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# Spatiotemporal Heterogeneity of Water and Dissolved Organic Carbon Sourcing in a Snow-dominated, Headwater Catchment

A Hydrologic Investigation in Owyhee County, Idaho

by

Anna G. Radke

A thesis

submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Geosciences Idaho State University Spring 2018 Copyright (2018) Anna G. Radke

### Committee Approval

To the Graduate Faculty:

The members of the committee appointed to examine the thesis of Anna Radke find it satisfactory and recommend that it be accepted.

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## Dedication

To my family and friends, for your support and senses of humor.

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#### Abstract

## Spatiotemporal Heterogeneity of Water and Dissolved Organic Carbon Sourcing in a Snow-dominated, Headwater Catchment

Thesis Abstract—Idaho State University (2018)

To understand coupled hydrological and carbon dynamics in heterogeneous, snowdriftdominated headwater catchments, we determine stream water and dissolved organic carbon (DOC) sources and fluxes from hydrometric and hydrochemical signals of soil water, saprolite water, and groundwater at the Reynolds Creek Critical Zone Observatory, Idaho, USA. We interpret flowpaths during the snowmelt period and summer drying using end-member mixing analysis in light of inferred subsurface structure from geophysical transects. Our findings indicate: (1) rapid loss of soil water connectivity with groundwater, and (2) an unusually rapid and important groundwater flowpath along the soil/saprolite boundary. Previously stored soil water appears to be displaced into the saprolite and groundwater which source most DOC and integrate soil water across the catchment. That this catchment does not follow the expected "flushing" model indicates a need for more detailed analysis of water sourcing in carbon export studies.

#### Keywords:

Dissolved organic carbon, DOC, soil organic carbon, SOC, hydrologic connectivity, soil water, ground water, snowdrifts, snow, infiltration, headwaters, dryland ecosystems, arid, desert, Idaho, Owyhee, Reynolds Creek, Critical Zone Observatory, CZO

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#### **Chapter 1:** Introduction

#### 1.1. Snow in the Intermountain West

#### 1.1.1. Snowpack as a critical resource and reservoir

In mountainous landscapes, snow is often the dominant phase of precipitation (Barnett & Adam, 2005). High-elevation snowpacks act as reservoirs, holding water from winter storms and releasing it in the growing season (M. W. Williams, Losleben, & Hamann, 2002). It is estimated that up to one-sixth of humanity is dependent on seasonal snowpacks for their water needs (Barnett & Adam, 2005).

The United States' Intermountain West region, currently the fastest growing area of the country, is dependent on snowpack for the majority of its water needs (Lang et al., 2008). In addition to municipal supplies, water is needed for irrigation. In 2012, over 10 million acre-feet of water was used to irrigate 3.8 million acres of the Colorado and Great Basin regions. In addition, the Pacific Northwest region, which encompasses the dryland agriculture of Idaho, eastern Washington and eastern Oregon, used 13 million acre-feet of water on 6.7 million acres (USDA NASS, 2013).

#### 1.1.2. Mechanisms of snow drifting and hydrologic importance of drifts

Snowpacks are influenced at a small scale by wind and topography. Wind in particular is responsible for the creation of heterogeneous snowpack (Pomeroy et al., 1998). Snow is not evenly distributed across the landscape; it tends to be blown into large drifts in the lee of topographic highs (Winstral & Marks, 2014). Snowdrift areas thus receive more water than other portions of the watershed, while those areas from which the snow was removed (known as 'scours') receive little to no water. This results in a heterogeneity of effective precipitation which

affects weathering rates, vegetative communities, and soil development across the watershed (Chorover et al., 2011).

Snowdrifts increase the amount of water available in the immediate vicinity of the drift. In soils with sufficiently high permeability, most of this water will infiltrate rather than becoming overland flow (Kormos et al., 2015; McNamara, Chandler, Seyfried, & Achet, 2005). From there, the water may flow along the soil-bedrock interface (Stieglitz et al., 2003) or enter a bedrock aquifer.

A large body of research exists on the physical aspects of snowdrift formation and melt (e.g. Årnason et al., 1970; Pomeroy, 1991; Grünewald et al., 2010). The total snowpack in a given catchment is a function of snowfall, sublimation, and canopy interception (MacDonald, Pomeroy, & Pietroniro, 2010; Pomeroy et al., 1998); however, redistribution is the dominant cause of small-scale spatial variability in snow depth (Pomeroy et al., 1998). Snow is transported by saltation and suspension, much as sediment is in water, when wind speed exceeds the velocity necessary to overcome the effects of surface roughness and gravity (e.g. Buffington, 2013; Pomeroy, 1989). Flat areas with long "fetch", windward slopes and hilltops, and unvegetated areas are subject to erosion, with the depth of snow in these areas being a function of snowfall, sublimation, and wind removal (Pomeroy, 1989, 1991). Snow accumulates on leeward slopes and in topographic depressions, or in areas of high surface roughness such as forested or shrubcovered areas (Essery, Li, & Pomeroy, 1999; MacDonald et al., 2010; Pomeroy et al., 1998). Sublimation, especially from vegetation, and snowfall are again the primary controls on snowpack depth in these locations, but here wind redistribution acts as a net gain rather than a net loss (MacDonald et al., 2010; Pomeroy, 1989; Pomeroy et al., 1998).

In mountainous regions, where topographic roughness is the major control on snow redistribution, snowdrift locations are relatively consistent from year to year (Hiemstra, Liston, & Reiners, 2002; MacDonald, Pomeroy, & Pietroniro, 2009; Sturm & Wagner, 2010), which means that there is more water available for chemical weathering of the bedrock at those locations, potentially leading to greater weathering depths and more conductive aquifers beneath and downgradient of snowdrifts (Anderson, Anderson, Tucker, & Dethier, 1998).

In many snow-dominated systems, the largest hydrologic event on an annual basis is the spring melt (Boyer, Hornberger, Bencala, & McKnight, 1997; Nayak, Marks, Chandler, & Seyfried, 2010; M. W. Williams et al., 2002), though other systems experience large rain-on-snow events or seasonal monsoons (Pomeroy et al., 2007; Viviroli, Dürr, Messerli, Meybeck, & Weingartner, 2007). The majority of snowmelt infiltrates to become soil and groundwater, though the pattern of melt is dependent on location, topography, and snowpack size (Harpold & Molotch, 2015). In general, melting proceeds slowly early in the season, and the areas of lesser snow depth melt out first; as the snowpack in areas of greater depth becomes isothermal, melt proceeds more rapidly in these areas of remaining snow (Dingman, 2015; Harpold & Molotch, 2015). Meltwater initiates hydrologic connectivity, 'flushing' solutes from the soil into the stream (Boyer et al., 1997). In mountain systems with little to no summer precipitation, melt may be the only event capable of significant leaching (McNamara et al., 2005).

#### **1.1.3.** Response of mountain snowpacks to changes in climate

Mountainous regions have experienced or are projected to experience larger impacts from a changing climate than most other regions of the world (Barnett & Adam, 2005; Beniston, 2003; M. W. Williams et al., 2002). Seasonal snowpacks, especially in mountainous regions, could become vulnerable to climate change (Brooks et al., 2011; Mote, Hamlet, Clark, & Lettenmaier,

2005), although the magnitude and direction of change for a given mountain catchment is dependent on local topographic factors, wind direction, and vegetation (Tennant et al., 2017).

Climate change is projected to bring about shifts in the seasonality of precipitation and in the relative amounts of solid and liquid precipitation phases (Beniston, 2003). In mountainous regions, this can take the form of a shorter snow-covered season and smaller snowpacks (Harpold et al., 2012; Tennant et al., 2017), as well as changes in the elevation of the rain/snow transition—the level at which a storm's precipitation changes from rain to snow (Klos, Link, & Abatzoglou, 2014). Some models have also predicted a long-term climate shift wherein earlier snowmelt overwhelms reservoir storage capacity, further reducing water supplies (Barnett & Adam, 2005). Declines in snowpack have already been noted for many snow measurement stations in the western United States, and the magnitude and spatial extent of the change has increased in just the last five years (Mote, Li, Lettenmaier, Xiao, & Engel, 2018).

A shift from snow to rain in a given watershed has implications for both hydrology and ecology. Rain is not stored aboveground, as snow is; if aquifer storage and soil infiltration rates are sufficient, it may instead be stored in the subsurface, but this has implications for the magnitude and timing of water delivery to streams (Barnett & Adam, 2005). The timing of snowmelt affects soil moisture, and thus aquifer recharge and plant water availability (Harpold & Molotch, 2015; Huntington & Niswonger, 2012). Rain which falls in winter does not remain on the landscape in the way that snow does, unless it adds to a snowpack already present (Dingman, 2015); if it falls on bare, saturated soil, it may run off. This lost reservoir of snow contributes to reduced soil moisture in the growing season (Smith et al., 2011; C. J. Williams, McNamara, & Chandler, 2008). Even without a complete shift to rain, changes in the size or location of a drift could trigger shifts in vegetation communities affecting patterns of evapotranspiration and also

further affecting snowdrift location (Harpold et al., 2017; Huntington & Niswonger, 2012), with concurrent effects on soil moisture.

One of the effects of changing snowpack, changing soil moisture, and changing vegetation is a change in the accumulation and storage of carbon in the soil (Doetterl et al., 2015; Edwards, Scalenghe, & Freppaz, 2007; Harpold & Molotch, 2015; Mavris et al., 2015; Stielstra et al., 2015).

#### 1.2. Carbon in Soils and Streams

In the global carbon cycle, soil is an important reservoir, locus of transformation, and sometimes serves as a carbon sink. It is estimated that soils store up to three times more carbon than aboveground biomass does, over 1500 Pg worldwide (Carvalhais et al., 2014; Eswaran, Berg, Reich, Van Den Berg, & Reich, 1993; Lal, 2004; Schimel, 1994; Wickland, Neff, & Aiken, 2007). Soil carbon content is a function of soil forming factors (climate, organismal community, parent material, topography, age) and human impacts (tillage, amendments, etc.) (Jenny, 1941). Carbon in soils exists in both organic and inorganic forms (Lal, 2004), though the former is more commonly considered as a measure of soil health. Soil organic carbon (SOC), in the form of soil organic matter (SOM), performs several functions important to maintaining the fertility of the soil: it acts as a binder for soil aggregates, increasing aeration and infiltration capacity; holds nutrients by absorption or adsorption; and increases the water-holding capacity (Doran, 2002).

SOC can be lost either to heterotrophic respiration or by leaching from the soil profile (Stielstra et al., 2015). While respiration represents a significant loss (Schlesinger & Andrews, 2000), in this thesis I instead focus on leaching losses, specifically the export of SOC by streams. This choice was made both to avoid overlap with existing eddy-covariance and partial

pressure/forced-diffusion chamber studies in the watershed, and to account for an oftenneglected source of carbon export. Leached SOC that is respired downstream can artificially inflate estimates of stored carbon in an ecosystem from gas exchange measurements (Cole et al., 2007).

Additionally, SOC is often a major source of dissolved organic carbon (DOC) to headwater stream ecosystems (Bunn, Balcombe, Davies, Fellows, & McKenzie-Smith, 2006; Fiebig, Lock, & Neal, 1990), and plays an important role in the export of certain nutrients and minerals (McIntosh et al., 2017).

DOC is one of the two common forms of carbon in fluvial systems, along with dissolved inorganic carbon (DIC, e.g., carbon dioxide, carbonate) (Fiebig et al., 1990). A major source of stream DOC is SOC (Boyer et al., 1997). Precipitation infiltrates into the soil, and the resulting soil water leaches carbon as it moves from upslope recharge zones to the stream and riparian discharge zones. This carbon is assimilated into aquatic food webs, where heterotrophic respiration eventually releases it to the atmosphere. Conservative estimates indicate that around half of the carbon entering fluvial systems is processed within the system, rather than exported to the sea—and most of this lost carbon is respired (Cole et al., 2007).

The other major source of DOC is in-stream production. In-stream production is considered a minor source of DOC in headwater systems (Fiebig et al., 1990), though some algal growth was observed at our site during low flow. The amount of autochthonous DOC produced varies with sunlight and nutrient availability in a given system; in-stream production occurs mostly in summers, while we expect flushing of SOC earlier in the season during snowmelt.

Given that SOC is a primary component of DOC in streams, the major impact of precipitation regimes on carbon export lies in the capacity of water to leach SOC and carry it to

the stream. This is strongly affected by water residence times in the soil (Chorover et al., 2011). Where residence times are short (generally in coarser-textured or well-aggregated soils, or with short hillslope lengths), there is less opportunity for leaching; these soils may export less DOC. Where residence times are longer (e.g., in loamy or silty soils), leaching is more likely, and DOC export may be higher (Chorover et al., 2011).

Standard models of allochthonous carbon transport to streams invoke both overland flow and subsurface hydrologic connectivity (Sanderman, Lohse, Baldock, & Amundson, 2009; Stieglitz et al., 2003; Stielstra et al., 2015). Subsurface connectivity occurs as precipitation infiltrates into soils, eventually reaching a saturation threshold at which hillslopes begin passing water into the riparian zones (Tromp-Van Meerveld & McDonnell, 2006).

Much of the existing work on carbon cycling in snowdrift-dominated watersheds has taken place at the Niwot Ridge Long-Term Ecological Research station (NWT LTER) in Colorado (e.g. Bowling et al., 2009; Liptzin et al., 2009; Williams et al., 2009). This site has provided an extensive understanding of carbon dioxide dynamics within and beneath snowpacks and clarified many aspects of high-elevation snowpack hydrology. Boyer et al. (1997) and Hornberger, Germann, & Beven (1991) have contributed work on the intersection of hydrology and DOC export, primarily using DOC concentrations in stream and soil waters to estimate carbon sources in the watershed. However, DOC is not a conservative tracer, being biologically mediated, and exhibits chemostatic behavior in many systems that suggests complicated interactions between hydrologic connectivity and geochemistry (Creed et al. 2015; Li, Bao, et al., 2017). The additional complication of an ancient rock glacier in the NWT LTER system makes it an imperfect analog for many lower-elevation snow-dominated watersheds.

In a snow-free system, Sanderman et al. (2009) found evidence for DOC supply limitation in upper hillslopes following large hydrologic events, with late summer DOC deriving from near-stream soils which are saturated year-round. In snowdrift-dominated systems, drift locations may become similarly supply-limited, due to the greater amount of water available for leaching.

Research in the flow of carbon from soils to streams has been conducted in many places, including the coastal regions of California and the Shale Hills Critical Zone Observatory in Pennsylvania (e.g. Sanderman et al., 2009; Herndon et al., 2015). In neither of these regions is the combination of climate, elevation, and topography conducive to the formation of large snowdrifts. Again, these studies give some insight into the controlling factors of soil carbon export, but they are not sufficient to understand carbon dynamics in the Intermountain West.

#### **1.2.1.** Carbon dynamics and a changing climate

With a shift from snow to rain comes the possibility for a shift in soil carbon storage. Shifting precipitation regimes impact vegetative productivity, changing the amount carbon sequestered by plants; they also impact the amount of water available for soil respiration (Carvalhais et al., 2014; Chorover et al., 2011). Shifts in vegetative communities due to drought can occur on surprisingly short timescales, on the order of decades (Fellows & Goulden, 2012), and microbial communities can respond even faster (Zogg et al., 1997). Temperatures can have similar impacts on vegetative and microbial communities (Abatzoglou & Kolden, 2011; Zogg et al., 1997), changing the quality and quantity of SOC (Bauhus, Paré, & Côté, 1998). A baseline measure of system carbon dynamics is necessary before the impacts of change can be assessed.

#### 1.3. Paths Forward in Drift-Dominated Snow Hydrology and Carbon Export

We propose to combine hydrologic investigations in a snowdrift-dominated, headwater catchment with an exploration of carbon sourcing in the stream draining this watershed. Similar

work has been performed in the Colorado Front Range (Boyer et al., 1997; Hornberger, Bencala, & McKnight, 1994), and we extend this past work by applying end-member mixing analysis to our water sourcing model, and comparing water sources with inferred carbon sources.

We use a robust suite of environmental observations and chemical tracers to tease out patterns of hydrologic connectivity, and link DOC sourcing to spatial patterns of soil carbon distribution and snowdrift accumulation.

Another control on leaching is the amount of water available. Snowdrifts melt out gradually over months, due to the greater amounts of solar energy required to melt the mass of snow as opposed to shallower snowpacks in scoured areas (Barnhart et al., 2016; Harpold et al., 2012; Winstral & Marks, 2014), providing large amounts of water to the soils below them. Soils directly below and adjacent to snowdrifts support significant vegetative communities, including high-altitude forests (Winstral & Marks, 2014). These soils may be richer in carbon and associated nutrients, but may also see significant export of dissolved compounds if the cation-exchange capacity is satiated by hydrogen from infiltrating water (Herndon et al., 2015a, 2015b).

Scoured areas are spatiotemporally consistent, and occur primarily on windward slopes and summits (Winstral & Marks, 2014). These areas also tend to be less vegetatively productive (Seyfried, Harris, Marks, & Jacob, 2001; Winstral & Marks, 2014). They are unlikely to contribute much DOC to streams, as they lack both a significant source of carbon and sufficient moisture to leach what is there.

#### **1.3.1.** Research questions

Our research focuses on a small, snow-dominated headwater catchment called Reynolds Mountain East located in southwestern Idaho, USA. Drifting is common in this catchment with most drifts forming on the north-facing, leeward side of slopes. This catchment experiences little to no overland flow (Grant, Seyfried, & McNamara, 2004), and so our questions relate primarily

to subsurface water. 1: What are the patterns of dissolved organic carbon concentrations in stream and source waters? Do they follow the "flushing" model, or are there other factors driving carbon export? 2: What paths does meltwater from seasonal snowdrifts follow on its way to the stream? 3: Is soil water a major component of the hydrograph in drift-dominated systems, or is carbon being brought into the stream by another subsurface flowpath?

#### 1.3.2. Specific goals

To answer these questions, we aim to 1: Assess DOC for concentration, aromaticity, and fluorescence over the year-long hydrograph; 2: Identify the end-members contributing to stream flow over an annual timescale to estimate the relative importance of groundwater, laterally-transmitted soil water, and saprolite water to total flow over time; 3: Compare DOC of source and stream waters to determine the relationship between lateral flow of soil water and the export of soil carbon.

#### **1.4. Site Description**

Research was conducted at the Reynolds Creek Critical Zone Observatory (RC-CZO) in Owyhee County, Idaho (Figure 1.1). The Critical Zone Observatories (CZOs) are a National Science Foundation program designed to study the zone of the planet "from the tops of the trees to the bottom of the groundwater" (Anderson et al., 2010). Reynolds Creek CZO takes advantage of a long-running United States Department of Agriculture-Agricultural Research Service (USDA-ARS) experimental watershed, and the many years of data collected at this site (Reba et al., 2011).

#### 1.4.1. Reynolds Creek Experimental Watershed

The Reynolds Creek Experimental Watershed (RCEW) is a 239 km<sup>2</sup> catchment located 80 km SW of Boise, ID. The experimental watershed has been operated by the United States USDA-ARS Northwest Watershed Research Center since 1960 (McNamara et al., 2005).

Elevations vary by almost a kilometer, and average precipitation changes with elevation from less than 250 mm to more than 1100 mm annually, creating a gradient from mesic, udic headwaters to xeric flats (Marks, 2001).

Data from a network of meteorological stations, seven sub-catchment-defining weirs, winter snow-pack measurements, vegetation surveys, soil surveys, and bedrock extent maps for the watershed is publicly available through the USDA-ARS: https://www.ars.usda.gov/pacific-west-area/boise-id/watershed-management-research/.

#### 1.4.2. Reynolds Creek Critical Zone Observatory

RC-CZO was implemented in 2013 to study carbon fluxes. It is spatially contiguous with the Experimental Watershed and makes use of much of the ARS infrastructure. The CZO is managed jointly by the ARS, Idaho State University, and Boise State University. Data collected from the CZO includes spatially extensive maps of predicted soil carbon (Patton, 2016), and stream chemistry datasets, which can be found on the RCCZO website: http://criticalzone.org/reynolds/infrastructure/field-area/reynolds-creek-experimental-watershed/.

#### 1.4.3. Reynolds Mountain East catchment

The headwaters of Reynolds Creek are divided between two watersheds, Reynolds Mountain West (RMW) and Reynolds Mountain East (RME). RME is the more thoroughly studied of the two (Figure 1.1). It ranges from 2020 m to 2140 m in elevation over an area of 0.38 km<sup>2</sup>; slopes vary from 0 to 40%.

RME receives approximately 900 mm of precipitation annually, principally in the form of snow, and exports ~520 mm of this as stream flow (Seyfried, Grant, Marks, Winstral, & McNamara, 2009). Snow commonly accumulates in deep (>2 m) drifts in sheltered areas (Winstral & Marks, 2014). Snowdrifts occupy <10% of the total surface area of the catchment, but contribute 15-20% of total snow water input; another 25% of snow water input is provided

by snow in sheltered areas not deep enough to be considered drifts (Grant et al., 2004) One large drift, the East drift, forms at the eastern end of the catchment, on the leeward side of an unnamed peak (Figure 1.2, No. 1). A smaller drift forms at the base of the steep hill below the cabin (Figure 1.2, No. 2); little to no drifting occurs in the Douglas-fir forest below this drift; but in exceptionally snowy years, a smaller drift forms farther downhill in a bog (Figure 1.2, No. 2b). Another drift forms in an aspen stand downhill of the East drift (Figure 1.2, No. 3). An exceptionally large drift (>10 m in depth) is formed just outside the surface watershed divide (Figure 1.2, No. 4), and is referred to as the Springhouse drift; it feeds a perennial stream (in which is located the springhouse for which the drift is named) and cow pond. While this drift is technically outside the surface watershed, the divide is topographically muted (a ridge ~40 cm in height), and likely does not accurately reflect subsurface connectivity. The bog in this catchment is a "cryptic" wetland in a dryland ecosystem, possibly initiated by beaver dams, though no beaver activity was observed during the study.

Lithology in this catchment consists of multiple layers of volcanic rocks, primarily andesite and rhyolite with some basalt (McIntyre, 1972). There are no well logs extant, and the relative thicknesses and degrees of fracturing of these rock layers are unknown. Soils are primarily loams and silt loams, poorly developed, and highly permeable (Seyfried et al., 2001). NRCS classifications list most of the soils as mollisols, but the author disputes this classification after examining the soils in person, and prefers to class them as inceptisols. Vegetative communities are dominated by sagebrush (*Artemesia* spp.), along with various forbs and grasses. There are areas of willow (*Salix* spp.) in the riparian corridor, quaking aspen (*Populus tremuloides* Michx.) in wetter sites, and conifers (principally Douglas fir, *Pseudotsuga menzeii* (Mirb.) Franco) in scattered stands at intermediate elevations (Seyfried et al., 2009).

#### 1.4.3.1. Instruments and measurement locations.

Long-term ARS instrumentation in RME includes two meteorological stations (precipitation, snow depth, wind direction, relative humidity, soil moisture, air and soil temperature, and solar radiation) (Reba et al., 2011), four monitoring wells (depth to water table), and a v-notch weir at the outlet with TROLL 9500 (In-Situ Inc., Fort Collins, CO) continuous sensors and a Sigma 900 automated sampler (Hach Company, Loveland, CO) for stage, discharge, temperature, particulate and non-purgeable organic carbon, nutrients, and total suspended solids (total suspended solids are measured both continuously by inferometry and from samples) (Nayak et al., 2010). Additional data collected by the ARS includes snow depth measurements and soil moisture models (Grant et al., 2004; Seyfried et al., 2009; Winstral & Marks, 2014). The monitoring wells were used for groundwater sampling, and consist of three 15m-deep wells (Drift, West, and Aspen wells) and one 30m-deep well, the Cabin well (Figure 1.3).

In addition to the ARS instruments, we installed three nests of lysimeters, soil moisture probes, and matric potential sensors at locations along a hillslope gradient from the smaller snowdrift below the cabin to the riparian zone and bog. At each of these locations we also installed drive-point piezometers, with an additional piezometer in the artesian spring. We also installed a rain collector near the ARS meteorological station for rain chemistry and isotope sampling (Figure 1.3).

Dr. Steven Holbrook and a crew from the University of Wyoming collected geophysical data, including electrical resistance tomography and seismic velocity data, along multiple transects in the watershed in fall 2015 (Figure 1.4). This data, along with Dr. Holbrook's interpretations, were used to determine placement of the lysimeter nests and to interpret hydrochemical data.



Figure 1.1: Orthophoto of RME and its location with the larger RC-CZO and the state of Idaho, USA. Scales vary.



Figure 1.2: Map of snow depth in RME (shown in black outline) on March 19, 2009 (late winter of an average snow year). White areas show snow drift,s with numbers 1, 2a&b, 3, and 4 marking drifts examined throughout this thesis. Although drift 4 (the "Springhouse Drift") is located outside the boundaries of RME, note that it is quite large and separated from the catchment only by a ~40-cm surface divide. Snow depth ata from Shrestha, 2016.



Figure 1.3: Instrument and measurement locations in RME. "PZ" indicates piezometer; piezometers installed at the soil pit locations (Drift, Conifer, and Bog pits) are not shown separately from the pits themselves. "176" is the meteorology station and JUDD snow-depth ("exposed ridge") sensor site, "RMSP" is the Reynolds Mountain snow-pillow ("wind-sheltered") site. Sites with solid white background text boxes were installed for this thesis, and the remaining sites were installed previously and are maintained by the USDA-ARS.



Figure 1.4: Locations of electrical-resistance tomography (ERT) and seismic velocity transects in RME, from Steven Holbrook

#### 1.5. Background on Approaches for Analysis and Interpretation of Drift-

#### **Dominated System Carbon Fluxes**

#### 1.5.1. Hydrologic source identification: PCA and EMMA

Principal Component Analysis (PCA) is a multivariate factor analysis technique used to determine the primary entities in a mixture (Davis, 1973). In hydrology, it is used to find the lowest possible n-dimensional space in which all observations (e.g., ionic concentrations in streamwater) will fit within the bounds of a specified accuracy (Christophersen & Hooper, 1992). PCA yields matrices used to identify the expected number of components for an end-member mixing model (see below), and the "best" (in the sense of containing the largest amount of distinct information or explanatory power to explain stream chemical signatures) solutes to identify possible end-members.

End-Member Mixing Analysis (EMMA) is a method to determine which non-stream waters of a catchment (originally soil waters, since expanded) are contributing to stream flow (Hooper et al., 1990). It can also be used to determine if a source water has been missed in sampling. The key assumption in EMMA is that stream water is derived from some combination of source waters whose chemical compositions are unvarying in time and space (Hooper et al., 1990). When PCA is used to determine the "best" solutes for EMMA, the concentrations of those solutes in the suspected end-members are used to construct a bounding polygon in n-dimensional space, where the number of vertices (end members) is equal to the number of solutes plus one. The space is defined by the concentrations of the stream samples, and then the end-member concentrations are adjusted using the PCA matrix to project them into that end-member "Uspace" (Hooper, 2001). EMMA is assumed to be successful when the majority of stream water chemistry points fall within the bounds of the shape defined by end-member concentrations (Christophersen & Hooper, 1992); stream water points that do not fall within this space can be

projected onto the line between the two closest end-members (Christophersen & Hooper, 1992). A more detailed explanation of how we ran PCA and EMMA is found in sections 4.4 and 4.5 in the appendices.

#### 1.5.2. Carbon indices: SUVA and FI

Specific ultra-violet absorbance (SUVA) is a measure of the amount of light at 254nm absorbed by a water sample (Weishaar et al., 2003). It is strongly correlated to the aromaticity of DOC in the water, which can be used as a proxy for decomposition (McKnight et al., 2001). The assumption is that stream water samples with lower SUVA are derived from soils with more-decomposed organic material, generally the lower portions of the soil profile (Gabor, Eilers, McKnight, Fierer, & Anderson, 2014).

The fluorescence index (FI) is the ratio of emission at 450nm vs. 500nm, when a water sample is excited at 370nm (McKnight et al., 2001). It serves as a proxy for the source of DOC in a sample, with lower FI corresponding to more microbially derived DOC (autochthonous or decomposed), and higher FI corresponding to terrestrial (allochthonous) DOC (McKnight et al., 2001).

#### 1.6. Summary of Thesis Contents

This thesis is laid out as follows: chapter one, literature review of snow and carbon work; chapter two, study design, methods, results, discussion, and conclusions; chapter three: summary of chapter two with expanded conclusions and directions for future work.

The Appendices include detailed protocols for lysimeter installation; soil, water, and snow sampling and sample processing; and PCA/EMMA methodology and R code. Additionally, there are safety protocols for RC-CZO, and potentially helpful hints for future graduate students.

#### 1.7. Works Cited

- Abatzoglou, J. T., & Kolden, C. A. (2011). Climate change in Western US deserts: Potential for increased wildfire and invasive annual grasses. *Rangeland Ecology and Management*, 64(5), 471–478. https://doi.org/10.2111/REM-D-09-00151.1
- Anderson, R. S., Anderson, S. P., Aufdenkampe, A. K., Bales, R., Brantley, S. L., Duffy, C. J., ... Yoo, K. (2010). Future Directions for Critical Zone Observatory (CZO) Science. *Earth Science*, 1–6.
- Anderson, S. P., Anderson, R. S., Tucker, G. E., & Dethier, D. P. (1998). Climate and exhumation in the Colorado Front Range, *33*(1), 1–32. https://doi.org/10.1130/2013.0033(01).
- Årnason, B., Buason, T., Martinec, J., & Theodorsson, P. (1970). Movement of water through snow pack traced by deuterium and tritium. *IASH Publication*, *1*(107), 299–312.
- Barnett, T. P., & Adam, J. C. (2005). Potential impacts of a warming climate on water availability in snow-dominated regions. *Nature*, 438(7066), 303–309. https://doi.org/10.1038/nature04141
- Barnhart, T. B., Molotch, N. P., Livneh, B., Harpold, A. A., Knowles, J. F., & Schneider, D. (2016). Snowmelt rate dictates streamflow. *Geophysical Research Letters*, 43, 8006–8016. https://doi.org/10.1002/2016GL069690
- Bauhus, J., Paré, D., & Côté, L. (1998). Effects of tree species, stand age and soil type on soil microbial biomass and its activity in a southern boreal forest. *Soil Biology and Biochemistry*, 30(8–9), 1077–1089. https://doi.org/10.1016/S0038-0717(97)00213-7
- Beniston, M. (2003). Climatic change in mountain regions: A review of possible impacts. *Climate Change*, *59*, 5–31.
- Bowling, D. R., Massman, W. J., Schaeffer, S. M., Burns, S. P., Monson, R. K., & Williams, M. W. (2009). Biological and physical influences on the carbon isotope content of CO2 in a subalpine forest snowpack, Niwot Ridge, Colorado. *Biogeochemistry*, 95(1), 37–59. https://doi.org/10.1007/s10533-008-9233-4
- Boyer, E. W., Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1997). Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes*, 11, 1635– 1647. https://doi.org/10.1002/(SICI)1099-1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H
- Brooks, P. D., Grogan, P., Templer, P. H., Groffman, P., Öquist, M. G., & Schimel, J. (2011). Carbon and Nitrogen Cycling in Snow-Covered Environments. *Geography Compass*, 5(9), 682–699. https://doi.org/10.1111/j.1749-8198.2011.00420.x

- Buffington, J. M. (2013). 9.36 Geomorphic Classification of Rivers. In *Treatise on Geomorphology* (Vol. 9, pp. 730–767).
- Bunn, S. E., Balcombe, S. R., Davies, P. M., Fellows, C. S., & McKenzie-Smith, F. J. (2006). Aquatic productivity and food webs of desert river ecosystems. In R. Kingsford (Ed.), *Ecology of Desert Rivers* (pp. 76–99). Cambridge, England: Cambridge University Press.
- Carvalhais, N., Forkel, M., Khomik, M., Bellarby, J., Jung, M., Migliavacca, M., ... Reichstein, M. (2014). Global covariation of carbon turnover times with climate in terrestrial ecosystems. *Nature*, 514(7521), 213–217. https://doi.org/10.1038/nature13731
- Chorover, J., Troch, P. A., Rasmussen, C., Brooks, P. D., Pelletier, J. D., Breshears, D. D., ... Durcik, M. (2011). How Water, Carbon, and Energy Drive Critical Zone Evolution: The Jemez–Santa Catalina Critical Zone Observatory. *Vadose Zone Journal*, 10(3), 884. https://doi.org/10.2136/vzj2010.0132
- Christophersen, N., & Hooper, R. P. (1992). Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem. *Water Resources Research*, 28(1), 99–107. https://doi.org/10.1029/91WR02518
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., ... Melack, J. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10, 172–185. https://doi.org/10.1007/s10021-006-9013-8
- Davis, J. C. (1973). Statistics and Data Analysis in Geology. New York: Wiley.
- Dingman, S. L. (2015). Physical Hydrology (3rd ed.). Long Grove, IL: Waveland Press.
- Doetterl, S., Stevens, A., Six, J., Merckx, R., Oost, K. Van, Pinto, M. C., ... Boeckx, P. (2015). Soil carbon storage controlled by interactions between geochemistry and climate. *Nature Geoscience*, 8(10), 780–783. https://doi.org/10.1038/NGEO2516
- Doran, J. W. (2002). Soil health and global sustainability: Translating science into practice. *Agriculture, Ecosystems and Environment, 88*(2), 119–127. https://doi.org/10.1016/S0167-8809(01)00246-8
- Edwards, A. C., Scalenghe, R., & Freppaz, M. (2007). Changes in the seasonal snow cover of alpine regions and its effect on soil processes: A review. *Quaternary International*, *162–163*, 172–181. https://doi.org/10.1016/j.quaint.2006.10.027
- Essery, R. L. H., Li, L., & Pomeroy, J. W. (1999). A distributed model of blowing snow over complex terrain. *Hydrological Processes*, *13*, 2423–2438. https://doi.org/10.1002/(SICI)1099-1085(199910)13:14/15<2423::AID-HYP853>3.0.CO;2-U
- Eswaran, H., Berg, E., Reich, P., Van Den Berg, E., & Reich, P. (1993). Organic carbon in soils of the world. *Soil Science Society of America Journal*, 57, 192–194.

