

QUANTIFYING SPATIAL VARIABILITY OF SNOW WATER EQUIVALENT,
SNOW CHEMISTRY, AND SNOW WATER ISOTOPES:
APPLICATION TO SNOWPACK WATER BALANCE

By

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ABSTRACT

This study quantifies spatial and temporal patterns in snow water equivalent (SWE), chemistry, and water isotopes associated with snowpack shading due to aspect and vegetation in the Valles Caldera National Preserve, New Mexico. Depth, density, stratigraphy, temperature, and snow chemistry, isotope, and biogeochemical nutrient samples were collected and analyzed from five snowpit locations on approximate monthly intervals between January-April 2007. SWE showed little variability between sites in January (~10mm) but differences expanded to 84mm (30%) by max accumulation in open sites and 153mm (45%) between all sites. Sulfate varied by 22% (10.6–13.5 $\mu\text{eq/L}$), Cl^- by 35% (17.4–26.9 $\mu\text{eq/L}$), and $\delta^{18}\text{O}$ by 17% (-16.3–-13.5‰), with SWE exhibiting inverse correlations with $\delta^{18}\text{O}$ ($r^2=0.96$), SO_4^{2-} ($r^2=0.75$), and Cl^- ($r^2=0.60$) at max accumulation. Regression relationships suggest variability in SWE and solutes/water isotopes are primarily driven by sublimation. Mass balance techniques estimate sublimation ranges from 1-16% between topographically- and non-shaded open sites.

1. INTRODUCTION

The introduction to my thesis will begin by outlining the overarching relevance of studying snow hydrology and snow chemistry/water isotopes. The introduction will proceed to broadly discuss factors which affect the spatial variability of snow water equivalent (SWE), snow chemistry, and snow water isotopes over snow accumulation and melt. Hopefully the introduction of my thesis will aid the reader in understanding factors influencing both snow cover distribution and snow chemistry/water isotopes.

1.1 TOPIC RELEVANCE

Seasonal snowpacks of the mountainous western United States provide water for stream flow generation, groundwater recharge, vegetation growth, and biogeochemical fluxes as well as contributing to global and regional climate variability. The storage and release of snowpack water through snowmelt acts as the dominant control on the timing and magnitude of spring runoff. The timing of snowmelt is also important for both natural riparian and human agricultural and urban water supplies as it comes when demand is increasing and controls water resource management practices (Elder et al., 1991). Hydrologic feedbacks in the mountains of the semi-arid southwestern U.S. are unique from those in lower-elevation or humid regions due to the sharp wet-dry seasonal transitions, steep temperature and precipitation gradients with elevation, and high interannual water availability (Bales et al., 2006). Groundwater recharge from snowmelt is especially important in the southwestern U.S. due to the nature of the summer monsoon, which produces high-intensity short-duration rainfall likely to produce a higher

percentage of overland flow versus infiltration (Wilson et al., 1980). As rising populations of the southwestern U.S. continue, our ability to accurately quantify seasonal snowpack water storage will be of critical importance for municipal, agricultural, riparian and groundwater resources (Carroll and Cressie, 1996). However, the amount of water storage is not the only concern in seasonal snowpacks.

Similar to other high elevation sites, the mountains of the western U.S. have been exposed to an increasing number of pollutants and atmospheric trace substances in recent decades. Gaining knowledge of the chemical composition of atmospheric deposition is critical for understanding regional and local air pollution and its effects on hydrologic systems (Turk et al., 2001). Seasonal snowpacks have the unique ability to accumulate and store both wet and dry deposition of chemical mass which is then flushed early and rapidly in the melt season (Pomeroy et al., 2005). The spatial variability of snow chemical loads, similar to SWE, can vary significantly over mountain catchments (Rohrbough et al., 2003). If industrial pollutants are scavenged and deposited in snow cover the resulting meltwaters provide a low pH contribution to mountain soils, lakes, and streams. Due to the low acid neutralizing capacity of high-elevation soils the water quality of seasonally snow covered catchments is sensitive to changes in deposition (Wolford and Bales, 1996). Quantifying the solute storage in the snowpack is therefore important to quantify the effect of snowmelt water inputs on the hydrochemistry and aquatic and terrestrial biota of these basins. (Williams and Melack, 1991).

