carried than a smaller sub-basin. For example, if a total of 30 mg/day NO₃ was deposited to a particular sub-basin and the instream concentration of NO₃ is 5 mg/L, a comparison of these values is not recommended because the denominators do not match. If the stream discharge is 100 L/s, the total load of the stream would be 500 mg/s NO₃; using the assumption that the flux/time must be 10% or greater than the load/time, the 30 mg/day flux would not be considered a significant influence on this sub-basin water-quality. By multiplying the concentration by discharge the units become mass/time for both the flux totals and the streams measurements allowing a direct comparison.

$$\text{Equation 4: Total Load} = \text{WQ concentration} * \text{Stream Discharge}$$

Results and Discussion

The discussion of the results is divided into three parts: elevation, aspect, and additional calculations. These results are followed a summary and conclusions.

The results of the water quality analyses are presented as bar charts with error bars representing standard deviation. The statistically significant differences determined by the Tukey's HSD test are represented using letters (i.e., "a", "b", "c"), to denote the group to which a result belongs. These groups could also be represented using symbols or numbers, this notation is simply a personal choice, to distinguish the various statistical groups. If a result cannot be distinguished statistically from more than one group, it is assigned the "letters" of both groups. Figure 19 is an illustration of this denotation of statistical groups. In this example, samples 1 and 3 are statistically different from each other (sample 3 being significantly higher than 1) and therefore belong to different groups: "a" and "b". Sample 4 is significantly higher than all three other samples and belongs to its own group: "c". Sample 2 falls between samples 1 and 3 and could not be statistically distinguished from either group, therefore, this is denoted by assigning it the letters ("a" and "b") of both groups (Figure 19). If two samples results share a symbol (in this case a letter) it means the sample results belong to the same statistical group.

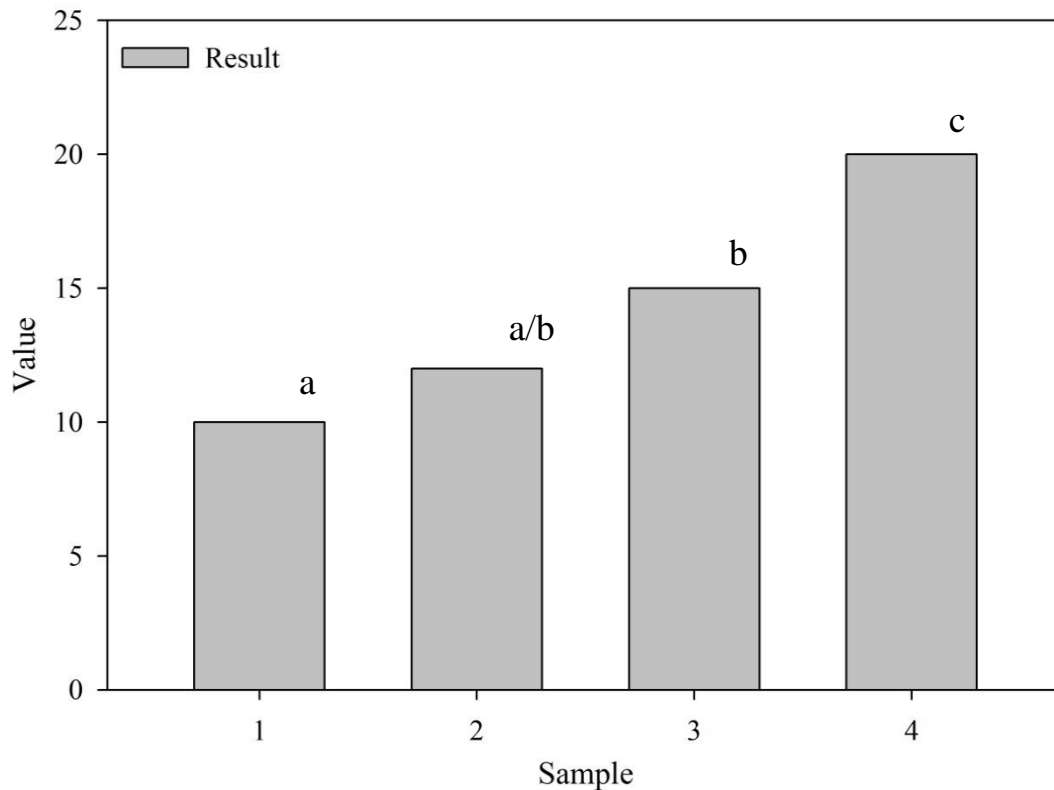


Figure 19. This example figure illustrates how significant differences are denoted based on Tukey’s HSD results. Sample 1, denoted by the letter “a” is one statistical group. Samples 3 and 4 are both significantly larger than sample 1 and are denoted using different letters (“b” and “c”) from “a”. The sample 2 result falls between samples 1 and 3 and cannot be statistically distinguished from either, therefore, it is denoted as belonging to both groups and assigned the notation of both groups (“a” and “b”).

Elevation

On the north aspect, multiple significant differences occurred for the in-situ and lab measured water quality parameters between different elevations. Whereas sites O1, O2, and O3 are on Red Mountain Creek, which drains into the Uncompaghre River, sites O4 and O5 are located on the Uncompaghre River.

The four in-situ measurements taken for each stream sample at the time of collection (T, DO, pH, and Sp. Cond.) were compared between. On the Ouray aspect, the mean T, DO, pH, and Sp. Cond in-situ measurements all had significant differences between elevations. On the southern (Silverton) aspect however, significant differences were only detected for the in-situ pH and Sp. Cond (Figures 20-23).

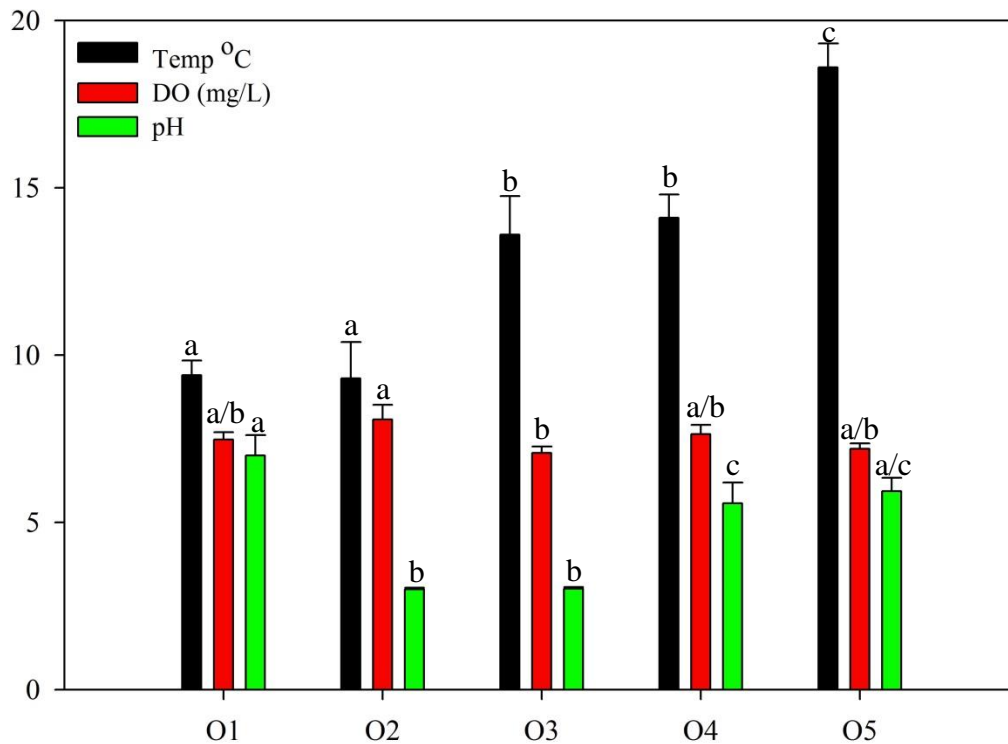


Figure 20. Mean \pm SD (n=3) in-situ water quality results (except Specific Conductance) for the north-facing aspect streams (Red Mountain Creek and the Uncompaghre River). The letters denote to which statistical group a site belongs by constituent.

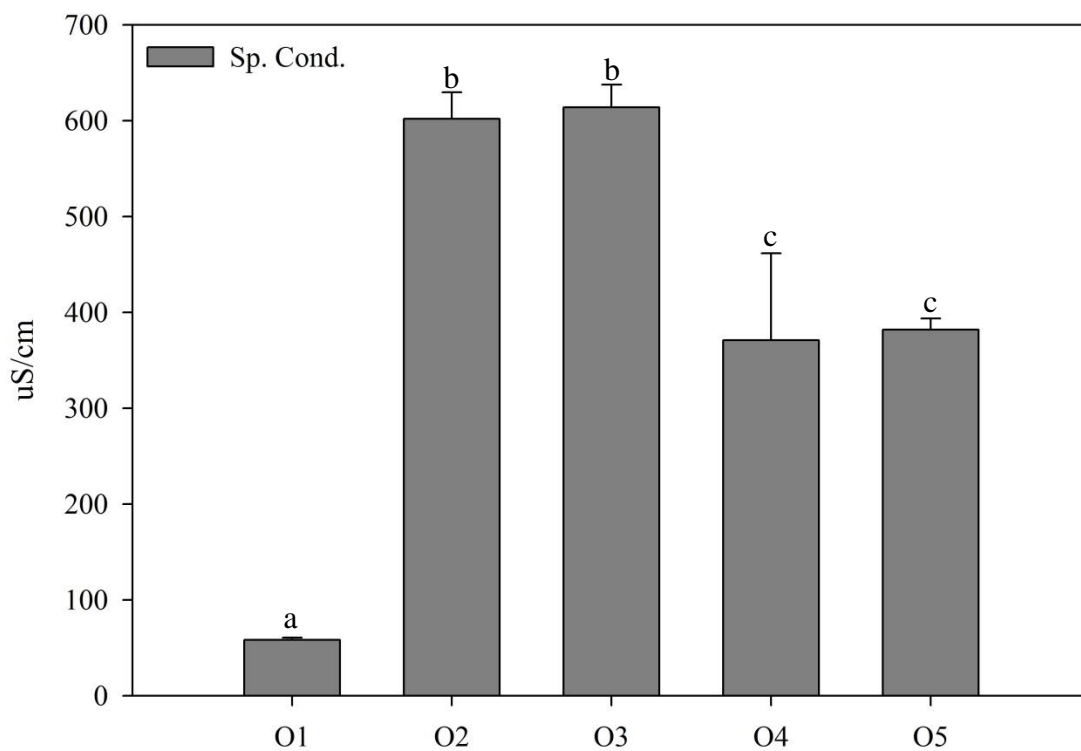


Figure 21. Mean \pm SD (n=3) in-situ Specific Conductance for the north-facing aspect streams (Red Mountain Creek and the Uncompaghre River). The letters denote to which statistical group a site belongs by constituent.