https://doi.org/10.2136/sssaj1993.03615995005700010034x

- Fellows, A. W., & Goulden, M. L. (2012). Rapid vegetation redistribution in Southern California during the early 2000s drought. *Journal of Geophysical Research: Biogeosciences*, 117, 1– 11. https://doi.org/10.1029/2012JG002044
- Fiebig, D. M., Lock, M. A., & Neal, C. (1990). Soil water in the riparian zone as a source of carbon for a headwater stream. *Journal of Hydrology*, *116*, 217–237. https://doi.org/10.1016/0022-1694(90)90124-G
- Gabor, R. S., Eilers, K., McKnight, D. M., Fierer, N., & Anderson, S. P. (2014). From the litter layer to the saprolite: Chemical changes in water-soluble soil organic matter and their correlation to microbial community composition. *Soil Biology and Biochemistry*, 68, 166– 176. https://doi.org/10.1016/j.soilbio.2013.09.029
- Grant, L. E., Seyfried, M. S., & McNamara, J. P. (2004). Spatial variation and temporal stability of soil water in a snow-dominated, mountain catchment. *Hydrological Processes*, 18, 3493– 3511. https://doi.org/10.1002/hyp.5798
- Grünewald, T., Schirmer, M., Mott, R., & Lehning, M. (2010). Spatial and temporal variability of snow depth and SWE in a small mountain catchment. *The Cryosphere Discussions*, *4*, 1–30. https://doi.org/10.5194/tcd-4-1-2010
- Harpold, A. A., Brooks, P. D., Rajagopal, S., Heidbuchel, I., Jardine, A., & Stielstra, C. M. (2012). Changes in snowpack accumulation and ablation in the intermountain west. *Water Resources Research*, 48(11). https://doi.org/10.1029/2012WR011949
- Harpold, A. A., Kaplan, M. L., Klos, P. Z., Link, T. E., McNamara, J. P., Rajagopal, S., ... Steele, C. M. (2017). Rain or snow: Hydrologic processes, observations, prediction, and research needs. *Hydrology and Earth System Sciences*, 21(1), 1–22. https://doi.org/10.5194/hess-21-1-2017
- Harpold, A. A., & Molotch, N. P. (2015). Sensitivity of soil water availability to changing snowmelt timing in the western U.S. *Geophysical Research Letters*, 42, 8011–8020. https://doi.org/10.1002/2015GL065855
- Herndon, E. M., Dere, A. L., Sullivan, P. L., Norris, D., Reynolds, B., & Brantley, S. L. (2015a). Biotic controls on solute distribution and transport in headwater catchments. *Hydrology and Earth System Sciences Discussions*, 12(1), 213–243. https://doi.org/10.5194/hessd-12-213-2015
- Herndon, E. M., Dere, A. L., Sullivan, P. L., Norris, D., Reynolds, B., & Brantley, S. L. (2015b). Landscape heterogeneity drives contrasting concentration-discharge relationships in shale headwater catchments. *Hydrology and Earth System Sciences*, 19(8), 3333–3347. https://doi.org/10.5194/hess-19-3333-2015
- Hiemstra, C. A., Liston, G. E., & Reiners, W. A. (2002). Snow Redistribution by Wind and Interactions with Vegetation at Upper Treeline in the Medicine Bow Mountains, Wyoming,

U.S.A. Arctic, Antarctic, and Alpine Research, 34(3), 262–273. https://doi.org/10.2307/1552483

- Hooper, R. P. (2001). Applying the scientific method to small catchment studies: a review of the Panola Mountain experience. *Hydrological Processes*, 15, 2039–2050. https://doi.org/10.1002/hyp.255
- Hooper, R. P., Christophersen, N., Peters, N. E., Neal, C., Hooper, R. P., Vogt, R. D., ... Peters, N. E. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members - An application to the Panola Mountain catchment, Georgia, U.S.A. *Journal of Hydrology*, *116*, 321–343. https://doi.org/10.1016/0022-1694(90)90131-G
- Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1994). Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry*, 25(3), 147–165. https://doi.org/10.1007/BF00024390
- Hornberger, G. M., Germann, P. F., & Beven, K. J. (1991). Throughflow and solute transport in an isolated sloping soil block in a forested catchment. *Journal of Hydrology*, 124, 81–99. https://doi.org/10.1016/0022-1694(91)90007-5
- Huntington, J. L., & Niswonger, R. G. (2012). Role of surface-water and groundwater interactions on projected summertime streamflow in snow dominated regions: An integrated modeling approach. *Water Resources Research*, 48(11), 1–20. https://doi.org/10.1029/2012WR012319
- Jenny, H. (1941). *Factors of soil formation: A system of quantitative pedology*. New York: McGraw-Hill.
- Klos, P. Z., Link, T. E., & Abatzoglou, J. T. (2014). Extent of the rain-snow transition zone in the western U.S. under historic and projected climate. *Geophysical Research Letters*, 41, 4560–4568. https://doi.org/10.1002/2014GL060500
- Kormos, P. R., McNamara, J. P., Seyfried, M. S., Marshall, H. P., Marks, D., & Flores, A. N. (2015). Bedrock infiltration estimates from a catchment water storage-based modeling approach in the rain snow transition zone. *Journal of Hydrology*, 525, 231–248. https://doi.org/10.1016/j.jhydrol.2015.03.032
- Lal, R. (2004). Soil carbon sequestration impacts on global climate change and food security. *Science (New York, N.Y.)*, 304(5677), 1623–1627. https://doi.org/10.1126/science.1097396
- Lang, R. E., Muro, M., Sarzynski, A., Muro, M., Sarzynski, A., & Muro, M. (2008). Mountain Megas: America's Newest Metropolitan Places and a Federal Partnership to Help Them Prosper. Washington D.C.: Brookings Institution.

- Li, L., Bao, C., Sullivan, P. L., Brantley, S. L., Shi, Y., & Duffy, C. J. (2017). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. *Water Resources Research*, 53(3), 2346–2367. https://doi.org/10.1002/2016WR018935
- Liptzin, D., Williams, M. W., Helmig, D., Seok, B., Filippa, G., Chowanski, K., & Hueber, J. (2009). Process-level controls on CO2 fluxes from a seasonally snow-covered subalpine meadow soil, Niwot Ridge, Colorado. *Biogeochemistry*, 95(1), 151–166. https://doi.org/10.1007/s10533-009-9303-2
- MacDonald, M. K., Pomeroy, J. W., & Pietroniro, A. (2009). Parameterizing redistribution and sublimation of blowing snow for hydrological models: tests in a mountainous subarctic catchment. *Hydrological Processes*, 23, 2570–2583. https://doi.org/10.1002/hyp.7356
- MacDonald, M. K., Pomeroy, J. W., & Pietroniro, A. (2010). On the importance of sublimation to an alpine snow mass balance in the Canadian Rocky Mountains. *Hydrology and Earth System Sciences*, 14(7), 1401–1415. https://doi.org/10.5194/hess-14-1401-2010
- Marks, D. (2001). Introduction to Special Section: Reynolds Creek Experimental Watershed. *Water Resources Research*, 37(11), 2817–2817. https://doi.org/10.1029/2001WR000941
- Mavris, C., Furrer, G., Dahms, D., Anderson, S. P., Blum, A., Goetze, J., ... Egli, M. (2015). Decoding potential effects of climate and vegetation change on mineral weathering in alpine soils: An experimental study in the Wind River Range (Wyoming, USA). *Geoderma*, 255– 256, 12–26. https://doi.org/10.1016/j.geoderma.2015.04.014
- McIntosh, J. C., Schaumberg, C., Perdrial, J. N., Harpold, A. A., Vázquez-Ortega, A., Rasmussen, C., ... Chorover, J. (2017). Geochemical evolution of the Critical Zone across variable time scales informs concentration-discharge relationships: Jemez River Basin Critical Zone Observatory. *Water Resources Research*, 53(5), 4169–4196. https://doi.org/10.1002/2016WR019712
- McIntyre, D. H. (1972). Cenozoic geology of the Reynolds Creek Experimental Watershed, Owyhee County, Idaho. *Pamphlet 151*. Moscow, ID. Retrieved from https://ngmdb.usgs.gov/Prodesc/proddesc\_46206.htm
- McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., & Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46, 38–48. https://doi.org/10.4319/lo.2001.46.1.0038
- McNamara, J. P., Chandler, D. G., Seyfried, M. S., & Achet, S. (2005). Soil moisture states, lateral flow, and streamflow generation in a semi-arid, snowmelt-driven catchment. *Hydrological Processes*, *19*, 4023–4038. https://doi.org/10.1002/hyp.5869
- Mote, P. W., Hamlet, A. F., Clark, M. P., & Lettenmaier, D. P. (2005). Declining mountain snowpack in western north America. *Bulletin of the American Meteorological Society*, 86(1), 39–49. https://doi.org/10.1175/BAMS-86-1-39
- Mote, P. W., Li, S., Lettenmaier, D. P., Xiao, M., & Engel, R. (2018). Dramatic declines in snowpack in the western US. *Npj Climate and Atmospheric Science*, *1*(1), 2. https://doi.org/10.1038/s41612-018-0012-1
- Nayak, A., Marks, D., Chandler, D. G., & Seyfried, M. S. (2010). Long-term snow, climate, and streamflow trends at the reynolds creek experimental watershed, Owyhee Mountains, Idaho, United States. *Water Resources Research*, 46(6). https://doi.org/10.1029/2008WR007525
- Patton, N. R. (2016). *Topographic Controls on Total Mobile Regolith and Total Soil Organic Carbon in Complex Terrain* (master's thesis). Idaho State University.
- Pomeroy, J. W. (1989). A process-based model of snow drifting. *Annals of Glaciology*, 13(January), 237–240. https://doi.org/10.1017/S0260305500007965
- Pomeroy, J. W. (1991). Transport and Sublimation of Snow in Wind-Scoured Alpine Terrain. Snow Hydrology and Forests in High Alpine Areas, Proceedings of the Vienna Symposium, August 1991, IAHS Publ. No. 205, 0(Snow Hydrology and Forests in High Alpine Areas, Proceedings of the Vienna Symposium, August 1991, IAHS Publ. 205), 131–140.
- Pomeroy, J. W., Gray, D. M., Brown, T., Hedstrom, N., Quinton, W. L., Granger, R. J., & Carey, S. K. (2007). The cold regions hydrological model: a platform for basing process representation and model structure on physical evidence. *Hydrological Processes*, 21, 2650–2667. https://doi.org/10.1002/hyp.6787
- Pomeroy, J. W., Gray, D. M., Shook, K. R., Toth, B., Essery, R. L. H., Pietroniro, A., & Hedstrom, N. (1998). An Evaluation of Snow Processes for Land Surface Modelling. 55th Eastern Snow Conference, 2367(September), 2339–2367. https://doi.org/10.1002/(SICI)1099-1085(199812)12:15<2339::AID-HYP800>3.0.CO;2-L
- Reba, M. L., Marks, D., Seyfried, M. S., Winstral, A., Kumar, M., & Flerchinger, G. (2011). A long-term data set for hydrologic modeling in a snow-dominated mountain catchment. *Water Resources Research*, 47(7), 1–7. https://doi.org/10.1029/2010WR010030
- Sanderman, J., Lohse, K. A., Baldock, J. A., & Amundson, R. (2009). Linking soils and streams: Sources and chemistry of dissolved organic matter in a small coastal watershed. *Water Resources Research*, 45(3), W03418. https://doi.org/10.1029/2008WR006977
- Schimel, D. S. (1994). Climatic, edaphic, and biotic controls over storage and turnover of carbon in soils. *Global Biogeochemical Cycles*, 8(3), 279–293. https://doi.org/10.1029/94GB00993.This

Schlesinger, W. H., & Andrews, J. A. (2000). Soil Respiration and the Global Carbon Cycle.

Biogeochemistry, 48(1), 7–20. https://doi.org/10.1023/A:1006247623877

- Seyfried, M. S., Grant, L. E., Marks, D., Winstral, A., & McNamara, J. P. (2009). Simulated soil water storage effects on streamflow generation in a mountainous snowmelt environment, Idaho, USA. *Hydrological Processes*, 23, 858–873. https://doi.org/10.1002/hyp.7211
- Seyfried, M. S., Harris, R., Marks, D., & Jacob, B. (2001). Geographic database, Reynolds Creek Experimental Watershed, Idaho, United States. *Water Resources Research*, 37(11), 2825– 2829. https://doi.org/10.1029/2001WR000414
- Shrestha, Rupesh. (2016). 2009 Im Snow Depth for Reynolds Mountain East, Reynolds Creek Experimental Watershed, Idaho [Data set]. http://doi.org/10.18122/B28597
- Smith, T. J., McNamara, J. P., Flores, A. N., Gribb, M. M., Aishlin, P. S., & Benner, S. G. (2011). Small soil storage capacity limits benefit of winter snowpack to upland vegetation. *Hydrological Processes*, 25, 3858–3865. https://doi.org/10.1002/hyp.8340
- Stieglitz, M., Shaman, J., McNamara, J. P., Engel, V., Shanley, J. B., & Kling, G. W. (2003). An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. *Global Biogeochemical Cycles*, 17(4), 1–15. https://doi.org/10.1029/2003GB002041
- Stielstra, C. M., Lohse, K. A., Chorover, J., McIntosh, J. C., Barron-Gafford, G. A., Perdrial, J. N., ... Brooks, P. D. (2015). Climatic and landscape influences on soil moisture are primary determinants of soil carbon fluxes in seasonally snow-covered forest ecosystems. *Biogeochemistry*, 123(3), 447–465. https://doi.org/10.1007/s10533-015-0078-3
- Sturm, M., & Wagner, A. M. (2010). Using repeated patterns in snow distribution modeling: An Arctic example. *Water Resources Research*, 46(12), 1–15. https://doi.org/10.1029/2010WR009434
- Tennant, C. J., Harpold, A. A., Lohse, K. A., Godsey, S. E., Crosby, B. T., Larsen, L. G., ... Glenn, N. F. (2017). Regional sensitivities of seasonal snowpack to elevation, aspect, and vegetation cover in western North America. *Water Resources Research*, 53(8), 6908–6926. https://doi.org/10.1002/2016WR019374
- Tromp-Van Meerveld, H. J., & McDonnell, J. J. (2006). Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. *Water Resources Research*, 42(2), 1–11. https://doi.org/10.1029/2004WR003800
- USDA NASS. (2013). Table 4. Estimated Quantity of Water Applied By Source: 2013 and 2008. 2012 Census of Agriculture, 2013 FRIS Entire Farm Data, 11–14.
- Viviroli, D., Dürr, H. H., Messerli, B., Meybeck, M., & Weingartner, R. (2007). Mountains of the world, water towers for humanity: Typology, mapping, and global significance. *Water Resources Research*, 43(7), 1–13. https://doi.org/10.1029/2006WR005653

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003).

Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. *Environmental Science & Technology*, *37*, 4702–4708. https://doi.org/10.1021/es030360x

- Wickland, K. P., Neff, J. C., & Aiken, G. R. (2007). Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability. *Ecosystems*, 10(8), 1323– 1340. https://doi.org/10.1007/s10021-007-9101-4
- Williams, C. J., McNamara, J. P., & Chandler, D. G. (2008). Controls on the temporal and spatial variability of soil moisture in a mountainous landscape: the signatures of snow and complex terrain. *Hydrology and Earth System Sciences Discussions*, 5(4), 1927–1966. https://doi.org/10.5194/hessd-5-1927-2008
- Williams, M. W., Helmig, D., & Blanken, P. (2009). White on green: Under-snow microbial processes and trace gas fluxes through snow, Niwot Ridge, Colorado Front Range. *Biogeochemistry*, 95(1), 1–12. https://doi.org/10.1007/s10533-009-9330-z
- Williams, M. W., Losleben, M. V, & Hamann, H. B. (2002). Alpine areas in the Colorado Front Range as monitors of climate change and ecosystem response. *Geographical Review*, 92, 180–191. https://doi.org/10.1111/j.1931-0846.2002.tb00003.x
- Winstral, A., & Marks, D. (2014). Long-term snow distribution observations in a mountain catchment: Assessing variability, time stability, and the representativeness of an index site. *Water Resources Research*, *50*(1), 293–305. https://doi.org/10.1002/2012WR013038
- Zogg, G. P., Zak, D. R., Ringelberg, D. B., White, D. C., MacDonald, N. W., & Pregitzer, K. S. (1997). Compositional and Functional Shifts in Microbial Communities Due to Soil Warming. Soil Science Society of America Journal, 61, 475. https://doi.org/10.2136/sssaj1997.03615995006100020015x

# Chapter 2: Spatiotemporal Heterogeneity of Water and Dissolved Organic Carbon Sourcing in a Snow-dominated, Headwater Catchment

#### 2.1. Abstract

The non-uniform distribution of water in snowdrift-driven systems can drive spatial heterogeneity in vegetative communities and soil development, as snowdrifts may locally increase weathering. The focus of this study is to understand the coupled hydrological and carbon dynamics in a heterogeneous, snowdrift-dominated headwater catchment (Reynolds Mountain East, Reynolds Creek Critical Zone Observatory, Idaho, USA). We determine the sources and fluxes of stream water and dissolved organic carbon (DOC) at this site, deducing likely flowpaths from hydrometric and hydrochemical signals of soil water, saprolite water, and groundwater measured through the snowmelt period and summer drying. We then interpret flowpaths using end-member mixing analysis in light of inferred subsurface structure derived from geophysical transects. Streamwater is sourced primarily from groundwater (averaging 25% of annual streamflow), snowmelt (50%), and water travelling along the saprolite/bedrock boundary (25%). The latter is comprised of the prior year's soil water, which accumulates DOC in the soil matrix through the summer before flushing to the saprolite during snowmelt. DOC indices indicate that it is sourced from terrestrial carbon, and the hydrologic dominance of subsurface flowpaths suggests that this DOC was originally soil organic carbon (SOC). Multiple aquifers in the catchment contribute differentially to streamflow as the season progresses; sources shift from the saprolite/bedrock interface to deeper bedrock aquifers from the snowmelt period into summer. Unlike most studied catchments, this year's soil water (moving by lateral flow) is not a primary source of streamflow. Instead, saprolite and groundwater act as integrators of soil water. Our results do not support the flushing hypothesis proposed for similar systems,

and suggest possible temporal variation in connectivity as a cause of the similarly unexpected dilution behavior displayed by DOC in this catchment. While our conclusions on carbon sourcing broadly correspond to the existing literature, we suggest an unusually rapid groundwater flowpath and a relative absence of soil-stream connectivity in this watershed might indicate a need for more detailed analysis of water sourcing in carbon export studies.

#### **2.2. Introduction**

In mountainous headwater catchments, snow is often the dominant phase of precipitation (Barnett & Adam, 2005). High-elevation snowpacks act as reservoirs, storing water from winter storms and releasing it later, often sustaining streamflow through the growing season at downstream locations (Nayak et al., 2010; M. W. Williams et al., 2002). One major impact of climate change is a shift in the elevation of the rain-snow transition (Klos et al., 2014; Marks, Winstral, Reba, Pomeroy, & Kumar, 2013), the range of elevations that commonly receives a mixture of rain and snow during precipitation events, with snow dominating at higher elevations and rain at lower elevations (Marks et al., 2013). The location of the rain-snow transition can shift between and during storm events, but commonly has a characteristic range of elevations in a given geographic region (Marks et al., 2013). Any change in the elevation of the rain-snow transition will affect snowpack size and location (Klos et al., 2014; Tennant et al., 2017), and the different hydrologic response of the basin to rain versus snow will affect streamflow and groundwater supplies (Marks et al., 2013).

Snowmelt and snowdrifts dominate the hydrology of mountain regions around the world (Viviroli et al., 2007). Snowdrifts are created by the intersection of wind and topography, as wind removes snow from exposed areas and drops it on lee slopes (Winstral & Marks, 2002). This amounts to 'drift' (accumulation) areas receiving a precipitation subsidy from 'scour'

(removal) areas (Winstral & Marks, 2014). Drifts tend to form in the same locations annually (visible on LiDAR imagery or in person), resulting in greater spatial heterogeneity of precipitation in snowdrift-dominated catchments than in those where drifting does not occur (Grünewald et al., 2010; Sturm & Wagner, 2010; Winstral & Marks, 2014). This impacts hydrologic flowpaths in these systems (Pomeroy et al., 2007).

Hydrologic flowpaths are constrained by topography, soil and bedrock porosity, and evapotranspiration (Soulsby, Tetzlaff, Rodgers, Dunn, & Waldron, 2006; Tetzlaff, Malcolm, & Soulsby, 2007). In a system with several large upstream snowdrifts and only one stream, meltwater that does not evaporate or sublimate from the drift surface must flow downhill into the stream from the melting drifts, unless it is lost to deep regional aquifers. Therefore, we know that the stream water derives from the drift, but the key question is *how* it gets to the stream. What does it flow through? How long does it take? What solutes does it acquire en route?

If snowdrifts can be considered aboveground "water towers" in mountainous systems (Viviroli et al., 2007), then aquifers can be thought of as belowground "storage tanks". Bedrock aquifers, where present, are considered the major source of stream baseflow during periods of little precipitation (Dingman, 2015). In snow-dominated systems, it is common for snowmelt to be the dominant aquifer-recharge event (Fleckenstein, Niswonger, & Fogg, 2006; Seyfried et al., 2009). Water from the drifts infiltrates through the soil, where soil is present in the catchment, dissolving minerals and organic material from the soil matrix (Lohse, Brooks, McIntosh, Meixner, & Huxman, 2009). The water may recharge the bedrock aquifer, or it may run along the bedrock/soil interface into the stream (Stieglitz et al., 2003). The paths water follows affect the species and quantity of solutes it carries.

After the initial pulse of snowmelt, snow-dominated watersheds may begin to dry out from the ridgetops down (Stieglitz et al., 2003). In drier areas, soil water continues to accumulate solutes, but this water will not reach the stream until sufficient hydrologic connectivity is restored through soil saturation (Li, Bao, et al., 2017; Sanderman et al., 2009; Stieglitz et al., 2003; Stielstra et al., 2015). Since hydrologic connectivity is not uniform across most catchments, patterns in solute concentration in stream waters will be influenced by patterns in connectivity (Li et al., 2017).

A solute of interest, particularly for connection to in climate change, is dissolved organic carbon (DOC). In headwater catchments, especially those where subsurface flow predominates, the primary source of DOC is soil organic carbon (SOC) leached by precipitation and carried to the stream (Boyer et al., 1997). DOC is an important component of aquatic food webs, while SOC in the form of soil organic matter (SOM) increases the availability of water and nutrients for plant growth (Cole et al., 2007; Crimmins, Dobrowski, Greenberg, Abatzoglou, & Mynsberge, 2011; Doran, 2002). Loss of SOM can reduce soil fertility, while much of the SOC lost to rivers is eventually respired to the atmosphere in the form of carbon gasses such as carbon dioxide and methane (Cole et al., 2007; Doran, 2002).

Climate change has the potential to cause particularly large changes in mountainous regions, including altering the level of the rain-snow transition, and the proportions of rain and snow on an annual basis (Beniston, 2003; Tennant et al., 2017). Changes in the proportions of rain and snow in a catchment can impact hydrologic flowpaths; and insofar as hydrology affects carbon transport, these changes can also impact the export of DOC from mountainous headwater catchments (Boyer et al., 1997; Jones et al., 2005; Tennant et al., 2017). Rising atmospheric concentrations of methane and carbon dioxide in the past few centuries have already altered

world climate, affecting temperature and water availability worldwide (Intergovernmental Panel on Climate Change, 2014). The stability of SOM is influenced by temperature and water availability, and as SOM represents a major store of carbon worldwide, there exists a potential feedback loop—climate change leading to greater release of soil carbon, which then changes the climate further (Cox, Betts, Jones, Spall, & Totterdell, 2000; Eswaran et al., 1993; Jones et al., 2005; Zogg et al., 1997).

At the intersection of snow hydrology and carbon export is the "flushing" hypothesis (Boyer et al., 1997). While the snowpack remains frozen, only limited export of soil water occurs, and soil pore waters accumulate solutes, including SOC. In spring, snowmelt flushes this concentrated soil water into the stream, along with the solutes it carries. This is a major control on carbon export (e.g. Boyer et al., 1997; Hornberger, Bencala, & McKnight, 1994). However, these previous studies generally used the carbon concentrations themselves as an indicator of water sourcing. We expanded on this idea by tracing water flowpaths separately through more conservative tracers, creating an end-member mixing model that we then compared with known carbon concentrations. Comparing the relative contributions of water and DOC of these source waters will allow us to evaluate previous assumptions on DOC transport and flowpaths—that SOC the primary source of DOC in streams because soil water is the primary source of water to the stream (Boyer et al., 1997).

In this study, we explore how the hydrologic dynamics of snow-dominated watersheds interact with carbon stores to affect stream carbon export, specifically:

1: What are the patterns of dissolved organic carbon concentrations in stream and source waters? Do they follow the "flushing" model, or is there another factor driving carbon export?

2: What paths does meltwater from seasonal snowdrifts follow on its way to the stream?

3: Is soil water a major component of the hydrograph in drift-dominated systems, or is carbon being brought into the stream by another subsurface flowpath?

## 2.3. Methods

#### 2.3.1. General approach

To answer the questions outlined above, we sampled all likely end-members (soil water, saprolite water, deeper groundwater, rain, and snow) and compared cation and anion concentrations to those in stream water to determine the flow paths in this watershed. Carbon sourcing in this study was determined using the DOC concentrations in end-members determined by end-member mixing analysis (EMMA), the specific ultraviolet absorbance (SUVA) and fluorescence index (FI) of stream water and end-members, and estimates of SOC stocks in the watershed (Q1). To determine hydrologic response, we measured soil moisture and matric potentials in three soil pits at three depths; depth to water table in wells drilled in the bedrock aquifer; and isotopic composition of waters taken from soil, saprolite, bedrock, snowpack, rainfall, and stream. These likely end-members were quantified using EMMA and a mixing model to indicate the primary sources of stream flow (Q2). Once questions one and two were addressed, we compared the relative contributions of carbon and water to the stream by each end-member to answer Q3.

#### 2.3.2. Site Description

Reynolds Mountain East (RME) is a 0.38 km<sup>2</sup> headwater catchment in the Reynolds Creek Experimental Watershed (RCEW)/Reynolds Creek Critical Zone Observatory (RC-CZO) (Figure 2.1). It ranges from 2020 m to 2140 m in elevation over an area of 0.38 km<sup>2</sup>; slopes vary from 0 to 40% (Seyfried et al., 2009). RME has been intensively monitored as a USDA-ARS

experimental watershed for over 50 years, and as a National Science Foundation Critical Zone Observatory for the past five years.

RME receives approximately 900 mm of precipitation annually, of which more than 70% is delivered in the form of snow, and exports ~520 mm of this as stream flow (Seyfried et al., 2009). Snow commonly accumulates in deep (>2 m) drifts in sheltered areas (Winstral & Marks, 2014). One large drift, the East drift, forms at the eastern end of the catchment, on the leeward side of an unnamed peak (Figure 2.2, No. 1). A smaller drift forms at the base of the steep hill below the cabin (Figure 2.2, No. 2); little to no drifting occurs in the Douglas-fir forest below this drift, but in exceptionally snowy years, a smaller drift forms farther downhill in a bog (Figure 2.2, No. 2b). Another drift forms just east of this drift, downhill of the East drift, in an aspen stand (Figure 2.2, No. 3). An exceptionally large drift (>10m in depth) is formed just outside the catchment boundary (Figure 2.2, No. 4); this is referred to as the Springhouse drift, which feeds a perennial stream adjacent to a springhouse for which the drift is named. While this drift is technically outside the catchment, the divide is a ridge only ~40cm in height, and we hypothesize that subsurface connectivity may not reflect the surface topography (Figure 2.3, indicated by near-zero slopes within the blue circle).

Lithology and soils in this catchment are relatively consistent, while vegetation is more variable. Multiple layers of volcanic rocks, primarily andesite and rhyolite with some basalt, compose the bedrock (Ekren, McIntyre, Bennet, & Malde, 1981; McIntyre, 1972). Soils are primarily poorly developed, highly permeable loams and silt loams (Seyfried et al., 2001). The stream in RME is perennial from the weir to a point approximately 100m upstream of the bog site; above this point, the stream is intermittent. There is at least one perennial, seasonally artesian spring, which was sampled in this study. Most slopes are dominated by sagebrush

(*Artemesia* spp.) and various forbs and grasses. However, willow (*Salix* spp.) dominates the riparian corridor, and quaking aspen (*Populus tremuloides*) and conifers (principally Douglas fir, *Pseudotsuga menzeii*) are found in scattered stands at intermediate elevations (Seyfried et al., 2009). Bog vegetation consists of shrubby willow, aspen, and various forbs and sedges, with some algal growth in the channel during summer low flow. Large branches were preserved in the bog's organic soil layer, and roots penetrated to significant depth; non-woody organic material was unidentifiable. Toothmarks on the ends of some of the branches suggest that they were deliberately placed by beavers. No beavers were active in RME during WY2016-2017, but they are currently active farther downstream on Reynolds Creek.



Figure 2.1: Orthophoto of Reynolds Mountain East catchment, in context of the larger Reynolds Creek CZO and the state of Idaho



Figure 2.2: Snow depth in RME, March 2009 (an average snow year). White areas show snow drifts, with numbers 1, 2a&b, 3, and 4 marking drifts examined throughout this thesis). Snow depth data from Shrestha (2016).



Figure 2.3: Slope map of RME, with surface between catchment boundary and external drift indicated by the blue circle. Note near-zero slopes in this location.



Figure 2.4: Map of RME, showing instrument and sampling locations. 176 is the "exposed ridge" meteorology station and JUDD snow-depth site; "RMSP" is the "wind-sheltered" snow pillow. "PZ" stands for "piezometer"; the piezometers at the soil pits are co-located with the soil moisture and matric-potential probes.



Figure 2.5: Geophysics (seismic velocity and electrical-resistance tomography) transects completed by Steven Holbrook and the University of Wyoming, 2015

## 2.3.2.1. Instrumentation

## Meteorological, soil, discharge, and groundwater monitoring

As part of the Reynolds Creek Experimental Watershed, RME boasts long-term ARS instrumentation, including two meteorological stations (precipitation, snow depth, wind direction, relative humidity, soil moisture, air and soil temperature, and solar radiation), four monitoring wells (depth to water table), and a v-notch weir at the outlet with TROLL 9500 (In-Situ Inc., Fort Collins, CO) continuous sensors (stage, discharge, temperature, and total suspended solids) and a Sigma 900 automated sampler (Hach Company, Loveland, CO) for water chemistry sampling (anions, total suspended solids, particulate organic carbon, non-purgeable organic carbon). Additional data collected by the ARS includes snow depth measurements and soil moisture (Nayak et al., 2010; Seyfried et al., 2009). The monitoring wells are used for groundwater sampling, and include three 15m-deep wells (Drift, West, and Aspen wells) and one 30m-deep well (Cabin well). Locations of all monitoring equipment are noted on Figure 2.4.

## Soil Pits, Sensors, and Water Collectors

In August and September 2016, we excavated three soil pits along geophysics transect 4 from snowdrift 2a to stream (Figure 2.2, Figure 2.4, Figure 2.5 No. 4). Each pit was hand-dug to refusal, described, and sampled by horizon (Table 2.2). The regolith contact was defined as where digging reached consolidated bedrock, which could not easily be removed by hand. We also recorded the soil-saprolite boundary: saprolite is here defined as unconsolidated bedrock, where the orientation of rocks in the surrounding matrix shows they were weathered in place, and not considered mobile regolith for the purpose of soil studies previously conducted in RME (Patton, 2016).

We selected pit locations in order to collect soil water along a hypothesized hydrologic flowpath incorporating three distinct combinations of topography and vegetation: a snowdrift area dominated by grasses, forbs, and sagebrush; a mid-slope "conifer" location in a Douglas fir stand; and a toeslope/riparian location in an aspen/willow/sedge bog. An additional piezometer was installed at a spring near the transect to sample groundwater. Through visual inspection, it was determined that the regolith for all pits was rhyolitic volcanic rock, which is consistent with the geologic maps of the area (McIntyre, 1972). The "snowdrift" and "conifer" soils were loams and silt loams to depths of 125 cm and 95 cm, respectively; while the "bog" pit contained 32 cm of hemic organic material overlying silt loam to 50 cm. The conifer pit was considerably drier than the snowdrift or the bog during excavation. Photos of the pits are shown in Figure 2.6.

Three Prenart SuperQuartz (Prenart Equipment ApS, Buen, Denmark) tension lysimeters were installed in each pit: at approximately 30 cm below the soil surface, at the soil-saprolite boundary, and in saprolite. Decagon EC-5 (METER Environment Group, USA) soil moisture probes were installed at the same depths as the lysimeters, and Decagon MPS-1 and MPS-2 soil matric potential probes were installed alongside the lysimeters at the soil-saprolite boundary and 10 cm below the soil surface, respectively. Each pit setup also incorporated a stainless-steel drive-point piezometer which was hand-driven to refusal, placing the screened interval in the saprolite near the top of the consolidated bedrock. The piezometers were intended to capture water flowing along the bedrock surface, which is a flowpath that McNamara et al. (2005) report from the Dry Creek watershed, also located in southeastern Idaho (Table 2.1, Figure 2.6). Soil moisture and matric-potential data from the sensors were collected at 10-minute intervals on Decagon EM-50 dataloggers; piezometer diameter was too small to install water level loggers.

A rain sampler was installed at the end of winter in 2017, and collected rain from May through September 2017, minimizing isotopic fractionation by using a foam float inside of a Nalgene bottle housed within an insulating cooler (B. Finney, personal communication, May 2017). Large particles were excluded from the sample bottle by a plastic screen, but dust was not removed. National Atmospheric Deposition Program (NADP) dust data from the ID11 site (Reynolds Creek) were compared to the RME results to account for the effects of wet and dry deposition.



Figure 2.6: Soil pits from the snowdrift (left), conifer (middle) and bog (right) sites with delineated horizon boundaries, including saprolite. The soil directly beneath snowdrift is much deeper than at the other locations and the organic horizons are much thicker in the bog than at the other locations. Large roots and branches are visible in the bog organic horizons, and redox features are visible, especially in the bog saprolite. Overlaid on the photos are the locations of instruments (Table 2.1)

Table 2.1: Depths of soil contacts and instrument installation for each soil pit.

Pit Name	Depth to Bedrock (cm)	Depth to Saprolite (cm)	Depth of Piezometer Screened Interval (cm)	Depths of Lysimeters and Co-Installed Probes (cm)							
				MPS-2, EC-5	MPS-1, EC-5	EC-5					
Drift	165	125	143-120	23.3	75.5	151.1					
Conifer	110	95	103-80	34	70	77.6					
Bog	70	50	83-60	34.9	48.6	82.4					
Spring	125*	60*	120-100	n/a	n/a	n/a					
* Determined using soil corer prior to installing piezometer											

## 2.3.3. Sample Collection

#### 2.3.3.1. Soil Sampling, Processing and Analysis

Bulk density cores and bulk soil samples were collected by horizon when pits were dug in fall 2016. Samples were double-bagged in zip-top bags and stored at 0°C until analysis. Bulk soil samples were split prior to analysis in order to preserve a portion of the sample for possible future analysis with the reserved portion immediately returned to the freezer. Wet soil was sieved to separate coarse (> 2 mm dia.) and fine fractions; these were air dried, weighed, and subjected to textural analysis by a modified hydrometer method, and the sand portion further quantified using a 53  $\mu$ m sieve (Lohse, Seyfried, McCorkle, & Patton, 2014).

A separate sieved portion of each sample was used to measure pH and electrical conductivity in a 1:1 soil:deionized water solution using a Fisher Scientific XL50 Dual Channel pH/Ion/Conductivity Meter. The dried fine fraction of each sample was processed to determine soil organic matter/total soil carbon by loss on ignition at 400°C. Elemental C and carbon-13 were measured in the Idaho State University Stable Isotope Laboratory. Samples were freeze-dried and homogenized before measuring; samples were not treated for carbonates, as all pH measurements were below 6.5 (Table 2.2). Measurements were obtained using an Elemental Combustion System 4010 (Costech Analytical Technologies, Inc., Cernusco S/Nav–MI, Italy)

interfaced to a Delta V Advantage mass spectrometer through a ConFlo IV system (Thermo Fisher Scientific, Waltham, MA). Bulk density samples were weighed, and bulk density calculated using the known volume of the sample rings (Patton, 2016).

#### 2.3.3.2. Water Sampling, Processing and Analysis

Samples were collected at least monthly from January to October 2017, after allowing a 3-month settling period for lysimeters (Lohse, Sanderman, & Amundson, 2013). During the melt and recession period from March to September 2017, samples were collected bi-weekly. Stream water grab samples were collected at the weir and in the bog area upstream of the soil pits during each sampling effort. One sample was taken from the Springhouse stream in October 2017.

Lysimeters were sampled by applying 60kPa of tension by hand pump for a minimum of 3 hours. Piezometers were sampled with a MasterFlex peristaltic pump (ColeParmer Inc., Vernon Hills, IL), and groundwater wells with a stainless-steel bailer (WildCo Inc., Yulee, FL) or polypropylene ball valve bailer. Heavy snowfall precluded sample collection at the bog until May of 2017; the drift and conifer sites could be sampled during this period, as the lysimeter lines extended to areas of low snow accumulation. Similar lines set up in the bog were initially inaccessible because of treefall, but collection resumed as early as possible in May. Wells were also sampled throughout the entire period with a handful of exceptions: the Cabin well was not sampled when the generator running its electric well pump failed, and the West well was buried by snow until March 2017 and blocked in September 2017.

Rain samples were collected directly from the rain sampler, after homogenizing the sample bottle contents. Snow samples were collected from pits dug to the base of the snowpack in the snowdrift near the drift pit, with density samples taken every 30 cm and depth-integrated samples used for analyses. One sample, from the East drift (Figure 2.2, Drift No. 1), was collected using a snow survey tube. Snow samples were double-bagged in zip-top bags and

stored at 0°C until analysis. Liquid water samples were collected in Nalgene bottles and stored at 4°C until analyzed. All water samples were vacuum filtered through pre-combusted 0.7μm Whatman glass fiber filters within 72 hours of collection or thaw. Samples were split into portions for carbon, ion, and isotope analyses. Carbon samples were not further processed. For ion and isotopic analyses, samples were filtered through 0.45μm Puradisc syringe filters.

Water samples were analyzed for anions, cations, isotopes of oxygen and hydrogen, total nitrogen, and carbon species. Anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>) were measured using a Dionex (Sunnyvale, California, USA) ICS-5000, at dilutions from 0 to 1:20, with final dilutions depending on signal strength. A full spectrum of stable cations was measured in the Center for Archaeology, Materials, and Applied Spectroscopy (CAMAS) lab at Idaho State University on a Thermo X-II series Inductively Coupled Plasma Mass Spectrometer (ICP-MS) equipped with a Cetac 240-position liquid autosampler (ThermoFisher Scientific); dilution was 1:10 sample:de-ionized water. A subset of stream samples, and end-members from both May and July 2017 were selected for water isotope analysis. A Delta V Advantage mass spectrometer with a ConFlo IV system (Thermo Fisher Scientific) at the CAMAS lab was used to measure deuterium and  $\delta^{18}$ O for water samples. All isotope values are reported as per mille (‰) of  $\delta$ D and  $\delta^{18}$ O relative to Vienna Mean Standard Ocean Water (VS.MOW).  $\delta$ D vs.  $\delta^{18}$ O plots of precipitation (rain and snow) samples were regressed to determine the local meteoric waterline (LMWL) (Dansgaard, 1964).

Dissolved/non-purgeable organic carbon, dissolved inorganic carbon, and total nitrogen were run in the ISU Lohse Soil and Biogeochemistry (LSB) lab on a Shimadzu Corp (Kyoto, Japan) TOC-V CSH equipped with an ASI-V autosampler and TNM-1 chemiluminescence detector for total nitrogen. No dilutions were required. Samples selected for absorbance and

fluorescence spectroscopy were sent to the University of Vermont Pedrial lab, where a Horiba Aqualog Fluorescence Spectrometer (Horiba, Irvine CA, USA) was used to characterize DOC. Absorbance runs were conducted on undiluted samples, while fluorescence analysis (EM 212.62-619.21 nm emission, 3.336 nm increment; EX 240-600 nm excitation, 3 nm increment) required dilution to a value between 0.1 and 0.3 (absorbance, unitless) (Miller & Blair, 2009; Ohno, 2002). FI was computed as the quotient of excitation intensity at 370 nm and emission intensity at 470nm divided by the emission intensity at 520 nm (Cory & McKnight, 2005; McKnight et al., 2001).

#### 2.3.4. Principal Component and End-Member Mixing Analysis

Principal Component Analysis (PCA) is a multivariate factor analysis technique used to determine the primary entities in a mixture (Davis, 1973). In hydrology, it is used to find the lowest possible n-dimensional space in which all observations (e.g., ionic concentrations) will fit within the bounds of a specified accuracy (Christophersen & Hooper, 1992). PCA can be used to identify the expected number of components for an end-member mixing model as described below, and assists in selecting solutes that best identify possible end-members.

End-member mixing analysis (EMMA) is a method to determine which non-stream waters of a catchment are contributing to stream flow (Hooper et al., 1990). Originally focused on soil water contributions, it has expanded to include all possible sources and can also be used to determine if an end-member that supplies water to the stream was missed in sampling. The key assumption in EMMA is that stream water is derived from some combination of source waters, or end-members, whose chemical compositions are unvarying in time and space (Hooper et al., 1990). After PCA is used to determine how many and which solutes are used for EMMA, the concentrations of those solutes in the suspected end-members are used to construct a bounding polygon in n-dimensional space, where the number of vertices (representing each endmember) is equal to the number of solutes plus one. EMMA must be adjusted when stream water chemistry points fall outside the bounds of the shape defined by end-member concentrations, typically by projecting the points to the closest n-1-dimensional space (Hooper, 2001), which we adopted for the handful of points that fell outside the best-fit end-member space identified by PCA (Liu et al. 2004; Christophersen & Hooper, 1992).

PCA and EMMA were performed using the "stats" package in the R statistical software (Liu, Williams, & Caine, 2004; Martins, 2013). Isotopes, carbon, and nitrogen were not used for these analyses due to sampling limitations and non-conservative behavior. Analytes where fewer than 50% of samples showed measurable concentrations were also excluded. Non-detects in the included analytes were replaced by half the detection limit, after Farnham, Singh, Stetzenbach, & Johannesson (2002). Wilcoxon tests were used to determine which potential end-members could be grouped, and stream samples taken at the bog were excluded on this basis. EMMA analysis was conducted in scaled-and-centered "solute space", rather than in U-space, for the sake of visualization—U-space models gave nearly identical results. EMMA plots in the results section below are shown in concentration-space for ease of interpretation.

We performed hydrograph separation based on the concentrations of tracers in source and streamwater at each date, using a program which calculates the percent of streamflow for which each end-member was responsible. The fractional contributions of each end-member were then used to calculate a modeled carbon concentration for that stream sample based on end-member DOC concentrations. The modeled DOC was compared to the measured value at each date, using the fractional contribution of each end-member and the carbon concentrations in the end-members on that date, to create a predicted carbon concentration for streamwater and assess the importance of source mixing vs. riparian and in-stream processing of carbon.

#### 2.3.5. Geophysical Characterization

Electrical resistivity (ER) and seismic velocity (SV) data were collected along a 500 m transect from between the upper snowdrifts to the bog (Figure 2.5, line 4) in summer of 2015. Holbrook (personal communication, October 18, 2017) conducted this work with a team using University of Wyoming equipment, interpreted the data, and shared inferred ERT and SV profiles along the closest geophysical transect for the purposes of this thesis.

# 2.4. Results

# 2.4.1. Carbon Sourcing

# 2.4.1.1. Soil Carbon

Soil profiles in the drift, conifer, and bog pits differed substantially in texture and soil carbon content. Carbon and textures in the drift pit were fairly uniform throughout its depth, with a sharp decline in carbon at approximately 80 cm below the soil surface (Figure 2.7, Table 2.2). Several burrows (> 5 cm dia.) were present in the upper 70 cm. The conifer pit shows distinct horizonation in SOM, with the surface litter layer and the A containing much more organic matter than deeper layers. SOM decreases sharply at 10cm below the surface in the conifer pit (Figure 2.7). Finally, the bog pit has a highly organic surface to 32 cm below the soil surface, a thin mineral horizon, and a very distinct transition to saprolite at 50 cm depth. There is almost no organic matter in the saprolite, while the soil horizons are both very high in organic material (Figure 2.7). Redoximorphic features were present in the saprolite layer (Figure 2.8) and the bog soils are not more acidic (pH 5.8) than those in the upland pits (pH 5.2 for drift, 5.8 for conifer).

Sito	Horizon	Field Texture (Whole Soil)	Particle Size Analysis			~	Cond.	% SOM
Site	Horizon	Field Texture (Whole Soll)	% Sand	% Silt	% Clay	рп	(µS/cm)	70 30101
Drift	0-7	Gravelly Loam	39.7	46.6	13.7	5.1	27.2	10.1
	7-24	Very Gravelly Silt Loam	36.3	50.3	13.3	5.2	17.7	9.8
	24-50	Very Gravelly Loam	46.8	44.8	8.4	4.7	16.7	8.3
	50-79	Very Gravelly Silt Loam	42.8	51.3	5.8	5.5	8.1	6.5
	79-125	Extremely Gravelly Sandy Loam	67.9	28.9	3.2	5.5	6.7	2.4
	125-165	Extremely Gravelly Sandy Loam	69.4	27.4	3.2	5.1	13.8	2.1
Conifer	0-6	Fibric (Duff)						42.4
	6-9	Gravelly Loam	41.9	43.6	14.5	6.2	89.2	22.6
	9-29	Gravelly Loam	37.9	48.8	13.3	5.6	33.4	7.2
	29-33	Very Gravelly Loam	39.8	48.5	11.7	5.8	23.4	7
	33-42	Very Gravelly Loam	41.3	48	10.7	5.5	27.4	5.5
	42-55	Very Gravelly Loam	43.8	44.7	11.5	5.7	21.6	4.3
	55-95	Very Cobbly Sandy Loam	50.9	42.3	6.8	5.7	18.4	2.1
	95-110	Extremely Stony Sandy Loam	49.7	44	6.3	6.0	21.7	0.8
Bog	0-32	Hemic Silt Loam	34.1	51.5	14.4	5.7	65.7	50.8
	32-50	Silt Loam	32.7	50.8	16.5	5.7	36.9	33.2
	50-80	Very Channery Loam	48.7	43.1	8.2	6.0	19.2	0.6

Table 2.2: Texture, organic matter, and pH by horizon for soil pits in RME



Figure 2.7: Soil texture (grey stacked bars, left vertical axis) and percent organic matter (black narrow bars, right vertical axis) by horizon: (a) drift pit, (b) conifer pit, and (c) bog pit. Vertical scale of organic matter varies to accommodate observed large differences in organic matter, especially in the bog pit.



Figure 2.8: Saprolite layer in bog pit, showing clear redox features (grey matrix of reduced iron with red-orange mottles of oxidized iron, near scale bar)



Figure 2.9: Organic layer in bog pit. Note abundant roots and large branches

# 2.4.1.2. Dissolved Organic Carbon Concentrations and indices

DOC concentrations are higher at low flows than at high, and shows a similar pattern to DIC and the C:N ratio (Figure 2.10a, Figure 2.11a, b, and c). The slope of the log-log plot of DOC vs. discharge is  $-0.2 \pm 0.03$  (R<sup>2</sup><sub>adj</sub> = 0.63), which is significantly different from zero (p < 0.001 at  $\alpha$  = 0.05). SUVA and FI increase nonlinearly with discharge (Figure 2.10b and c) and exhibit similar scatter throughout the year (Figure 2.11d and e). The best fit model for a log-log plot of SUVA (based on R<sup>2</sup><sub>adj</sub>) is quadratic, R<sup>2</sup><sub>adj</sub>= 0.49:  $log_{10}$  SUVA = 0.997 + 0.108 ×  $log_{10}$  Q –

 $0.065 \times (log_{10}Q + 2.44)^2$ 

For a log-log plot of FI, the best-fit model has 6 parameters,  $R^{2}_{adj} = 0.77$ :  $log_{10} FI = -0.221 - 0.2 \times log_{10} Q - 0.326 \times (log_{10} Q + 2.44)^{2} + 0.36 \times (log_{10} Q + 2.44)^{3} - 0.307 \times (log_{10} Q + 2.44)^{4} - 0.145 \times (log_{10} Q + 2.44)^{5} - 0.094 \times (log_{10} Q + 2.44)^{6}$ 



Figure 2.10: Concentration of dissolved organic carbon, SUVA, and FI versus discharge at the outlet to RME, plotted in log-log space. DOC is highly variable at low flows and exhibits slight dilution at high flows, SUVA increases with Q, and FI remains relatively unchanged. DOC, SUVA, FI, and C:N for all waters in RME are shown in Figure 2.12.



Figure 2.11: Time series of DIC, DOC, C:N ratio, SUVA, FI, and tracers in streamwater samples, with lower panel showing contributions of each end-member to streamflow from March to October, 2017. Spline fits for DIC, DOC, C:N, SUVA, FI:  $\lambda = 0.05$ ; for Rb, Sr, Ba:  $\lambda = 0.0002$ . Samples could not be run for DIC or TN after August due to equipment failure.



End Member

Figure 2.12: Medians, ranges, and IQRs for DIC, DOC, C:N ratio, SUVA, FI, and selected tracers for EMMA for all potential water sources in RME. Note that only one sample was collected from the Springhouse drift. Missing boxplots for lysimeters are due to insufficient sample to run all analyses.

#### 2.4.2. Water

#### 2.4.2.1. Well and soil moisture responses to snowpack

Precipitation events in RME were concentrated in the fall, winter, and early spring (Figure 2.13a), consistent with prior observations of strong seasonality of discharge (Figure 2.13e). During WY2017 snow began accumulating in December 2016 and was entirely melted by mid-June 2017. Timing of melt was determined from ARS snow depth observations and is defined as the timespan from peak to zero snow depth (mid-March to mid-June 2017).

Soil moisture increased briefly with the onset of snowmelt, and decreased quickly following it, except in the bog (Figure 2.13b). This pattern is more pronounced in the conifer pit, and more attenuated in the drift pit. In both of these pits, soil moisture remained higher at depth throughout WY2017. Extraction of soil water at 60 kPa from the conifer pit was impossible by June 6<sup>th</sup>, 2017; the saprolite lysimeter at the drift site was only able to collect very small (less than 20 mL) samples after June 6<sup>th</sup>, and all other lysimeters remained dry throughout the rest of the summer. Piezometers at the conifer and drift sites were never saturated, and the mud present at the bottoms dried out by July 2017.

In contrast, the bog pit was wet throughout the water year. Soil moisture dropped from ~60% to ~45% (volume per volume) in the surface layer between July and October 2017 but remained around 40% at the soil-saprolite interface. We cannot rule out the possibility that the excursion toward zero at the soil/saprolite interface (dashed line in Figure 2.13b) in late winter 2016 may be an artifact because it coincides with the failure of the other probes. The soil moisture sensor in the bog saprolite failed in mid-January 2017, but data from the previous year, which included an extremely dry summer shows little to no change in saprolite water content in the bog (data not shown). The surface soil moisture sensor in the bog also failed in mid-January, but resumed data collection in April, and appeared to work properly. This may be

due to the aforementioned burial and settling affecting the connection of the probe to the logger. Matric potential at the surface dropped quickly at all sites following melt-out, while it remained higher at the soil-saprolite interface at all sites (Figure 2.13c). Piezometers in the bog and spring remained saturated throughout the year.

Wells in RME usually respond to snowmelt nearly as rapidly as soil moisture (Figure 2.13d). Piezometers were not instrumented, but during frequent field visits (at least biweekly), water levels in the Bog piezometer were always approximately at the surface of the stream, while those in the Spring piezometer were above the ground surface from March to June 2017. Discharge at the weir is near-zero for most of the year, increasing at the start of melt (March 2017) and peaking during the fastest melt period (May 2017). Discharge drops precipitously after all snow has melted, and remains near-zero for the remainder of the year (Figure 2.13e). Peak discharge occurs in spring or early summer, when snowdrifts in the catchment melt. Flow declines following melt-out until mid to late summer, and then remains fairly consistent—often nearly dry—until the next spring melt, except for brief events associated with late fall snow melt or rain-on-snow events.



Figure 2.13: Precipitation at RME from October 2016 to October 2017, and its effects on various water reservoirs in the system. (a) Hyetograph on inverse right vertical axis and snow depth on left vertical axis at two sites, the exposed ridge (light gray line) meteorological station (176) and the wind-sheltered snow pillow site (dark gray line, station "rmsp"); (b) Soil moisture in soil pits—solid lines represent the near-surface measurement, dashed lines represent the soil/saprolite interface, and dotted lines represent the saprolite at all three sites; (c) Matric potential in soil pits—solid line is the sensor at the soil/saprolite boundary, dotted line is the 30 cm depth, anomalous readings in the conifer pit at the end of 2016 are attributed to settling after installation; (d) Water table elevation in four monitoring wells in RME; (e) Discharge at the catchment-defining weir. Vertical red lines highlight (i) the early March melt event and (ii) peak snow accumulation and rises in soil moisture and water table elevation associated with these events, and (iii) the end of snowmelt, with succeeding drops in soil moisture and water tables. Smoothers all  $\lambda = 0.05$ , except wells and discharge  $\lambda = 0.00001$ ; y-axis of discharge plot is logarithmic.

# 2.4.2.2. Hydrochemistry and End-Member Mixing Analysis

Principal components analysis showed that three tracers explain 59% of the variation between samples. We selected tracers with the longest, orthogonal eigenvectors to explain as much variance in stream chemistry as possible and to minimize covariance between factors (Barthold et al., 2011). Strontium (Sr), barium (Ba), and rubidium (Rb) were selected as likely tracers based on the PCA, allowing distinction between four possible end-members. The concentrations of these tracers in the stream and potential end-member waters are shown in Figure 2.12, panels f, g, and h.

We plotted median concentrations of the three tracers from all sampled end-members with individual stream samples (Figure 2.14). We identified snowmelt, piezometer (saprolite) water, and groundwater from the Drift and Aspen wells as the end members that best explained observed variations in stream water chemistry (see Figure 2.4 for well locations). Based on the EMMA results, we calculated proportional contributions of each end-member to stream flow at each sampling date. Our results suggest that snowmelt contributions dominate until mid-June when both groundwater and saprolite contributions become dominant (Figure 2.15). This proportional mixing model was used to generate the carbon concentration model shown in Figure 2.17.



Figure 2.14: End-member mixing analysis shown in: a) the 3D concentration space, b) the Ba-Sr plane of concentration space, c) the Rb-Sr plane of concentration space. Error bars on end-member median concentrations represent the interquartile range (IQR) of concentration distributions for each end-member, and are not shown if smaller than markers. Points that fall outside the represented figure (as in [c]) are still within the concentration range of each end-member (maximum Rb concentrations for PZs and Drift W, 10.3 and 13.8 ppb, respectively). To solve for the fractional contribution, those points are projected onto the closest plane and values are assumed to be a fractional mix of the 3 end-members comprising that plane (adaptation of the 2D method applied by Liu et al. 2004). The circled points are discussed further in the Discussion section on EMMA.



Figure 2.15: Percent contribution of each end-member to stream flow during 2017. From top to bottom: Aspen well (black), Drift well (light gray), Saprolite flow (dark gray), Snowmelt (dotted white).

# 2.4.2.3. Isotopic Signatures and Melt Patterns

The slope of the regression line for the local meteoric water line (LMWL) is  $6.9 \pm 0.5$  SE, and the intercept is  $-10.1 \pm 7.0$  SE (R<sup>2</sup>= 0.98), within the range of values expected in the Continental United States (Kendall & Coplen, 2001). The isotopic regression line for stream water samples in RME has a slope of  $6.0 \pm 0.5$  SE (Figure 2.16b), which does not differ significantly from the slope of the LMWL (p = 0.22). Stream water isotopes become heavier as the summer progresses, indicative of evaporation (Kendall & Coplen, 2001). Water collected from the suction lysimeters in the soil has a slight evaporative signal, with a regression slope of  $6.5 \pm 0.5$  SE (Figure 2.16c) that also does not differ from the slope of the LMWL (p = 0.53) or the stream (p = 0.54). Water drawn from the piezometers in saprolite, on the other hand, is highly evaporated, with a slope of  $3.1 \pm 0.9$  SE, which is significantly different from the LMWL, streamwater, and soil water (p = 0.0048, 0.001, and 0.0069, respectively) (Figure 2.16d).
Isotopic signatures of water in the wells at RME are heavier during the early melt stages in May and become lighter and closer to the local meteoric water line (LMWL) as the snowpack disappears in July (Figure 2.16e). The regression slope of all well samples is  $4.8 \pm 0.8$  SE, which does not significantly differ from the piezometer (p = 0.18) or lysimeter (p = 0.10) regression line slopes, but differs from the LMWL and stream water slopes (p = 0.047, 0.037, respectively).



Figure 2.16: Water isotopes for all waters in RME, by source, a) Precipitation, b) Stream, c) Soil water, d) Saprolite water, e) Groundwater. Points represent samples; colors progress from blue to red as the sample dates shift from March to July, 2017.

#### 2.4.2.4. Modeling carbon export in streamwater

We compared measured stream DOC to the DOC concentration predicted by the concentrations of carbon in source waters identified by EMMA and a resulting proportional mixing model (Section 2.4.2.2, above), and found the model significantly under-predicted carbon concentrations, especially during melt (Figure 2.17).



Figure 2.17: Modeled and measured DOC concentrations for Reynolds Creek streamwater, based on outcomes of the proportional-mixing model. Thick error bars are for modelled concentrations, where visible; thin error bars are 10% analytical error of carbon measurements (this error is conservative, actual error may be less)

# 2.4.3. Geophysics: Electrical Resistivity and Seismic Velocity Data

Electrical resistivity along Transect 4 decreased from log values of 4 ohm-m at the surface to values near 0 ohm-m at depths of 5 to >50 m below the surface (shown by the transition from red to blue in Figure 2.18). Seismic velocity increased with depth from surface values of 0 m/s to deep values of over 5000 m/s (white contour lines in Figure 2.18). The velocity in low-resistivity areas is lower than would be expected for solid igneous rock (O'Connell & Budiansky, 1974).



Figure 2.18: ER and SV in the top 125 m of Transect 4 at RME. Colors represent electrical resistivity, while contours (white) indicate seismic velocity in m/s. Areas of low resistivity (blue) are inferred to be aquifers, and the 2000 m/s contour is interpreted as the base of the saprolite layer.

# 2.5. Discussion

### 2.5.1. What are the patterns of dissolved organic carbon concentrations in

#### stream and source waters?

While soil organic carbon is, as expected, the primary carbon source in RME

streamwater, the patterns it exhibits are far from what we thought to see.

### 2.5.1.1. Dissolved organic carbon in the stream

In contrast to our expectation that DOC would show concentration behavior with

increasing discharge (Sanderman et al., 2009), a dilution pattern was observed where increasing discharge led to lower DOC concentrations. Discharge in RME peaks with peak snowmelt, then declines until mid to late summer. DOC concentrations, in contrast, are highest during late summer and lowest during the melt period. This is inconsistent with the flushing hypothesis, where DOC-rich riparian zones become saturated and flush DOC into streams during snowmelt

(Boyer et al., 1997; Sanderman et al., 2009). Rather DOC appears to concentrate in soil water during dry periods and be flushed vertically by piston-flow mechanism to the saprolite/bedrock interface during snowmelt. From there it moves laterally to the stream, which accounts for the observed dilution pattern, as surface snowmelt is contributing significantly to streamflow during this period.

Weak DOC dilution at high flows is also inconsistent with emergent chemostatic behavior for DOC, and may be explained by the factors invoked in Creed et al. (2015)—at the event scale, they invoke stability in flowpaths to explain chemostasis; we surmise flowpaths in RME are not stable at the event scale, and so create non-chemostatic conditions. We suggest that saprolite/bedrock interface flow is temporally variable (as shown by changes in Rb concentration with time, this data not shown), and soil water flushed to this interface during melt mixes nonconservatively with other soil waters.

Higher discharges are associated with higher SUVA, indicating that snowmelt carries "fresher", less-decomposed carbon into the stream. Both higher discharges and higher SUVA are correlated with higher FI in 2014-2016 (Figure 2.11), suggesting that this fresh carbon is terrestrially derived (McKnight et al., 2001). SUVA, FI, and discharge decrease together as the summer progresses. This suggests one of several possibilities: 1) delivery of highly decomposed organic carbon from deep soil horizons (Neff et al., 2006), accounting for lower SUVA but not lower FI; 2) bog and near-bog saturated soils as the major source of DOC and water in late summer as in Sanderman et al. (2009), explaining lower FI but perhaps not lower SUVA; or 3) algae in the channel as the primary DOC source during low-flow, explaining both low SUVA and low FI, but not DOC dynamics during winter low-flow. With better characterization of DOC during low-flow conditions, we could be more certain of the situation. However, given the high

concentrations of carbon in saprolite and groundwater (Figure 2.12), it seems likely that the majority of DOC in RME is derived from decomposed soil organic matter of terrestrial origin.

Regardless of the DOC source, we can be confident that there is little to no leaching of SOM from surface soil horizons during the summer months. The lack of precipitation (Figure 2.13a) and hydrologic connectivity, as shown by extremely low soil moisture during the summer months (Figure 2.13b, and modeled in Grant et al., 2004), mean that there is no mechanism for leaching these horizons until snowmelt.

#### 2.5.1.2. Carbon Mixing

Comparing modeled DOC concentrations based on EMMA partitioning to measured DOC values for streamwater on the same dates shows a consistent model under prediction of carbon content (Figure 2.17). This could suggest a significant in-stream production component of carbon concentration, extensive subsurface processing, or an incomplete hydrological model. Given that the PCA used to generate the EMMA accounted for only 59% of total variance in streamwater chemistry, we cannot exclude modeling error.

# 2.5.1.3. Summary

Carbon exported by Reynolds Creek flowing from RME is derived ultimately from SOC, but the dilution behavior displayed by DOC with increasing discharge suggests some form of source or rate limitation for carbon export during the melt period.

# 2.5.2. What paths does meltwater from seasonal drifts follow on its way to the stream?

Stream water in RME shows little evidence of lateral soil connectivity, which we did not expect, given the importance of this mechanism in other studies. Instead we found significant groundwater contributions via unexpected flowpaths.

# 2.5.2.1. End-member mixing analysis and hydrogeochemistry

We expected a significant groundwater contribution to flow in Reynolds Creek, given the perennial nature of the stream in an area with little to no summer precipitation. This expectation was supported by an end-member mixing analysis that found up to 50% of streamflow on an annual basis deriving from various groundwater flowpaths (Figure 2.15). Previous work in the catchment had suggested an absence of overland flow and localized soil saturation only in the riparian corridor (Grant et al., 2004); our findings support a lack of saturated soil connectivity, but suggest that overland flow, even if quickly routed into ephemeral channels, is a significant component of streamflow during the melt period.

Of the end-members (groundwater from two wells, saprolite water, snowmelt), groundwater has the highest concentrations of strontium and rubidium, consistent with a bedrock aquifer potentially located in rhyolite or andesite. From inferred flowpaths based on surface topography, water in the Drift well would have a short travel time from the East snowdrift directly uphill (Figure 2.2, No. 1), while water in the Aspen well could also potentially consist of water from the East drift and another drift located between the two wells (Figure 2.2, Nos. 1 and 3, respectively). If the Aspen well were fed by the East drift, that water would have to travel a longer distance, and all else equal, would be expected to have a longer travel time. During the snowmelt period of 2017, the soils surrounding the Aspen well were saturated, and formed and ephemeral wetland feeding an intermittent channel into Reynolds Creek. The wetland dried as the summer progressed and the water table dropped, and the initiation of surface flow in the channel moved farther downstream.

Saprolite likely formed from weathered rhyolite and andesite (McIntyre, 1972), and is generally high in clay (Figure 2.7). This would explain the similar concentrations of rubidium and barium in saprolite waters and groundwater. Strontium is much lower in saprolite water than

in groundwater; this may be related to a reduced tendency for Sr release from feldspars in colder, acidic soils compared to Rb and Ba (Salminen et al., 2005).

The presence of barium in snowmelt, our third end-member, suggests there is some atmospheric deposition of this element in RME, but we lack data to test this theory (the NADP does not test for barium at ID11, the closest National Trends Network site). Snow is almost entirely lacking in strontium or rubidium, indicating little interaction with the igneous bedrock of the catchment. Snow is only slightly more dilute than soil water samples from the drift and conifer pits, suggesting that soil water moves quickly through the soil to the saprolite during the wetter portions of the year (Grant et al., 2004). This is consistent with both the "flushing" and "fill and spill" hypotheses (Boyer et al., 1997; Tromp-Van Meerveld & McDonnell, 2006).

Barium is the 14<sup>th</sup> most common element in crustal rocks; it concentrates in felsic magmas and can substitute for Ca in feldspars (Salminen et al., 2005). Strontium and rubidium are both associated with hydrothermal alteration of felsic rocks, and can substitute for potassium in feldspars, micas, and clays (Salminen et al., 2005). Given the tendency of all the tracers used for our EMMA to concentrate in felsic rocks, it is reasonable to assume the majority of streamwater in RME is interacting with the soil and with the surface bedrock layers, rhyolite and andesite (McIntyre, 1972). The presence of hydrothermal alteration in RME is attested to by the occurrence of hydrothermally emplaced mineral deposits in the nearby DeLamar mine (Halsor, Bornhorst, Beebe, Richardson, & Strowd, 1988), and by opal observed during field work in a gully draining into the stream.

The snowmelt signal dominates during the melt period, making up as much as 90% of streamflow. Snow remains high in the variable-contribution mixing analysis (Figure 2.15) through the summer period, during a time of little to no rainfall. This snowmelt signal may

derive from the Springhouse drift outside the watershed; October samples from a stream fed directly from this drift have Ba, Sr, and Rb concentrations very similar to snow. It is possible that soils and rocks along the flowpath from this drift have been so thoroughly leached by several meters of annual precipitation that they now contribute few dissolved ions: perhaps the clays are already deeply weathered and the more soluble elements have long ago been flushed downstream.

An alternate explanation for this improbable snowmelt signal lies with the Cabin well. This well is deeper (30 m) than other wells in the catchment and may intersect flowpaths coming from the Springhouse drift. The Cabin well plots in the center of the stream samples in our EMMA. The concentrations of tracers in the Cabin well samples are not variable enough to explain all the variation in stream water chemistry (Figure 2.12f, g, and h), but the median concentration is not different enough to identify the Cabin well as an end-member. It is possible that the majority of late-season streamflow is derived from this source, but that it cannot be distinguished by the EMMA we used.

Samples taken on May 8<sup>th</sup>-11<sup>th</sup> and June 19<sup>th</sup> are anomalously high in strontium, falling outside the mixing polygon (Figure 2.14c). However, they fall within the range of Sr in saprolite water; and piezometer samples on those same dates are also higher than usual in Sr. We posit that on those dates, saprolite water is arriving at the stream by a different (unknown) flowpath, one which is higher in Sr. There is no clear correlation to melt or rainfall events.