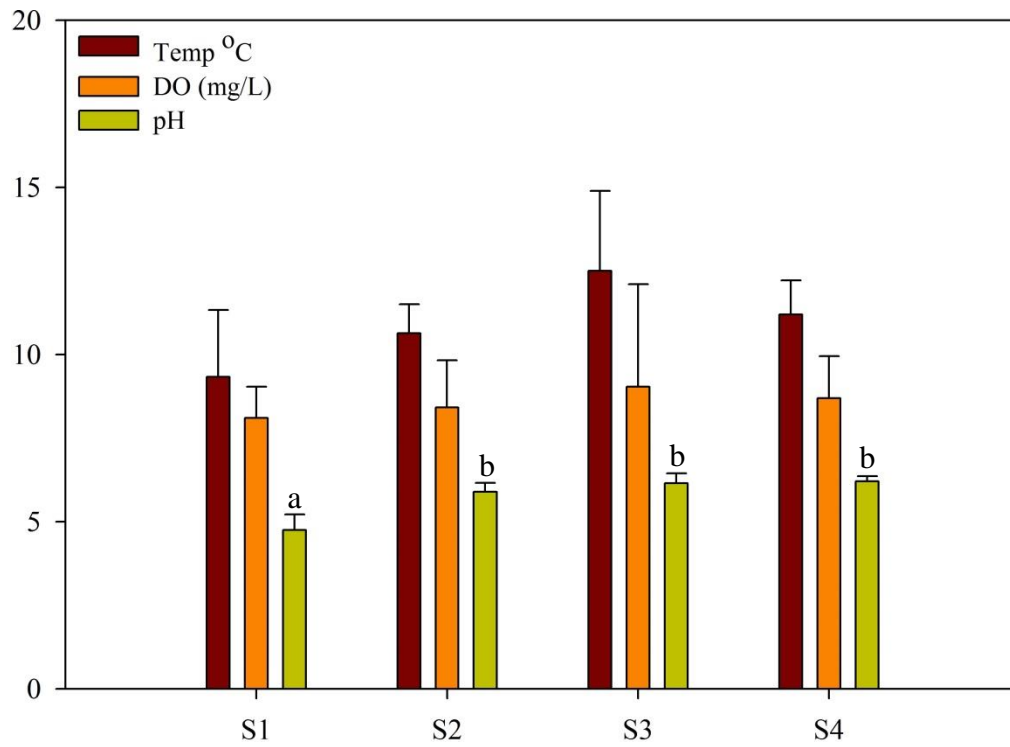


Figure 22. Mean \pm SD (n=3) in-situ water quality results (except Specific Conductance) for the south-facing aspect stream (Mineral Creek). The letters denote to which statistical group a site belongs by constituent.

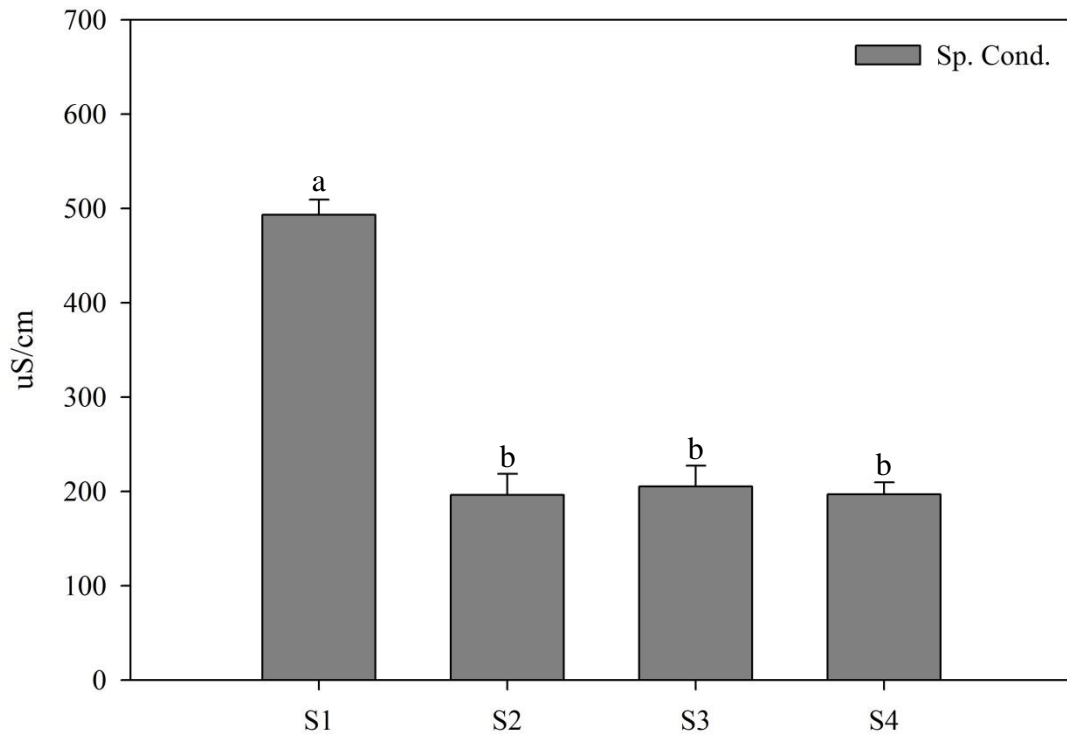


Figure 23. Mean \pm SD (n=3) in-situ Specific Conductance for the south-facing aspect stream (Mineral Creek). The letters denote to which statistical group a site belongs by constituent.

The differences in T between elevations on the northern aspect increased with decreasing elevations. This could be explained by the generally higher air temperatures at lower elevations, the method of collecting samples highest to lowest elevations each day (meaning the lowest elevation sample was collected latest in the day each time), or a combination of both factors. Because the highest elevation sites also had the lowest mean discharge, these sites would have been more susceptible to the influence of local air temperature; by sampling these low-flow high-elevation streams earlier in the day, it is not surprising the temperatures are significantly lower than those measured in the higher-discharge lower-elevation sample sites later in the day (Figure 20). On the

Silverton aspect, mean T between elevations was not significantly different, though S1 had observably lower T than the other three points within the same stream at lower elevations. This is likely a result of S1 being the highest elevation site, and being sampled first during the day. Additionally, this point in Mineral Creek had the lowest volume of discharge, making it more likely to be strongly affected by the air temperature.

On the Ouray aspect, the mean DO concentrations at the different elevations showed a different trend from T, decreasing as the T increased (Figure 20). This is not surprising as DO is directly affected by temperature; cold water can hold more dissolved oxygen than warm water (Cech, 2010). The mean DO at the Silverton aspect elevations was not significantly different, but, neither were the in-situ temperature measurements (Figure 22).

The pH along the Ouray aspect follows the same trend as DO, with sites O2 and O3 having the lowest mean pH, corresponding with the highest mean pollutant concentrations (Figure 20). On the Silverton aspect, site S1 had a significantly lower mean pH than the three lower elevation sites. I think this lower pH at S1 correlates with the local geology of this site just as was seen at sites O2 and O3 on the Ouray aspect (Figure 22). The highly mineralized San Juan formation contains large amounts of sulfides. The oxidation of these sulfides leaves free H^+ in solution, which explains the low pH measured at the sample sites which correlate with this formation (Figure 16) (Neubert et al., 2011).

Unfortunately, low pH can have serious negative environmental effects such as making some contaminants (such as metals) stay in a dissolved state within the water column rather than precipitating out thereby increasing exposure to aquatic organisms (Mast et al., 2007; Runkel et al., 2007). Low pH is also closely tied to low DO, which can negatively affects aquatic life (Kramer, 1987; Olsvik, Vikeså, Lie, & Hevrøy, 2013).

Specific conductance, the ability of water to pass an electric current, is typically directly correlated with the presence of dissolved and suspended solids (Hem, 1985). Spec. Cond. itself is not a constituent which causes direct positive or negative environmental effects, it is simply an indicator of the presence of dissolved and suspended particles within water (Hem, 1985). Relationships have been verified between various dissolved and suspended constituents in a host of studies, however, Sp. Cond. does not have predictive power regarding what is present (Hem, 1985; Pilgrim, Huff, & Steele, 1979). It is used in this study as a verification of the laboratory results; when collecting samples in the field, a high Sp. Cond. value is indicative of the presence of a high concentration of “things” within the water. In this study area where metal contamination is a known problem, in-situ Sp. Cond. measurements could be employed as a preliminary site selection method for sites being considered for further analysis, monitoring, and remediation.

Within the water samples brought back to Texas A&M for further analysis, only five of the six constituents of interest (SO_4 , NO_3 , Al, Mn and Fe) were examined because PO_4 was below detection level in all but three stream samples (Appendix N). PO_4 tends to be a limiting nutrient in many aquatic ecosystems because of its tendency to

be naturally scarce. One of the reasons for this natural scarcity is actually a lack of PO_4 availability rather than a lack of PO_4 being present. In aquatic systems with aluminum or iron rich soils, PO_4 tends to react with and bind to the underlying soil (under aerobic conditions) making it unavailable within the water column (E. E. Burns, Comber, Blake, Goddard, & Couldrick, 2015; Jin et al., 2013; Lu et al., 2013; Smil, 2000). A water column with DO concentration of 2 mg/L or greater is considered aerobic; if the DO concentration falls below 2 mg/L, the system becomes anaerobic and trapped PO_4 is released into the water column (Smil, 2000; Wu, Wen, Zhou, & Wu, 2014). This process is similar to that of metals precipitating out of solution at neutral to basic pH (Mast et al., 2007; Seo, Cheong, Yim, Min, & Geroni, 2016).

On the northern aspect, a general spike occurs in measured constituents at site O2 which is followed by a decrease downstream (down elevation) (Figure 24). On the southern aspect, the highest elevation site (S1) had the highest mean concentrations of all constituents measured with the exception of NO_3 . NO_3 was highest at site S3 (Figure 25). Significant differences exist between sites for SO_4 , Al, Mn, and Fe. No significant differences were detected for NO_3 or PO_4 between sites.

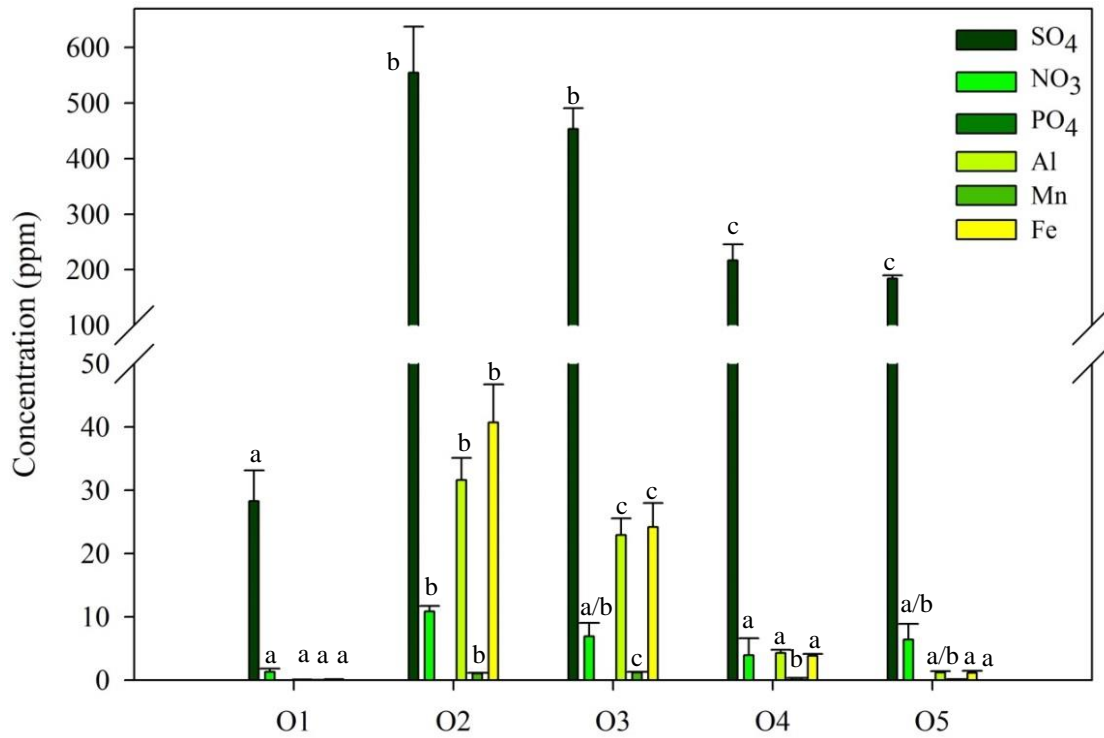


Figure 24. North-facing aspect stream sample means \pm SD (n=3) by elevation for sulfate (SO₄), nitrate (NO₃), phosphate (PO₄), aluminum (Al), manganese (Mn), and iron (Fe). The letters denote to which statistical group a site belongs by constituent.

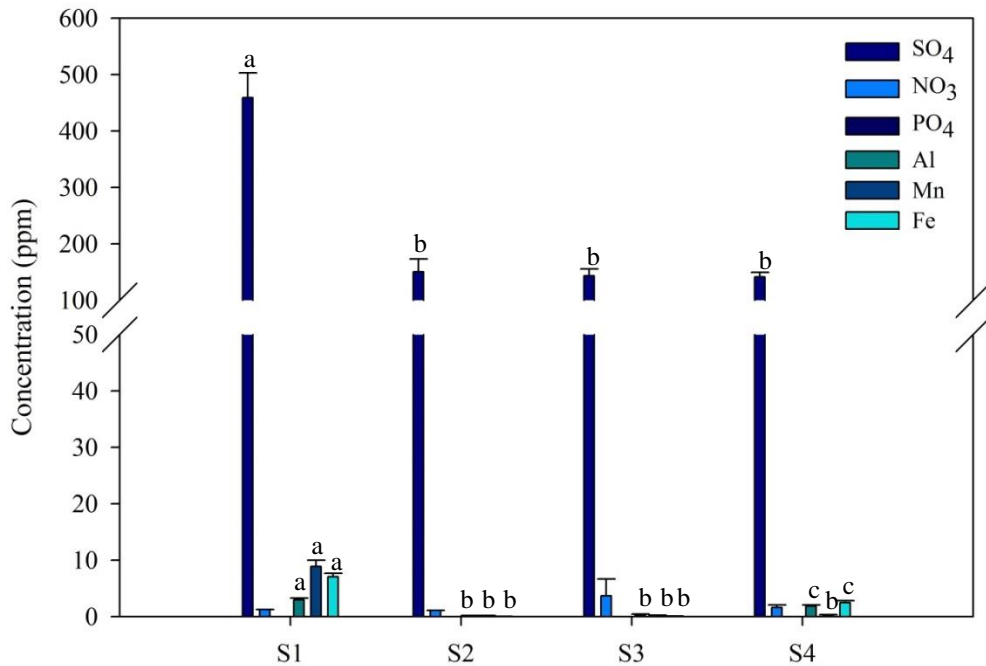


Figure 25. South-facing aspect stream sample means \pm SD (n=3) by elevation for sulfate (SO₄), nitrate (NO₃), phosphate (PO₄), aluminum (Al), manganese (Mn), and iron (Fe). The letters denote to which statistical group a site belongs by constituent.

A comparison of the water-quality results by elevation for each aspect showed site O1 has a significantly lower SO₄ concentration than the downstream sites. A spike of SO₄ occurs at sites O2 and O3, whereas lower concentrations were present downstream; that downstream decrease, while significantly lower than sites O2 and O3, is still significantly higher than the SO₄ concentration measured at site O1. This high SO₄ concentration, especially within the range of sites O2 and O3, may be influenced by the local lithology (the San Juan Formation), which contains large quantities of sulfides (Figure 16) (Burbank & Luedke, 2008; Shin, Ryu, Mayer, Lee, & Lee, 2014). On the south aspect site S1 had a significantly higher concentration of SO₄ than the three

downstream sites, which are not statistically significantly different from each other (Figure 25). Site S1 is also intersects the San Juan formation (Figure 16).

The SO_4 measured at sites O2, O3, and S1 is most likely directly from the San Juan formation. The limited discharge of Mineral Creek at site S1 and of Red Mountain Creek at sites O2 and O3 suggests these streams are mostly made up of baseflow (water seeping directly out of the local lithology) at these high elevation headwater portions of their respective watersheds. The high concentration of SO_4 measured at these sites is then reduced downstream by dilution and distance from the source. The Uncompahgre, Cuttler, and Hermosa formations are sedimentary and do not contain the notable concentrations of sulfides contained within the younger, higher elevation formations (Figure 16) (Blair, 1996a, 1996b; Cross & Larsen, 1935).

Sulfate is a secondary drinking water contaminant according to the USEPA, and it is known to cause non-toxic detriments to drinking water above a specific concentration: 250 mg/L. Water with a SO_4 concentration greater than 250 mg/L may have a salty taste but no known health detriments (Dietrich & Burlingame, 2015). The SO_4 at sites O2 and O3 and S1 exceed the drinking-water standards for this constituent (Dietrich & Burlingame, 2015). Atmospherically transported SO_4 , which lowers the pH of falling precipitation, can result in acid rain, which has widespread detrimental effects on the environment (Lee, 1981).

The NO_3 concentration within Red Mountain Creek and the Uncompahgre River follow the same general trend as SO_4 , which is a spike at site O2 and then a decrease in concentration in the downstream sites. The NO_3 concentration at sites O1 and O4 fall

into Tukey's group "a" for significant differences, so they can only be distinguished from site O2. Site O2 has a significantly higher concentration of NO_3 than site O1, but cannot be statistically distinguished from sites O3 and O5 (meaning those concentrations fall between the concentrations of sites O1/O4 and O2) (Figure 24). On the southern aspect, site S3 had the highest mean NO_3 concentration of the four sites monitored, however, all four sites on the southern aspect had NO_3 levels below EPA drinking-water standards (Figure 25).

The most common anthropogenic sources of NO_3 into surface waterways are treated wastewater effluent discharge, soil fertilization, and atmospheric deposition (Shin et al., 2014; Waldner et al., 2014). In addition to anthropogenic sources, NO_3 may also be naturally leached from local bedrock, especially in areas with thick sedimentary or metasedimentary beds (J. Holloway, Dahlgren, Hansen, & Casey, 1998; J. M. Holloway & Dahlgren, 2002; Morford, Houlton, & Dahlgren, 2011). Igneous lithologies, while able to contain/leach nitrogen, are typically minor contributors to surface water NO_3 concentrations (J. Holloway et al., 1998).

NO_3 must be monitored because it can cause widespread health issues in humans and animals (Bruning-Fann & Kaneene, 1993; Jamaludin, Sham, & Ismail, 2013; Su, Wang, & Zhang, 2013). The USEPA drinking water standards prohibit NO_3 from exceeding 10 mg/L in water intended for human consumption (Knobeloch, Salna, Hogan, Postle, & Anderson, 2000). Effects of excess NO_3 to humans include methemoglobinemia (Blue Baby Syndrome) and have been investigated as a potential source of some cancers (Galloway, Schlesinger, Levy, Michaels, & Schnoor, 1995;

Knobeloch et al., 2000; Su et al., 2013). Any NO_3 in excess of the environmental need is sufficient to cause environmental harm such as promoting eutrophication of surface waters, therefore, NO_3 is typically monitored in conjunction with other nutrients and the presence of algal populations in at risk surface waters (Galloway et al., 1995). In all sites but O2, the mean nitrate concentrations are below the USEPA drinking water standard (Figure 24) (USEPA, 2016b). All of these sites, but especially O2, have the potential to be causing environmental harm.

The Al concentrations within the Red Mountain Creek and Uncompaghre watersheds follow the same general trend as SO_4 and NO_3 . In this area, and especially at these elevations, an abundance of aluminum bearing rocks were left over from the now extinct volcanoes which were active at this location until the Pleistocene (Blair, 1996b). On the Silverton aspect, site S1 had the highest mean concentration of Al detected, however, the levels of Al detected were low enough that they are unlikely to cause environmental degradation (Organization, 2003). The frequency of mining and mine waste on the Ouray side are likely acting as additional sources of pollutants to the streams on that aspect which are less prevalent on the Silverton aspect, even though the geology is the same. As with the SO_4 concentrations measured at the sample sites which intersect the San Juan formation, the highest metal concentrations also coincide with the local lithology (Figure 16).

Aluminum is important environmentally because it can inhibit the uptake of nutrients by flora and fauna and has the ability to travel up the food chain through bioaccumulation (Sivakumar & Prasad, 2012). Fish and aquatic invertebrates are

especially susceptible to Al toxicity as high concentrations of Al affect the ability of gills to uptake necessary ions and making it difficult or impossible to regulate the osmotic pressure (Rosseland, Eldhuset, & Staurnes, 1990; Sivakumar & Prasad, 2012). In humans, the toxicity of Al is still being researched, but correlations have been found between aluminum and degenerative neurological diseases, such as Alzheimer's (Bhattacharjee, Zhao, Hill, Percy, & Lukiw, 2014).

Like Al, the concentration of Mn within Red Mountain Creek and the Uncompaghe River is likely being driven by the local lithology. The same trend exists for Mn as was seen for Al and SO₄ where the mid-elevation sites have the highest concentrations (San Juan formation). Sites O1 and O5 were statistically the same and significantly lower than the other three mid-elevation sites. These two sites, the headwater location within the Burns formation (above the influence of the San Juan formation and most of the historic and current mining activity) and the lowest elevation site which coincides with the Cuttler Formation (a sedimentary formation) and is influenced by a drainage basin than the higher elevation sites allowing for dilution of the metals and sulfides from the younger igneous formations upstream have understandably the lowest concentrations of metals and sulfur compounds. Sites O2 and O4 also statistically belong to the same group and site O3 contained the highest concentration of the five sites for Mn. This suggests the Mn concentration measured at site O3 is under the influence of the immediate environment as well as the upstream O2 site. The reduction in concentration at site O4 suggests between sites O3 and O4 is where the

introduction of Mn to the local stream starts to decline and dilution starts to have a greater influence on the water quality of Red Mountain Creek (Figure 24).

On the Silverton aspect, as was observed for Al, the Mn concentrations detected are significantly higher at site S1 than the downstream (lower elevation) sites (Figure 25). The mean Mn concentrations for all Silverton aspect sites except S1 are below 1 mg/L; these levels are low enough that this constituent is unlikely to be causing environmental harm, especially considering Mn is not considered a highly toxic metal (USEPA, 2016a). Though lower than the concentrations measured on the northern (Ouray) aspect, the trend continues of the site coinciding with the San Juan formation having the highest concentrations of the constituents of interest, including Mn (Figure 16).

Mn is considered a secondary water quality hazard, meaning it is not strictly regulated by the United States Environmental Protection Agency (USEPA, 2016a). Mn may cause discoloration and taste abnormalities in drinking water, but the organisms (including humans) are good at processing ingested Mn (Organization, 2004). Most studies which have found detrimental health effects (typically neurological) from Mn exposure involved long-term inhalation exposure, not ingestion exposure (Organization, 2004). Studies involving the effects of chronic Mn exposure within the environment are quite limited, however, the World Health Organization (WHO) has determined adult humans can tolerate daily Mn intakes as high as 11 mg/day (Organization, 2004). The mean Mn levels at all sample sites except are below 3 mg/L (most sites it is below 1

mg/L), therefore, it is unlikely Mn is causing environmental degradation on its own (Organization, 2004).