#### 2.5.2.2. Isotopic evidence

In order to explain the preponderance of soil carbon in the saprolite and groundwater, we turn to water isotopes to explain the movement of water from soil to the saprolite and bedrock. Water isotopes (deuterium and oxygen-18) are commonly used in hydrology as indicators of evapoconcentration (Kendall & Coplen, 2001). Lighter isotopes evaporate more readily, and so

water that has been subject to evaporation will show a larger proportion of the heavier isotopes. Transpiration does not have this effect (Hsieh, Chadwick, Kelly, & Savin, 1998).

Water isotopes in the stream show the expected evaporative signal, with a slope of 5.9 which differs significantly from both the global meteoric water line (slope of 8) and the local meteoric water line (slope of 7). The slope of the local meteoric water line could be due to evaporation of rainfall in the atmosphere under extremely low-humidity summer conditions (B. Finney, personal communication, October 30, 2017). The slope of the stream is within the range of slopes expected for surface waters in North America (Kendall & Coplen, 2001)

Soil water within the capillary fringe is also subject to evapoconcentration, and should show an increase in heavy isotopes (Allison, 1998). This is not the case in RME, suggesting that water sampled by lysimeters was not evaporated. However, the isotopic signature of saprolite water is highly evaporative, which may indicate that it derived from soil water that remained in small soil pores through the prior summer and was flushed to the saprolite by spring melt. This would explain both the larger evaporative signal and the higher concentrations of Sr, Ba, and Rb in saprolite waters than in sampled soil waters.) The offset of the stream samples from the local meteoric water line suggests that the source of streamwater has already fractionated, which is consistent with saprolite water providing a major portion of streamflow (Kendall & Coplen, 2001; Sklash & Farvolden, 1979).

Isotopes in groundwater became lighter over the course of snowmelt (Figure 2.16e). This could also be indicative of the presence of last summer's soil water in the aquifer, or it could reflect isotopic fractionation in the snowpack (Taylor et al., 2001). In the latter case, snowpacks become lighter as melt progresses, and groundwater also becomes lighter from the beginning to the end of melt, as the lighter isotopes eventually enter the aquifer. In either case, this suggests a

rapid response of the water table to melt. If, in fact, it also reflects evapoconcentrated soil water in the aquifer, this is further evidence for the displacement of old soil water by fresh meltwater.

#### 2.5.2.3. Integrating Hydrological and Geophysical Data

From our EMMA and geophysics data (Figure 2.18), we developed conceptual models for flowpaths and water table dynamics in RME. In the geophysics data, resistive areas are interpreted as dry, unconsolidated sediment (e.g., soil), while less-resistive areas are interpreted as wet areas rather than consolidated bedrock. The 2000 m/s line is interpreted as the approximate lower boundary of the saprolite based on the seismic velocity, while ERT data suggests an aquifer (low resistivity zone) at approximately 20 m depth (S. Holbrook, personal communication, Oct. 18, 2017). While the low-resistivity zones appear disconnected in this transect, we believe they are in fact the same aquifer, with areas of connection outside the plane of the ERT transect. It is unclear if there is a deeper aquifer in the watershed. There is sufficient ambiguity in the ERT data that this aquifer may be intersected by all or none of the 15 m deep wells or the 30 m deep Cabin well. This data does not allow us to definitively conclude that the Cabin well draws on a separate aquifer from the other wells in the watershed.

Three subsurface flowpaths that could occur in RME: shallow soil, saprolite/bedrock interface, and bedrock aquifer (Figure 2.19). Our EMMA suggests that of these three possible flowpaths, only the saprolite/bedrock interface flow and flow through the aquifer contribute significantly to streamflow. Overland flow is not observed in this catchment. When the catchment is dry (late summer through winter), the water table is below the soil profile, and soil water on the hillslope is disconnected from the stream (Figure 2.20, top). During the melt period, the water table rises, wetting the soil, as soil water from the previous summer is flushed into the deeper saturated zone, whence it flows to the stream and snowmelt (Figure 2.20, bottom).

# 2.5.2.4. Summary

Streamflow in RME is primarily derived from snowmelt and groundwater, with the groundwater flowpaths being divided between shallow saprolite flow and flow through a deeper fractured-bedrock aquifer system. Groundwater is derived from soil water displaced by snowmelt by piston-type flow, where melting snow drives antecedent soil water down through the profile into the saprolite and bedrock aquifers. This is shown by the soil carbon-like carbon signatures of saprolite and groundwater, and the distinct geochemical fingerprints of water from these aquifers.



Figure 2.19: Conceptual model of hypothesized flowpaths in RME (blue arrows). From top to bottom, the blue arrows represent shallow soil flow, saprolite/bedrock interface flow, and bedrock aquifer flow. Aquifer locations inferred from geophysics data (Figure 2.18). Only saprolite/bedrock interface flow and bedrock aquifer flows contribute significantly to streamflow in RME.



Figure 2.20: Water table elevation in late summer compared to during snowmelt. Summer water tables (top) are lower, leaving soil water stranded in the unsaturated zone and unable to reach the stream. With the onset of melt, the water table rises (bottom) and soil water is flushed to the stream. Groundwater in aquifer may be from adjacent catchment.

# 2.5.3. Is soil water a major component of the hydrograph, or is carbon being transported along another subsurface flowpath?

At the beginning of this study, we expected to see SOC become DOC through lateral connectivity of soils and streams. This was not at all what we found. Soil water is not a significant end-member contributor to streamflow, but soil is the major reservoir and source of DOC—thus, DOC must be carried to the stream by saprolite water or groundwater. DOC is higher in the Aspen and Drift wells than in the stream, and very similar in the Bog piezometer, though the Spring piezometer has much lower DOC concentrations (Figure 2.12). Saprolite water DOC quality was the most similar to stream water of the potential sources, suggesting that saprolite water is the major source of DOC to Reynolds Creek (Figure 2.12). Thus, we conclude that while SOC is the primary carbon source for stream DOC in this system, the flowpaths are not controlled by lateral soil connectivity to the riparian zone, but rather by infiltration to the saprolite layer underlying the soil.

#### **2.6.** Conclusions

In this study, we used indices of DOC composition, performed end-member mixing analysis using more-conservative tracers, and combined the results to determine the sources of both stream water and DOC in a snowdrift-dominated headwater catchment. This has led us to conclude that soil water is not a major source of streamflow in this catchment, although soil organic carbon is the primary carbon source. The explanation for this apparent inconsistency in sources requires a fuller understanding of the hydrological processes at work in the study catchment.

In Reynolds Mountain East (RME), more than 70% of precipitation falls as snow, and is stored in the form of wind-created snowdrifts (Nayak et al., 2010; Reba et al., 2011). These drifts are the ultimate source of stream flow in RME, but the different paths that water takes to the

stream determine stream water chemistry and DOC content. SOC leached to the groundwater throughout the catchment reaches the stream through deep flowpaths as well as flowpaths that follow the soil-bedrock interface. DOC concentration varies little in time, but sources are increasingly affected by microbial processing as the summer progresses.

The use of DOC quality or quantity to determine end-members in RME would not give the same results as the use of cations in an EMMA, as can be seen from the attempt to create a carbon model using the fractional contributions of end-members to streamflow (Figure 2.17). Based on quantity alone, one would expect a larger contribution from the Aspen well than is indicated by the Ba/Sr/Rb EMMA. Alternatively, the use of SUVA would yield a larger proportion of piezometer water. In the EMMA, the contributions of both groundwater sources are much smaller than those of snowmelt. This may suggest that SOC is more soluble than the tracers used during the snowmelt period, and so the groundwaters export more DOC than might be expected based on the EMMA alone. It may also indicate unsampled preferential flowpaths high in SOC that route meltwaters to the stream, perhaps along root channels. Snowdriftdominated, dryland headwater catchments may largely bypass near-surface flowpaths, but still export large DOC fluxes if SOC can be readily flushed during the melt period.

#### 2.7. Works Cited

- Allison, G. B. (1998). Stable isotopes in soil and water studies. *Colloques et Séminaires Institut Français de Recherche Scientifique Pour Le Développement En Coopération*, 23–38. Retrieved from http://cat.inist.fr/?aModele=afficheN&cpsidt=2279868
- Barnett, T. P., & Adam, J. C. (2005). Potential impacts of a warming climate on water availability in snow-dominated regions. *Nature*, 438(7066), 303–309. https://doi.org/10.1038/nature04141
- Barthold, F. K., Tyralla, C., Schneider, K., Vaché, K. B., Frede, H. G., & Breuer, L. (2011). How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis. *Water Resources Research*, *47*(8), 1–14. https://doi.org/10.1029/2011WR010604
- Beniston, M. (2003). Climatic change in mountain regions: A review of possible impacts. *Climate Change*, *59*, 5–31.
- Boyer, E. W., Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1997). Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes*, 11, 1635– 1647. https://doi.org/10.1002/(SICI)1099-1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H
- Christophersen, N., & Hooper, R. P. (1992). Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem. *Water Resources Research*, 28(1), 99–107. https://doi.org/10.1029/91WR02518
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., ... Melack, J. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10, 172–185. https://doi.org/10.1007/s10021-006-9013-8
- Cory, R. M., & McKnight, D. M. (2005). Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environmental Science & Technology*, 39, 8142–8149. https://doi.org/10.1021/es0506962
- Cox, P. M., Betts, R. A., Jones, C. D., Spall, S. A., & Totterdell, I. J. (2000). Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature*, 408(6809), 184–187. https://doi.org/10.1038/35041539
- Creed, I. F., McKnight, D. M., Pellerin, B. A., Green, M. B., Bergamaschi, B. A., Aiken, G. R., ... Stackpoole, S. M. (2015). The river as a chemostat: Fresh perspectives on dissolved organic matter flowing down the river continuum. *Canadian Journal of Fisheries and Aquatic Sciences*, 72, 1272–1285. https://doi.org/10.1139/cjfas-2014-0400
- Crimmins, S. M., Dobrowski, S. Z., Greenberg, J. A., Abatzoglou, J. T., & Mynsberge, A. R. (2011). Changes in climatic water balance drive downhill shifts in plant species' optimum elevations. *Science*, *331*(6015), 324–327. https://doi.org/10.1126/science.1199040

- Dansgaard, W. (1964). Stable isotopes in precipitation. *Tellus*, *16*, 436–468. https://doi.org/10.3402/tellusa.v16i4.8993
- Davis, J. C. (1973). Statistics and Data Analysis in Geology. New York: Wiley.
- Dingman, S. L. (2015). Physical Hydrology (3rd ed.). Long Grove, IL: Waveland Press.
- Doran, J. W. (2002). Soil health and global sustainability: Translating science into practice. *Agriculture, Ecosystems and Environment*, 88(2), 119–127. https://doi.org/10.1016/S0167-8809(01)00246-8
- Ekren, E. B., McIntyre, D. H., Bennet, E. H., & Malde, H. E. (1981). Geologic map of Owyhee County, Idaho, west of longitude 116° W [map]. 1:125,000. Miscellaneous investigations series, map I-1256. Denver, CO: U.S. Geological Survey.
- Eswaran, H., Berg, E., Reich, P., Van Den Berg, E., & Reich, P. (1993). Organic carbon in soils of the world. *Soil Science Society of America Journal*, *57*, 192–194. https://doi.org/10.2136/sssaj1993.03615995005700010034x
- Farnham, I. M., Singh, A. K., Stetzenbach, K. J., & Johannesson, K. H. (2002). Treatment of nondetects in multivariate analysis of groundwater geochemistry data. *Chemometrics and Intelligent Laboratory Systems*, 60, 265–281. https://doi.org/10.1016/S0169-7439(01)00201-5
- Fleckenstein, J. H., Niswonger, R. G., & Fogg, G. E. (2006). River-aquifer interactions, geologic heterogeneity, and low-flow management. *Ground Water*, 44, 837–852. https://doi.org/10.1111/j.1745-6584.2006.00190.x
- Grant, L. E., Seyfried, M. S., & McNamara, J. P. (2004). Spatial variation and temporal stability of soil water in a snow-dominated, mountain catchment. *Hydrological Processes*, *18*, 3493–3511. https://doi.org/10.1002/hyp.5798
- Grünewald, T., Schirmer, M., Mott, R., & Lehning, M. (2010). Spatial and temporal variability of snow depth and SWE in a small mountain catchment. *The Cryosphere Discussions*, *4*, 1–30. https://doi.org/10.5194/tcd-4-1-2010
- Halsor, S. P., Bornhorst, T. J., Beebe, M., Richardson, K., & Strowd, W. (1988). Geology of the DeLamar silver mine, Idaho - a volcanic dome complex and genetically associated hydrothermal system. *Economic Geology*, 83, 1159–1169. https://doi.org/10.2113/gsecongeo.83.6.1159
- Hooper, R. P. (2001). Applying the scientific method to small catchment studies: a review of the Panola Mountain experience. *Hydrological Processes*, 15, 2039–2050. https://doi.org/10.1002/hyp.255

Hooper, R. P., Christophersen, N., Peters, N. E., Neal, C., Hooper, R. P., Vogt, R. D., ... Peters,

N. E. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members - An application to the Panola Mountain catchment, Georgia, U.S.A. *Journal of Hydrology*, *116*, 321–343. https://doi.org/10.1016/0022-1694(90)90131-G

- Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1994). Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry*, 25(3), 147–165. https://doi.org/10.1007/BF00024390
- Hsieh, J. C. C., Chadwick, O. A., Kelly, E. F., & Savin, S. M. (1998). Oxygen isotopic composition of soil water: Quantifying evaporation and transpiration. *Geoderma*, 82, 269– 293. https://doi.org/10.1016/S0016-7061(97)00105-5
- Intergovernmental Panel on Climate Change. (2014). *Climate Change 2013 The Physical Science Basis*. (Intergovernmental Panel on Climate Change, Ed.). Cambridge: Cambridge University Press. https://doi.org/10.1017/CBO9781107415324
- Jones, C. D., McConnell, C., Coleman, K., Cox, P. M., Falloon, P., Jenkinson, D., & Powlson, D. (2005). Global climate change and soil carbon stocks; predictions from two contrasting models for the turnover of organic carbon in soil. *Global Change Biology*, 11, 154–166. https://doi.org/10.1111/j.1365-2486.2004.00885.x
- Kendall, C., & Coplen, T. B. (2001). Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrological Processes*, 15, 1363–1393. https://doi.org/10.1002/hyp.217
- Klos, P. Z., Link, T. E., & Abatzoglou, J. T. (2014). Extent of the rain-snow transition zone in the western U.S. under historic and projected climate. *Geophysical Research Letters*, 41, 4560–4568. https://doi.org/10.1002/2014GL060500
- Li, L., Bao, C., Sullivan, P. L., Brantley, S. L., Shi, Y., & Duffy, C. J. (2017). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. *Water Resources Research*, 53(3), 2346–2367. https://doi.org/10.1002/2016WR018935
- Liu, F., Williams, M. W., & Caine, N. (2004). Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. *Water Resources Research*, 40(9), 1–16. https://doi.org/10.1029/2004WR003076
- Lohse, K. A., Brooks, P. D., McIntosh, J. C., Meixner, T., & Huxman, T. E. (2009). Interactions between biogeochemistry and hydrologic systems. *Annual Review of Environment and Resources*, 34, 65–96. https://doi.org/10.1146/annurev.environ.33.031207.111141
- Lohse, K. A., Sanderman, J., & Amundson, R. (2013). Identifying sources and processes influencing nitrogen export to a small stream using dual isotopes of nitrate. *Water*

Resources Research, 49(9), 5715–5731. https://doi.org/10.1002/wrcr.20439

- Lohse, K. A., Seyfried, M. S., McCorkle, E. P., & Patton, N. R. (2014). Soil Texture Protocol. Retrieved from http://info.reynoldscreekczo.org/dokuwiki/doku.php?id=protocols
- Marks, D., Winstral, A., Reba, M., Pomeroy, J., & Kumar, M. (2013). An evaluation of methods for determining during-storm precipitation phase and the rain/snow transition elevation at the surface in a mountain basin. *Advances in Water Resources*, 55, 98–110. https://doi.org/10.1016/j.advwatres.2012.11.012
- Martins, T. G. (2013). Computing and visualizing PCA in R. Retrieved from http://tgmstat.wordpress.com/2013/11/28/computing-and-visualizing-pca-in-r/
- McIntyre, D. H. (1972). Cenozoic geology of the Reynolds Creek Experimental Watershed, Owyhee County, Idaho. *Pamphlet 151*. Moscow, ID.
- McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., & Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46, 38–48. https://doi.org/10.4319/lo.2001.46.1.0038
- McNamara, J. P., Chandler, D. G., Seyfried, M. S., & Achet, S. (2005). Soil moisture states, lateral flow, and streamflow generation in a semi-arid, snowmelt-driven catchment. *Hydrological Processes*, *19*, 4023–4038. https://doi.org/10.1002/hyp.5869
- Miller, R. E., & Blair, P. D. (2009). *Input-Output Analysis: Foundations and Extensions* (2nd ed.). Cambridge, England: Press, Cambridge University.
- Nayak, A., Marks, D., Chandler, D. G., & Seyfried, M. S. (2010). Long-term snow, climate, and streamflow trends at the reynolds creek experimental watershed, Owyhee Mountains, Idaho, United States. *Water Resources Research*, *46*(6). https://doi.org/10.1029/2008WR007525
- Neff, J. C., Finlay, J. C., Zimov, S. A., Davydov, S. P., Carrasco, J. J., Schuur, E. A. G., & Davydova, A. I. (2006). Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams. *Geophysical Research Letters*, 33. https://doi.org/10.1029/2006GL028222
- O'Connell, R. J., & Budiansky, B. (1974). Seismic velocities in dry and saturated cracked solids. *Journal of Geophysical Research*, 79, 5412–5426. https://doi.org/10.1029/JB079i035p05412
- Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environmental Science & Technology*, *36*, 742–746. https://doi.org/10.1021/es0155276
- Patton, N. R. (2016). Topographic Controls on Total Mobile Regolith and Total Soil Organic

Carbon in Complex Terrain (master's thesis). Idaho State University.

- Pomeroy, J. W., Gray, D. M., Brown, T., Hedstrom, N., Quinton, W. L., Granger, R. J., & Carey, S. K. (2007). The cold regions hydrological model: a platform for basing process representation and model structure on physical evidence. *Hydrological Processes*, 21, 2650–2667. https://doi.org/10.1002/hyp.6787
- Reba, M. L., Marks, D., Seyfried, M. S., Winstral, A., Kumar, M., & Flerchinger, G. (2011). A long-term data set for hydrologic modeling in a snow-dominated mountain catchment. *Water Resources Research*, 47(7), 1–7. https://doi.org/10.1029/2010WR010030
- Salminen, R., Batista, M. J., Bidovec, M. D., Demetriades, A., De Vivo, B., De Vos, W., ... Tarvainen, T. (2005). FOREGS Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps. Retrieved from http://weppi.gtk.fi/publ/foregsatlas/
- Sanderman, J., Lohse, K. A., Baldock, J. A., & Amundson, R. (2009). Linking soils and streams: Sources and chemistry of dissolved organic matter in a small coastal watershed. *Water Resources Research*, 45(3), W03418. https://doi.org/10.1029/2008WR006977
- Seyfried, M. S., Grant, L. E., Marks, D., Winstral, A., & McNamara, J. P. (2009). Simulated soil water storage effects on streamflow generation in a mountainous snowmelt environment, Idaho, USA. *Hydrological Processes*, 23, 858–873. https://doi.org/10.1002/hyp.7211
- Seyfried, M. S., Harris, R., Marks, D., & Jacob, B. (2001). Geographic database, Reynolds Creek Experimental Watershed, Idaho, United States. *Water Resources Research*, 37(11), 2825– 2829. https://doi.org/10.1029/2001WR000414
- Shrestha, R. (2016). 2009 1m Snow Depth for Reynolds Mountain East, Reynolds Creek Experimental Watershed, Idaho [Data set]. http://doi.org/10.18122/B28597
- Sklash, M. G., & Farvolden, R. N. (1979). The role of groundwater in storm runoff. *Journal of Hydrology*, 43, 45–65. https://doi.org/10.1016/0022-1694(79)90164-1
- Soulsby, C., Tetzlaff, D., Rodgers, P., Dunn, S. M., & Waldron, S. (2006). Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: An initial evaluation. *Journal of Hydrology*, 325, 197–221. https://doi.org/10.1016/j.jhydrol.2005.10.024
- St. Clair, J., Moon, S., Holbrook, W. S., Perron, J. T., Riebe, C. S., Martel, S. J., ... Richter, D. deB. (2015). Geophysical imaging reveals topographic stress control of bedrock weathering. *Science*, 350(6260), 534–538. https://doi.org/10.1126/science.aab2210
- Stieglitz, M., Shaman, J., McNamara, J. P., Engel, V., Shanley, J. B., & Kling, G. W. (2003). An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. *Global Biogeochemical Cycles*, 17(4), 1–15. https://doi.org/10.1029/2003GB002041

- Stielstra, C. M., Lohse, K. A., Chorover, J., McIntosh, J. C., Barron-Gafford, G. A., Perdrial, J. N., ... Brooks, P. D. (2015). Climatic and landscape influences on soil moisture are primary determinants of soil carbon fluxes in seasonally snow-covered forest ecosystems. *Biogeochemistry*, 123(3), 447–465. https://doi.org/10.1007/s10533-015-0078-3
- Sturm, M., & Wagner, A. M. (2010). Using repeated patterns in snow distribution modeling: An Arctic example. *Water Resources Research*, 46(12), 1–15. https://doi.org/10.1029/2010WR009434
- Taylor, S., Feng, X., Kirchner, J. W., Osterhuber, R., Klaue, B., & Renshaw, C. E. (2001). Isotopic evolution of a seasonal snowpack and its melt. *Water Resources Research*, 37(3), 759–769. https://doi.org/10.1029/2000WR900341
- Tennant, C. J., Harpold, A. A., Lohse, K. A., Godsey, S. E., Crosby, B. T., Larsen, L. G., ... Glenn, N. F. (2017). Regional sensitivities of seasonal snowpack to elevation, aspect, and vegetation cover in western North America. *Water Resources Research*, 53(8), 6908–6926. https://doi.org/10.1002/2016WR019374
- Tetzlaff, D., Malcolm, I. A., & Soulsby, C. (2007). Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments. *Journal of Hydrology*, 346, 93–111. https://doi.org/10.1016/j.jhydrol.2007.08.016
- Tromp-Van Meerveld, H. J., & McDonnell, J. J. (2006). Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. *Water Resources Research*, 42(2), 1–11. https://doi.org/10.1029/2004WR003800
- USDA ARS Northwest Watershed Research Center. (2017). [Reynolds Creek 166 hourly streamflow]. Unpublished raw data.
- USDA ARS Northwest Watershed Research Center. (2017). [Reynolds Mountain East meteorological data.] Unpublished raw data.
- Viviroli, D., Dürr, H. H., Messerli, B., Meybeck, M., & Weingartner, R. (2007). Mountains of the world, water towers for humanity: Typology, mapping, and global significance. *Water Resources Research*, 43(7), 1–13. https://doi.org/10.1029/2006WR005653
- Williams, M. W., Losleben, M. V, & Hamann, H. B. (2002). Alpine areas in the Colorado Front Range as monitors of climate change and ecosystem response. *Geographical Review*, 92, 180–191. https://doi.org/10.1111/j.1931-0846.2002.tb00003.x
- Winstral, A., & Marks, D. (2002). Simulating wind fields and snow redistribution using terrainbased parameters to model snow accumulation and melt over a semi-arid mountain catchment. *Hydrological Processes*, *16*, 3585–3603. https://doi.org/10.1002/hyp.1238
- Winstral, A., & Marks, D. (2014). Long-term snow distribution observations in a mountain catchment: Assessing variability, time stability, and the representativeness of an index site. *Water Resources Research*, *50*(1), 293–305. https://doi.org/10.1002/2012WR013038

Zogg, G. P., Zak, D. R., Ringelberg, D. B., White, D. C., MacDonald, N. W., & Pregitzer, K. S. (1997). Compositional and Functional Shifts in Microbial Communities Due to Soil Warming. Soil Science Society of America Journal, 61, 475. https://doi.org/10.2136/sssaj1997.03615995006100020015x

#### **Chapter 3:** Conclusions

#### 3.1. Summary

While many studies have focused on the importance of snow in mountainous headwater catchments, or carbon dynamics with regards to hydrologic activity, very few have combined these two focus areas to investigate how snow-driven systems export carbon (e.g. Boyer et al., 1997; Hornberger et al., 1994; Liptzin et al., 2009; MacDonald et al., 2010; Pomeroy, 1991; M. W. Williams, Helmig, et al., 2009). Those that have focused primarily on using the carbon itself as a tracer of water movement—a potentially inaccurate method, given that carbon is a reactive tracer which can be removed by groundwater processes (Li, Maher, et al., 2017).

In this study, we have used indices of dissolved organic carbon (DOC) composition, performed end-member mixing analysis using more-conservative tracers, and combined the results to determine the sources of both stream water and DOC. This has lead us to conclude that while the majority of DOC is, as expected, derived from SOC, it is not transported to the stream by lateral flow through the soil. Rather, soil pore-water is flushed to the saprolite/bedrock interface by snowmelt, then carried to the stream via flow either along this interface or through bedrock aquifers.

In Reynolds Mountain East (RME), more than 70% of precipitation falls as snow, and is stored in the form of wind-created snowdrifts (Nayak et al., 2010; Reba et al., 2011). These drifts are the ultimate source of stream flow in RME, but the different paths that water takes to the stream determine stream water chemistry and DOC content.

From soil moisture sensors, and tension lysimeters, we see that the soil water available at less than 60kPa tension at the hillslope (conifer and drift) sites is relatively un-evolved meltwater, with few dissolved solutes distinguishing it from snowpack. Isotopic analysis

suggests that little to no evaporative fractionation occurs in soil water during the melt-out period. Combined with the coarse-textured, high-permeability soils in RME, this suggests that melt water infiltrates relatively quickly through the soil to the soil-saprolite boundary, and thus that laterally flowing soil water does not contribute directly to streamflow. The results of our EMMA support this conclusion—while DOC in the stream and source waters is clearly soil-derived, the geochemistry of the waters indicates further evolution of vertically displaced soil water in the bedrock.

Water sampled in the saprolite showed greater chemical differences from snowpack than soil water did. We found saprolite water is one of the end-members for streamflow, and carbon indices suggest it is the major source of DOC. We hypothesize that saprolite water represents soil water from the previous summer that remained trapped in small soil pores or around particles until the spring snowmelt flushed it down through the soil profile (Boyer et al., 1997; Oshun, Dietrich, Dawson, & Fung, 2016). During the summer period, while this water was too tightly bound to be sampled by tension lysimeters, it equilibrated with the soil matrix (Li, Bao, et al., 2017). This accounts for the distinct chemical signal, the increase in dissolved organic carbon, and the fact that saprolite water isotopes show the evaporative signal we would expect from soil water, and which soil water does not show (Barnes, Allison, & Osmond, 1988).

Below the saprolite layer are multiple layers of fractured bedrock, as shown by geophysical data (McIntyre, 1972; Steven Holbrook, personal communication, October 19, 2017). Our study found that at least one aquifer exists in this fractured bedrock zone. Wells in this catchment respond quickly to snowmelt, consistent with rapid percolation of meltwater through the soil. The saprolite intercepts enough percolating soil water to act as an aquifer, while allowing some of the water to pass on to the bedrock aquifer below. At snowdrift locations, more

water is available to pass through saprolite into bedrock aquifers; seismic velocity data also suggest a thinner saprolite layer at these locations compared to farther downslope, further reducing saprolite interception of meltwater. The snowdrift locations are likely to act as recharge zones for bedrock aquifers, while saprolite water is recharged throughout the watershed. Although the concentration of solutes in snow is uniform throughout the watershed, the drift areas would experience a larger flux of windblown dust, potentially increasing the concentrations of chemical species sorbed to the dust (e.g., nitrate, sulfate) in the topsoil at these locations to levels not seen elsewhere.

Three wells in the watershed are drilled to 15m below the soil surface, and have similar chemical signatures to each other. The Drift well is located immediately downhill of the large southeastern drift and has the least-evolved water chemistry; the Aspen and West wells appear to derive from the same drift and intercept the same aquifer, but along different flow paths. The Drift and Aspen wells are end-members, while the West well is not. The vicinity of the Aspen well was saturated near the surface for much of spring and summer 2017, suggesting that stream water originating in this area could be influenced by soil and the atmosphere before reaching the stream. The West and Drift wells experienced a shorter period of surface saturation. There is also another snowdrift between the Drift and Aspen wells (Figure 3.1, no. 3) which could alter the chemistry of the Aspen well.



Figure 3.1: Snow depth in RME, March of 2009 (an average snow year). Numbers indicate snowdrifts mentioned in the thesis. Adapted from Shrestha (2016)

Little to no surface runoff occurs in RME (McNamara et al., 2005). Meltwater flows almost immediately into ephemeral channels, which dry downstream as the summer progresses. However, for the duration of melt, snowmelt is a primary end-member in the stream. The low concentrations of both conservative tracers and DOC in snowmelt mean it acts as a diluting factor for stream water chemistry.

Even in late August, snowmelt comprises up to 20% of streamflow in our proportionalmixing plot (Figure 3.2), two months before the first snowfall of the year and a month after the last measurable rain event. Water collected in the stream draining the Springhouse drift area in late October 2017 was similar in composition to snowmelt. This drift likely feeds the Cabin well immediately downslope of it, which at 30m is deeper than the other wells in the watershed. Given that the chemistry of the Cabin well is similar to that of stream samples, and the location of the Cabin well uphill of the perennial channel heads, we assume that this well may intersect a different aquifer than the others, and that it provides dilute water to the stream at low-flow. This signal is overprinted by snowmelt signals during the melt period, but becomes more obvious as saprolite water contributions diminish in late summer.



Figure 3.2: Percent contribution of each end-member to stream flow during 2017. From top to bottom: Aspen well (black), Drift well (light gray), Saprolite flow (dark gray), Snowmelt (dotted white).

Most of the DOC, as noted above, seems to be derived from saprolite water. Both the carbon compound complexity and the degree of microbial processing suggest a primarily terrestrial source for DOC in RME, consistent with previous findings (McKnight et al., 2001; Sanderman et al., 2009; Stielstra et al., 2015). While the 2015-2016 data show clear trends in carbon sourcing, with more-processed carbon (likely from deeper soil horizons) predominating at low-flow, the 2016-2017 data show consistent levels of microbial processing throughout the year. This may be due to an unusually wet (200% of normal snowfall) year allowing greater

leaching of all soil horizons, or perhaps due to the longer period of stream flow allowing more sampling and thus better constraints on variability. In any case, autochthonous carbon does not appear to be a major component of the total DOC budget in RME during wet or dry years.

#### **3.2. Implications**

The fast throughput of water in this system, as indicated by well responsiveness and the fact that soils quickly dry after the end of snowmelt, suggests this watershed may be vulnerable to climate change in the near term. Reduced snowpack leads not only to lower peak discharges, but also to lower baseflow (Nayak et al., 2010). The stream is perennial in most years, but the quantity of flow varies widely depending on the wetness of the year (USDA-ARS Northwest Watershed Research Center, 2017a, b).

Carbon storage in RME is likely a balancing act of water availability. There must be enough water to allow plant growth, and thus carbon sequestration; but too much water will increase the amount of soil carbon lost during spring snowmelt. The implications of changing snow regimes for carbon storage are unknown, as the interplay of vegetation and precipitation was beyond the scope of this study—other than to note that the most vegetatively productive areas are adjacent to snowdrifts, where any impact of climate change will be more acutely felt.

#### **3.3. Opportunities for Future Work**

Perhaps the clearest outcome of this study was clarifying how much more work needs to be done to fully characterize even a small, seemingly 'simple' catchment. I present below several areas of study that would greatly improve our understanding of RME, and how it (and similar areas of the Intermountain West) may be affected by climatic shifts:

#### **3.3.1.** Better mapping of lithology

Existing geologic maps of RME were produced for the entirety of Owyhee County, or for the RCEW as a whole (Ekren et al., 1981; McIntyre, 1972). The lack of significant bedrock

outcrops in RME make more detailed mapping difficult. Boreholes in RME would allow better characterization of the thickness and degree of fracturing of the geologic units present, as well as providing a more detailed map of their spatial distribution. Geochemical measurements of the bulk bedrock rather than just surface and groundwater would also be useful, as a way to predict from well water chemistry what layer of rock the aquifer is hosted in.

Additional examination of existing geophysical (seismic velocity and ERT) data in RME would also be helpful as a means of mapping fracturing and water content of rock and soil, perhaps including the fluctuation in the water table over several seasons.

#### **3.3.2.** Better constraints on hydrology

This was a limited study in many ways. Our selection of study locations was determined by the geophysical data and by restrictions on the time and funding available for the study. A more thorough investigation would require the installation of lysimeter and piezometer nests at multiple locations, preferably capturing suspected flowpaths from all the major snowdrifts in the watershed as well as soils in the scour areas.

Additional wells, installed in the drier portions of the watershed and at differing depths, would allow better estimation of the extent of the aquifer(s) in this watershed. The use of slug tests in these wells would assist in determining the degree of fracturing in the aquifer, and the application of tracers to snowdrifts would clarify both flowpaths and residence times in the aquifer. Hydraulic head measurements at multiple locations in the watershed would also make the connections between recharge and discharge zones clearer. In particular, characterization of flowpaths from the Springhouse drift may clarify what contribution, if any, this drift makes to the stream in RME.

Examination of well cores would also allow us to distinguish potential aquifers and aquitards on the basis of porosity. There may be more than one aquitard affecting this basin—the

piezometer at the spring site had a hydraulic head consistently above the ground surface, suggesting confined flow. A detailed characterization of bedrock hydraulic conductivity in RME would be a useful future study.