The third metal examined, Fe, varies between elevations in a similar trend as SO₄, Al, and Mn, further supporting the hypothesis that these constituents are controlled by the local lithology in this historic mining area, because all four constituents are found in large quantities in the local rock formations and the alterations which produced the metal ores in this area (Neubert et al., 2011). Statistically, sites O1, O4, and O5 are indistinguishable. The concentrations of Fe at these three sites are significantly lower than the concentrations measured at sites O2 and O3, of which O3 has the highest concentration of Fe. This is the same trend detected for Al; this suggests these two metals may be from similar or the same sources (local lithology) and interact with the surface waterways in a similar manner.

On the Silverton aspect, the mean Fe concentration was highest at site S1 and lowest at sites S2 and S3, following a similar trend as the other constituents measured (Figure 25). This suggests the sources of the compounds, which were all found in highest concentrations at the highest elevation site on this aspect, are likely from the same source. Along with being from the same source, the mechanism by which these constituents are moving into Mineral Creek is likely the same (e.g., leaching from bedrock/base flow).

As previously discussed, the low pH of these upper-elevation sites will have caused the naturally occurring metals to remain in solution rather than precipitating out (Mast et al., 2007; Seo et al., 2016). The drop in concentration of all the metals

measured downstream from the source rock (San Juan Formation) on both aspects may be explained by both dilution from greater discharge and the increase in pH associated with the change in local geology from mineralized igneous/metamorphic formations to sedimentary limestone and sandstone formations at the lower elevation sites.

Determining the source of Fe into this system, as with the other metals and anions examined in this study, is important because iron, in addition to staining rocks and turning the local waters orange, can have serious environmental and human health impacts (Lieu, Heiskala, Peterson, & Yang, 2001; Vuori, 1995). Like many essential nutrients in humans, Fe can be fatal at high doses and has been linked to DNA damage, neurological impairment, diabetes, and some cancers (Britton, Leicester, & Bacon, 2002; Fraga & Oteiza, 2002). Excessive iron in the water can bind to the gills of some aquatic organisms, such as some species of trout, inhibiting the ability to breath (Dalzell & Macfarlane, 1999).

At many of the sites sampled no significant differences were detected for any constituent. Some of the sites sampled (e.g., O2 and O3; S2 and S3; S4 and S5) are very close to each other (i.e., <150 meters elevation difference between sites). This lack of difference in elevation, one of the parameters by which samples were being compared, may be the primary reason differences were not detected between these sites.

Aspect

A comparison of the in-situ water quality parameters between aspects showed no statistically significant differences. Though no significant differences were detected, T and Sp. Cond. were higher and DO and pH were lower on the Ouray aspect than the Silverton aspect, respectively (Figures 26 and 27). This trend coincides with the higher concentrations of metals and anions on the Ouray aspect than on the Silverton aspect (Figure 28). This further supports the discussion of how the pH of this system is the likely driver of the metal concentrations measured (i.e., low pH is correlated with higher concentrations of dissolved metals).

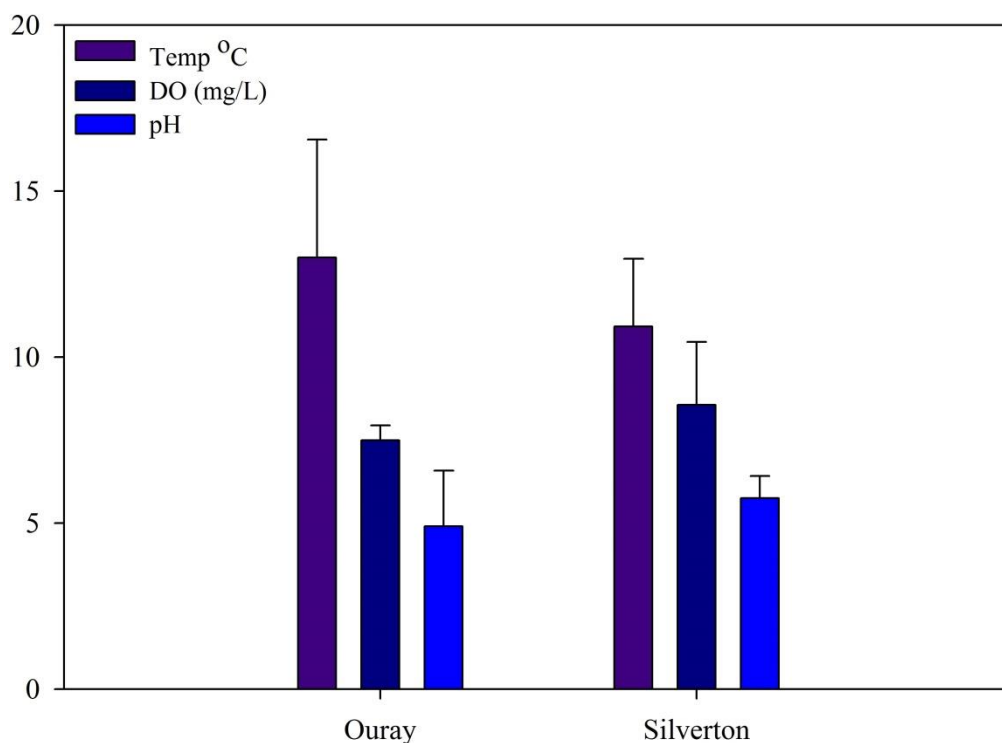


Figure 26. Mean \pm SD (Ouray: n=15; Silverton: n=12) in-situ water quality results (except Specific Conductance) between aspects. No significant differences were detected between aspects.

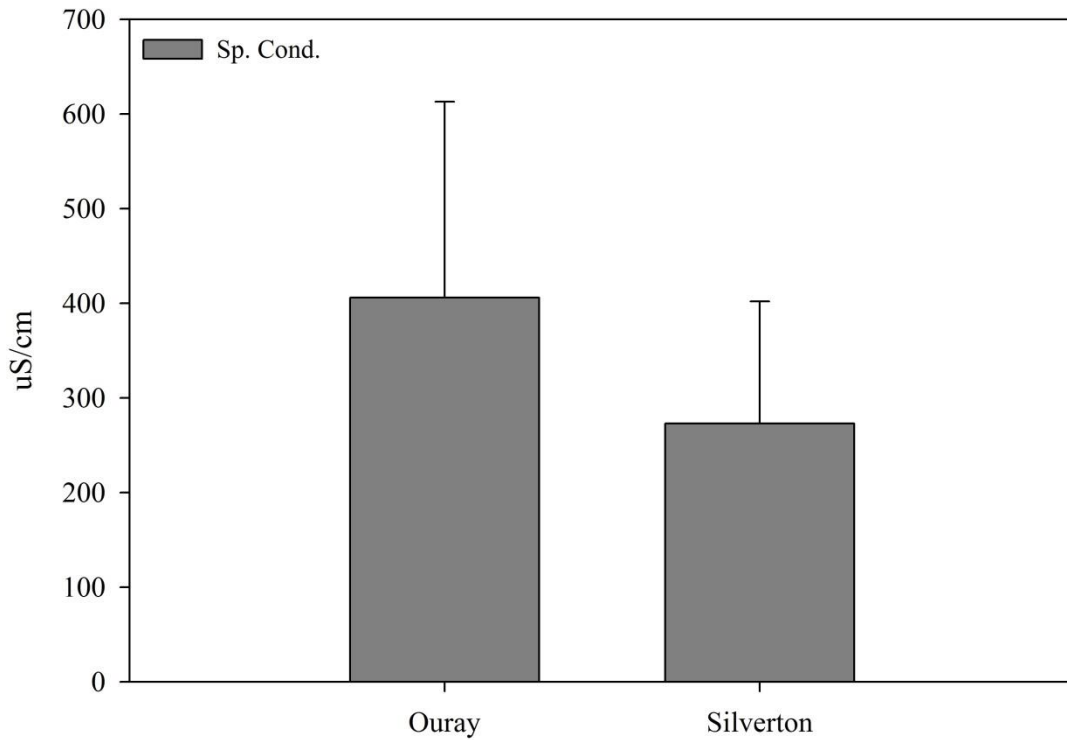


Figure 27. Mean \pm SD (Ouray: n=15; Silverton: n=12) in-situ Specific Conductance between aspects. No significant differences were detected between aspects.

The aspect mean water quality parameters followed the same general trend as the in-situ parameters, where the quality tended to be worse on the Ouray aspect than on the Silverton aspect (Figures 26-28). A comparison of the mean concentrations of the water-quality constituents between aspects shows higher concentrations on the Ouray side of Red Mountain for all but Mn (Figure 28). The mean concentrations for three of the six constituents were significantly higher on the Ouray (north facing) aspect than on the Silverton (south facing) aspect. This finding corresponds with the atmospheric flux results which generally showed a higher flux of constituents on the Ouray aspect than on the Silverton aspect (Price, 2015).

A possible explanation for the higher concentrations of constituents within the streams on the Ouray aspect, besides influence of atmospheric input, is the increased mining activity and tailing ponds present on the Ouray side of the mountain. These abandoned mine portals and tailings can be seen discharging water throughout the year; the increased surface area of the tailings means more surface area for dislodging the natural metals, sulfides, minerals, etc. which can enter into surface water.

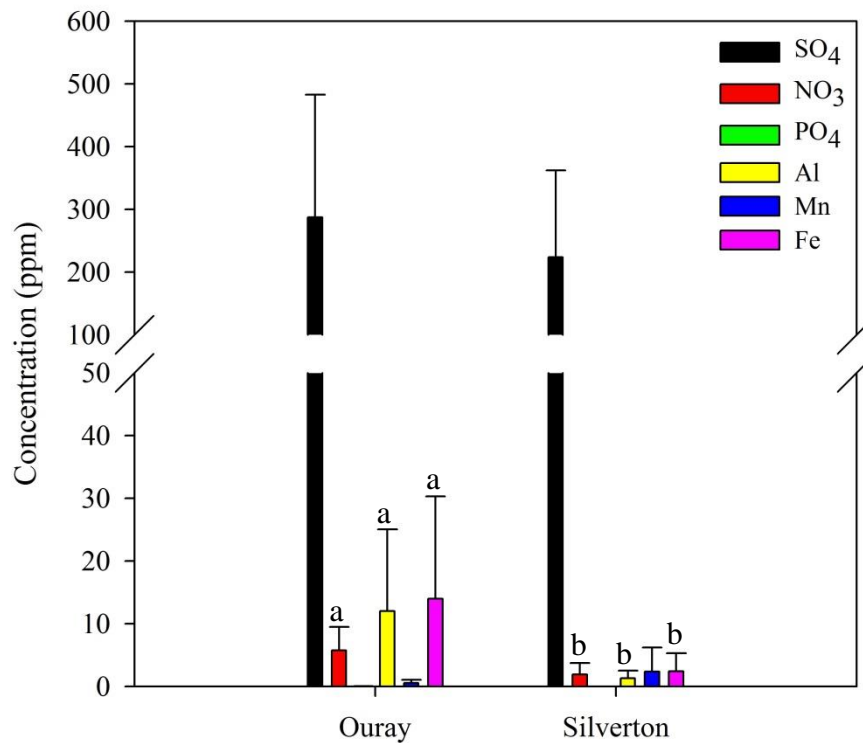


Figure 28. Stream sample means \pm SD (Ouray n=15, Silverton n=12) by aspect for sulfate (SO₄), Nitrate (NO₃), Phosphate (PO₄), aluminum (Al), manganese (Mn), and iron (Fe). The letters denote to which statistical group a site belongs by constituent.

Between the north and south aspects, several significant differences were found. NO₃, Al, and Fe were significantly higher on the Ouray aspect than on the Silverton side

of Red Mountain Pass (Figure 28). SO_4 was also higher on the norther (Ouray) side than the southern (Silverton), but it was not statistically significant. Whereas technically higher on the north aspect than the south aspect, PO_4 was found in such low concentrations, below detection at multiple sites, that is it not surprising no significant difference occurred between aspects for PO_4 . Mn was the only constituent to have a higher concentration, though not statistically significant, on the south aspect (Figure 28).

I think the greater mining activity on the Ouray aspect as compared to the Silverton aspect may explain most of these aspect differences in water quality. The differences in atmospheric flux between aspects, however, were also higher on the Ouray aspect than on the Silverton aspect, so the atmospheric flux could also be contributing to these water quality differences (Price, 2015).

Additional Calculations Results

Some additional calculations were performed to attempt to tie together the atmospheric flux and water quality measurements. The goal was to determine how much of each constituent examined would be fluxed onto each sub-basin within the watershed if the assumption is made that the flux rate measured at each sample site could be applied to the entire sub-basin. The size of the sub-basins directly affected the results of these calculations (Equation 5); in this equation, the area of each sub-basin was multiplied by the atmospheric flux and the result (in ug/day) was multiplied by a conversion factor (1000 ug/mg) to get the answer into a more familiar, usable unit (mg). The area of the sub-basins within the study area means the rate of flux at the sub-basin or

watershed level could be quite high (i.e., NO₃ would have been fluxed at a rate of over almost twenty grams per day in sub-basin O2 during this study) (Tables 1 and 2).

Equation 5: $[\text{Area of sub-basin (cm}^2\text{)} * \text{Flux (ug/cm}^2\text{/day)}] * 1000 \text{ ug/mg}$

Table 1. The mean total atmospheric flux (mg/day) associated with the area of the sub-basin in which each sample site resided for the northern (Ouray) aspect.

Site	Area (Hectares)	Total Flux (mg/day)					
		SO ₄	NO ₃	PO ₄	Al	Mn	Fe
O1	23.6	32.9	104.6	0.4	1.1	0.3	1.6
O2	2575.3	6892.1	19483.1	586.4	47.0	44.3	266.5
O3	2018	775.9	2435.5	34.6	13.9	4.8	20.4
O4	14832	2850.7	6777.2	223.1	747.8	112.2	802.1
O5	15205.1	1397.0	4036.1	54.0	265.6	34.1	228.6

On the southern aspect, the same trend as was noted on the northern aspect is observed. Site S1 had the highest measured concentration of all measured constituents except PO₄ and Mn, however, this site has the lowest measured total flux of all constituents by an order of magnitude or more (Figure 25 and Table 2). Unfortunately, as was the case for this entire study, there are no water quality results available for site S5 for which to compare these total flux results. As was seen for the northern aspect, the lowest elevation site also occupied the largest sub-basin and thereby had the greatest total flux results; it would have been an interesting comparison to see if the same trend (lower concentrations of constituents associated with higher total flux) was seen on the southern aspect as was seen on the northern aspect.

Table 2. The mean total atmospheric flux (mg/day) associated with the area of the sub-basin in which each sample site resided for the southern (Silverton) aspect.

Site	Area (Hectares)	Total Flux (mg/day)					
		SO ₄	NO ₃	PO ₄	Al	Mn	Fe
S1	44.2	0.9	2.3	0.0	0.1	0.0	0.2
S2	2474.1	844.5	2449.0	0.0	17.9	2.4	19.4
S3	342	167.4	478.4	0.0	5.5	1.9	8.6
S4	10535.7	1110.7	3281.8	69.2	34.3	7.4	50.8
S5	24362.5	13041.8	33549.9	1639.5	544.9	151.5	867.7

The second calculation performed investigated how much (at what rate) flux would need to occur to affect the surface water quality in this study area. The first assumption made for this calculation was that 10% of the streams total load (concentration*discharge) must have originated from atmospheric flux for it to be considered a significant source. The second assumption was that all fluxed material (constituent) was available for runoff into a local surface stream which would drain to the sub-basin pour point (which was based on the sample site location).

The results of this calculation show, with these assumptions, the 10% total load of the streams examined are exceeded at multiple sites, for multiple constituents, on both aspects (Tables 3 and 4). On the northern (Ouray) aspect, the NO₃ and PO₄ total fluxes exceed the 10% stream total load at all five sample sites. At some sites, the total flux even exceeds the raw total load of the stream. Of the three metals examined, only Fe had a total flux which exceeded the 10% total load calculated for these streams, and it was only at sites O4 and O5, which had the lowest measured Fe concentration of all the sites, with the exception of site O1 (Table 3).

On the southern, (Silverton) aspect, NO_3 and PO_4 were the only constituents for which total flux exceeded the 10% total load for the sample sites examined. As on the northern aspect, NO_3 total flux exceeded the 10% total load at all sample sites; PO_4 however only exceeded the total load at site S4 (Table 4). This site (S4) was also the only site at which any PO_4 was detected on the southern aspect in either the stream or atmospheric flux samples

These results suggest that though the flux measured in this study was small as compared to other studies, it is possible the quantities of NO_3 and PO_4 , and possibly Fe, would be sufficient to impact surface water quality in the event runoff occurred (Tables 3 and 4). The sub-basins which, because of their size, would have had the most atmospherically fluxed material to contribute to the surface water quality are associated with sites which had some of the lowest concentrations of these constituents. For example, the highest total fluxed SO_4 and NO_3 results occur at sites O4 and O5, however, the SO_4 and NO_3 water quality peaks occurred at sites O2 and O3 (Table 1 and Figure 24). These calculations support the hypothesis that there are multiple sources acting upon the water quality of these surface streams, and that at some of the sites examined, atmospheric flux could be contributing to surface water quality when runoff occurs. Further research would be necessary to examine this connection between atmospheric flux and surface water quality in more detail.

Table 3. The total flux (TF) of each constituent compared to the 10% total load (TL) of each constituent shows the TF exceeds 10% TL (red) for NO₃ and PO₄ at all sample sites and Fe for sites O4 and O5.

Sample Site	SO ₄ (mg/t)			NO ₃ (mg/t)			PO ₄ (mg/t)			Al (mg/t)			Mn (mg/t)			Fe (mg/t)		
	Total Load (TL)	10% TL	Total Flux (TF)	TL	10% TL	TF	TL	10% TL	TF	TL	10% TL	TF	TL	10% TL	TF	TL	10% TL	TF
O1	1,812.7	181.3	32.9	85.3	8.5	104.6	3.2	0.3	0.4	595.5	59.5	1.1	99.4	9.9	0.3	153.2	15.3	1.6
O2	145,127.8	14,512.8	6,892.1	2,829.8	283.0	19,483.1	0.0	0.0	586.4	8,860,686.0	886,068.6	47.0	299,129.7	29,913.0	44.3	5,410,467.2	541,046.7	266.5
O3	160,648.9	16,064.9	775.9	2,443.2	244.3	2,435.5	17.7	1.8	34.6	8,875,279.4	887,527.9	13.9	459,947.3	45,994.7	4.8	2,881,811.7	288,181.2	20.4
O4	416,440.1	41,644.0	2,850.7	7,539.5	753.9	6,777.2	76.9	7.7	223.1	44,890.6	4,489.1	747.8	632,795.9	63,279.6	112.2	1,557.9	155.8	802.1
O5	625,632.0	62,563.2	1,397.0	19,293.1	1,929.3	4,036.1	0.0	0.0	54.0	600,972.2	60,097.2	265.6	367,111.7	36,711.2	34.1	0.0	0.0	228.6

Table 4. The total flux (TF) of each constituent compared to the 10% total load (TL) of each constituent shows the TF exceeds 10% TL (red) for NO₃ at all sample sites and PO₄ for site S4.

Sample Site	SO ₄ (mg/t)			NO ₃ (mg/t)			PO ₄ (mg/t)			Al (mg/t)			Mn (mg/t)			Fe (mg/t)		
	Total Load (TL)	10% TL	Total Flux (TF)	TL	10% TL	TF	TL	10% TL	TF	TL	10% TL	TF	TL	10% TL	TF	TL	10% TL	TF
S1	137.7	13.8	0.9	0.4	0.0	2.3	0.0	0.0	0.0	908.9	90.9	0.1	2,739.8	274.0	0.0	1,384.1	138.4	0.2
S2	51,198.6	5,119.9	844.5	371.8	37.2	2,449.0	0.0	0.0	0.0	18,612.7	1,861.3	17.9	57,373.3	5,737.3	2.4	1,606.8	160.7	19.4
S3	115,175.6	11,517.6	167.4	2,933.6	293.4	478.4	0.0	0.0	0.0	45,009.3	4,500.9	5.5	166,679.0	16,667.9	1.9	996.6	99.7	8.6
S4	285,376.3	28,537.6	1,110.7	3,230.1	323.0	3,281.8	0.0	0.0	69.2	29,656.0	2,965.6	34.3	586,075.3	58,607.5	7.4	1,979,364.3	197,936.4	50.8

Summary and Conclusions

Overall, many differences were detected amongst the sample sites (elevations) and between the two aspects of the study area for the water-quality parameters measured. The significant differences detected between elevations align with the previously discussed geologic and hydrologic differences within the area. The samples sites are associated with the geologic formations in which mining has (and is currently) taken place: sites O2, O3, and S1 located geographically correspond with the highest measure concentrations of metals and sulfate, as well as the lowest pH measurements and highest measured specific conductance (Figures 20-25). The further correspondence of low measured stream discharge at these highest elevation sites means there is less opportunity for the dilution of the baseflow seeping from the local lithology laden with dissolved metals, minerals, anions, and cations.

It was not surprising the Sp. Cond. correlates closely with the mean metal and anion concentrations found at the various sample sites. For the Ouray aspect elevations, the Sp. Cond. at sites O2 and O3 was significantly higher than that found at the other three sites, with site O1 having the lowest Sp. Cond. and lowest concentrations of measured constituents (Figure 21 and 24). The same trend was seen on the Silverton aspect with site S1 having a statistically higher Sp. Cond. than the three lower elevation sites, which is directly correlated with significantly higher metals and anions at site S1 than the lower elevation sites (Figure 23 and 25).

The lower elevation sample sites, O4, O5, S2, S3, and S4, which are associated with geologic formations such as limestone and sandstone (which also do not have the

economical mineralization found at the higher elevation sites), are likely acting as a natural buffering system to these low pH, metal laden headwater streams. The increased discharge associated with the larger contributing watershed along with the natural buffering capacity of water which has interacted with limestone raise the pH of the lower-order headwater streams causing the previously dissolved metals to precipitate out. The concentrations of the metals and other anions measured in this study which remain in solution are diluted by the increased hydrologic contribution (Figures 17-18 and 24-25).