#### 3.3.3. Modeling the Rain-Snow Transition

The rain-snow transition has been modeled for another portion of the RCEW (Enslin, 2016), but not for RME. Modeling the impacts of a switch from snow to rain as the primary form of precipitation in RME would require knowledge of the aquifer potential of rocks underlying scoured areas, the transmissivity and storage of existing aquifers, and the transit time of groundwater in the system. With this data, a modeler could predict the impacts of the loss of snowdrifts on streamflow on the seasonal-to-decadal scale.

# 3.3.4. A More Complex EMMA

End-member mixing analysis can theoretically extend into an infinite number of dimensions of U-space (Hooper, 2001). With a dataset like ours, where the first four endmembers capture just over half of the variability of streamwater chemistry, a more complex model might be able to do a better job of constraining the relative proportions of end-members in streamflow throughout the season.

EMMA assumes temporally invariant solute concentrations in end-members. In RME, variability in the end-members is sufficiently small to allow us to use EMMA, but the creation of a mixing model that allows end-member solute concentrations to vary along with stream chemistry might better capture shifting flowpaths over the course of the year. This would be particularly applicable to the piezometer/saprolite water, which shows considerable variability, particularly in rubidium.

#### **3.3.5.** Modeling the Interaction of Precipitation and Carbon

A model of the changes in precipitation and climate, combined with existing models of soil carbon storage in RME, may be used to predict any changes in carbon storage or export due to the switch from snow to rain. Adding a component to predict shifts in vegetative communities could further improve the usefulness of the model, allowing the modeler to predict if and when such shifts could occur. This would have implications for plant growth (if precipitation arrives out of sync with the growing season) and invasion by non-native species, and for possible shifts in carbon distribution throughout the watershed.

#### 3.3.6. Dust

NADP data from ID11 does not include the rare-earth elements. The presence of barium in snow suggests that dust might be a source of rare-earth elements (REEs) in RME. Measuring the concentrations of REEs in the soil may also provide guidance in selecting natural tracers for soil water chemistry, particularly if drift areas accumulate dust as well as they do snow.

#### 3.3.7. Mapping Associations of Snowdrifts and Curvature/Weathering

# Profiles

Snowdrifts increase the amount of water available for chemical weathering beneath themselves. In RME, there is a visual correlation between snowdrifts and concave topography. Using geophysical data and boreholes, a geomorphologic study could determine if the concavities are created by increased weathering (depth to bedrock) or not. This would have implications for soil formation, as well as for geomorphologic models in other systems (e.g. St Clair et al., 2015).

### 3.4. Works Cited

- Barnes, C. J., Allison, G. B., & Osmond, P. O. G. (1988). Tracing of Water Movement in the Unsaturated Zone Using Stable Isotopes of Hydrogen and Oxygen. *Journal of Hydrology*, 100, 143–176. https://doi.org/10.1016/0022-1694(88)90184-9
- Boyer, E. W., Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1997). Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes*, 11, 1635– 1647. https://doi.org/10.1002/(SICI)1099-1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H
- Ekren, E. B., McIntyre, D. H., Bennet, E. H., & Malde, H. E. (1981). Geologic map of Owyhee County, Idaho, west of longitude 116° W [map]. 1:125,000.shre Denver, CO: U.S. Geological Survey.
- Enslin, C. L. (2016). Understanding the rain-to-snow transition zone: modeling snowmelt and the spatial distribution of water resources in southwestern Idaho (master's thesis). Idaho State University.
- Hooper, R. P. (2001). Applying the scientific method to small catchment studies: a review of the Panola Mountain experience. *Hydrological Processes*, 15, 2039–2050. https://doi.org/10.1002/hyp.255
- Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1994). Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry*, 25(3), 147–165. https://doi.org/10.1007/BF00024390
- Li, L., Bao, C., Sullivan, P. L., Brantley, S. L., Shi, Y., & Duffy, C. J. (2017). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. *Water Resources Research*, 53(3), 2346–2367. https://doi.org/10.1002/2016WR018935
- Li, L., Maher, K., Navarre-Sitchler, A., Druhan, J., Meile, C., Lawrence, C., ... Beisman, J. (2017). Expanding the role of reactive transport models in critical zone processes. *Earth-Science Reviews*, 165, 280–301. https://doi.org/10.1016/j.earscirev.2016.09.001
- Liptzin, D., Williams, M. W., Helmig, D., Seok, B., Filippa, G., Chowanski, K., & Hueber, J. (2009). Process-level controls on CO2 fluxes from a seasonally snow-covered subalpine meadow soil, Niwot Ridge, Colorado. *Biogeochemistry*, 95(1), 151–166. https://doi.org/10.1007/s10533-009-9303-2
- MacDonald, M. K., Pomeroy, J. W., & Pietroniro, A. (2010). On the importance of sublimation to an alpine snow mass balance in the Canadian Rocky Mountains. *Hydrology and Earth System Sciences*, *14*(7), 1401–1415. https://doi.org/10.5194/hess-14-1401-2010

McIntyre, D. H. (1972). Cenozoic geology of the Reynolds Creek Experimental Watershed,

Owyhee County, Idaho. *Pamphlet 151*. Moscow, ID. Retrieved from https://ngmdb.usgs.gov/Prodesc/proddesc\_46206.htm

- McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., & Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46, 38–48. https://doi.org/10.4319/lo.2001.46.1.0038
- McNamara, J. P., Chandler, D. G., Seyfried, M. S., & Achet, S. (2005). Soil moisture states, lateral flow, and streamflow generation in a semi-arid, snowmelt-driven catchment. *Hydrological Processes*, *19*, 4023–4038. https://doi.org/10.1002/hyp.5869
- Nayak, A., Marks, D., Chandler, D. G., & Seyfried, M. S. (2010). Long-term snow, climate, and streamflow trends at the reynolds creek experimental watershed, Owyhee Mountains, Idaho, United States. *Water Resources Research*, 46(6). https://doi.org/10.1029/2008WR007525
- Oshun, J., Dietrich, W. E., Dawson, T. E., & Fung, I. (2016). Dynamic, structured heterogeneity of water isotopes inside hillslopes. *Water Resources Research*, *52*(1), 164–189. https://doi.org/10.1002/2015WR017485
- Pomeroy, J. W. (1991). Transport and Sublimation of Snow in Wind-Scoured Alpine Terrain. Snow Hydrology and Forests in High Alpine Areas, Proceedings of the Vienna Symposium, August 1991, IAHS Publ. No. 205, (Snow Hydrology and Forests in High Alpine Areas, Proceedings of the Vienna Symposium, August 1991, IAHS Publ. 205), 131–140.
- Reba, M. L., Marks, D., Seyfried, M. S., Winstral, A., Kumar, M., & Flerchinger, G. (2011). A long-term data set for hydrologic modeling in a snow-dominated mountain catchment. *Water Resources Research*, 47(7), 1–7. https://doi.org/10.1029/2010WR010030
- Sanderman, J., Lohse, K. A., Baldock, J. A., & Amundson, R. (2009). Linking soils and streams: Sources and chemistry of dissolved organic matter in a small coastal watershed. *Water Resources Research*, 45(3), W03418. https://doi.org/10.1029/2008WR006977
- Shrestha, R. (2016). 2009 Im Snow Depth for Reynolds Mountain East, Reynolds Creek Experimental Watershed, Idaho [Data set]. http://doi.org/10.18122/B28597
- St. Clair, J., Moon, S., Holbrook, W. S., Perron, J. T., Riebe, C. S., Martel, S. J., ... Richter, D. deB. (2015). Geophysical imaging reveals topographic stress control of bedrock weathering. *Science*, 350(6260), 534–538. https://doi.org/10.1126/science.aab2210
- Stielstra, C. M., Lohse, K. A., Chorover, J., McIntosh, J. C., Barron-Gafford, G. A., Perdrial, J. N., ... Brooks, P. D. (2015). Climatic and landscape influences on soil moisture are primary determinants of soil carbon fluxes in seasonally snow-covered forest ecosystems. *Biogeochemistry*, 123(3), 447–465. https://doi.org/10.1007/s10533-015-0078-3

USDA ARS Northwest Watershed Research Center. (2017a). [Reynolds Creek 166 hourly

streamflow]. Unpublished raw data.

- USDA ARS Northwest Watershed Research Center. (2017b). [Reynolds Mountain East meteorological data.] Unpublished raw data.
- Williams, M. W., Helmig, D., & Blanken, P. (2009). White on green: Under-snow microbial processes and trace gas fluxes through snow, Niwot Ridge, Colorado Front Range. *Biogeochemistry*, 95(1), 1–12. https://doi.org/10.1007/s10533-009-9330-z

# **Chapter 4: Appendices**

# 4.1. Table of Analyte Concentrations in All Sampled Waters

Table 4.1: Median, interquartile range, and range of concentrations for all measured analytes in all sampled waters. TIC, NPOC, TN, and anions are reported in mg/L; SUVA in L mgC<sup>-1</sup> m<sup>-1</sup>; FI and C:N are unitless ratios; isotopes are reported in per mille relative to VSMOW, and cations are reported in  $\mu$ g/L. Stream samples were taken near the bog soil pit and at the catchment-defining weir (Figure 2.4).

Analyte	Snow			Rain		
	Median	IQR	Range	Median	IQR	Range
TIC	0.37	0.14	0.22	2.74	4.97	4.97
NPOC	0.99	2.11	6.58	4.33	4.17	4.27
SUVA	1.29	0.78	0.81	1.40	0.94	0.94
FI	1.05	7.96	10.41	1.40	0.33	0.33
TN	0.42	0.18	0.24	0.27	0.08	0.08
C:N	4.84	13.18	26.88	11.09	16.69	16.69
δD	-121.70	33.03	33.03	-64.69	43.76	43.76
δ¹ <sup>8</sup> Ο	-15.66	4.05	4.05	-7.38	8.10	8.10
D-excess	6.82	3.87	3.87	-5.65	21.04	21.04
F <sup>-</sup>	0.08	0.04	0.10	0.01	0.03	0.03
Cl⁻	0.20	0.15	7.52	0.53	0.60	0.75
NO3 <sup>2-</sup>	0.10	0.20	0.59	2.20	3.46	4.06
SO4 <sup>2-</sup>	0.09	0.18	0.39	1.41	3.61	4.27
Li <sub>7</sub>	0.23	0.21	2.74	0.30	0.28	0.28
Be <sub>9</sub>	0.37	0.47	1.28	0.05	3.69	3.69
B <sub>11</sub>	9.20	5.93	12.19	15.40	10.13	10.13
Na <sub>23</sub>	534.95	309.79	4913.10	703.90	523.26	584.34
Mg <sub>24</sub>	70.88	28.51	47.27			
Mg25	69.74	55.61	133.84	207.76	285.36	310.39
Al <sub>27</sub>	141.29	137.40	244.51	59.97	112.13	125.87
Si <sub>29</sub>	2855.20	3356.61	3579.31	103.82	363.56	478.96
P <sub>31</sub>	619.37	213.72	347.59	355.20	1245.20	1245.20
S <sub>33</sub>	2399.00	1240.00	1654.00	5194.50	3515.00	3515.00
K <sub>39</sub>	540.60	888.26	1112.45	1152.54	3578.78	4287.40
Ca <sub>44</sub>	373.24	236.19	513.14	955.01	755.90	851.20
Sc <sub>45</sub>	1.62	1.74	2.42	0.20	0.51	0.67
Ti <sub>47</sub>	0.75	4.14	8.08	3.37	2.71	2.71
V <sub>51</sub>	0.24	0.22	0.53	0.16	0.40	0.47
Cr <sub>52</sub>	1.22	1.13	2.28	0.55	0.70	0.89
Mn <sub>55</sub>	2.30	5.82	20.63	9.90	44.17	56.66
Fe <sub>57</sub>	96.47	331.09	391.58	30.82	62.40	81.60
Co <sub>59</sub>	0.07	0.07	0.81	0.22	0.33	0.35

Ni <sub>60</sub>	0.73	0.66	87.56	0.50	59.05	78.70
Cu <sub>65</sub>	1.07	5.78	290.67	8.56	136.52	180.71
Zn <sub>66</sub>	31.83	39.26	430.84	39.27	32.06	39.89
Ga <sub>69</sub>	1.86	1.48	5.12	2.41	4.27	5.07
Ge <sub>72</sub>	0.20	0.36	0.45			
As <sub>75</sub>	3.68	4.53	7.64	17.20	11.53	14.17
Se <sub>82</sub>	5.20	5.01	84.83	3.61	2.19	2.80
Rb <sub>85</sub>	0.22	0.41	6.65	1.96	2.83	3.31
Sr <sub>88</sub>	1.08	0.80	2.97	6.04	6.82	7.39
Y <sub>89</sub>	0.04	0.03	0.21	0.03	0.03	0.03
Zr <sub>90</sub>	0.45	0.57	0.67	0.16	0.15	0.15
Nb <sub>93</sub>	6.25	7.57	11.70	0.36	0.00	0.00
Mo <sub>95</sub>	0.49	0.59	1.23	0.26	0.70	0.93
Ag <sub>107</sub>	0.05	0.07	0.55	0.10	0.53	0.53
Cd <sub>111</sub>	0.09	0.09	0.61	0.07	0.26	0.34
Sn <sub>182</sub>	0.88	1.10	2.46	0.82	1.48	1.69
Sb <sub>121</sub>	1.68	1.34	2.94	1.50	0.77	0.98
Te <sub>125</sub>	0.16	0.07	0.08			
Cs <sub>133</sub>	0.04	0.02	0.11	0.01	0.02	0.02
Ba <sub>137</sub>	30.25	31.29	93.34	43.30	79.11	92.92
La <sub>139</sub>	0.04	0.03	0.18	0.02	0.02	0.02
Ce <sub>140</sub>	0.06	0.04	0.28	0.06	0.14	0.18
Pr <sub>141</sub>	0.01	0.01	0.14	0.01	0.09	0.12
Nd <sub>146</sub>	0.05	0.05	0.94	0.04	0.08	0.10
Sm <sub>147</sub>	0.06	0.08	0.65	0.61	1.22	1.22
Eu <sub>153</sub>	0.02	0.02	0.33	0.03	0.20	0.26
Gd <sub>157</sub>	0.03	0.04	0.06	0.01	0.11	0.14
Tb <sub>159</sub>	0.22	0.27	0.29	0.44	0.71	0.72
Dy <sub>163</sub>	0.02	0.03	0.49	0.01	0.33	0.44
Ho <sub>165</sub>	0.01	0.01	0.09	0.00	0.07	0.07
Er <sub>166</sub>	0.01	0.01	0.17	0.01	0.14	0.18
Tm <sub>169</sub>	0.01	0.02	0.09	0.00	0.04	0.04
Yb <sub>172</sub>	0.02	0.03	0.05	0.00	0.27	0.36
Lu <sub>175</sub>	0.01	0.02	0.08	0.00	0.05	0.07
TI <sub>205</sub>	0.55	0.56	1.05	0.07	0.00	0.00
Pb <sub>208</sub>	0.13	0.15	0.62	0.09	0.14	0.16
Bi <sub>209</sub>	0.01	0.01	0.02			
Th <sub>232</sub>	0.25	0.43	0.66	0.03	0.00	0.00
U <sub>238</sub>	0.01	0.00	0.04	0.01	0.01	0.01

Analyte	Springhouse Stream (1 sample)			Drift Lysimeters		
	Median	IQR	Range	Median	IQR	Range
TIC						
NPOC	3.79			2.33	7.05	8.76
SUVA	1.81			0.92	0.00	0.00
FI	1.33			1.70	0.00	0.00
TN						
C:N						
δD				-129.46	30.86	30.86
0''0				-17.36	4.45	4.45
D-excess	0.01			9.43	4.73	4.73
F	0.01			0.03	0.05	0.70
Cl	0.44			0.24	0.17	0.56
NO <sub>3</sub> <sup>2-</sup>				0.84	0.91	2.37
SO4 <sup>2-</sup>	1.47			0.35	0.14	1.60
Li7	0.40			8.13	29.67	83.43
Be <sub>9</sub>				0.05	0.31	0.53
B <sub>11</sub>	6.26			6.65	9.22	91.37
Na <sub>23</sub>	1813.00			930.60	597.97	14845.30
Mg <sub>24</sub>				141.43	9.99	17.74
Mg <sub>25</sub>	443.60			117.00	57.13	172.24
Al <sub>27</sub>	50.04			59.96	107.60	259.94
Si <sub>29</sub>	4413.00			3568.00	2060.00	5399.00
P <sub>31</sub>	3.06			170.38	245.87	271.63
S <sub>33</sub>	3230.00			616.80	1052.35	1226.90
K <sub>39</sub>	1081.00			495.40	705.09	1116.30
Ca <sub>44</sub>	2406.00			656.10	324.76	1593.60
<b>SC</b> 45	1.92			1.98	1.50	2.65
Ti <sub>47</sub>	6.57			2.17	4.42	7.83
V <sub>51</sub>	0.17			0.12	0.31	1.35
Cr <sub>52</sub>	0.27			0.62	1.29	11.30
Mn <sub>55</sub>	44.89			2.69	5.25	9.56
Fe <sub>57</sub>	112.20			35.07	283.63	356.49
Co <sub>59</sub>	0.17			0.17	0.19	0.95
Ni <sub>60</sub>	0.53			1.44	4.79	11.39
Cu <sub>65</sub>	1.55			0.91	0.79	9.15
Zn <sub>66</sub>	33.89			31.01	38.50	439.12
Ga <sub>69</sub>	1.35			2.29	1.87	33.75
Ge <sub>72</sub>				0.12	0.11	0.11
As <sub>75</sub>	7.87			0.68	0.85	5.52
Se <sub>82</sub>	4.96			5.60	5.84	12.32
Rb <sub>85</sub>	0.39			0.93	0.40	1.29
14.19			5.58	2.79	10.47	
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0.08			0.02	0.03	0.07	
0.09			0.36	0.60	1.10	
			0.74	2.65	5.70	
0.11			0.32	0.72	2.26	
			0.02	0.05	0.10	
0.07			0.06	0.08	0.16	
0.04			0.30	0.62	1.23	
0.47			3.28	2.31	18.86	
0.01			0.02	0.02	0.11	
22.48			43.57	30.85	686.74	
0.04			0.02	0.02	0.05	
0.15			0.04	0.04	0.10	
0.01			0.01	0.01	0.04	
0.07			0.02	0.02	0.07	
0.02			0.03	0.07	0.13	
0.01			0.01	0.01	0.17	
0.01			0.01	0.03	0.07	
0.64			0.21	0.37	1.22	
0.01			0.01	0.02	0.05	
0.00			0.00	0.01	0.03	
0.01			0.01	0.02	0.03	
0.00			0.00	0.01	0.03	
0.00			0.01	0.02	0.04	
0.00			0.00	0.01	0.03	
			0.14	0.44	0.97	
0.05			0.08	0.11	0.54	
			0.01	0.01	0.01	
			0.19	0.30	0.62	
0.00			0.01	0.01	0.03	
	14.19 0.08 0.09 0.11 0.07 0.04 0.47 0.04 0.47 0.01 22.48 0.04 0.15 0.01 0.07 0.02 0.01 0.07 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01	14.19       0.09       0.11       0.11       0.07       0.04       0.04       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.02       0.01       0.02       0.01       0.02       0.01       0.02       0.01       0.02       0.03       0.04       0.05       0.00       0.00       0.00       0.00	14.19        0.08        0.09        0.11        0.07        0.04        0.04        0.04        0.04        0.04        0.04        0.01        0.01        0.04        0.05        0.01        0.02        0.01        0.02        0.01        0.01        0.01        0.01        0.00        0.00        0.00        0.00	14.19     5.58      0.08      0.02      0.09      0.36      0.01      0.32      0.07      0.32      0.07      0.02      0.07      0.06      0.04      0.30      0.47      3.28      0      0.02      22.48      0.02      0.15      0.02      0.15      0.01      0.01      0.02      0.02      0.01      0.01      0.02      0.02      0.01      0.01      0.02      0.02      0.01      0.01      0.01      0.01      0.01 <t< td=""><td>14.19      5.58    2.79      0.08      0.02    0.03      0.99      0.36    0.60      0.11      0.32    0.72      0.07      0.32    0.72      0.07      0.32    0.05      0.07      0.30    0.62      0.47      0.30    0.62      0.47      3.28    2.31      0.01      3.28    2.31      0.01      0.02    0.02      0.15      0.02    0.02      0.15      0.01    0.01      0.01      0.02    0.02      0.02      0.01    0.01      0.01      0.01    0.01      0.01      0.01    0.02      0.02      0.0</td></t<>	14.19      5.58    2.79      0.08      0.02    0.03      0.99      0.36    0.60      0.11      0.32    0.72      0.07      0.32    0.72      0.07      0.32    0.05      0.07      0.30    0.62      0.47      0.30    0.62      0.47      3.28    2.31      0.01      3.28    2.31      0.01      0.02    0.02      0.15      0.02    0.02      0.15      0.01    0.01      0.01      0.02    0.02      0.02      0.01    0.01      0.01      0.01    0.01      0.01      0.01    0.02      0.02      0.0	

Analuta	Conifer Lysimeters			Bog Lysimeter at 35 cm		
Analyte	Median	IQR	Range	Median	IQR	Range
TIC						
NPOC	1.09	0.00	0.00	1.26	3.17	6.45
SUVA				2.12	3.14	3.14
FI				1.71	0.91	0.91
TN						
C:N						
δD	-112.25	0.87	0.87	-119.08	2.90	2.90
δ'°0	-14.74	0.06	0.06	-15.78	1.55	1.55
D-excess	5.65	0.36	0.36	7.16	9.53	9.53
F <sup>-</sup>	0.23	0.47	0.60	0.08	0.04	0.16
Cl⁻	0.84	0.82	1.09	0.36	0.07	0.44
NO <sub>3</sub> <sup>2-</sup>	0.10	0.11	0.11	0.06	0.12	0.26
SO4 <sup>2-</sup>	3.17	3.72	5.03	1.07	0.46	1.31
Li7	13.08	22.49	38.93	2.05	1.40	6.46
Be <sub>9</sub>	0.02	0.05	0.08	0.09	0.23	0.31
B <sub>11</sub>	11.38	15.82	43.06	8.86	4.63	8.02
Na <sub>23</sub>	2179.50	1631.50	2628.00	4262.00	652.61	1581.00
Mg <sub>24</sub>				1373.71	121.88	131.93
Mg <sub>25</sub>	65.35	66.42	126.59	1353.40	173.05	525.00
Al <sub>27</sub>	66.43	32.19	85.62	46.33	127.18	261.24
Si <sub>29</sub>	6771.00	9356.75	15032.00	8963.00	1927.67	5078.67
P <sub>31</sub>	7.74	0.00	0.00	213.91	166.29	211.39
S <sub>33</sub>	348.75	490.78	547.20	918.75	1299.03	2275.00
K <sub>39</sub>	4343.00	464.00	2094.00	2177.75	437.25	1940.07
Ca <sub>44</sub>	346.10	269.90	1430.00	3720.68	447.34	3164.00
<b>SC</b> 45	3.24	4.21	6.90	4.53	0.80	2.01
Ti <sub>47</sub>	1.16	2.11	4.05	1.12	5.78	10.12
V <sub>51</sub>	0.17	0.02	0.08	0.07	0.47	0.53
Cr <sub>52</sub>	0.28	0.17	2.68	0.52	1.84	6.85
Mn <sub>55</sub>	3.32	6.50	17.20	87.87	12.27	50.66
Fe <sub>57</sub>	32.54	0.00	0.00	685.09	2389.41	3575.08
Co <sub>59</sub>	0.23	0.14	0.25	1.16	0.16	2.06
Ni <sub>60</sub>	0.48	0.83	0.95	61.90	22.13	185.44
Cu <sub>65</sub>	1.61	2.99	13.80	0.42	0.63	4.56
Zn <sub>66</sub>	57.80	65.05	79.84	36.77	34.59	96.57
Ga <sub>69</sub>	1.14	1.43	32.81	1.05	0.36	3.80
Ge <sub>72</sub>				0.25	0.00	0.00
As <sub>75</sub>	0.88	1.27	1.62	1.38	0.92	1.92
Se <sub>82</sub>	2.13	0.98	0.98	2.05	5.02	7.24
Rb <sub>85</sub>	3.80	0.75	2.61	4.17	1.41	2.34

Sr <sub>88</sub>	2.81	2.79	4.63	37.74	4.18	41.94
Y <sub>89</sub>	0.08	0.04	0.29	0.04	0.08	0.39
Zr <sub>90</sub>	0.45	0.26	0.46	0.13	0.52	18.43
Nb <sub>93</sub>	0.28	0.92	0.92	1.57	2.25	3.62
Mo <sub>95</sub>	0.30	0.58	0.76	0.48	0.33	1.27
Ag <sub>107</sub>	0.01	0.01	0.01	0.02	0.03	0.17
Cd <sub>111</sub>	0.02	0.03	0.11	0.03	0.06	0.19
Sn <sub>182</sub>	0.47	1.27	2.27	0.32	0.49	1.81
Sb <sub>121</sub>	3.51	2.29	3.88	2.26	1.99	11.15
Te <sub>125</sub>				0.05	0.08	0.08
Cs <sub>133</sub>	0.03	0.01	0.01	0.05	0.04	0.08
Ba <sub>137</sub>	21.83	31.02	682.88	19.00	2.00	80.96
La <sub>139</sub>	0.04	0.03	0.28	0.02	0.02	0.23
Ce <sub>140</sub>	0.11	0.09	0.58	0.04	0.03	0.51
Pr <sub>141</sub>	0.02	0.01	0.07	0.01	0.01	0.05
Nd <sub>146</sub>	0.08	0.10	0.40	0.02	0.03	0.24
Sm <sub>147</sub>	0.02	0.03	0.07	0.03	0.06	0.09
Eu <sub>153</sub>	0.01	0.02	0.18	0.01	0.01	0.02
Gd157	0.02	0.03	0.09	0.02	0.02	0.07
Tb <sub>159</sub>	0.73	0.71	3.87	0.27	0.47	3.62
Dy <sub>163</sub>	0.01	0.01	0.06	0.01	0.02	0.04
Ho <sub>165</sub>	0.00	0.01	0.01	0.00	0.01	0.01
Er <sub>166</sub>	0.01	0.01	0.05	0.01	0.02	0.03
Tm <sub>169</sub>	0.00	0.00	0.00	0.00	0.01	0.01
Yb <sub>172</sub>	0.01	0.01	0.05	0.01	0.02	0.03
Lu <sub>175</sub>	0.00	0.00	0.00	0.00	0.01	0.01
TI <sub>205</sub>	0.08	0.13	0.16	0.11	0.29	0.87
Pb <sub>208</sub>	0.10	0.41	0.93	0.10	0.07	0.28
Bi <sub>209</sub>				0.01	0.00	0.00
Th <sub>232</sub>	0.03	0.06	0.07	0.14	0.22	0.30
U <sub>238</sub>	0.00	0.02	0.03	0.01	0.01	0.02

A see but a	Bog Lysimeter at 49 cm			Bog Lysimeter at 82 cm (saprolite)		
Analyte	Median	IQR	Range	Median	IQR	Range
TIC						
NPOC	3.87	2.35	3.01	4.33	4.25	4.25
SUVA						
FI						
TN						
C:N	440.00	0.00	0.00	440.40	0.00	0.00
δD 5180	-118.30	0.00	0.00	-119.10	0.00	0.00
0 <sup>.0</sup> 0	-15.76	0.00	0.00	-15.85	0.00	0.00
D-excess	7.77	0.00	0.00	7.72	0.00	0.00
F CI-	0.07	0.02	0.08	0.03	0.05	0.09
	0.05	0.11	0.22	0.11	0.24	0.44
NO3 <sup>2-</sup>	0.02	0.29	0.42	0.08	0.61	0.61
SO42-	0.09	0.21	1.43	0.11	0.19	0.35
Li7	2.66	1.18	6.98	5.29	4.02	9.48
Be <sub>9</sub>	0.08	0.05	0.38	0.06	0.06	0.51
B <sub>11</sub>	8.66	3.82	8.84	9.31	2.93	6.16
Na <sub>23</sub>	4527.00	875.75	1854.00	5185.00	778.00	1102.00
Mg <sub>24</sub>	1516.46	0.00	0.00	2256.22	0.00	0.00
Mg <sub>25</sub>	1287.50	580.00	1000.00	2252.50	352.35	1248.00
Al <sub>27</sub>	50.80	18.89	159.71	70.17	49.40	169.19
Si <sub>29</sub>	10157.50	2413.23	3889.00	8861.50	2561.75	3534.00
P <sub>31</sub>	22.78	283.50	283.50	7.91	279.68	279.68
S <sub>33</sub>	990.00	910.93	1933.32	491.65	851.73	1462.19
K <sub>39</sub>	463.75	179.53	1320.00	1984.50	479.75	1507.00
Ca <sub>44</sub>	4749.00	2341.50	4741.00	6425.50	1197.50	3412.00
SC45	4.92	1.40	2.82	4.26	1.55	3.32
Ti <sub>47</sub>	1.95	1.94	7.26	2.06	5.61	7.03
V <sub>51</sub>	0.07	0.10	0.34	0.05	0.04	0.37
Cr <sub>52</sub>	1.06	1.43	2.57	0.36	0.40	1.48
Mn <sub>55</sub>	105.90	48.67	138.34	39.80	17.22	47.50
Fe <sub>57</sub>	4344.00	5455.58	6619.30	110.70	445.97	884.23
Co <sub>59</sub>	1.16	0.43	1.09	0.64	0.28	0.54
Ni <sub>60</sub>	3.32	2.35	66.67	7.10	1.67	4.82
Cu <sub>65</sub>	0.55	0.48	0.94	0.46	0.47	0.82
Zn <sub>66</sub>	29.87	19.65	128.23	7.96	14.32	45.71
Ga <sub>69</sub>	2.50	1.37	2.44	1.33	0.38	0.97
Ge <sub>72</sub>						
As <sub>75</sub>	4.40	4.91	5.77	1.20	0.63	1.77
Se <sub>82</sub>	1.94	1.38	6.50	1.80	1.78	3.21
Rb <sub>85</sub>	2.59	1.16	1.61	4.65	1.86	2.88

Sr <sub>88</sub>	56.09	30.92	59.63	71.07	15.90	35.50
Y <sub>89</sub>	0.17	0.21	0.50	0.01	0.01	0.03
Zr <sub>90</sub>	0.17	0.18	0.96	0.10	0.16	0.97
Nb <sub>93</sub>	1.40	2.62	7.56	1.11	1.98	6.67
Mo <sub>95</sub>	0.49	0.61	1.43	0.40	0.25	0.63
Ag <sub>107</sub>	0.02	0.02	0.11	0.01	0.03	0.08
Cd <sub>111</sub>	0.03	0.04	0.21	0.03	0.02	0.24
Sn <sub>182</sub>	0.45	0.76	1.96	0.27	0.61	7.63
Sb <sub>121</sub>	3.51	1.79	3.54	3.37	1.45	4.05
Te <sub>125</sub>	0.03	0.00	0.00			
Cs <sub>133</sub>	0.03	0.04	0.06	0.04	0.04	0.08
Ba <sub>137</sub>	46.21	25.56	46.00	25.37	4.98	14.84
La <sub>139</sub>	0.09	0.12	0.81	0.01	0.01	0.02
Ce <sub>140</sub>	0.20	0.26	1.74	0.02	0.03	0.04
Pr <sub>141</sub>	0.03	0.03	0.16	0.00	0.01	0.01
Nd <sub>146</sub>	0.09	0.15	0.58	0.02	0.02	0.08
Sm <sub>147</sub>	0.04	0.06	0.13	0.00	0.01	0.09
Eu <sub>153</sub>	0.02	0.01	0.04	0.01	0.00	0.03
Gd157	0.04	0.05	0.12	0.01	0.01	0.04
Tb <sub>159</sub>	1.87	2.23	6.54	0.46	0.31	0.39
Dy <sub>163</sub>	0.03	0.04	0.08	0.00	0.01	0.03
Ho <sub>165</sub>	0.01	0.00	0.01	0.00	0.01	0.01
Er <sub>166</sub>	0.02	0.03	0.06	0.00	0.01	0.02
Tm <sub>169</sub>	0.00	0.01	0.01	0.00	0.01	0.01
Yb <sub>172</sub>	0.03	0.03	0.05	0.00	0.01	0.02
Lu <sub>175</sub>	0.00	0.01	0.01	0.00	0.01	0.01
TI <sub>205</sub>	0.11	0.33	1.49	0.09	0.22	1.26
Pb <sub>208</sub>	0.10	0.11	0.49	0.04	0.07	0.13
Bi <sub>209</sub>	0.01	0.00	0.00	0.01	0.00	0.00
Th <sub>232</sub>	0.08	0.16	0.90	0.05	0.08	0.79
U <sub>238</sub>	0.01	0.01	0.02	0.01	0.01	0.02