Along with the geologic and pH influences on stream water quality, the interaction of soils and DO upon PO_4 can be seen in these results. Under aerobic conditions PO_4 is trapped in Fe and Al rich soils, such as those found in this study area and under anaerobic conditions, the trapped PO_4 is released into the water column (E. E. Burns et al., 2015; Jin et al., 2013; Wu et al., 2014). However, in this study, the water was aerobic ($\text{DO} > 2 \text{ mg/L}$) during all in-situ measurements (Figures 20 and 22). Because more PO_4 was measured in the atmospheric flux than within the stream samples for all sites (at which PO_4 was detected), I think the PO_4 which is entering the study area through atmospheric flux, and that which is already present, is being trapped within the soils and only being released when soils undergo anaerobic conditions.

Lastly, the additional calculations performed to examine hypothetically how atmospheric flux within the study area could be affecting surface water quality during periods of runoff showed some interesting results. Scaling the atmospheric flux measurements up to the sub-basin area illustrated the potential for large ($>1000 \text{ mg/day}$

for some constituents) contributions of the constituents examined (SO_4 , NO_3 , PO_4 , Al, Mn, and Fe) from atmospheric flux to the sub-basins examined. The second part of these calculations examined whether enough flux occurred for any of the constituents to exceed 10% of the total load of the streams for each constituent during this study. For three of the six constituents measured, the total flux did exceed the 10% mean total load of the stream for multiple sites. For NO_3 and PO_4 , this result is supported by numerous studies throughout the world which have found the atmospheric transport of NO_3 and PO_4 , common ingredients in fertilizer, is widespread (Anderson & Downing, 2006; D. A. Burns, 2004; Fowler et al., 2013; Michalak et al., 2013). I think the Fe flux which exceeded the 10% total load of the Uncompaghre River at sites O4 and O5 is most likely from a local source considering how iron-rich this study area is. However, not discounting the probability of local inputs, I think it is likely some or most of the atmospheric NO_3 and PO_4 measured in this study may have originated from agricultural or confined animal feeding operations (CAFOs) outside the study area.

Therefore, I have reached the following conclusions regarding the water quality within this study area and sample period:

1. Differences in surface water quality are associated more at the individual site level than between aspects for SO_4 , Mn, Sp. Cond., pH, T, and DO.
2. A direct relationship between the local geology of the sample sites and water quality can be observed.

CHAPTER IV

OVERALL SUMMARY AND CONCLUSIONS

The San Juan Mountains, like any ecosystem, are fragile and are affected by numerous inputs, outputs, pathways and drivers. This study examined atmospheric flux and water quality individually within this system and then looked to determine if there was a potential link between the two. The atmospheric flux measured in this study at ten sample sites, five elevations on two generally opposing aspects, showed that for two of the six constituents measured, atmospheric flux significantly varies between multiple elevations. Figure 12 within Chapter II showed the atmospheric flux of both NO_3 and SO_4 to be significantly higher at sample sites O1 and O2 than the other three lower elevation sites examined. Though other variations in mean flux for this study period are observable between sample sites, no other statistically significant differences were detected for atmospheric flux.

A comparison of the results from this study with those from other similar studies (studies which examined the flux of these same constituents in high elevation systems) showed these results to be universally lower. I think these differences may have multiple causes, but the cause I think most likely to have significantly affected the flux was the ongoing drought conditions during this study period. During the summer of 2015, the state of Colorado was in the midst of an El Niño driven drought causing below average precipitation. Lack of precipitation is correlated with low atmospheric flux (Gunawardena et al., 2013; Lynam et al., 2014; Zhu et al., 2015). Likewise, the lack of

precipitation associated with these drought conditions meant no runoff was predicted to have occurred during the study period. One of the objectives of this research was to determine if the atmospheric flux occurring in this study area of the San Juan Mountains was impacting surface water quality. Though no runoff occurred, surface water quality was still examined at each of the same sample locations as the atmospheric flux samples were collected and follow-up calculations were performed to examine the potential hypothetical effect of the atmospheric flux measured to surface water quality had runoff occurred.

Surface water quality was assessed for both in-situ parameters (temperature (T), dissolved oxygen (DO), pH, and specific conductance (Spec. Cond.) and six lab analyzed constituents (sulfate (SO₄), nitrate (NO₃), phosphate (PO₄), aluminum (Al), manganese (Mn), and iron (Fe)). The results of these measurements, and the lack of runoff washing atmospherically fluxed constituents into the streams sampled, are telling of how impacted these local waters are by the local environment itself. Being located within a highly mineralized geologic area, these streams are naturally influenced by the high concentrations of metal and sulfide bearing ores (Blair, 1996b). The sample sites which coincide with the historically and currently mined geologic formations are the sites at which all three metals examined and sulfate was found to have the highest concentrations. These sites also have the highest mean Spec. Cond. and lowest mean pH. These water quality indicators (pH and Spec. Conductance) are important for two reasons. First, the low pH is most likely being driven by the oxidation of the sulfur bearing minerals throughout these formations. Low pH (as measured in this study)

cause metals to remain in a dissolved state within a water column. Second, high Spec. Cond. indicates the presence of dissolved and or suspended material within a water column. Therefore, the highest Spec. Cond. measurements support the findings of the highest measured concentrations of SO_4 , Al, Mn, and Fe at the same sites, with which the high Spec. Cond. measurements correlate (Figures 21 and 23-25).

The significant differences detected between elevations and aspects for these water quality parameters support the discussion that the surface water quality during this study was lithologically driven. Sample sites O2, O3 and S1 were consistently higher than the other sites on their respective aspects with regards to the mean concentrations of SO_4 , Al, and Fe (Figures 24 and 25). PO_4 was consistently below detection levels for the surface water samples collected from all but three sites: O1, O3, and O4, each of which produced one PO_4 measurement (Appendix N). This indicates that PO_4 present within the system being examined, but is being sequestered either within the biological material within the study area (PO_4 is commonly a limiting nutrient within ecosystems) or is being entrapped through another, non-biological, chemical process: soil entrapment (Jin et al., 2013; Wu et al., 2014).

The parent materials for the soils in this study area are primarily the local geologic formations. It is safe to assume these soils will contain significant amounts of Fe and Al. Because PO_4 interacts with, and binds to, Al and Fe bearing soils under aerobic conditions, it is not surprising PO_4 was difficult to measure in these streams of interest, as they typically maintained aerobic conditions ($\text{DO} > 2 \text{ mg/L}$) (Smil, 2000; Wu et al., 2014).

Though PO_4 was difficult to detect in the surface water samples, it, along with the other five constituents examined, were measured in the atmospheric flux samples. This begs the question, if runoff had occurred during the sample period, would PO_4 have been found in the surface streams? Though I cannot answer that question directly, the stochastic environmental model performed to examine whether enough atmospheric flux occurred to have potentially affected the surface water quality of the streams being examined does show (using the assumptions of the calculations) that enough PO_4 was deposited on the norther aspect to have potentially affected the PO_4 concentration had runoff occurred. Along with PO_4 , NO_3 and Fe were found to have been fluxed in sufficient quantities during this sample period to have potentially had an effect on surface water quality if the conditions had been right and the assumptions of these calculations were correct (Tables 3 and 4). Though these calculated results, based on multiple assumptions, are in no way conclusive, it is interesting to see that even though the flux measured during this study was lower than the results of other studies, the potential may exist for the influence of atmospheric flux on surface water quality in this study area. Further research would be necessary to examine this relationship between atmospheric flux and surface water quality in more detail.

Therefore, I have come to the following overall conclusions:

1. During this study, local lithology/mining activity is the primary driver of water quality within this system in regards to pH, specific conductance, nitrate, phosphate, sulfate, aluminum, manganese, and iron.

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2. The potential does exist for atmospherically deposited materials and constituents to affect these streams.

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APPENDIX A

NORTH AND SOUTH ASPECT ATMOSPHERIC SULFATE FLUX

North Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
O1 8/12	8.678E-06	O2 8/12	1.422E-05	O3 8/12	1.880E-06	O4 8/12	0.000E+00	O5 8/12	0.000E+00
O1 8/17	9.270E-06	O2 8/17	2.191E-05	O3 8/17	4.996E-06	O4 8/17	0.000E+00	O5 8/17	2.605E-06
O1 8/22	2.387E-05	O2 8/22	4.416E-05	O3 8/22	4.657E-06	O4 8/22	5.766E-06	O5 8/22	1.515E-07
Mean	1.39E-05	Mean	2.68E-05	Mean	3.84E-06	Mean	1.92E-06	Mean	9.19E-07
Std. Dev.	7.03E-06	Std. Dev.	1.27E-05	Std. Dev.	1.40E-06	Std. Dev.	2.72E-06	Std. Dev.	1.19E-06

South Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
S1 8/13	0.000E+00	S2 8/13	8.445E-06	S3 8/13	1.358E-06	S4 8/13	2.757E-06	S5 8/13	0.000E+00
S1 8/18	0.000E+00	S2 8/18	0.000E+00	S3 8/18	1.332E-05	S4 8/18	0.000E+00	S5 8/18	7.249E-06
S1 8/23	5.909E-07	S2 8/23	1.796E-06	S3 8/23	0.000E+00	S4 8/23	4.054E-07	S5 8/23	8.810E-06
Mean	1.97E-07	Mean	3.41E-06	Mean	4.89E-06	Mean	1.05E-06	Mean	5.35E-06
Std. Dev.	2.79E-07	Std. Dev.	3.63E-06	Std. Dev.	5.98E-06	Std. Dev.	1.22E-06	Std. Dev.	3.84E-06

APPENDIX B

NORTH AND SOUTH ASPECT ATMOSPHERIC NITRATE FLUX

North Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
O1 8/12	2.335E-05	O2 8/12	4.123E-05	O3 8/12	5.408E-06	O4 8/12	0.000E+00	O5 8/12	0.000E+00
O1 8/17	2.211E-05	O2 8/17	6.689E-05	O3 8/17	1.470E-05	O4 8/17	0.000E+00	O5 8/17	7.504E-06
O1 8/22	8.765E-05	O2 8/22	1.188E-04	O3 8/22	1.609E-05	O4 8/22	1.371E-05	O5 8/22	4.594E-07
Mean	4.44E-05	Mean	7.57E-05	Mean	1.21E-05	Mean	4.57E-06	Mean	2.65E-06
Std. Dev.	3.06E-05	Std. Dev.	3.23E-05	Std. Dev.	4.74E-06	Std. Dev.	6.46E-06	Std. Dev.	3.43E-06

South Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
S1 8/13	0.000E+00	S2 8/13	2.408E-05	S3 8/13	4.039E-06	S4 8/13	8.237E-06	S5 8/13	0.000E+00
S1 8/18	0.000E+00	S2 8/18	0.000E+00	S3 8/18	3.792E-05	S4 8/18	0.000E+00	S5 8/18	1.698E-05
S1 8/23	1.593E-06	S2 8/23	5.612E-06	S3 8/23	0.000E+00	S4 8/23	1.108E-06	S5 8/23	2.433E-05
Mean	5.31E-07	Mean	9.90E-06	Mean	1.40E-05	Mean	3.11E-06	Mean	1.38E-05
Std. Dev.	7.51E-07	Std. Dev.	1.03E-05	Std. Dev.	1.70E-05	Std. Dev.	3.65E-06	Std. Dev.	1.02E-05

APPENDIX C

NORTH AND SOUTH ASPECT ATMOSPHERIC PHOSPHATE FLUX

North Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
O1 8/12	0.000E+00	O2 8/12	0.000E+00	O3 8/12	0.000E+00	O4 8/12	0.000E+00	O5 8/12	0.000E+00
O1 8/17	5.164E-07	O2 8/17	1.436E-06	O3 8/17	3.607E-07	O4 8/17	0.000E+00	O5 8/17	9.486E-08
O1 8/22	0.000E+00	O2 8/22	5.395E-06	O3 8/22	1.543E-07	O4 8/22	4.512E-07	O5 8/22	1.161E-08
Mean	1.72E-07	Mean	2.28E-06	Mean	1.72E-07	Mean	1.50E-07	Mean	3.55E-08
Std. Dev.	2.43E-07	Std. Dev.	2.28E-06	Std. Dev.	1.48E-07	Std. Dev.	2.13E-07	Std. Dev.	4.22E-08

South Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
S1 8/13	0.000E+00	S2 8/13	0.000E+00	S3 8/13	0.000E+00	S4 8/13	1.660E-07	S5 8/13	0.000E+00
S1 8/18	0.000E+00	S2 8/18	0.000E+00	S3 8/18	0.000E+00	S4 8/18	0.000E+00	S5 8/18	9.572E-07
S1 8/23	0.000E+00	S2 8/23	0.000E+00	S3 8/23	0.000E+00	S4 8/23	3.103E-08	S5 8/23	1.062E-06
Mean	0.00E+00	Mean	0.00E+00	Mean	0.00E+00	Mean	6.57E-08	Mean	6.73E-07
Std. Dev.	0.00E+00	Std. Dev.	0.00E+00	Std. Dev.	0.00E+00	Std. Dev.	7.21E-08	Std. Dev.	4.78E-07

APPENDIX D

NORTH AND SOUTH ASPECT ATMOSPHERIC ALUMINUM FLUX

North Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
O1 8/12	2.476E-08	O2 8/12	1.617E-07	O3 8/12	2.361E-08	O4 8/12	0.000E+00	O5 8/12	0.000E+00
O1 8/17	2.263E-07	O2 8/17	1.462E-07	O3 8/17	6.730E-08	O4 8/17	0.000E+00	O5 8/17	4.683E-07
O1 8/22	1.209E-06	O2 8/22	2.390E-07	O3 8/22	1.156E-07	O4 8/22	1.513E-06	O5 8/22	5.570E-08
Mean	4.87E-07	Mean	1.82E-07	Mean	6.88E-08	Mean	5.04E-07	Mean	1.75E-07
Std. Dev.	5.17E-07	Std. Dev.	4.06E-08	Std. Dev.	3.76E-08	Std. Dev.	7.13E-07	Std. Dev.	2.09E-07

South Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
S1 8/13	0.000E+00	S2 8/13	9.227E-08	S3 8/13	3.318E-08	S4 8/13	7.124E-08	S5 8/13	0.000E+00
S1 8/18	0.000E+00	S2 8/18	0.000E+00	S3 8/18	4.473E-07	S4 8/18	0.000E+00	S5 8/18	1.121E-07
S1 8/23	7.605E-08	S2 8/23	1.246E-07	S3 8/23	0.000E+00	S4 8/23	2.639E-08	S5 8/23	5.589E-07
Mean	2.53E-08	Mean	7.23E-08	Mean	1.60E-07	Mean	3.25E-08	Mean	2.24E-07
Std. Dev.	3.58E-08	Std. Dev.	5.28E-08	Std. Dev.	2.03E-07	Std. Dev.	2.94E-08	Std. Dev.	2.41E-07

APPENDIX E

NORTH AND SOUTH ASPECT ATMOSPHERIC MANGANESE FLUX

North Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
O1 8/12	1.274E-08	O2 8/12	2.784E-08	O3 8/12	3.396E-09	O4 8/12	0.000E+00	O5 8/12	0.000E+00
O1 8/17	3.660E-08	O2 8/17	7.807E-08	O3 8/17	2.830E-08	O4 8/17	0.000E+00	O5 8/17	5.948E-08
O1 8/22	3.369E-07	O2 8/22	4.102E-07	O3 8/22	4.002E-08	O4 8/22	2.269E-07	O5 8/22	7.793E-09
Mean	1.29E-07	Mean	1.72E-07	Mean	2.39E-08	Mean	7.56E-08	Mean	2.24E-08
Std. Dev.	1.47E-07	Std. Dev.	1.70E-07	Std. Dev.	1.53E-08	Std. Dev.	1.07E-07	Std. Dev.	2.64E-08

South Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
S1 8/13	0.000E+00	S2 8/13	1.438E-08	S3 8/13	4.516E-08	S4 8/13	1.673E-08	S5 8/13	0.000E+00
S1 8/18	0.000E+00	S2 8/18	0.000E+00	S3 8/18	1.188E-07	S4 8/18	0.000E+00	S5 8/18	5.435E-08
S1 8/23	7.207E-09	S2 8/23	1.463E-08	S3 8/23	0.000E+00	S4 8/23	4.252E-09	S5 8/23	1.322E-07
Mean	2.40E-09	Mean	9.67E-09	Mean	5.46E-08	Mean	7.00E-09	Mean	6.22E-08
Std. Dev.	3.40E-09	Std. Dev.	6.84E-09	Std. Dev.	4.89E-08	Std. Dev.	7.10E-09	Std. Dev.	5.42E-08

APPENDIX F

NORTH AND SOUTH ASPECT ATMOSPHERIC IRON FLUX

North Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
O1 8/12	3.384E-08	O2 8/12	4.107E-07	O3 8/12	2.702E-08	O4 8/12	0.000E+00	O5 8/12	0.000E+00
O1 8/17	2.521E-07	O2 8/17	5.761E-07	O3 8/17	1.184E-07	O4 8/17	0.000E+00	O5 8/17	4.075E-07
O1 8/22	1.764E-06	O2 8/22	2.117E-06	O3 8/22	1.584E-07	O4 8/22	1.622E-06	O5 8/22	4.344E-08
Mean	6.83E-07	Mean	1.03E-06	Mean	1.01E-07	Mean	5.41E-07	Mean	1.50E-07
Std. Dev.	7.69E-07	Std. Dev.	7.69E-07	Std. Dev.	5.50E-08	Std. Dev.	7.65E-07	Std. Dev.	1.83E-07

South Aspect									
Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux	Sample Site	Atmos. Flux
S1 8/13	0.000E+00	S2 8/13	1.074E-07	S3 8/13	5.650E-08	S4 8/13	1.112E-07	S5 8/13	0.000E+00
S1 8/18	0.000E+00	S2 8/18	0.000E+00	S3 8/18	6.953E-07	S4 8/18	0.000E+00	S5 8/18	2.589E-07
S1 8/23	1.436E-07	S2 8/23	1.275E-07	S3 8/23	0.000E+00	S4 8/23	3.349E-08	S5 8/23	8.096E-07
Mean	4.79E-08	Mean	7.83E-08	Mean	2.51E-07	Mean	4.82E-08	Mean	3.56E-07
Std. Dev.	6.77E-08	Std. Dev.	5.60E-08	Std. Dev.	3.15E-07	Std. Dev.	4.66E-08	Std. Dev.	3.38E-07

APPENDIX G

NORTH AND SOUTH ASPECT STREAM DISCHARGE MEASUREMENTS

North Aspect									
Sample Site	m ³ /s	Sample Site	m ³ /s	Sample Site	m ³ /s	Sample Site	m ³ /s	Sample Site	m ³ /s
O1 8/12	0.07	O2 8/12	0.17	O3 8/12	0.45	O4 8/12	2.35	O5 8/12	4.19
O1 8/17	0.06	O2 8/17	0.35	O3 8/17	0.31	O4 8/17	1.78	O5 8/17	3.03
O1 8/22	0.06	O2 8/22	0.26	O3 8/22	0.30	O4 8/22	1.64	O5 8/22	2.97
Mean	0.06	Mean	0.26	Mean	0.35	Mean	1.92	Mean	3.40
Std. Dev.	0.00	Std. Dev.	0.07	Std. Dev.	0.07	Std. Dev.	0.31	Std. Dev.	0.56

South Aspect							
Sample Site	m ³ /s	Sample Site	m ³ /s	Sample Site	m ³ /s	Sample Site	m ³ /s
S1 8/13	0.00030	S2 8/13	0.28	S3 8/13	0.54	S4 8/13	2.36
S1 8/18	0.00029	S2 8/18	0.38	S3 8/18	1.17	S4 8/18	1.54
S1 8/23	0.00031	S2 8/23	0.36	S3 8/23	0.70	S4 8/23	2.16
Mean	0.00030	Mean	0.34	Mean	0.80	Mean	2.02
Std. Dev.	0.00001	Std. Dev.	0.04	Std. Dev.	0.27	Std. Dev.	0.35

APPENDIX H

NORTH AND SOUTH ASPECT STREAM IN-SITU TEMPERATURE MEASUREMENTS

North Aspect									
Sample Site	°C	Sample Site	°C	Sample Site	°C	Sample Site	°C	Sample Site	°C
O1 8/12	9.8	O2 8/12	10.2	O3 8/12	14.9	O4 8/12	13.9	O5 8/12	19
O1 8/17	9.6	O2 8/17	10	O3 8/17	13.8	O4 8/17	15	O5 8/17	19.2
O1 8/22	8.8	O2 8/22	7.8	O3 8/22	12.1	O4 8/22	13.3	O5 8/22	17.6
Mean	9.40	Mean	9.33	Mean	13.60	Mean	14.07	Mean	18.60
Std. Dev.	0.43	Std. Dev.	1.09	Std. Dev.	1.15	Std. Dev.	0.70	Std. Dev.	0.71

South Aspect							
Sample Site	°C	Sample Site	°C	Sample Site	°C	Sample Site	°C
S1 8/13	11.7	S2 8/13	11.2	S3 8/13	11.5	S4 8/13	12.4
S1 8/18	9.5	S2 8/18	11.3	S3 8/18	15.8	S4 8/18	11.3
S1 8/23	6.8	S2 8/23	9.4	S3 8/23	10.2	S4 8/23	9.9
Mean	9.33	Mean	10.63	Mean	12.50	Mean	11.20
Std. Dev.	2.00	Std. Dev.	0.87	Std. Dev.	2.39	Std. Dev.	1.02

APPENDIX I

NORTH AND SOUTH ASPECT STREAM IN-SITU DISSOLVED OXYGEN MEASUREMENTS

North Aspect									
Sample Site	mg/l	Sample Site	mg/l	Sample Site	mg/l	Sample Site	mg/l	Sample Site	mg/l
O1 8/12	7.77	O2 8/12	8.06	O3 8/12	7.33	O4 8/12	8.02	O5 8/12	7.05
O1 8/17	7.4	O2 8/17	7.57	O3 8/17	6.92	O4 8/17	7.4	O5 8/17	7.13
O1 8/22	7.24	O2 8/22	8.62	O3 8/22	6.95	O4 8/22	7.48	O5 8/22	7.42
Mean	7.47	Mean	8.08	Mean	7.07	Mean	7.63	Mean	7.20
Std. Dev.	0.22	Std. Dev.	0.43	Std. Dev.	0.19	Std. Dev.	0.28	Std. Dev.	0.16

South Aspect							
Sample Site	mg/l	Sample Site	mg/l	Sample Site	mg/l	Sample Site	mg/l
S1 8/13	9.41	S2 8/13	10.41	S3 8/13	13.36	S4 8/13	10.44
S1 8/18	7.31	S2 8/18	7.38	S3 8/18	6.61	S4 8/18	7.55
S1 8/23	7.58	S2 8/23	7.47	S3 8/23	7.12	S4 8/23	8.08
Mean	8.10	Mean	8.42	Mean	9.03	Mean	8.69
Std. Dev.	0.93	Std. Dev.	1.41	Std. Dev.	3.07	Std. Dev.	1.26