Applyto	Bog Piezometer			Spring Piezometer		
Analyte	Median	IQR	Range	Median	IQR	Range
TIC	2.80	1.01	3.05	2.95	1.24	1.87
NPOC	3.91	3.89	8.88	0.92	0.45	2.94
SUVA	8.06	11.09	11.09	5.37	2.17	2.17
FI	1.46	1.85	1.85	1.28	0.28	0.28
TN	0.42	0.35	0.48	0.83	0.08	0.16
C:N	8.51	12.09	18.46	0.95	0.52	0.91
δD	-119.13	0.29	0.29	-120.00	1.25	1.25
δ'°O	-16.04	0.27	0.27	-16.18	0.38	0.38
D-excess	9.19	1.87	1.87	9.44	1.79	1.79
F.	0.30	0.52	0.63	0.06	0.16	1.02
Cl⁻	1.16	0.56	1.75	0.97	0.23	1.52
NO <sub>3</sub> <sup>2-</sup>	1.17	1.05	4.25	3.53	0.31	2.37
SO4 <sup>2-</sup>	2.72	1.91	3.71	1.48	0.82	2.46
Li <sub>7</sub>	3.00	2.24	4.72	1.11	0.40	0.75
Be <sub>9</sub>	0.27	1.74	2.43	0.16	1.08	3.17
B <sub>11</sub>	28.25	7.25	70.36	16.24	3.89	14.70
Na <sub>23</sub>	4572.50	940.68	3883.68	3851.61	888.87	2312.97
Mg <sub>24</sub>	418.53	209.36	209.36	333.91	0.00	0.00
Mg <sub>25</sub>	422.92	338.22	686.92	327.68	111.14	254.60
Al <sub>27</sub>	97.91	131.90	184.40	91.06	127.37	278.58
Si <sub>29</sub>	9148.74	2185.61	3328.50	9189.41	1142.58	3151.63
P <sub>31</sub>	193.37	265.25	289.90	25.11	53.57	53.57
S <sub>33</sub>	3746.00	4729.56	7808.11	2780.50	3159.78	6015.10
K <sub>39</sub>	2120.65	938.66	1696.31	1839.50	481.52	792.16
Ca <sub>44</sub>	1801.33	1166.73	2784.49	1222.77	605.55	1135.56
SC <sub>45</sub>	4.70	1.33	8.00	4.39	1.71	7.27
Ti <sub>47</sub>	7.69	6.31	29.51	6.51	12.36	45.98
V <sub>51</sub>	0.72	0.51	1.12	0.39	0.65	1.04
Cr <sub>52</sub>	0.87	1.85	2.90	0.74	1.78	3.62
Mn <sub>55</sub>	7.87	4.19	10.74	2.89	2.84	45.01
Fe <sub>57</sub>	70.54	138.19	313.90	67.53	150.04	347.72
Co <sub>59</sub>	0.14	0.29	0.77	0.24	0.56	1.75
Ni <sub>60</sub>	1.87	52.38	72.89	3.70	68.13	90.28
Cu <sub>65</sub>	1.40	44.23	256.60	2.69	147.09	187.77
Zn <sub>66</sub>	52.45	80.54	277.47	249.83	491.35	1652.32
Ga <sub>69</sub>	9.83	5.81	13.78	2.60	5.96	15.28
Ge <sub>72</sub>	0.11	0.00	0.00			
AS <sub>75</sub>	1.39	2.07	10.64	1.67	5.00	9.56
Se <sub>82</sub>	4.71	15.37	32.50	4.09	24.59	58.44
Rb <sub>85</sub>	5.12	3.60	5.90	3.56	4.52	7.95

Sr <sub>88</sub>	13.50	9.67	21.90	10.71	5.23	9.55
Y <sub>89</sub>	0.25	0.55	1.50	0.37	0.88	1.32
Zr <sub>90</sub>	0.23	0.73	1.06	0.30	0.59	0.80
Nb <sub>93</sub>	0.65	3.57	4.18	0.52	0.85	1.03
Mo <sub>95</sub>	0.40	1.03	2.20	0.22	0.79	4.03
Ag <sub>107</sub>	0.04	0.79	1.24	0.10	0.67	1.61
Cd <sub>111</sub>	0.06	0.46	2.03	0.10	0.91	2.37
Sn <sub>182</sub>	0.30	0.99	5.12	0.41	1.60	8.55
Sb <sub>121</sub>	1.91	1.28	2.31	1.07	0.90	4.85
Te <sub>125</sub>	0.11	0.00	0.00	0.02	0.00	0.00
Cs <sub>133</sub>	0.05	0.03	0.06	0.05	0.09	0.14
Ba <sub>137</sub>	206.58	163.98	307.15	74.30	74.97	283.31
La <sub>139</sub>	0.08	0.12	0.31	0.12	0.26	0.45
Ce <sub>140</sub>	0.18	0.39	0.81	0.40	0.46	0.70
Pr <sub>141</sub>	0.03	0.06	0.18	0.10	0.26	0.55
Nd <sub>146</sub>	0.12	0.19	0.83	0.45	0.98	2.10
Sm <sub>147</sub>	0.09	0.33	0.78	0.14	0.66	1.06
Eu <sub>153</sub>	0.06	0.07	0.44	0.09	0.12	0.38
Gd157	0.06	0.36	1.28	0.21	0.65	1.22
Tb <sub>159</sub>	1.39	2.63	6.91	2.11	4.75	13.08
Dy <sub>163</sub>	0.06	0.30	0.51	0.10	0.13	0.81
Ho <sub>165</sub>	0.01	0.02	0.12	0.06	0.12	0.21
Er <sub>166</sub>	0.06	0.12	0.46	0.18	0.32	0.60
Tm <sub>169</sub>	0.01	0.05	0.09	0.05	0.09	0.17
Yb <sub>172</sub>	0.04	0.12	0.29	0.08	0.19	0.46
Lu <sub>175</sub>	0.01	0.03	0.11	0.05	0.10	0.14
TI <sub>205</sub>	0.05	0.56	2.08	0.34	0.84	1.40
Pb <sub>208</sub>	0.13	0.14	0.49	0.26	0.28	2.02
Bi <sub>209</sub>	0.01	0.01	0.01			
Th <sub>232</sub>	0.07	0.22	0.49	0.09	0.20	0.32
U <sub>238</sub>	0.01	0.02	0.06	0.02	0.04	0.06

Angluta	Aspen Well			Cabin Well		
Analyte	Median	IQR	Range	Median	IQR	Range
TIC	12.15	11.18	16.18	3.32	0.54	0.70
NPOC	4.89	1.69	20.26	0.67	2.99	3.06
SUVA	0.86	3.87	3.87	1.19	3.97	3.97
FI	1.51	0.07	0.07	1.30	0.36	0.36
TN	0.24	0.08	0.19	1.07	0.05	0.07
C:N	17.08	1.62	6.73	0.54	0.25	0.33
δD	-120.83	6.04	6.04	-117.02	0.32	0.32
δ¹®Ο	-16.18	1.50	1.50	-15.75	0.68	0.68
D-excess	8.61	5.96	5.96	8.98	5.12	5.12
F <sup>-</sup>	0.15	0.08	0.25	0.11	0.19	0.19
Cl⁻	0.74	0.35	1.18	0.97	0.26	0.49
NO <sub>3</sub> <sup>2-</sup>	0.20	0.40	0.78	4.45	1.15	2.06
SO4 <sup>2-</sup>	1.24	0.73	1.66	1.41	0.37	0.69
Li <sub>7</sub>	12.36	13.07	17.18	1.70	0.39	0.62
Be <sub>9</sub>	0.19	0.44	1.74	0.41	1.29	2.54
B <sub>11</sub>	10.80	7.05	13.07	14.03	8.49	12.45
Na <sub>23</sub>	6667.65	4548.66	6372.79	5189.50	934.40	3373.89
Mg <sub>24</sub>	2788.52	3004.64	3693.98	562.88	51.82	51.82
Mg <sub>25</sub>	2920.55	2496.76	4029.19	566.50	109.83	478.17
Al <sub>27</sub>	88.01	182.00	618.98	70.31	215.40	226.88
Si <sub>29</sub>	8289.00	1415.42	2934.26	10770.00	1470.86	2578.06
P <sub>31</sub>	298.84	266.18	428.93	317.79	288.10	288.10
S <sub>33</sub>	2714.00	4500.38	5690.10	2166.40	3691.20	3691.20
K <sub>39</sub>	1335.54	1247.74	2172.24	2226.08	641.02	759.84
Ca <sub>44</sub>	12290.26	9220.55	13291.65	1777.23	415.03	1925.64
<b>Sc</b> <sub>45</sub>	4.40	2.29	7.11	7.11	2.87	5.83
Ti <sub>47</sub>	7.80	6.96	16.79	10.35	12.65	25.77
V <sub>51</sub>	1.32	1.14	1.87	0.39	0.46	0.59
Cr <sub>52</sub>	1.24	1.36	2.40	1.54	2.41	2.47
Mn <sub>55</sub>	6.79	7.86	44.68	25.24	23.18	30.53
Fe <sub>57</sub>	334.17	261.45	483.99	323.26	327.63	345.26
Co <sub>59</sub>	0.13	0.07	0.80	0.32	0.35	1.20
Ni <sub>60</sub>	1.72	0.86	77.10	4.07	61.65	70.95
Cu <sub>65</sub>	2.35	13.23	199.83	102.10	60.56	223.79
Zn <sub>66</sub>	11.53	22.43	42.65	564.74	126.81	399.40
Ga <sub>69</sub>	4.96	6.49	12.09	2.48	2.93	4.74
Ge <sub>72</sub>	0.13	0.15	0.20	0.09	0.07	0.07
As <sub>75</sub>	1.37	1.26	6.56	1.18	3.88	9.09
Se <sub>82</sub>	5.65	3.17	37.51	6.93	18.83	39.31
Rb <sub>85</sub>	4.48	4.78	9.17	2.34	2.97	3.28

Sr <sub>88</sub>	96.00	62.17	110.55	11.54	1.38	12.17
Y <sub>89</sub>	0.16	0.35	1.21	0.07	0.08	0.17
Zr <sub>90</sub>	0.68	1.13	1.61	0.97	0.99	1.07
Nb <sub>93</sub>	1.65	4.06	5.92	1.94	5.58	6.47
M0 <sub>95</sub>	1.37	1.37	2.55	0.76	0.70	1.22
Ag <sub>107</sub>	0.05	0.06	0.75	0.11	0.53	0.63
Cd <sub>111</sub>	0.06	0.14	2.03	0.53	0.52	1.33
Sn <sub>182</sub>	1.03	1.02	2.88	0.58	0.79	1.29
Sb <sub>121</sub>	4.63	2.02	6.25	4.80	3.74	4.97
Te <sub>125</sub>	0.08	0.09	0.09	0.25	0.00	0.00
Cs <sub>133</sub>	0.17	0.23	0.42	0.05	0.06	0.08
Ba <sub>137</sub>	91.56	123.76	227.48	54.72	51.72	66.14
La <sub>139</sub>	0.09	0.11	0.23	0.06	0.08	0.26
Ce <sub>140</sub>	0.20	0.24	0.62	0.07	0.07	0.21
Pr <sub>141</sub>	0.03	0.06	0.28	0.01	0.03	0.03
Nd <sub>146</sub>	0.11	0.11	0.81	0.07	0.70	0.82
Sm <sub>147</sub>	0.10	0.12	1.44	0.07	0.16	0.41
Eu <sub>153</sub>	0.04	0.03	0.28	0.02	0.32	0.33
Gd <sub>157</sub>	0.05	0.08	0.13	0.07	0.36	0.43
Tb <sub>159</sub>	0.64	1.49	1.86	0.01	0.12	0.12
Dy <sub>163</sub>	0.03	0.07	0.40	0.03	0.04	0.08
Ho <sub>165</sub>	0.01	0.01	0.02	0.01	0.03	0.08
Er <sub>166</sub>	0.02	0.03	0.22	0.03	0.37	0.45
Tm <sub>169</sub>	0.00	0.01	0.06	0.02	0.06	0.10
Yb <sub>172</sub>	0.02	0.04	0.15	0.04	0.23	0.30
Lu <sub>175</sub>	0.01	0.01	0.02	0.01	0.06	0.08
TI <sub>205</sub>	0.34	0.53	6.58	0.95	2.20	3.24
Pb <sub>208</sub>	0.17	0.21	0.86	0.30	0.12	0.25
Bi <sub>209</sub>	0.00	0.01	0.01	0.01	0.00	0.00
Th <sub>232</sub>	0.10	0.40	1.25	0.05	0.64	0.72
U <sub>238</sub>	0.05	0.03	0.06	0.02	0.02	0.02
-	•					

Analuta	Drift Well			West Well		
Analyte	Median	IQR	Range	Median	IQR	Range
TIC	10.17	2.13	7.04	15.35	7.50	8.33
NPOC	0.63	0.34	16.59	6.97	1.21	1.77
SUVA	0.30	3.00	3.00	3.44	5.22	5.22
FI	1.13	0.59	0.59	1.33	0.13	0.13
TN	0.09	0.07	0.15	0.47	0.28	0.47
C:N	8.91	5.20	16.03	14.03	6.77	10.96
δD	-123.85	0.68	0.68	-121.15	5.07	5.07
δ'°0	-16.76	0.45	0.45	-16.20	0.98	0.98
D-excess	10.19	2.93	2.93	8.46	2.77	2.77
F	0.56	0.71	1.69	0.18	0.11	0.19
Cl	1.11	0.99	1.53	1.09	0.99	2.99
NO <sub>3</sub> <sup>2-</sup>	1.26	3.09	3.09	0.80	1.71	2.54
SO4 <sup>2-</sup>	24.44	17.03	36.40	2.42	2.06	3.97
Li <sub>7</sub>	10.91	3.28	5.83	6.43	1.77	3.23
Be <sub>9</sub>	0.24	1.48	2.51	0.30	1.15	2.44
B <sub>11</sub>	8.13	4.16	6.92	22.10	12.09	15.48
Na <sub>23</sub>	12847.59	2744.49	15079.44	8112.00	3661.09	12036.58
Mg <sub>24</sub>	1849.01	149.97	258.88	1770.25	956.38	956.38
Mg <sub>25</sub>	1950.47	416.66	2342.33	2095.00	987.83	3095.43
Al <sub>27</sub>	71.19	184.61	231.39	293.31	287.50	397.94
Si <sub>29</sub>	13540.00	2225.06	6778.90	8660.00	1581.55	4239.72
P <sub>31</sub>	249.32	146.51	181.65	298.42	94.72	94.72
S <sub>33</sub>	883.00	1075.10	1075.10			
K <sub>39</sub>	2722.63	499.72	2499.85	4492.97	3479.59	6327.53
Ca <sub>44</sub>	13599.08	3398.88	22407.51	12876.19	3560.17	21481.13
<b>SC</b> 45	6.80	1.79	11.18	5.21	2.44	8.07
Ti <sub>47</sub>	6.73	7.28	21.46	26.89	25.33	114.59
V <sub>51</sub>	0.43	0.61	1.13	1.46	0.50	3.36
Cr <sub>52</sub>	2.15	2.19	4.31	1.73	1.71	2.62
Mn <sub>55</sub>	29.81	19.91	167.67	3.30	2.97	6.35
Fe <sub>57</sub>	217.60	252.97	430.52	458.46	367.21	486.64
Co <sub>59</sub>	0.79	0.52	1.58	0.16	0.11	0.90
Ni <sub>60</sub>	3.07	2.49	108.17	2.48	44.07	74.98
Cu <sub>65</sub>	1.59	2.01	271.55	10.35	127.86	249.67
Zn <sub>66</sub>	27.16	36.84	63.81	14.61	17.89	23.84
Ga <sub>69</sub>	2.67	3.23	5.00	14.00	7.61	8.26
Ge <sub>72</sub>	0.13	0.20	0.20	0.14	0.00	0.00
As <sub>75</sub>	1.40	2.56	9.80	1.89	2.46	12.29
Se <sub>82</sub>	5.86	4.64	35.14	8.33	80.44	108.92
Rb <sub>85</sub>	6.00	1.70	9.61	12.20	8.70	15.28

Sr <sub>88</sub>	82.49	16.20	106.15	82.29	24.32	107.29
Y <sub>89</sub>	0.05	0.06	1.46	0.60	0.77	2.37
Zr <sub>90</sub>	0.42	0.80	5.40	1.39	1.70	2.91
Nb <sub>93</sub>	2.34	2.56	3.42	2.18	4.23	6.62
Mo <sub>95</sub>	0.87	0.82	9.69	1.12	0.49	3.33
Ag <sub>107</sub>	0.03	0.10	0.94	0.09	1.70	1.76
Cd <sub>111</sub>	0.10	0.20	1.72	0.23	1.53	1.78
Sn <sub>182</sub>	1.56	2.37	10.96	1.73	3.28	5.75
Sb <sub>121</sub>	8.05	9.89	17.47	9.51	7.66	9.12
Te <sub>125</sub>	0.16	0.00	0.00			
Cs <sub>133</sub>	0.18	0.12	0.25	0.30	0.19	0.20
Ba <sub>137</sub>	59.81	56.83	94.22	266.60	312.81	437.72
La <sub>139</sub>	0.01	0.04	0.23	0.32	0.52	0.77
Ce <sub>140</sub>	0.05	0.09	0.22	0.62	0.86	1.29
Pr <sub>141</sub>	0.01	0.02	0.23	0.09	0.13	0.43
Nd <sub>146</sub>	0.04	0.07	0.59	0.45	0.51	1.30
Sm <sub>147</sub>	0.09	0.49	0.93	0.18	0.64	1.19
Eu <sub>153</sub>	0.03	0.01	0.36	0.08	0.16	0.51
Gd157	0.02	0.04	0.88	0.14	0.83	0.95
Tb <sub>159</sub>	0.01	0.08	0.14	0.05	3.79	5.67
Dy <sub>163</sub>	0.02	0.04	0.51	0.14	0.09	0.58
Ho <sub>165</sub>	0.01	0.06	0.12	0.02	0.11	0.16
Er <sub>166</sub>	0.01	0.01	0.29	0.08	0.40	0.54
Tm <sub>169</sub>	0.01	0.04	0.12	0.01	0.20	0.23
Yb <sub>172</sub>	0.02	0.03	0.41	0.05	0.05	0.06
Lu <sub>175</sub>	0.01	0.04	0.13	0.01	0.10	0.24
TI <sub>205</sub>	0.16	0.27	17.27	0.42	8.92	16.52
Pb <sub>208</sub>	0.11	0.28	1.52	0.28	0.28	0.48
Bi <sub>209</sub>	0.01	0.01	0.01	0.01	0.00	0.00
Th <sub>232</sub>	0.09	0.28	3.93	0.34	0.76	3.61
U <sub>238</sub>	0.01	0.01	0.04	0.13	0.05	0.08

Applyto	Stream at Bog			Stream at Weir		
Analyte	Median	IQR	Range	Median	IQR	Range
TIC	2.89	0.74	1.59	2.69	2.70	5.40
NPOC	1.87	2.51	4.23	3.11	7.32	13.92
SUVA	4.56	4.81	5.47	5.72	4.09	5.19
FI	1.41	0.34	0.44	1.45	0.15	0.60
TN	0.67	0.13	0.13	0.24	0.12	0.82
C:N	2.41	1.23	1.23	12.31	5.69	24.58
δD	-119.98	1.51	1.51	-121.37	7.22	16.35
δ'°O	-16.09	0.76	0.76	-16.13	0.89	2.72
D-excess	8.75	4.57	4.57	7.62	2./1	8.57
F.	0.03	0.15	0.18	0.06	0.04	0.15
Cl⁻	0.73	0.32	0.45	0.52	0.29	2.15
NO <sub>3</sub> <sup>2-</sup>	2.22	0.58	1.51	0.20	0.25	0.75
SO4 <sup>2-</sup>	1.07	0.28	1.30	0.70	0.41	0.77
Li <sub>7</sub>	1.29	0.41	3.50	1.25	0.31	1.16
Be <sub>9</sub>	0.08	0.54	2.86	0.20	0.54	3.61
B <sub>11</sub>	14.78	7.38	16.69	14.38	4.20	14.19
Na <sub>23</sub>	3967.00	882.21	4098.63	3634.56	1409.07	3476.34
Mg <sub>24</sub>	379.66	118.53	131.20	502.84	306.66	386.37
Mg <sub>25</sub>	348.42	115.41	437.66	566.05	695.78	1608.99
Al <sub>27</sub>	203.10	133.37	301.11	275.52	146.88	507.23
Si <sub>29</sub>	8235.24	1364.66	3076.06	9535.50	1975.83	4203.11
P <sub>31</sub>	236.35	238.33	360.92	481.57	525.00	640.38
S <sub>33</sub>	479.90	2830.70	2830.70	257.05	302.30	302.30
K <sub>39</sub>	1997.02	723.57	1593.10	1835.54	912.60	5161.40
Ca <sub>44</sub>	1246.63	409.85	1646.30	1940.90	1751.54	4312.81
SC45	4.54	1.75	5.40	4.73	1.65	3.83
Ti <sub>47</sub>	11.56	8.34	18.67	12.03	8.10	33.82
V <sub>51</sub>	0.44	0.42	1.00	1.24	0.55	1.44
Cr <sub>52</sub>	1.36	3.02	3.83	1.32	1.97	4.22
Mn <sub>55</sub>	4.37	4.28	11.16	4.25	6.24	30.27
Fe <sub>57</sub>	137.30	243.22	303.18	244.30	200.41	377.50
Co <sub>59</sub>	0.11	0.18	0.79	0.19	0.24	1.00
Ni <sub>60</sub>	0.62	1.14	58.30	0.76	35.90	94.26
Cu <sub>65</sub>	1.30	1.45	223.90	1.47	97.70	288.83
Zn <sub>66</sub>	36.45	37.01	91.64	24.78	19.52	433.73
Ga <sub>69</sub>	4.61	3.27	6.18	2.85	3.63	4.72
Ge <sub>72</sub>	0.14	0.17	0.17	0.42	0.10	0.15
As <sub>75</sub>	1.32	2.57	8.81	1.75	2.10	8.95
Se <sub>82</sub>	3.32	3.97	48.05	5.99	17.11	85.82
Rb <sub>85</sub>	3.20	0.98	5.24	3.23	4.56	7.39

Sr <sub>88</sub>	10.33	3.01	12.58	16.70	17.37	42.61
Y <sub>89</sub>	0.58	0.40	1.28	0.57	0.14	5.92
Zr <sub>90</sub>	0.59	0.56	1.01	0.70	0.13	0.78
Nb <sub>93</sub>	1.93	4.30	8.76	2.14	3.37	6.40
Mo <sub>95</sub>	0.25	0.93	4.08	0.43	0.53	6.33
Ag <sub>107</sub>	0.04	0.13	1.37	0.03	0.27	1.47
Cd <sub>111</sub>	0.12	0.25	0.88	0.13	0.24	2.08
Sn <sub>182</sub>	0.16	0.86	2.95	0.55	0.85	3.02
Sb <sub>121</sub>	1.36	0.75	2.26	2.37	1.05	3.05
Te <sub>125</sub>	0.05	0.00	0.00	0.14	0.22	0.29
Cs <sub>133</sub>	0.06	0.06	0.09	0.06	0.02	0.06
Ba <sub>137</sub>	86.94	59.09	75.55	37.89	79.46	93.46
La <sub>139</sub>	0.19	0.12	0.51	0.27	0.10	0.45
Ce <sub>140</sub>	0.32	0.26	0.47	0.45	0.29	0.92
Pr <sub>141</sub>	0.07	0.05	0.27	0.07	0.05	0.34
Nd <sub>146</sub>	0.34	0.20	1.71	0.43	0.31	1.64
Sm <sub>147</sub>	0.16	0.12	0.99	0.13	0.23	0.88
Eu <sub>153</sub>	0.03	0.07	0.49	0.04	0.06	0.22
Gd157	0.14	0.12	0.79	0.14	0.17	0.97
Tb <sub>159</sub>	3.43	7.84	8.62	0.10	6.80	10.29
Dy <sub>163</sub>	0.14	0.09	0.70	0.12	0.03	0.48
Ho <sub>165</sub>	0.03	0.07	0.13	0.02	0.02	0.23
Er <sub>166</sub>	0.10	0.12	0.24	0.11	0.11	0.46
Tm <sub>169</sub>	0.01	0.07	0.23	0.01	0.03	0.17
Yb <sub>172</sub>	0.10	0.06	0.57	0.07	0.05	0.46
Lu <sub>175</sub>	0.02	0.04	0.23	0.01	0.02	0.11
TI <sub>205</sub>	0.08	0.59	1.44	0.12	0.33	0.83
Pb <sub>208</sub>	0.15	0.19	0.50	0.15	0.10	0.37
Bi <sub>209</sub>	0.01	0.00	0.00	0.01	0.01	0.02
Th <sub>232</sub>	0.08	0.32	0.88	0.10	0.13	0.40
U <sub>238</sub>	0.02	0.01	0.08	0.03	0.02	0.03

# 4.2. Lysimeter Bottle Setup and Installation

# 4.2.1. Vacuum Bottles

- 1. See spreadsheet (4.2.4) for necessary supplies, and check against current inventory.
- 2. Wash all bottles, lids, tubing, adapters, and connectors thoroughly Milli-Q water (<18

M $\Omega$  conductivity, Millipore filtration system) See protocol below.

## Bottle-washing protocols for Lysimeters

# **Bottles**

- 1. Remove lid from bottle and place in Ziploc bag for storage.
- 2. Rinse bottle with ~100 mL Millipore water five (5) times
- 3. Fill bottle with Millipore water and allow to leach for a minimum of 24 hrs.
- 4. Rinse bottle with  $\sim 100$  mL Millipore water five (5) times
- 5. Dry bottles upside-down and bag until needed

Venting Caps/Lids

- 1. Rinse with Millipore water five (5) times
- 2. Place in washtub (NEVER used for acid rinse--I will label them) full of Millipore water, allow to leach for a minimum of **24** hrs.
- 3. Rinse with Millipore water five (5) times
- 4. Dry under KimWipes, bag until needed

Small parts of Venting Caps, Stopcocks, etc.

- 1. Place in clean bottle (see above) of Millipore water, allow to leach for at least 24 hrs.
- 2. Dry under KimWipes and bag.

Tubing/Hoses: Prime with Millipore water in field

3. Set up work space: Clean work surface, wipe cutting board and X-acto knife with isopropyl, plug in heat gun, prep silicone sealant, don gloves.

isopropyi, plug in neat gun, prep sincone sealant, don gloves.

4. Cut tubing. Each lid needs: 9mm OD antistatic tubing, 1 30cm and 1 10cm length; 5mm

OD Tygon tubing, 1 10cm length; stiff 8mm OD tubing. For each lysimeter: 10cm Tygon

tubing.

5. Lid assembly: for each ported lid, in addition to tubing: 1 6mm to 3mm ID tubing adapter, 1 pinch-clamp flow regulator, 1 stopcock, 1 port cover.

- 6. Heat one end of the 10cm length of antistatic tubing until it can slide over one of the long ports on the ported lid. Make sure not to heat it too long, or it will melt.
- 7. Heat the other end of the 10cm antistatic tubing, and insert the large side of the adapter.
- 8. Heat one end of the Tygon tubing, and slide over the small side of the adapter.
- 9. Heat one end of the 30cm length of antistatic tubing, and insert the unthreaded end of the stopcock.
- 10. Slide pinch clamp onto 30cm antistatic tubing.
- 11. Heat other end of 30cm antistatic tubing, slide over other long port of lid.
- 12. Apply silicone sealant inside port cover, and place port cover over short (untoothed) port in lid.

#### 4.2.2. Lysimeters

- 1. Wearing clean gloves, slightly loosen nut on top of lysimeter
- 2. Place lysimeters in bucket of Millipore water.
- 3. Slide Tygon tubing over end of lysimeter line.
- 4. Fill 60cc syringe with Millipore water, and attach to Tygon tubing.
- Push Millipore water through lysimeter line until no more air bubbles emerge from lysimeter. This may require refilling the syringe.
- 6. Fold and clamp Tygon tube.
- Tighten nut on lysimeter, and place in sealed container with additional Millipore water (gallon Ziploc bags work well), approximately 100mL.

#### 4.2.2.1. Additional prep

 Cut stiff tubing into 10cm lengths to cover junction of lysimter line and Tygon tubing at bottles.

- 2. Cut extra 10cm lengths of Tygon tape for joining lysimeter lines, and extra 15cm lengths of stiff tubing to protect these junctions.
- Prep whatever material you will be using as an outer casing for the lysimeter lines.
  Suggestions: split electrical conduit, PVC conduit (easier to use than plumbing pipe).

## 4.2.2.2. Silica Slurry

- 1. If the soil is sufficiently wet or clayey, you may not need Si slurry.
- 2. If it is not, weigh out two bags of silica powder in the lab for each lysimeter (and some extras).
  - a. 30g, bag should be large enough to completely enclose the lysimeter (quart size)
  - b. 200g in another bag, gallon-sized
- 3. Carry at least 500mL of Milli-Q water for each lysimeter to be installed

### 4.2.3. Preparation of soil pit

- 1. Dig a soil pit large enough to work in while installing your lysimeters (you will need room for inserting a pipe into the pit wall at a 45-degree angle).
  - a. Save the tailings on a tarp or plastic bag, sorting by horizon where possible
  - b. Make note of any clay-rich horizons for use as packing material
- If you are describing the soil pit, I recommend you take photos and samples and finish your description before installing anything. Soil colors change as they dry, and it's also easier to not work around your tubing and wiring.
- Follow the protocol on the next page (modified from Lohse lab protocol) to install the lysimeters.

# 4.2.4. Prenart Lysimeter Installation Protocol

# Lysimeter components:

Prenart lysimeter, pre-loaded with Milli-Q, with 1.5 m PTFE tubing

in gallon-sized Ziploc bag, with Tygon tubing/Teflon cap

Lysimeter Si flour loading Ziploc bag, quart sized (30 g Si)

Slurry Si flour Ziploc bag, gallon sized (200 g Si)

Lysimeter vacuum bottle assembly in 1 gallon Ziploc bag

DI H<sub>2</sub>O, 250 mL

100 mL graduated cylinder

# General field equipment:

Field book

Pencil/pen/sharpie

Tape measure (metric)

Pin flagging

Flashlight

# **Coring equipment:**

3/4" step probe corer or 1" metal pipe

2" Soil auger with protractor

Soil drill bit

Protractor

Soil PVC packing rod

2" PVC sleeve

3/4" PVC tube for Lysimeter installation (AKA loading rod)

Field gloves

2 mm soil sieve

Garbage bags or tarp for holding soil

Shovel for digging soil pit if needed

DI H<sub>2</sub>O, 1 L, for rinsing

Nitrile gloves

Sharpies

Clean Knife

Calculator

# Lysimeter/bottle installation equipment:

Field vacuum bottle assembly

Nitrile gloves

Clean utility knife for cutting PTFE tubing

Teflon tape

DI H<sub>2</sub>O, 0.5 L per lysimeter

Hand pumps

Field table

## Step 1: Site Selection/Coring

## **Checklist:**

3/4" step probe corer or 1" metal pipe

2" soil auger

Protractor

Soil drill bit

Field gloves

Garbage bags or tarp for holding soil (tarps work better)

Shovel for digging soil pit if needed

Nitrile gloves (1 pair per person per pit, plus one or two spare pairs)

Clean knife (Utility or X-Acto knives work best)

Field book

Site map for locating installation locations

Pencil/pen/sharpie

Tape measure/meter stick (metric)

Pin Flagging

Calculator

Flashlight

## **General Protocol:**

- Always stay outside the area upslope of the plots unless you need to work in it. Minimize trampling or cutting through this area.
- 1. General tasks to be assigned:
  - a. Corer

- b. Note taker and soil tailing sorter
- Lysimeter installation location will differ slightly depending on site. Lysimeters should ideally all be installed in the uphill face of the soil pit, to minimize the impact of disturbed soil on flowpaths sampled.
- 3. Record information in fieldbook including:

Date & time Site name and number Precipitation, vegetation, and soil depth Position in plot (e.g. SW corner, etc.) Field technician initials

- 4. Place garbage bag or tarp next to digging site to collect soil tailings. Dig pit if necessary, and describe. Make sure to collect soil tailings and place on garbage bag in approximate order of profile horizons. Make sure to keep any surface leaf litter or bunny droppings out of the soil tailings and out of the drill hole.
- 5. Have one person dig up clayey soil from off plot using the large soil auger or a shovel to be used for capping the lysimeter. Collect enough to use for several lysimeter installations and place in Ziploc bag. If necessary, bentonite may be used. (Or use clay from the soil pit.)
- 6. Calculate starting depth for auger hole in pit wall. Calculate again when you know how deep you augered, where you actually started, and the actual angle of the auger hole

Starting depth = desired depth - 
$$\left(\frac{cosine(45)}{Length \ of \ auger - 9cm}\right)$$

Ex: for a 40 cm installation depth, augered at a 45 degree angle, you will want to drill to a length of 47.5 cm (i.e. <u>56.5 - 9.0 cm)</u>.

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- a. The length of the auger will vary, the 9cm accounts for an additional core from the end to accommodate the lysimeter itself. Mark the length of auger you want to use on the auger itself with tape.
- b. Insert the step corer into the PVC pipe, and mark on the handle of the corer where it hits the pipe when 9cm of corer are sticking out the opposite side.
- 7. If installing in wall of pit:
  - a. Determine depth at which you wish to install the lysimeter.
  - b. Place auger at an angle of 45 degrees from the wall ABOVE the auger, and core until you reach the depth needed to place the lysimeter at your desired depth.
- 8. If installing lysimeter from surface:
  - a. Place 2" auger just behind pin flag location perpendicular to soil surface and proceed with augering to approximately 10 cm.
  - b. Next, lower soil auger to a 45 degree angle and proceed with coring until you reach the depth mark on the auger handle (mark with tape). When lowering auger, be careful not to lever the soil up next to hole -- try to disturb the surface soil as little as possible.
- 9. If the hole deviates from 45 degrees or is otherwise not a perfect hole to the specified depth, note the deviation in fieldbook. Double check hole depth with measuring tape or meter stick and record precise depth in fieldbook .

If you did not core at a 45-degree angle, or the drill hole length is incorrect, you will need to recalculate the actual depth of installation.

10. Again make sure the hole is clean (no organic material at bottom), carefully slide the 2"PVC sleeve into the hole to the desired depth.

- 11. Using the soil kick probe or 1" metal pipe, center the tip at the bottom of the hole (you may need a flashlight to see) and pound probe into soil maintaining the 45 degree angle for 9 cm (you should have this point marked on the handle of the probe). Record the total length of the hole and use this in your depth calculation.
- 12. Remove probe and place soil in probe in quart Ziploc bag for archiving. Label bag using a sharpie with plot #, date, and your initials. This concludes the coring protocol -- see slurry preparation protocol next.