APPENDIX J

NORTH AND SOUTH ASPECT STREAM IN-SITU PH MEASUREMENTS

North Aspect									
Sample Site		Sample Site		Sample Site		Sample Site		Sample Site	
O1 8/12	7.85	O2 8/12	3.01	O3 8/12	3.03	O4 8/12	5.08	O5 8/12	5.6
O1 8/17	6.44	O2 8/17	3.05	O3 8/17	3.07	O4 8/17	6.45	O5 8/17	6.5
O1 8/22	6.7	O2 8/22	2.93	O3 8/22	2.95	O4 8/22	5.19	O5 8/22	5.69
Median	6.70	Median	3.01	Median	3.03	Median	5.19	Median	5.69
Std. Dev.	0.61	Std. Dev.	0.05	Std. Dev.	0.05	Std. Dev.	0.62	Std. Dev.	0.40

South Aspect							
Sample Site		Sample Site		Sample Site		Sample Site	
S1 8/13	5.3	S2 8/13	5.88	S3 8/13	6.05	S4 8/13	6.3
S1 8/18	4.8	S2 8/18	6.23	S3 8/18	6.55	S4 8/18	6.34
S1 8/23	4.16	S2 8/23	5.57	S3 8/23	5.85	S4 8/23	6
Median	4.80	Median	5.88	Median	6.05	Median	6.30
Std. Dev.	0.47	Std. Dev.	0.27	Std. Dev.	0.29	Std. Dev.	0.15

APPENDIX K

NORTH AND SOUTH ASPECT STREAM IN-SITU SPECIFIC CONDUCTANCE MEASUREMENTS

North Aspect									
Sample Site	us/cm	Sample Site	us/cm	Sample Site	us/cm	Sample Site	us/cm	Sample Site	us/cm
O1 8/12	61.3	O2 8/12	580	O3 8/12	605	O4 8/12	281.2	O5 8/12	394.3
O1 8/17	56.1	O2 8/17	588	O3 8/17	591	O4 8/17	495.5	O5 8/17	366.7
O1 8/22	57.3	O2 8/22	638	O3 8/22	647	O4 8/22	337.1	O5 8/22	385.3
Mean	58.23	Mean	602.00	Mean	614.33	Mean	371.27	Mean	382.10
Std. Dev.	2.22	Std. Dev.	25.66	Std. Dev.	23.80	Std. Dev.	90.76	Std. Dev.	11.49

South Aspect							
Sample Site	us/cm	Sample Site	us/cm	Sample Site	us/cm	Sample Site	us/cm
S1 8/13	470.8	S2 8/13	171.6	S3 8/13	176.2	S4 8/13	186.1
S1 8/18	505	S2 8/18	191.3	S3 8/18	210.6	S4 8/18	190.8
S1 8/23	504	S2 8/23	225.9	S3 8/23	228.9	S4 8/23	215
Mean	493.27	Mean	196.27	Mean	205.23	Mean	197.30
Std. Dev.	15.89	Std. Dev.	22.44	Std. Dev.	21.85	Std. Dev.	12.66

APPENDIX L

NORTH AND SOUTH ASPECT STREAM SULFATE MEASUREMENTS

North Aspect									
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
O1 8/12	30.40	O2 8/12	452.97	O3 8/12	401.16	O4 8/12	179.52	O5 8/12	177.75
O1 8/17	32.85	O2 8/17	556.80	O3 8/17	482.00	O4 8/17	219.00	O5 8/17	183.89
O1 8/22	21.59	O2 8/22	654.93	O3 8/22	477.94	O4 8/22	251.03	O5 8/22	190.93
Mean	28.28	Mean	554.90	Mean	453.70	Mean	216.52	Mean	184.19
Std. Dev.	4.84	Std. Dev.	82.46	Std. Dev.	37.19	Std. Dev.	29.25	Std. Dev.	5.39

South Aspect							
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
S1 8/13	397.16	S2 8/13	123.18	S3 8/13	125.86	S4 8/13	130.93
S1 8/18	484.86	S2 8/18	147.23	S3 8/18	151.12	S4 8/18	151.32
S1 8/23	495.05	S2 8/23	179.82	S3 8/23	152.92	S4 8/23	141.83
Mean	459.03	Mean	150.08	Mean	143.30	Mean	141.36
Std. Dev.	43.94	Std. Dev.	23.21	Std. Dev.	12.35	Std. Dev.	8.33

APPENDIX M

NORTH AND SOUTH ASPECT STREAM NITRATE MEASUREMENTS

North Aspect									
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
O1 8/12	1.01	O2 8/12	12.06	O3 8/12	6.00	O4 8/12	2.58	O5 8/12	9.59
O1 8/17	0.97	O2 8/17	10.02	O3 8/17	9.83	O4 8/17	7.63	O5 8/17	3.50
O1 8/22	2.01	O2 8/22	10.39	O3 8/22	4.89	O4 8/22	1.55	O5 8/22	3.96
Mean	1.33	Mean	10.82	Mean	6.90	Mean	3.92	Mean	5.68
Std. Dev.	0.48	Std. Dev.	0.89	Std. Dev.	2.11	Std. Dev.	2.66	Std. Dev.	2.77

South Aspect							
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
S1 8/13	1.27	S2 8/13	1.10	S3 8/13	7.83	S4 8/13	1.26
S1 8/18	1.20	S2 8/18	1.09	S3 8/18	1.00	S4 8/18	1.27
S1 8/23	1.17	S2 8/23	1.07	S3 8/23	2.13	S4 8/23	2.25
Mean	1.22	Mean	1.09	Mean	3.65	Mean	1.60
Std. Dev.	0.04	Std. Dev.	0.01	Std. Dev.	2.99	Std. Dev.	0.46

APPENDIX N

NORTH AND SOUTH ASPECT STREAM PHOSPHATE MEASUREMENTS

North Aspect									
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
O1 8/12	0.05	O2 8/12	n.a.	O3 8/12	n.a.	O4 8/12	0.04	O5 8/12	n.a.
O1 8/17	n.a.	O2 8/17	n.a.	O3 8/17	n.a.	O4 8/17	n.a.	O5 8/17	n.a.
O1 8/22	n.a.	O2 8/22	n.a.	O3 8/22	0.05	O4 8/22	n.a.	O5 8/22	n.a.
Mean	0.05	Mean	n.a.	Mean	0.05	Mean	0.04	Mean	n.a.
Std. Dev.	0.00	Std. Dev.	n.a.	Std. Dev.	0.00	Std. Dev.	0.00	Std. Dev.	n.a.

South Aspect							
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
S1 8/13	n.a.	S2 8/13	n.a.	S3 8/13	n.a.	S4 8/13	n.a.
S1 8/18	n.a.	S2 8/18	n.a.	S3 8/18	n.a.	S4 8/18	n.a.
S1 8/23	n.a.	S2 8/23	n.a.	S3 8/23	n.a.	S4 8/23	n.a.
Mean	n.a.	Mean	n.a.	Mean	n.a.	Mean	n.a.
Std. Dev.	n.a.	Std. Dev.	n.a.	Std. Dev.	n.a.	Std. Dev.	n.a.

APPENDIX O

NORTH AND SOUTH ASPECT STREAM ALUMINUM MEASUREMENTS

North Aspect									
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
O1 8/12	14.74	O2 8/12	26597.38	O3 8/12	19099.52	O4 8/12	31.94	O5 8/12	177.37
O1 8/17	0.00	O2 8/17	32089.83	O3 8/17	23983.36	O4 8/17	5.24	O5 8/17	193.87
O1 8/22	13.12	O2 8/22	42949.95	O3 8/22	32113.05	O4 8/22	32.85	O5 8/22	159.54
Mean	9.29	Mean	33879.06	Mean	25065.31	Mean	23.34	Mean	176.93
Std. Dev.	6.60	Std. Dev.	6794.74	Std. Dev.	5367.55	Std. Dev.	12.81	Std. Dev.	14.02

South Aspect							
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
S1 8/13	2690.37	S2 8/13	42.16	S3 8/13	49.64	S4 8/13	14.84
S1 8/18	3253.95	S2 8/18	78.66	S3 8/18	91.97	S4 8/18	16.39
S1 8/23	3145.17	S2 8/23	42.87	S3 8/23	26.38	S4 8/23	12.84
Mean	3029.83	Mean	54.56	Mean	56.00	Mean	14.69
Std. Dev.	244.11	Std. Dev.	17.04	Std. Dev.	27.15	Std. Dev.	1.46

APPENDIX P

NORTH AND SOUTH ASPECT STREAM MANGANESE MEASUREMENTS

North Aspect									
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
O1 8/12	1.53	O2 8/12	909.60	O3 8/12	1059.39	O4 8/12	293.76	O5 8/12	127.13
O1 8/17	3.01	O2 8/17	1083.26	O3 8/17	1228.93	O4 8/17	312.27	O5 8/17	98.90
O1 8/22	0.12	O2 8/22	1438.34	O3 8/22	1608.59	O4 8/22	381.01	O5 8/22	98.22
Mean	1.55	Mean	1143.73	Mean	1298.97	Mean	329.01	Mean	108.08
Std. Dev.	1.18	Std. Dev.	220.05	Std. Dev.	229.62	Std. Dev.	37.53	Std. Dev.	13.47

South Aspect							
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
S1 8/13	7773.48	S2 8/13	159.10	S3 8/13	194.49	S4 8/13	256.19
S1 8/18	9829.26	S2 8/18	180.76	S3 8/18	198.50	S4 8/18	289.67
S1 8/23	9795.29	S2 8/23	164.67	S3 8/23	229.16	S4 8/23	325.07
Mean	9132.68	Mean	168.18	Mean	207.38	Mean	290.31
Std. Dev.	961.20	Std. Dev.	9.19	Std. Dev.	15.49	Std. Dev.	28.12

APPENDIX Q

NORTH AND SOUTH ASPECT STREAM IRON MEASUREMENTS

North Aspect									
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
O1 8/12	5.11	O2 8/12	14086.20	O3 8/12	5130.34	O4 8/12	0.63	O5 8/12	0.00
O1 8/17	0.00	O2 8/17	17084.15	O3 8/17	6358.63	O4 8/17	0.00	O5 8/17	0.00
O1 8/22	2.06	O2 8/22	30890.82	O3 8/22	12927.22	O4 8/22	1.81	O5 8/22	0.00
Mean	2.39	Mean	20687.06	Mean	8138.73	Mean	0.81	Mean	0.00
Std. Dev.	2.10	Std. Dev.	7318.22	Std. Dev.	3422.90	Std. Dev.	0.75	Std. Dev.	0.00

South Aspect							
Sample Site	ppm	Sample Site	ppm	Sample Site	ppm	Sample Site	ppm
S1 8/13	4085.31	S2 8/13	0.52	S3 8/13	1.29	S4 8/13	731.05
S1 8/18	5012.81	S2 8/18	12.05	S3 8/18	1.86	S4 8/18	908.55
S1 8/23	4742.83	S2 8/23	1.56	S3 8/23	0.57	S4 8/23	1301.82
Mean	4613.65	Mean	4.71	Mean	1.24	Mean	980.47
Std. Dev.	389.51	Std. Dev.	5.21	Std. Dev.	0.53	Std. Dev.	238.50