## Step 2: Slurry Installation

## Checklist:

Prenart lysimeter, pre-loaded, with 1.5 m PTFE tubing in quart sized Ziploc bag, Tygon

tubing/Teflon cap

Lysimeter Si flour loading Ziploc bag, quart sized (30 g Si)

Slurry Si flour Ziploc bag, gallon sized (200 g Si)

Lysimeter vacuum bottle assembly in 1 gallon Ziploc bag

Hand pump

DI H<sub>2</sub>O, 1 L for rinsing

100 mL for slurry

100 mL graduated cylinder

Nitrile gloves

Clean utility knife for cutting PTFE tubing

Teflon tape

Field book

Pencil/pen/sharpie

Tape measure (metric)

Flashlight

2" PVC sleeve

3/4" PVC tube for Lysimeter installation

Garbage bag with soil tailings

Shovel for filling soil core/pit

Field table (for pulling tension on lysimeters with)

Field vacuum bottle assembly (for pulling tension on lysimeters, see image below)

Squirt bottle

Toilet brush (for cleaning soil sleeve)

### **General Protocol:**

- All the lysimeter preparation should be done outside the plot (e.g. field table or tailgate).
- Do not draw water into pump -- pump will cease to function.
- 1. Make sure field vacuum bottle assembly is prepared and ready on field table. This includes attaching the hand pump to the long PTFE tubing.
- 2. Wearing gloves, and avoiding touching the lysimeter itself, pull out lysimeter line with protective Tygon tubing and Teflon at end. Each lysimeter with PTFE line should be in its own Ziploc.
- Attach Tygon tubing end of lysimeter to short PTFE tubing on vacuum bottle assembly, make sure stopcock and pinch clamp are closed.
- 4. The lysimeter should be in approximately 100 mL of water in the Ziploc bag -- add 30 g of silica flour to the lysimeter bag and mix into a milky slurry. This introduces the slurry into the lysimeter pores.

Note: **do not make slurry for drill hole at this time.** The slurry, if let sitting, will harden, so do not mix silica flour with water until slurry is needed.

- 5. After the lysimeter slurry is mixed and the lysimeter is attached to the vacuum bottle assembly, pull vacuum (60 kPa) to introduce the milky slurry to the lysimeter. Record lysimeter #, vacuum pressure and start time in fieldbook.
- 6. Work the slurry into the lysimeter gently with your hands, through the plastic bag.

- 7. Let this sit for 10 minutes. Check periodically to make sure lysimeter is pulling vacuum and no water has been introduced into the hand pump line.
- 8. After 10 minutes, record end vacuum pressure and time, and denote "OK" in fieldbook as evidence that water is being pulled through lysimeter line (see example at end of protocol). Then make sure hand pump stopcock is still closed and open center stopcock to release pressure from bottle. Disconnect the lysimeter Tygon and PTFE tubing (KEEP IT CLEAN!). Cover the end of the lysimeter line with a Tygon/Teflon tape cap. Empty vacuum bottle.
- At this point you or your field assistant should start preparing the hole slurry by pouring 100 mL of DI H<sub>2</sub>O (use graduated cylinder) into a Ziploc bag with 200 g of silica flour.
- 10. Mix slurry for 5-7 minutes with hands outside bag. You may feel it starting to get more viscous.
- 11. Prepare the lysimeter for loading by feeding the lysimeter line through the 3/4" PVC loading pole. Make sure to keep the lysimeter protected in the Ziploc bag and the PTFE tubing clean using the Tygon tubing and Teflon tape.
- 12. Pour slurry down clean 2" PVC sleeve and immediately install lysimeter into slurry.
- 13. Holding the lysimeter line that is feeding out of the back of the PVC pole to keep the lysimeter stable, load the lysimeter into the cored hole by embedding it into the slurry until it reaches the bottom of the hole. You will know you reached the appropriate insertion depth by the marked line or tape on the loading pole (and also probably the resistance of the soil at the bottom of the hole).

- 14. Once lysimeter is in place, extract the PVC sleeve using a twisting motion (be gentle) while holding lysimeter in place with <sup>3</sup>/<sub>4</sub>" loading PVC. If you wait more than a couple minutes, the slurry will pull out with the sleeve.
- 15. Hold the lysimeter in place for 2 minutes while the slurry solidifies further.
- 16. Wash the sleeve off with DI H<sub>2</sub>O immediately after finishing installation so that soil/slurry does not have time to setup and dry on PVC (outside and inside of sleeve must be well cleaned, do the rinsing away from plots).
- 17. Remove the lysimeter loading pole from the hole. Again, the tip of the pole will be in the slurry so use a gentle twisting motion. Note: make sure that as you withdraw the pole, the PTFE tubing is feeding through the pole and leaving the lysimeter in place (i.e. not dragging it out with the lysimeter pole).

# Step 3: Lysimeter Bottle Installation and Backfilling

# **Checklist:**

Tubing conduit

Protective plastic box for bottles

Nitrile gloves

Teflon Tape

DI H2O, 1 L

Hand pump

Field table

Field book

Pencil/pen/sharpie

Watch

Flashlight

Clean utility knife for cutting PTFE tubing

Soil PVC packing rod

Field gloves

Garbage bag with soil tailings

2 mm soil sieve

Shovel for filling soil pit

Duct tape or zip ties to hold box closed

# **Backfilling General protocol:**

• Wear nitrile gloves when working with clay and make sure not to incorporate any surface material into the clay.

- Use the clayey soil from the ~40 cm depth harvested from off plot OR from a clay layer in your soil pit
- 1. Ball up clay into small balls and send down the drill hole. Balling the clay minimizes the amount of surface soil scraped off and transported to the bottom of the hole.
- Tap the clay into a cap over the hardened silica slurry using dowel or PVC pipe. In some cases the clay will mix with the upper surface of the silica flour -- this is OK and you should continue to place clay balls on slurry surface.
- 3. Add a second set of clay balls to cap and pack again.
- 4. When you have a compact clay cap on the lysimeter, refill the hole with the soil removed -- make sure to replace the soil in the order it was removed (i.e. surface soil should end up back on the surface). Use soil from off plot to backfill if you run out. Use the PVC packing rod or wooden dowel to consolidate the soil every few inches as you backfill (ideally to approximately the same bulk density).
- 5. Make sure that the refilled soil is flush with the soil surface or slightly mounded to prevent ponding.

#### Lysimeter bottle installation General Protocol:

- The person working with lysimeter and PTFE line needs to wear Nitrile gloves.
- 1. Dig a small ditch to run the lysimeter lines from the pit to the location of your instrument box.
- 2. Run lysimeter line through whatever protective conduit you are using until you reach the end of the ditch, and run conduit into the box. Label the line with a metal tag and record the number in your field notebook.

- Remove Tygon tubing cover on end of Lysimeter PTFE tubing. If PTFE tip is damaged, rough, or dirty, use a clean utility knife to remove tip of PTFE tubing, cutting at an angle. Make sure vacuum bottle top is screwed on tightly and that the vacuum and lysimeter lines on bottle are clean.
- Place ¼" PTFE sleeve over 1/8" PTFE tubing. This will help prevent the Tygon tubing from crimping.
- 5. Insert lysimeter PTFE tubing into Tygon tubing on vacuum bottle after removing small clamp. Insert PTFE tubing into Tygon tubing until it reaches the coupler. Remember to put PTFE tubing through hole in plastic box before attaching it to the vacuum bottle. Wrap end of Tygon tubing with Teflon tape (see figure).
- 6. Attach hand pump to vacuum bottle line and pull 60 kPa of vacuum. Close large white clamp on vacuum line (must be clamped down all the way to hold vacuum) and then close hand pump stopcock.
- Detach hand pump and then cover the end of the vacuum line with quart Ziploc bag or Teflon tape to keep it clean (may need to use rubber bands to secure bag).
- Insert foam into gap for conduit to pass into plastic box to minimize dust and critters getting in, or seal with silicone sealant.
- Attach lid to box and place heavy object or rock on lid to secure it (may also need duct tape). It may be advisable to remove bottles when not in use, if weather is cold.

#### 4.2.4.1. Additional notes on installation of conduit

 After lysimeter is installed, determine if additional lysimeter line is needed. If not, thread it through the casing to the storage box. Make sure to keep the end of the lysimeter line covered with Tygon during this process!

- 2. If it is, determine if you can attach the line partway through the casing process (e.g., your casing material is in lengths short enough to thread part of the tubing through before needing more).
  - a. If so, thread the tube through the casing until you need to attach more, then see step 3.
  - b. If not, move immediately to step 3.
- Connect the ends of the lines with Tygon tubing. If space in outer casing material permits, wrap junction in Teflon tape, cover with length of stiff tubing (held in place with duct tape).
- 4. Write the lysimeter depth on a piece of label tape on the end of the tubing (or use colors to distinguish different depths).
- At storage box, attach a label tag to the lysimeter line with the number you are assigning to it and record what depth it was installed at. Slide a length of stiff tubing over the line. Replace Tygon cap.
- 6. To attach a vacuum bottle, remove the Tygon cap from the lysimeter line, slide the end of the line into the Tygon on the bottle, and slide the stiff tubing over this junction. Remove vacuum bottles when not sampling.

#### 4.2.5. Installing prong-style soil moisture probes and disk-style matric

#### potential probes

- 1. Select depth of installation (should be same as lysimeter depth)
- 2. Using a table knife or putty knife, excavate a small slot in the wall of the pit approximately 50% larger than the probe prongs or disks. The slot should be deep enough to install the entire probe flush with the wall of the pit, and wide enough at the near end to accommodate the rubber housing of the probe.

- Make mud from a clay layer in the pit, and cover the probe prongs or disks generously with it.
- 4. Insert the probe into the wall of the pit. The mud should ensure good contact with the soil.
- 5. Run the probe wire through conduit to the instrument box. If possible, install conduit close enough to rubber housing to ensure no wire is exposed. Label the plug end of the wire, and record its number and depth in your field book.
- 6. Backfill the hole around the rubber housing with mud, and pack it well

### 4.2.6. Backfilling the soil pit

- 1. Try, as much as possible, to return soil to the pit in the opposite order to how it was removed (that is, match the horizons).
- 2. It is usually best to fill the upslope side of the pit first. This also allows you to be more careful in packing the soil around your conduit.
- 3. You will probably have to tamp the soil down a little to support the conduit where it comes out of the pit wall, but try to avoid over-compacting the soil in the rest of the pit. Where possible, try to backfill to the same bulk density as the soil was originally.
- 4. Don't forget to fill in the ditch you ran the conduit through to your instrument box!

#### 4.2.7. Helpful hints

- If possible, use two sizes of conduit: one smaller, flexible size to cover the individual wires (or groups of wires and lysimeter lines coming from the same depth) in the pit, and a larger one (that will accommodate all the wires/lines, make sure to account for the size of the plugs on the wires) to run from the pit to the instrument box.
- 2. Shovels are not usually sufficient to dig soil pits. Bring a pick.
- 3. Your hands will get very muddy doing this. Bring a towel to wipe them on.
- 4. Consider using a wheeled caddy if terrain allows. There's a lot of stuff to haul.
- 5. Waterproof your instrument box if you can.
- 6. If possible, site the instrument box so that it is not significantly lower in elevation than the soil pit. Otherwise you may get water running down the conduit into the box.
- 7. Protect the datalogger INSIDE the box, too. Keep it in a Ziploc bag.
- Cold weather causes the tubing on the lysimeter bottles to shrink and break the seals.
  Remove the bottles in winter and install them only when actively sampling.

	Piece	For One Setup	Supplier	Item No.	Number/ Amount per Unit
Bottles	807 Nalgene heavy-duty vacuum hottle	1	Nalgene/US Plastics	69035	1
	Filling/venting closure with 3 ports for 1/4id tube	1	Nalgene/US Plastics	77111	1
	Antistatic White Polyurethane Tubing, 6 Mm Id, 9 Mm Od (Pumpline) (cm)	10	McMasterCarr	<u>5790K64</u>	1
	PTFE tubing, 6 Mm Id, 8 Mm Od, 1 Mm Wall, Semi-clear White (cm)		McMasterCarr	<u>52335K36</u>	1
	Laboratory Clear Tygon Pvc Tubing, 3 Mm Id, 5 Mm Od (cm)	10	McMasterCarr	<u>52335K53</u>	1
	Stopcocks	2	ColeParmer	30600 00	10
	Lysimeter Line (cm)	100	Free w/ lysimeters!		3-30 ft
Lysimeters	Soil Water Sampler	1	Prenart DK	NONE	1
	Silica flour				230 g
Installation	Conduit for protecting PTFE tubing	70	Grainger, 3/8"	<u>1YPF7</u>	100
	Zip ties for securing conduit in vacuum boxes	3	Grainger, 8"	<u>3XAT5</u>	100
	Ziploc sandwich bags for covering stopcocks	3	Grainger	<u>32GM81</u>	500
	Ziploc bags, 1 gal for holding wires	1	Grainger	<u>32GM82</u>	250
	Syringe, Sterile, Centered Tip, Capacity: 20mL	1	Fisher	22034507	100
	Vacuum bottle box	1			
Tools	Teflon tape		Grainger, 1/2", 520in	<u>31XH96</u>	1
	Trash bags for soil tailings (box)	_	Grainger	<u>2RRC7</u>	250
	Pin flags	_	Grainger	<u>3LUH4</u>	100
	Nitrile gloves large (box)	_	Grainger	<u>1RL58</u>	100
	Nitrile gloves medium (box)		Grainger	<u>1RL57</u>	100
	Duct tape for bottle racks		Grainger, 60yd	<u>3KHH7</u>	1
	Tarp		Grainger	<u>2ZJ45</u>	1

4.2.8. Spreadsheet: Supplies for Lysimeter Setups

### 4.3. Sampling, Sample Processing, and Sample Analysis Protocol

Everything you do will require a field notebook, a Sharpie, and a rubber mallet!

# 4.3.1. Digging and describing the soil pit, collecting soil samples

## **Equipment needed:**

Shovel and pick, and someone to help

Several tarps to put soil tailings on

Tape measure and pins

Bulk-density cores, wooden board, and rubber mallet

Ziploc bags—quart and gallon sizes

Saran wrap and rubber bands

Soil knife and towel

GPS and camera

Munsell color book and field data sheet (see end of appendix)

Buckets

Field notebook and Sharpie

### **Protocol:**

- Remove the sod or duff from an area approximately 1x2m, and set carefully aside on the far edge of a tarp.
- 2. Dig. Try to keep soil horizons together as much as possible. Do not pile soil uphill of the pit. It's usually a good idea to pile from the outside of the tarp in.
  - a. When you're fairly deep in the hole, it is helpful to scoop soil into a bucket and hand it to your assistant to dump.
  - b. Dig until you can dig no further. This is "refusal". (Refusal of the soil to yield, not refusal of you to dig any more.) Use the pick to get as far as you can.

- 3. Describe the soil pit. Use the Munsell book and the field data sheet (see section 4.3.6). If you are unfamiliar with soil pit description, find a soil scientist to help.
- 4. Sample spacing may be every 10cm or every horizon
  - a. Bulk soil: Collect approximately 1L of bulk soil in a Ziploc bag.
    - i. Note proportion of large coarse fragments (>5cm in diameter), but do not include in sample if possible.
    - ii. Label with depth/horizon, site, date, and initials.
  - b. Bulk density: Clear a shelf of soil at the top of the sampling depth.
    - i. Place the core onto this shelf, put the wooden board over the top, and drive the core in with the mallet.
    - ii. Carefully dig the core out of the soil with the soil knife, and slice underneath it.
    - iii. Wrap the core in saran wrap and secure with rubber bands. Place in quartZiploc, label with depth/horizon, site, date, and initials.

#### 4.3.2. Soil Sample Processing and Testing

- Homogenize soil in bag by hand-mixing, and split into two samples. Retain one sample in bag for archiving or additional tests.
- 2) Remove approximately 100g of wet sample and save, wet, for pH testing.
- 3) Dry remainder of second sample at 50°C for 24 hours.
- Sieve sample through a 1-cm mesh sieve, and save coarse and fine fractions in separate bags. Weigh them to calculate percent coarse fraction.
- 5) pH testing: Lohse lab
  - a. Weigh 10g of soil into a beaker.
  - b. Add 10g of water and mix. Let stand at least 10 minutes. (It is best to do all the samples at once, then measure the first one.)

- c. Insert pH probe. Wait for it to stabilize and record measurement and temperature.
- d. Rinse probe. Repeat measurements (3x per sample).
- e. Rinse probe again and go onto the next sample.
- Textural analysis is performed by the hydrometer method on 50mg of fine fraction in 1L of water and dispersant, following CZO procedures.
- Carbon content is measured after removing all roots from the fine fraction (except for organic horizons).
  - a. After root-picking, 1g of soil is packaged in a small aluminum tin, and soil carbon is measured by loss on ignition.
  - b. Root-picking is a tedious job, asking for help on this task is a good idea.
#### 4.3.3. Water Samples

Collection should always be in cleaned and leached Nalgene bottles, and samples should be stored as close to 4°C as possible until analyzed.

# 4.3.3.1. Lysimeter/Piezometer sampling

The procedure is written assuming you have removed the bottles from the boxes due to cold weather. If you haven't, after step 1.a, go to step 1.g. It's a good idea to sample the piezometers and lysimeters at the same time, because the lysimeters take a while to finish sampling and often need to have tension re-applied.

# Sampling equipment:

Individually-bagged vacuum lids for the all lysimeters-these should be labelled so that you

don't use the same lid on different lysimeters

Extra vacuum lids

Bag of nitrile gloves for handling vacuum lids (They get dirty, so have several sets)

Bagged vacuum bottles

Solid lids for vacuum bottles

Hand pump with attached tubing and pressure gauge

Field computer, cable, and extra batteries

250mL Nalgene bottles (1 per piezometer)

Geopump (ensure you have: battery, battery cord, sample tubing)

1 500mL bottle of Milli-Q water

Label tape and Sharpie

Field notebook

Icepack & Carry pack for all of this stuff (the Geopump fits nicely in a haul pack)

#### **Protocol:**

- 1. Choose a box. At the box:
  - a. Record time of arrival and state of box (if damaged, disturbed). Open box.
  - b. Gather the lysimeter lines.
  - c. Get out the bottles and active vacuum lids.
  - d. Put on nitrile gloves.
  - e. Attach vacuum lids to bottles
  - f. Attach bottles to lysimeter tubing, matching numbers on vacuum lids to tags on lysimeter lines. The small tubing caps on the lines should go in the bag in the box labeled "FOR LYS LINE CAPS".
  - g. The lysimeter lines attach to the short tube on the caps. Make sure the hard-tubing guards are over the connection to prevent it from kinking. Once the vacuum lids are on the bottles you can take the gloves off.
  - h. Attach hand pump to long tubing on vacuum bottle and apply 60kPa of tension.
  - Wait for a minute--if the pressure drops quickly, check connections on lid and bottle.
     If they are tight and it's still leaking, you will need to replace the lid (place it in a bag and write "fix me!" on it) with one of the extras and repeat pulling tension.
  - j. If everything's good, close the stopcock and pinch clamp, record the time you applied tension in your notebook, and go on to the next bottle/box.
- 2. Once all the lysimeters are under tension, it is a good idea to collect the data from the datalogger:

- a. Open EM50 and attach communications cable to com port. Connect the cable to the computer's USB port, and connect using ECH2O utility. Download new data, and copy to field backup flash drive.
- b. Check the batteries, note charge percent in field notebook, and replace if lower than 30% (unless you'll be checking again tomorrow).
- c. Disconnect the computer and close the EM50 datalogger box.
- 3. Now is as good a time as any to check your piezometers, too.
  - a. Set up the Geopump: plug the cable into the pump itself. **Be very careful** with the end that plugs into the battery--do not pull on the cable, only the plastic plug.
  - b. Run the tubing through the motor. If it does not start, loosen the motor and see if that helps.
  - c. Insert tubing into piezometer, placing the end just off the bottom to avoid sampling too much sediment.
  - d. Allow the water to run for a minute or so, rinse the bottle 3x, then run water in.
  - e. If you don't get enough water to fill the bottle in one go, turn off pump for about ten minutes to allow well to refill. It may take multiple tries to fill the bottle.
  - f. Rinse the line with ~500mL of Milli-Q before sampling the next piezometer.
  - g. Label bottles with site, "PZ", date, time, and your initials. Put on icepack if you have it with you.
- 4. Check on lysimeters and reapply tension as necessary, noting times. You may need to go do other things while they pull water. When you have about a half-hour of work time left:
  - a. Release tension by opening stopcock and pinch clamp.

- b. Wearing gloves, remove entire bottle setup from lysimeter line. Cap bottle with solid lid, and place vacuum lid back in its individual bag.
- c. Label bottle (if there's any sample) with site, "lys", lysimeter number, date, time, initials. Record this in your notebook as well.

# 4.3.3.2. Well Sampling

# **Equipment needed:**

Bailer (steel or polypropylene), small enough to have about 1cm of clearance all around itself.

500mL Nalgene bottles, one for each well

Label tape and Sharpie

Field notebook

Icepack

# **Protocol:**

At each well:

- 1. Remove cap and level logger (if present). Note time of logger removal in notebook.
- 2. Label bottle with well name/number, date, time, and your initials.
- 3. Drop bailer into well. If it has a trigger mechanism, use it.
- 4. Use first two bailersful to rinse bottle three times; this also rinses the bailer.
- 5. Fill bottle, leaving as little headspace as possible.
- 6. Place bottle on icepack if you have it, and move on to next well.

# 4.3.3.3. Stream sampling

# **Equipment Needed:**

500mL Nalgene bottle

Label tape and Sharpie

Notebook

Icepack

## **Protocol:**

- 1. Note the time you arrive at the stream in your notebook. Label the bottle with the date and time, your initials, and the location.
- 2. **Do not** walk in the stream! If you have walked in the stream, sample upstream of where you walked.
- Rinse bottle three times, fill, and cap with as little headspace as possible. Place on icepack.

#### 4.3.4. Snow Samples

Snow samples require the digging of a snow pit. This is easier than a soil pit, but only slightly. Make sure to pile excavated snow downhill of your pit, and to dig steps so you can get out.

# **Equipment needed:**

Density sampler, putty knife, and rubber mallet

Clean shovel for snow extraction

Ziploc bags

Tape measure and pins

Sharpie and field notebook

Waterproof gloves and boots

Hand warmers

#### **Protocol:**

 Note the location of your snow pit in your field notebook. Pile everything you don't want to get wet uphill and to one side, and dig.

- 2. Pin the tape measure over the uphill side of the pit and take a photo.
- 3. Record any dense layers in your notebook.
- 4. Decide how many samples you need, and label the bags accordingly with the depth for each sample, whether it is a bulk snow or density sample, and the date and location of collection.
  - a. Density samples:
    - i. Drive the density sampler into the wall of the pit. This may require a rubber mallet.
    - ii. Slide the lid along the top of the sampler to close it off.
    - Extract the sampler, and remove any loose snow from the outside with the putty knife.
    - iv. Scrape the snow from the sampler quantitatively into a Ziploc bag.
    - v. Seal the bag, and double-bag the sample (the labelled bag should be the outside one).
  - b. Bulk samples:
    - i. Open a Ziploc and roll the edge back so you don't get snow on the seal.
    - ii. Stab the sampling knife into the wall of the pit (away from your sampling location) several times to ensure it's clean.
    - iii. Fill the bag mostly full of snow from the designated level in the pit.
    - iv. Seal, double-bag with the labelled bag on the outside.
  - c. Snow samples should be kept frozen until you are ready to analyze them.

### 4.3.5. Sample Processing

- 1) Snow samples should be melted at room temperature right before processing.
- 2) All other samples should be filtered as soon as possible after collection.

- 3) Make a spreadsheet with the sample data, and give each sample a unique number. This is much preferable to rewriting all the data on the label every time you change bottles.
- 4) Filtering:
  - a. For all analytes:
    - i. Set up the vacuum apparatus and prepare 0.7µm Whatman filters.
    - ii. Homogenize sample (shake it like mad). Unless you have a lot of sediment, in which case it is better to leave it as-is until close to the end of the sample.
    - iii. Rinse entire setup, including filter, with part of the sample. Discard rinse water or use to rinse storage bottle.
    - iv. Filtering may require multiple filters. For exceptionally sediment-heavy samples, using a 1.5μm filter before the 0.7 can speed things up considerably.
    - v. Store filtered sample in a clean, sample-rinsed container. Label with sample number. Reserve >50mL of this filtrant for DOC analysis.
    - vi. Rinse vacuum setup with Milli-Q before next sample.
  - b. For anions, cations, and nutrients:
    - i. Use a 0.45µm syringe filter setup. Rinse syringe with sample before filtering.
    - ii. Filter into clean, sample-rinsed bottle. Label with sample number. Anion analysis requires 1-10mL of sample, depending on dilution, while nutrients require >30mL.
    - Cations require >2mL, with 5-15mL preferred. This sample should be filtered into a metal-free centrifuge tube.
  - c. Store samples at 4°C until analysis

Pit Name:			G	PS: °		_",N, 	°,  ,	3	W Da	te:	   In	itials:
Horizon	Lower Depth	Boundary	Dry Co	olor Wet	Structure	Texture (field)	Coarse Fraction	Clay films	Eŧ	Roots	Pores	Vegetation/ Notes

# 4.3.6. Soil Profile Description Sheet

# 4.4. PCA

## 4.4.1. Data preparation

Stream data should be gap-filled: any non-detected analytes should be replaced with the mean concentration of that analyte. Do the same with the end-member samples; make sure to use the median concentration of the analyte for that end-member (Farnham et al., 2002). Rare-earth and alkali-earth elements often make good tracers (Barthold et al., 2011), beware of those which are biologically active or transition metals exhibiting redox reactions in saturated soils.

### 4.4.2. R code

The R code in section 4.4.3 is designed to run PCA. Use at your own risk. Make sure you have prepared the data beforehand—gap filling, removing any blanks or errors.

# Files needed:

- Your stream water concentrations—in the code this is an Excel file called "AdjustedValues", and we specify the actual sheet with stream samples as "GrabsforPCA"
- 2. End-member concentrations—here an Excel file called "EMs2"

4.4.3. R Code

# PCA 2A.R

```
A. G. Radke, 2018
```

```
## Attempt PCA on Stream samples only
## Set Up Workspace
setwd("G:/Thesis data/PCA&EMMA")
library(readxl)
require(readx1)
library(stats)
require(stats)
library(ggplot2)
require(ggplot2)
library(caret)
require(caret)
library(sp)
require(sp)
library(ggfortify)
require(ggfortify)
library(gstat)
require(gstat)
library(ggbiplot)
require(ggbiplot)
## Here's the data
StreamSamples <- read excel("AdjustedVAlues.xlsx", sheet = "Weir") # This sho</pre>
uld be only stream samples
## Subset the data to only include analyte columns, not metadata
StreamIons = (StreamSamples[, 11:41])
## Call the PCA function
PCA <- prcomp(StreamIons, center = TRUE, scale. = TRUE)</pre>
# "True" scales and centers the data (subtracts the mean of the column, then
divides by the standard deviation)
print(PCA)
## Standard deviations (1, ..., p=21):
## [1] 3.214672e+00 2.241015e+00 1.839297e+00 1.686848e+00 1.477981e+00
## [6] 1.314868e+00 1.197963e+00 1.038050e+00 9.403337e-01 7.635844e-01
## [11] 6.514923e-01 5.831058e-01 5.045594e-01 4.254232e-01 4.063020e-01
## [16] 2.533493e-01 2.173605e-01 1.650180e-01 1.176871e-01 6.632413e-02
## [21] 4.616433e-16
##
## Rotation (n \times k) = (31 \times 21):
##
                  PC1
                               PC2
                                             PC3
                                                          PC4
                                                                        PC5
## F
          0.068732360 0.250788353 0.001858493 -0.317444173 0.014145001
## Cl
                       0.216270806 0.049782824 -0.194779690 -0.236504337
          0.197865298
## NO3 -0.242135893 0.093834860 -0.112420954 -0.123357834 -0.150831637
```

##	S04	-0.203131676	-0.	039847132	0.0	010041183	-0.006141481	0.056058757
##	7Li	-0.004895693	0.	260911426	0.3	202797593	-0.001815788	0.193979843
##	11B	-0.118643465	-0.	140699623	-0.	055917402	-0.190563961	-0.108154423
##	23Na	0.275188043	0.	108532215	0.0	091205898	0.117083821	-0.027826381
##	25Mg	0.286225811	0.	134709508	0.0	019062020	0.026258082	-0.062512612
##	27A1	-0.127793000	0.	061242042	0.	233024156	-0.348884159	0.101446138
##	29Si	-0.024120129	0.	044513786	0.	311860466	0.137071386	0.380362138
##	31P	-0.043441792	-0	114002796	0.	197829178	0.036311477	-0.070890837
##	39K	0 219278931	а. О	177995965	0	144757880	0 010566150	-0 306708076
<u>#</u> #	44Ca	0.213270351	о. а	143594722	a 1	030202185	0.010900190	-0 066049704
<u>#</u> #	455c	0.2013/2/00	_0.	256069000	а.	352788536	0.060537674	0.0000043704
ππ ##	455C 47Ti	-0.061661718	0. 0	256530155	Q.	1/21/8560	-0.015122871	0.055502500
##	4711 51V	0 1/2826/85	0. 0	058362200	0. 0	242148300	0.213122071	0.131020132
## ##	52Cn	0.142020403	0.	030302299	0.	249030349	0.2022040/1	0.20304/3/2
## ##		-0.22/00//30	0.	151628422	0.	117200717	0.170901042	-0.10/025155
##		0.100525705	0.	0010020422	0.	11/399/1/	-0.2/200001	0.400//1001
## ##	57Fe	0.0/3030354	-0.	200000220	0.	203303238	-0.25040/124	-0.2/250/1/5
## ##	5900	-0.1805/5422	0.	2544000238	-0.0	01402002990	0.0849/1869	-0.04/3810/3
## ##	6011	-0.234645724	0.	254498022	-0.0	014838002	0.163411469	-0.02/119140
##	65CU	-0.238123055	0.	250227961	-0.0	0315/63/1	0.161284344	-0.048551814
##	66ZN	0.031/14691	-0.	115398241	-0.	212640478	-0.1558/42/6	0.159358818
##	69Ga	0.222259078	0.	038469836	-0.	32/691950	0.0532196/9	0.081468373
##	75AS	0.020265824	0.	2/4905891	-0.0	024928890	-0.315329057	0.042834080
##	825e	-0.20555298/	0.	163938966	0.0	088226769	0.266433290	0.005556/43
##	85KD	-0.0648/4034	0.	38/250358	-0.0	004589770	0.192398896	-0.125/0292/
##	885r	0.277225004	0.	15581/289	-0.0	025/20908	0.11//06299	-0.028680293
##	90Zr	0.119644925	-0.	038123875	0.1	128921656	-0.026226525	-0.426796926
##	121Sb	0.258198302	-0.	056353226	0.0	095596959	0.205463598	0.102970268
##	137Ba	0.200184799	0.	078219640	-0.	359831648	0.041937257	0.117948906
##	_	PC6	-	PC7	-	PCE	PC9	PC10
##	F	-0.097967388	-0.	2670790686	0	.107016815	6 0.258407025	-0.385584137
##	CI	0.0/212/545	-0.	000381/6/8	-0	.261393189	0.045221421	-0.092809924
##	NO3	0.243617196	-0.	1813874984	-0	.094090155	6 0.125462878	8 0.042286618
##	S04	0.449479003	-0.	2391462394	-0	.112233434	0.262084731	-0.035285002
##	7Li	-0.175203783	0.	1903169027	-0	.423016787	0.301543948	0.295111542
##	11B	0.414454119	0.	3599984176	0	.116529027	0.262711577	0.026565666
##	23Na	0.152273285	-0.	0055299185	0	.094869303	3 -0.065200776	-0.073068389
##	25Mg	0.098333907	-0.	0731655113	-0	.045512387	7 -0.035178910	0.021671031
##	27A1	-0.082495482	0.	2148100873	-0	.292784692	2 -0.231957827	' -0.079149434
##	29Si	0.311876607	-0.	0155776329	0	.131518595	5 -0.100871629	-0.199780920
##	31P	0.392420341	-0.	2881797354	-0	.384842609	9 -0.423952743	0.010718843
##	39K	0.095245259	0.	0385861554	-0	.086122075	6 0.034855889	0.053265047
##	44Ca	0.117226480	-0.	0690961837	-0	.009653247	7 -0.035845269	0.010995548
##	45Sc	0.114804568	-0.	0092915553	0	.180378884	0.103483409	0.147865958
##	47Ti	-0.033399878	0.	2520546870	0	.257988782	2 -0.464714800	0.049514597
##	51V	0.022474429	0.	1575688958	0	.038666602	0.149802355	-0.105259257
##	52Cr	-0.005310799	0.	0508901154	0	.135298589	9 -0.112384162	-0.339979899
##								
	55Mn	0.022807947	-0.	1018896465	0	.049412502	0.212798177	-0.299273952
##	55Mn 57Fe	0.022807947 -0.130513456	-0. -0.	1018896465 0187910169	0 -0	.049412502 .105212756	2 0.212798177 5 -0.063762243	-0.299273952 0.023628668
## ##	55Mn 57Fe 59Co	0.022807947 -0.130513456 0.019348111	-0. -0. 0.	1018896465 0187910169 0076426902	0 -0 0	.049412502 .105212756 .148077298	2 0.212798177 5 -0.063762243 8 0.003864797	-0.299273952 0.023628668 0.205776080

##	65Cu	0.041730037 0.0180153505 0.021215903 -0.052913497 -0.107685985
##	66Zn	0.288297342 0.5130885345 -0.195488034 -0.024882766 -0.041058124
##	69Ga	0.052870178 0.0415459940 -0.130836444 -0.114318969 -0.222624786
##	75As	0.207051288 -0.1130552883 0.298278576 0.007043341 0.436967054
##	82Se	-0.076938476 0.1101293848 -0.283975937 0.211003142 -0.097373062
##	85Rb	0.111436702 0.1236651452 0.005136977 -0.042127407 0.045565701
##	88Sr	0.108310031 -0.0325135999 -0.018979298 -0.020473603 -0.007660451
##	90Zr	0.074647995 0.3362456381 0.216031491 0.155723860 -0.236545091
##	121Sb	0.047912354 0.0528421040 0.029655656 0.092786616 0.278362540
##	137Ba	0.062332470 0.0711951154 -0.074385280 -0.151293300 -0.111470186
##		PC11 PC12 PC13 PC14 PC15
##	F	0.0376590285 0.3145144081 0.3210525945 -0.056066558 0.02598542
##	C1	-0.0771139272 0.0150095047 -0.2376317022 0.153234550 -0.13894086
##	NO3	0.1382073772 -0.0328803298 0.0606292022 -0.118165911 -0.30834099
##	504	-0.0896929534 -0.2837482929 -0.1357125005 0.287903528 0.02229533
##	7Li	0.0009087538 -0.0430375425 -0.0586946903 0.007990810 -0.04267405
##	11B	0.1317237219 0.2971976364 -0.0663984021 0.100497027 0.26193255
##	23Na	0.1386473013 -0.1245361552 0.2149469607 -0.028231542 0.07346511
##	25Mg	0.0548003376 -0.2177679626 -0.0157923890 -0.128605714 0.06224628
##	2741	-0.1713577492 0.1191119893 0.0718592338 0.186864520 -0.18888141
##	295i	-0.2287939409 -0.0266244280 0.0627039923 -0.199786483 -0.38840253
##	31P	-0.0205625548 0.3493653119 -0.0659626836 -0.158096272 0.31360146
##	39K	0.0962941010 0.0041324337 0.0495102526 0.364912875 -0.16859899
##	44Ca	0.0639601402 -0.2154562118 -0.0001879087 -0.098765386 0.06099098
##	45Sc	-0.2396188558 0.0050741604 0.3198217879 0.154369835 -0.18540578
##	47Ti	0.0542283056 -0.0814491459 -0.2370505529 0.062564396 0.10788299
##	51V	0.5172986754 0.4230200889 -0.0794010035 -0.004447242 -0.06434141
##	52(r	0.2511973369 -0.2069295142 0.1032020562 0.300970395 0.07224271
##	55Mn	-0 0921896252 -0 1819550336 -0 1860824755 0 086092451 0 40105533
##	57Fe	0.0779540212 -0.1049485005 0.3295040193 -0.171070130 0.18021539
##	59Co	-0.2647138761 0.0713095210 0.4115521737 0.066070883 0.34426167
##	60Ni	0 0415606554 0 0007652763 -0 1513310110 -0 097369379 0 03148993
##	65Cu	-0.0741501541 -0.0140758058 0.0458775923 -0.033171537 0.03460302
##	667n	0.1770166281 -0.2891070017 0.3459730650 -0.162038942 0.03326802
##	69Ga	-0 1067381688 0 1680465670 0 1538287219 0 100786788 -0 07163895
##	75Δs	0 1169333438 0 1133627230 -0 0121968192 -0 220270598 -0 15469294
##	825e	-0 1106777972 0 0058181859 0 0619978989 -0 371608691 0 10660068
##	85Rh	-0 0739414158 0 0434724798 0 1140335234 0 224940371 -0 06145590
##	885r	0 0544384291 -0 1699207028 -0 0500959145 -0 164532797 0 03573772
##	907r	-0 4219088167 0 0647732370 -0 2561047762 -0 295149028 -0 04600749
##	121Sh	-0 2355995013 0 1230901245 -0 0420893739 0 189625603 0 25489979
##	137Ba	-0 1920624724 0 1735253640 0 0701213924 0 111996488 -0 06815687
##	15700	PC16 PC17 PC18 PC19 PC20
##	F	0 189352648 0 380725509 0 110749433 -0 165777374 0 127875987
##	C1	0 265625204 -0 042643420 -0 249829577 -0 271170359 -0 424542524
##	NOR	-0 392792370 0 172596724 -0 156312285 -0 117683134 -0 658266411
##	504	-0 046614110 0 114768019 0 023988953 0 201566245 _0 010197487
##	71 i	0 105789655 0 072460518 0 411851194 _0 062562539 0 070716640
##	11R	0 153443017 -0 136042968 0 283101648 0 013288975 -0 20224051
##	23Na	-0.087150045 0.149530038 0.424818613 -0.043239529 -0.009365400
	u	

##	25Mg	0.042610135	0.134429108	-0.052878626	0.163550387	0.008562135
##	27A1	-0.203891864	0.240301966	-0.077353656	0.368387378	-0.087055232
##	29Si	0.374593598	-0.157606805	-0.079229015	-0.087766230	-0.113341512
##	31P	0.011183792	0.047104131	0.084803447	-0.033730659	0.225913010
##	39K	-0.022028792	-0.286124076	-0.078015697	-0.142866400	0 487110044
##	44Ca	-0 004397236	0 100172989	0 007003743	0 193320768	-0 153945684
##	455c	-0 2357023/5	-0 03221/863	0.007003743	-0 1200/2656	-0 020252193
ππ ##	455C 47Ti	-0.200702040	0.161821702	0.170055015	-0.120042030	-0.020252155
##		0.1044J1100	0.101021792	0.122972520	0.150827781	0.0044554514
## ##	53Cp	0 156160010	0.115046225	0.00022080	0.202/91100	-0.000/40120 0 107096242
##	52CF FEMm	-0.130100010	0.115940525	0.020270449	-0.159060121	-0.13/300243
## ##		-0.245196015	-0.319433028	-0.125557799	0.000415145	0.1/0/05052
## ##	5/Fe	-0.032259290	-0.3/3599/88	-0.090420344	-0.051541406	-0.199425015
##	5900	0.14/4085/3	0.0018/4836	-0.265664363	0.242953058	-0.089916/25
##	60N1	0.012384124	-0.05426/3/6	0.021/63228	-0.359399931	0.088562180
##	65Cu	0.026610638	-0.0919/1604	-0.016/214/9	-0.023014508	0.094990514
##	66Zn	0.097841957	0.128538551	-0.254926497	-0.158780443	0.259834861
##	69Ga	-0.292148794	-0.141204118	0.090313546	-0.081090250	-0.184472659
##	75As	-0.235859507	-0.139513166	-0.030912964	-0.025891482	-0.027743626
##	82Se	-0.324175822	-0.091629032	0.018721910	-0.128056121	-0.171097131
##	85Rb	0.062190323	-0.075412656	0.057143329	0.196855250	0.083564383
##	88Sr	-0.020290220	0.066041339	0.076315411	0.174052569	-0.195200278
##	90Zr	-0.143080941	0.130004637	-0.004951627	0.143859331	0.232920915
##	121Sb	-0.137270046	0.372525975	-0.326349264	-0.389794128	-0.085441189
##	137Ba	-0 15/53631/	0 212/07002	0.120887091	-0.009857856	-0.056175830
	19704	-0.1)+))0)14	-0.213497002		0.000000,0000	0.0501,5050
##	19704	PC21	-0.213497002		0.009097090	0.0301/3030
## ##	F	PC21 -0.0637365871			0.00000000000	0.0301/3030
## ## ##	F Cl	PC21 -0.0637365871 -0.2897010329	-0.213497002 L L			0.000175050
## ## ## ##	F C1 NO3	PC21 -0.0637365871 -0.2897010329 -0.0341879888	-0.213497002 L L B			
## ## ## ## ##	F C1 N03 S04	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867	-0.213497002 L L J			
## ## ## ## ##	F C1 NO3 SO4 7Li	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761	-0.213497002 L D D D			
## ## ## ## ## ##	F Cl NO3 SO4 7Li 11B	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797	-0.213497002 L L 3 7			
## ## ## ## ## ## ##	F Cl NO3 SO4 7Li 11B 23Na	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246	-0.213497002 L L 3 7 L 7			
## ## ## ## ## ## ##	F Cl NO3 SO4 7Li 11B 23Na 25Mg	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314	-0.213497002 L J J J J J J			
## ## ## ## ## ## ## ##	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829240 -0.1461156314 0.2429794397	-0.213497002 L L ) } , L , ,			
## ## ## ## ## ## ## ##	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102	-0.213497002			
## ## ## ## ## ## ## ## ##	F Cl NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169	-0.213497002 L L 2 2 2			
# # # # # # # # # # # # # # # # # # #	F Cl NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595	-0.213497002			
# # # # # # # # # # # # # # # # # # #	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026	-0.213437002			
######################################	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139	-0.213497002			
# # # # # # # # # # # # # # # # # # #	F Cl NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305	- 0 . 213437002			
######################################	F Cl NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884	-0.213497002			
######################################	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804	- 0 . 213437002			
######################################	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr 55Mn	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829240 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804 -0.0123521106	- 0 . 213437002			
#######################################	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr 55Mn 57Fe	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804 -0.0123521106 0.1300057577	- 0 . 213437 002			
#######################################	F Cl NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr 55Mn 57Fe 59Co	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804 -0.0123521106 0.1300057577 -0.0686724476	-0.213497002			
#######################################	F Cl NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr 55Mn 57Fe 59Co 60Ni	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804 -0.0123521106 0.1300057577 -0.0686724476 0.1682885129	- 0 . 213437002			
#######################################	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr 55Mn 57Fe 59Co 60Ni 65Cu	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829240 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804 -0.0123521106 0.1300057577 -0.0686724476 0.1682885129 -0.0510647113	- 0 . 213437002			
#######################################	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr 55Mn 57Fe 59Co 60Ni 65Cu 66Zn	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829240 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804 -0.0123521106 0.1300057577 -0.0686724470 0.1682885129 -0.0510647113 -0.1183682702	- 0 . 213437002			
#######################################	F C1 NO3 SO4 7Li 11B 23Na 25Mg 27A1 29Si 31P 39K 44Ca 45Sc 47Ti 51V 52Cr 55Mn 57Fe 59Co 60Ni 65Cu 66Zn 69Ga	PC21 -0.0637365871 -0.2897010329 -0.0341879888 0.0150781867 -0.0051778761 0.1040213797 0.1854829246 -0.1461156314 0.2429794397 0.2223106102 -0.1162375169 0.1375805595 0.1036670026 -0.4481835139 -0.2101775305 -0.1393215884 -0.0363272804 -0.0123521106 0.1300057577 -0.0686724476 0.1682885129 -0.0510647113 -0.1183682702 0.3634849302	- 0 . 213437002			

## 82Se -0.0927206598
## 85Rb -0.0222750480
## 88Sr -0.0568431866
## 90Zr -0.0008536682
## 121Sb 0.2594896250
## 137Ba -0.3764669837

plot(PCA, type = "1") # This gives you your explained variance plot

PCA



summary(PCA) # This lists the PCs and the proportion of variance explained by
each

```
## Importance of components:
                                                            PC5
##
                             PC1
                                    PC2
                                            PC3
                                                    PC4
                                                                    PC6
## Standard deviation
                          3.2147 2.2410 1.8393 1.68685 1.47798 1.31487
## Proportion of Variance 0.3334 0.1620 0.1091 0.09179 0.07047 0.05577
## Cumulative Proportion
                          0.3334 0.4954 0.6045 0.69628 0.76675 0.82252
##
                              PC7
                                       PC8
                                               PC9
                                                      PC10
                                                              PC11
                                                                      PC12
## Standard deviation
                          1.19796 1.03805 0.94033 0.76358 0.65149 0.58311
## Proportion of Variance 0.04629 0.03476 0.02852 0.01881 0.01369 0.01097
## Cumulative Proportion 0.86881 0.90357 0.93209 0.95090 0.96459 0.97556
##
                             PC13
                                      PC14
                                              PC15
                                                      PC16
                                                              PC17
                                                                      PC18
## Standard deviation
                          0.50456 0.42542 0.40630 0.25335 0.21736 0.16502
## Proportion of Variance 0.00821 0.00584 0.00533 0.00207 0.00152 0.00088
                          0.98377 0.98961 0.99494 0.99701 0.99853 0.99941
## Cumulative Proportion
                             PC19
                                      PC20
##
                                                PC21
## Standard deviation
                          0.11769 0.06632 4.616e-16
## Proportion of Variance 0.00045 0.00014 0.000e+00
## Cumulative Proportion 0.99986 1.00000 1.000e+00
```

plot((PCA\$sdev)^2/sum(PCA\$sdev^2)) # Another plot of explained variance, with
a flipped y-axis



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print(g)



```
## Scale and center MEDIANS of end-members by the mean and S.D. of the stream
samples
ems<-read.csv("Medians_EMs-subset.csv", header = T)</pre>
medians<-ems[, 2:32] # Again, cutting out metadata</pre>
ScaledandCentered<-scale(medians, PCA$center, PCA$scale)</pre>
## Apply loadings to MEDIANS
loads<-PCA$rotation #This SHOuLD be the loadings, with each eigenvector as a
column, so does not need to be transposed
Projected Medians<-ScaledandCentered %*% loads</pre>
write.csv(Projected_Medians, "Medians_Projected.csv", col.names = T) # These
are your PCs
## Warning in write.csv(Projected_Medians, "Medians_Projected.csv", col.names
## = T): attempt to set 'col.names' ignored
## Apply loadings to ALL END-MEMBER SAMPLES
ems_all<-read_excel("AdjustedValues.xlsx", "End-Members")</pre>
all<-ems all[, 11:41]
ScaledandCenteredAll<-scale(all, PCA$center, PCA$scale)</pre>
Projected EndMembers<-ScaledandCenteredAll %*% loads</pre>
write.csv(Projected_EndMembers, "AllEMs_Projected.csv", col.names = T)
## Warning in write.csv(Projected EndMembers, "AllEMs Projected.csv",
## col.names = T): attempt to set 'col.names' ignored
## Export the Stream Points in U-space
head(PCA$x) # There should be the same number of columns as you have principa
l components
##
                         PC2
               PC1
                                   PC3
                                               PC4
                                                          PC5
                                                                     PC6
## [1,] -0.1489063 -1.257693 -3.002387 -1.21134885 0.5898644 -1.6634382
## [2,] -0.7052574 -2.180992 -3.090975 -2.07559707 0.8226261 1.5975183
## [3,] -1.5835159 -2.685488 -1.360916 -0.71995579 -1.4575021 -1.2003561
## [4,] -0.8584405 -3.007801 2.998239 0.05558744 -0.3046119 2.7650496
## [5,] -0.7858733 -2.751152 1.508217 0.09012777 -0.4711584 -0.3341643
## [6,] -0.8194233 -2.746467 1.699763 -0.30927017 -0.9816321 0.1236186
##
                PC7
                           PC8
                                      PC9
                                                PC10
                                                            PC11
                                                                         PC12
## [1,] -0.50361332 -0.8809264 -0.1369336 -0.4239569 -0.40664350 1.143792921
## [2,] 3.34237861 -1.3694522 -0.5875225 0.1186120 0.33013212 -0.516026126
## [3,] -1.42361567 -0.6725110 1.1774933 0.4585183 0.65161951 -0.827812947
## [4,] -1.67904856 -1.7030370 -1.5511967 0.6794846 -0.24725108 0.603553776
## [5,] 0.02009135 0.5360187 0.6544164 0.1710464 -0.04621089 -0.352697335
## [6,] 0.53996600 0.8812212 0.8727224 -0.1572158 -0.72889268 0.004335758
##
                PC13
                            PC14
                                        PC15
                                                     PC16
                                                                 PC17
## [1,] -0.820567131 0.72108253 0.07185071 -0.366756598 0.08874624
## [2,] 0.323888477 -0.15720726 -0.20592493 -0.024014169 0.01432660
## [3,] -0.523615675 0.13726806 0.37234846 0.438644024 0.10606292
## [4,] 0.006102869 -0.08748719 0.30798161 0.013452203 0.04266344
## [5,] 0.222274134 0.44163709 -0.23992521 0.003223088 -0.40671219
## [6,] -0.015064463 0.12034079 -0.85300470 -0.020390376 0.31603174
```

```
##PC18PC19PC20PC21##[1,]0.061965939-0.004317720-0.0405084293.885781e-16##[2,]-0.0576599030.010371301-0.0011313791.443290e-15##[3,]-0.1958524450.0475385660.0735148755.551115e-17##[4,]-0.002773425-0.0052247220.0054352569.436896e-16##[5,]-0.151613823-0.228917288-0.1585897836.106227e-16##[6,]0.228296291-0.1336238290.1195965424.440892e-16
```

```
write.csv(PCA$x, "StreamsinU-Space.csv")
```

#### 4.4.4. References

- Barthold, F. K., Tyralla, C., Schneider, K., Vaché, K. B., Frede, H. G., & Breuer, L. (2011). How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis. *Water Resources Research*, *47*(8), 1–14. https://doi.org/10.1029/2011WR010604
- Farnham, I. M., Singh, A. K., Stetzenbach, K. J., & Johannesson, K. H. (2002). Treatment of nondetects in multivariate analysis of groundwater geochemistry data. *Chemometrics and Intelligent Laboratory Systems*, 60, 265–281. https://doi.org/10.1016/S0169-7439(01)00201-5

#### 4.5. End-Member Mixing Analysis

#### 4.5.1. Identifying tracers

EMMA should be performed using the analytes the PCA identifies as best. These are seen in the plot output: choose the longest arrows (representative of the eigenvalues in PCA), and try to choose solutes that do not group closely together—ideally they should be orthogonal to one another (the angles represent the eigenvectors in the PCA).

From the two plots below (Figure 4.1), I chose Ba, Sr, and Rb as tracers. You may need to zoom in in R to see the individual tracer labels. This can be done in the above code using the coord\_cartesian command. The number of tracers you use is determined by the number of end-members you expect: there is always one more end-member than the number of selected tracers (Christophersen, Neal, Hooper, Vogt, & Andersen, 1990; Hooper et al., 1990).



Figure 4.1: PCA plots for RME samples

#### 4.5.2. U-space or concentration space?

While there is some debate over whether it is always necessary to perform EMMA using the loadings generated from the PCA, it is often better to create the plots for presentation in concentration-space, as this is more intuitive. Ideally, you will perform EMMA on both the raw concentrations and the transformed ones (loadings), and compare the results to choose endmembers.

#### 4.5.3. The actual analysis

Plot the median values of your suspected end-members, for the tracers you identified,

using the U-space loadings from the PCA. Now plot each individual stream point. Draw lines

between the end-members to try to contain all the stream points between them. If you are using

four end-members, this will require a software program like JMP to plot in 3D space.

When making figures, be sure to include the upper and lower quartiles of the ranges for each end-member you determine is contributing to streamflow.

#### 4.5.4. References

- Christophersen, N., Neal, C., Hooper, R. P., Vogt, R. D., & Andersen, S. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members — A step towards secondgeneration acidification models. *Journal of Hydrology*, *116*, 307–320. https://doi.org/10.1016/0022-1694(90)90130-P
- Hooper, R. P., Christophersen, N., Peters, N. E., Neal, C., Hooper, R. P., Vogt, R. D., ... Peters, N. E. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members - An application to the Panola Mountain catchment, Georgia, U.S.A. *Journal of Hydrology*, *116*, 321–343. https://doi.org/10.1016/0022-1694(90)90131-G

#### 4.6. Safety Plan and Visitor Sheet for Reynolds

# 4.6.1. Safety plan for field work at RCEW: Update and print out! <u>Emergency Plan for [NAME] and [NAME], [DATES OF FIELD WORK]</u>

# While [YOU AND YOUR ASSISTANT] are away from the Quonset together, they will:

- 1. Carry ARS SPOT receiver, 2-way radio, and all other necessary equipment for overnight survival should it be necessary.
- 2. Before any planned fieldwork, meet with Zane and get cabin keys, SPOT, radio, and drop off field work plans.
- 3. Send regular "OK" messages at start of work (sunrise or around 9am), lunchtime (around noon), and end of work/return to Quonset/cabin (around sunset) each day.
- 4. If [YOUR NAMES] are out and ok, but will miss their estimated return time, they will radio the ARS with their current location and expected return time.
- 5. If [YOUR NAMES] plan to stay at the cabin overnight, they will make and confirm plans beforehand, and carry the ARS satellite phone for emergency use. They will conform to the same radio protocols as above, with cabin as "camp" rather than Quonset.
- 6. If either of [YOUR NAMES] is in a non-immediately life-threatening situation (twisted ankles, severe sprain, other limited mobility injuries *that require additional help to return to the field station--*this presumes that either the vehicle is inoperable, the injured person is the only authorized driver,

or there is no vehicle), they will use the "helping hand" alert on their SPOT to notify (1) Zane, (2) Sarah Godsey, and (3) [YOUR EMERGENCY CONTACT] of their location and radio Zane or Barry with the specifics.

a. Zane or Barry will send out a search party, and be the primary assistance.

Sarah/[YOUR EMERGENCY CONTACT] will do nothing for 24 hours.

- b. Sarah will email RCEW if she does not receive confirmation from Zane and Barry or an OK SPOT signal within 24 hours. Sarah, Zane and Barry will cc: [YOUR EMERGENCY CONTACT] on all emails. [Note: If RCEW email is down, contact the ARS in Boise or call Zane or Barry's cell phones after 5pm-see below.]
- c. Zane and Barry will follow up again with regular updates to confirm conditions.
- d. If Zane and Barry are unable to immediately send help, they will arrange for someone else go out and communicate this to [YOUR NAMES]
- 7. If either of [YOUR NAMES] is in an immediately life-threatening situation (rattlesnake bite, animal attack, immobilizing injuries such as a serious fall, [be aware of hypo- or hyperthermia and dehydration], etc.), they will use the SOS button on their SPOT. This will immediately contact search and rescue, Sarah Godsey and [YOUR EMERGENCY CONTACT]. They will then follow up by pressing the "helping hand" button to alert Zane and Barry, and radio any additional information to the ARS for further instructions.
  - a. SPOT will automatically contact search and rescue via the Owyhee County Sheriff's office. [YOUR EMERGENCY CONTACT] and Sarah will NOT call since this may confuse rescue operation.
  - b. Sarah will email Zane and Barry immediately upon receipt of message.
  - c. If they receive word in time, Zane and Barry will await word from search and rescue who will be in charge of coordination. If not, they will proceed as if it's

a non-immediately life-threatening situation.

# Plan for [YOUR NAME], [YEARS OF STUDY]

#### While [YOUR NAME] is away from the Quonset ALONE, he/she will:

- 1. Carry SPOT receiver, radio, and all other necessary equipment for overnight survival should it be necessary.
- Before any planned fieldwork, confirm with Zane and Barry and discuss plan.
   Especially discuss differences with solo travel.
- 3. Send a regular "OK" message at start of work (sunup or leaving Quonset), lunchtime (around noon), and end of work (return to Quonset/cabin) each day.
- 4. If [YOUR NAME] is out and ok, but will miss her/his estimated return time, she/he will radio the ARS with her/his current location and expected return time.
- 5. If [YOUR NAME] plans to stay at the cabin overnight, she/he will make and confirm plans beforehand, and carry the ARS satellite phone for emergency use. She/he will conform to the same radio protocols as above, with cabin as "camp" rather than Quonset.
- 6. If [YOUR NAME] is in a non-immediately life-threatening situation (twisted ankles, severe sprain, other limited mobility injuries *that require additional help to return to the field station*--this presumes that either the vehicle is inoperable, the injured person is the only authorized driver and cannot drive, or there is no vehicle), she/he will use the "helping hand" alert on her/his SPOT to notify (1) Zane, (2) Sarah Godsey, and (3) [YOUR EMERGENCY CONTACT] of her/his location and radio Zane or Barry with the specifics.
  - a. Zane or Barry will send out a search party, and be the primary assistance.

Sarah/[YOUR EMERGENCY CONTACT] will do nothing for 24 hours.

- b. Sarah will email RCEW if she does not receive confirmation from Zane and Barry or an OK SPOT signal within 24 hours. Sarah, Zane and Barry will cc: [YOUR EMERGENCY CONTACT] on all emails. [Note: If RCEW email is down, contact the ARS in Boise or call Zane or Barry's cell phones after 5pm--see below.]
- c. Zane and Barry will follow up again with regular updates to confirm conditions.
- d. If Zane and Barry are unable to immediately send help, they will arrange for someone else go out and communicate this to [YOUR NAME].
- 7. If [YOUR NAME] is in an immediately life-threatening situation (rattlesnake bite, animal attack, immobilizing injuries such as a serious fall, [be aware of hypo- or hyperthermia and dehydration], etc.), she/he will use the SOS button on her/his SPOT. This will immediately contact search and rescue, Sarah Godsey and [YOUR EMERGENCY CONTACT]. She/he will then follow up by pressing the "helping hand" button to alert Zane and Barry, and radio any additional information to the ARS for further instructions.
  - a. SPOT will automatically contact search and rescue via the Owyhee County Sheriff's office. [YOUR EMERGENCY CONTACT] and Sarah will NOT call since this may confuse rescue operation.
  - b. Sarah will email Zane and Barry immediately upon receipt of message.
  - c. If they receive word in time, Zane and Barry will await word from search and rescue who will be in charge of coordination. If not, they will proceed as if it's a non-immediately life-threatening situation.

## [YOUR EMERGENCY CONTACT]'s contact info

Personal cell:

Home phone:

# [YOUR ASSISTANT'S EMERGENCY CONTACT]'s contact info

Personal cell:

Home phone:

**RCEW contact info** 

### 4.6.2. Visitor sheet for ARS

There will probably be an updated version of this each year, but here is an example. If you haven't had a government-sponsored defensive driving course, you will have to take one before driving an ARS vehicle. You will also have to attend a UTV training if you wish to drive one of the side-by-sides. I recommend doing so, they're fun. If you're going to be out in the winter, they may have you learn to drive a Sno-Cat as well.



#### **United States Department of Agriculture**

Research, Education and Economics Agricultural Research Service

# **RCEW** Visitor information

Name:	Email & Phone
Date:	
Affiliation :	(University/Gov't/CZO/other)
Affiliation contact name:	email & phone
Sponsoring NWRC Scientist:	
Emergency Contact #1 name & Phone:	
Emergency Contact #2 name & Phone:	
Medical instructions/allergies:	

# **2015 RCEW Projected Plans**

**Project Summary:** Please provide a short summary of your project and planned field activities, including objectives and hypotheses, field and lab methods (destructive or not, special tools or vehicles), data collection and site maintenance plan, field campaign time frames, etc...

Project Needs: Please provide an exhaustive list of tools, vehicles (ATV/UTV, 4x4, suburban) and infrastructure you may need from the RCEW and its crew. Computer/printer/wireless needs, housing, metal fabrication, equipment maintenance, etc...

**Training:** Driving a Gov't vehicle requires proof of a gov't sponsored "Defensive Driving" course and a valid drivers license. The RCEW offers ATV/UTV safety training, 4x4 beginner instruction, and trailer towing. Please indicate your individual training needs and any past training credential obtained...



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#### 4.7. Learn from my mistakes! Or, Love letters to future mountain hydrologists

So, you have decided to embark on the adventure of grad school. You may change your mind after you read this section (you're probably already rethinking it if you read the whole thesis!). If not, I hope this advice is helpful.

Without further ado: Handy hints for future grad students!

#### 4.7.1. Data Acquisition and Management

#### 4.7.1.1. Make a list of all the data you want

This will be based off of your initial literature review, and will evolve as your project does. Having some idea of what story you want to tell will help guide your data acquisition; it's also a good idea to look into sampling design before you start. And having a rough handle on the number of samples you'll have will also be useful for budgeting.

#### 4.7.1.2. Keep tabs on the data you have

Design a data recording system early on, and stick to it as much as possible. Keep a detailed field notebook, and set up a spreadsheet with all the metadata as a backup. This is also nice for sample processing, as it mean you can assign a unique identity number to your sample and not have to rewrite when, where, and by whom it was taken every time you split off an aliquot for an analysis.

While you're at it, make a brief list of what datasets you have, and where you've stored both the samples and the data.

#### 4.7.2. Field Work

#### 4.7.2.1. Equipment

Make lists of the field equipment you'll need, and check to make sure you can use it for the time you need it. Also check that it works. Keep the checklist handy while loading the truck. And be ready to improvise: chances are, you will forget something.

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# 4.7.2.2. Use the right equipment

Sometimes, jerry-rigging something to save a few bucks is a great idea. Sometimes, it results in your equipment breaking and ruining part of the study. Examples:

- Bailers for wells need at least a half-inch of clearance on all sides. There's one out at Reynolds down a well that no one can dislodge it from, because I didn't follow this advice.
- 2. Peristaltic pumps are not sufficient for pulling water from deeper than about ten meters.
- 3. Cold weather plays havoc on anything plastic or silicone. It's best to try to keep any of these objects somewhere slightly warmer, or to use metal hand pumps in cold weather.
- 4. Field computers break. Make sure to have a field flash drive, and back up data immediately. Also, always have the charging cord, the data cords, and extra batteries.

#### 4.7.2.3. There is no bad weather, only insufficient (or surplus!) clothing

Dress for the weather. Always bring rain gear and a warmer layer than you think you'll need. You **need** good boots for working on rocks, and gaiters are wonderful things. Hats are necessary. So is sunscreen, summer or winter. Make a checklist of your personal equipment, too. Don't forget food!

## 4.7.2.4. Always carry a first aid kit

It doesn't have to be huge, but it should have at least a few sheets of gauze. You'll want it for band-aids, if nothing else. It's a good idea to have a larger one in a vehicle or building that you can get to fairly quickly, in case something goes wrong.

And keep your radio on! It's a rescue beacon and alert system rolled into one.

# 4.7.2.5. Know <u>exactly</u> where your sites are!

GPS coordinates are not infallible, and can be significantly off. If you're working off of someone else's data, assume they may be completely wrong. Double-check your own points if you can.

Flagging tape is your friend. Tie it to your equipment, and to trees above your sites or long poles. Working in mountainous headwaters means snow. You may have to dig your equipment out. This is a lot less annoying if you know you're digging in the right spot. For that matter, keep in mind that short, springy shrubs get buried under snowdrifts. Don't put anything under them that you'll want to access before spring.

# 4.7.2.6. Underestimate yourself initially, you can always be daring later

If you're new to a site, you're better off being careful until you know it well, no matter how used you are to working in the great outdoors. Be careful with motor vehicles on twisty dirt roads. Don't overexert yourself until you have a feel for your limits. Bring snacks and water, avoid heat exhaustion and hypothermia, and you'll be a lot happier.

#### **4.7.3.** Working with Other People

## 4.7.3.1. Care and feeding of your field assistants

If you're lucky, you will have a field assistant to carry all the heavy stuff and do all the tedious work. Wait. Don't do that. You do have to pull your own weight, after all.

Your field assistant may be an undergraduate. Go over some basics of the science before you start. Even if you're working with another grad student who knows your science, *do not expect them to be psychic*. They do not know all the quirks of your setup—and it will have quirks. They don't know all of *your* quirks. They might not know the terminology you're using or the way you want things done. Explain. Be patient. You'll both be happier. When it comes to undergraduates in particular...If they've never been outside before, make sure you take them on a training run somewhere close to town. This will let them get a feel for your pace, and you can see how they hold up in the field. You're not their parent, but it may still behoove you to make sure they dress for the weather and pack a lunch and water. And their own first-aid kit.

#### 4.7.3.2. Be nice to the field station staff!

It makes for a much more pleasant experience. The ARS folks are very knowledgeable about the site and the equipment, and they're willing to help with just about anything if you ask nicely and give them a heads-up. I'm pretty certain Barry could fix just about anything with duct tape and glue...

## 4.7.3.3. Be nice to the office staff

They know all the ins and outs and tricks to make your life easier. Do your travel authorizations ahead of time, ask for help when you need it, and avoid being a jerk.

#### 4.7.3.4. Be nice to your fellow grad students

You'll be working around these people for at least a year. If you help them, they will help you with classes, teaching, field work, etc. Grad student friendships are formed from all-nighters and coffee runs, and I'm assured they stick with you for the rest of your life.

# 4.7.3.5. Be nice to yourself

It's a marathon, not a hundred-yard dash. Figure out your best working strategy early on—for example, I need breaks from staring at computer screens, and computer glasses are wonderful inventions. Do you write better at a coffee shop? In your office? Do you need to go for a walk to get the writing juices flowing?

Exercise and eat well, don't just sit all day. I mentioned coffee and all-nighters above, but try to avoid too much of one or too many of the other. Sleep is necessary. Give yourself mental

breaks as well. Get involved in a community group, a play, a band. Give back to the community if you can.

Look into ways to make your life easier. Get an apartment with a dishwasher. Synchronize shopping runs with your roommates. Academia offers flexible work schedules take advantage of this. If you're a night owl, you can try to avoid 8am classes. If you're not, you can avoid all-nighters!

You're here for at least 2 years, make friends—and not just in the department. The biology students are not our mortal enemies, many of them are great people. And see above re: community groups. Friendships keep you sane (-ish).

#### 4.7.3.6. Don't be TOO nice to your advisor

Don't not be nice, just don't try to pretend everything's perfect when it isn't. Don't set up unrealistic expectations for yourself or them. Be honest about what works and what doesn't, and what you need from them to make things work. You will probably have to say 'no' to things, good grief, don't make excuses, just say no!

Admit when you don't understand what's going on, or what is expected of you. Don't be afraid to ask for help. Make notes of what to discuss with them, and take good notes, but keep in mind that you may need to remind them of what you need when. (And consider bringing them food occasionally.)

Make sure they come to your field site at least once, and ideally before, during, and after you've installed your equipment. It makes communicating that much easier.

#### 4.7.4. Grad school is very self-motivated

Keeping track of your time is important, so you don't miss deadlines or end up typing your thesis at 2am. Consider scheduling or time-tracking apps, the Pomodoro method, or a paper

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planner. Figure out who it's dangerous to get into a conversation with—sometimes you'll start off with a research question, and end up discussing the merits of various coffee grinders or tea varieties...it's fun, but if you have things to do, it's a bit irksome.

# 4.7.4.1. Grad school is 10% intelligence, 25% planning, 15%

# improvisation, and 50% bloody-mindedness

If you're better at the first, learn the others. If you feel like an imposter:

1) squelch that thought, and 2) exult in stubbornness. Good luck!