Quantifying the potential tracers, both chemical and isotopic, of the snowpack and snowmelt are also important for determining the routing and fate of precipitation. The

route precipitation waters follow, either into or over the earth's surface, can be estimated using conservative tracers. These "flowpaths" are important for discerning factors influencing water quality, mineral weathering, and hydrologic properties such as residence time and recharge rate. The quantification of water routing depends on an accurate measure of the precipitation signature which can vary seasonally. Snowpacks are unique in that they store and release tracers through a consistent flow of snowmelt, whereas rainfall inputs are intermittent.

Linkages between the spatial variability of SWE, snow chemistry, and hydrologic routing are needed to anticipate the potential affects of changing climate, land cover, and land use on the hydrologic and hydrochemcial response of mountain basins. Currently, a lack of process understanding and a reliance on sparsely distributed observational networks limit the ability to accurately quantify, simulate, and predict hydrologic responses in the mountain regions of the west (Bales et al., 2006). Based on current knowledge the factors that may control the spatial distribution of SWE, snow chemistry, and snow water isotopes are outlined in the following sections.

1.2 – FACTORS INFLUENCING SWE DISTRIBUTION

The primary factors influencing SWE at maximum accumulation include: deposition, elevation, aspect, canopy interception, physical redistribution, sublimation, and periodic melt. The relative influence of each of these processes depends on physical characteristics of the local environment. For instance, the tundra will be greatly

influenced by wind redistribution as there are no structures (vegetation, mountains, etc...) to disrupt the wind field while slope plays a far greater role in topographically diverse catchments.

1.2.1 – *Elevation*

Elevation is normally considered the most important factor affecting snowcover distribution in mountain catchments (McKay and Gray, 1981). Changes in elevation influence temperature and climate. Air masses traveling over mountains are orographically forced upward (the Orographic effect) causing cooling and condensing leading to precipitation and/or snowfall depending on temperature. Linear associations between the amount of snowfall and specific elevation intervals are commonly found, relating to the localized adiabatic lapse rate (U.S. Army Corps of Engineers, 1956). During the winter season continuous low air temperatures combined with the orographic effect of mountainous regions create ideal conditions for the formation of deep mountain snowpacks.

1.2.2 – *Snowfall*

Snowcover comprises the net accumulation of snow on the ground resulting from precipitation deposited as snowfall. A significant amount of the spatial variation attributed to variability in snowfall is often linked to topography, elevation, and scale. Isolated mountain massifs can force additional orographic lifting which can enhance

precipitation locally on an individual massif (McKay and Gray, 1981). The southwestern U.S. has many localized mountain massifs called Sky Islands which receive significantly more precipitation, occasionally as snow, than adjacent lowlands (Brown-Mitic et al., 2007). The variability of snowfall is commonly considered on three scales ranging from macro or regional scale (up to 10^6 km²), mesoscale or local scale (10^2 to 10^3 m), and microscale (10 to 10^2 m) (Goodison et al., 1981). The study area described in this document focuses on the mesoscale, thus regional variability in snowfall is not considered. Spatial variability in snowfall at the mesoscale is often considered negligible, especially in relatively flat areas of mountain catchments or on large flat plains (Hedstrom and Pomeroy, 1998).

1.2.3 – *Aspect*

Aspect has two major effects on snow accumulation and ablation. The first is due to the enhancing or decreasing solar exposure and the second is the influence of snow redistribution from windward to leeward slopes. A significant portion of the early literature on aspects ability to enhance/decrease solar exposure places the importance of aspect into the snow melt period, suggesting it is predominantly a melt effect (McKay and Gray, 1981; Meiman, 1970). However, studies reporting these conclusions were not located in mid-latitude environments. The relative solar exposure of any aspect is a function of the solar zenith angle, which increases after the winter solstice. Mid-latitude environments experience higher net all-wave radiation which metastasizes from the rising solar zenith angle at winter solstice over the remainder of the snow accumulation period

eventually causing warming and snowmelt. In the Northern Hemisphere the winter sun is low in the southern sky, resulting in enhanced snow grain metamorphism, snow densification, and ablation preferentially on southern and western aspects over northern and eastern ones respectively. Overall, this result implies that the relative influence of aspect is gauged by both local slope and the sun's position in the sky. Diverse topography causes high variation in aspect which stimulates variability in localized snow cover. Snow cover modeling efforts have shown varying aspects primarily dictate the influence of solar radiation on snow accumulation and ablation (Link and Marks, 1999a; Molotch et al., 2004).

1.2.4 – *Physical Redistribution*

Physical redistribution of snow, including snow slides and wind redistribution, can significantly alter snow accumulation in a variety of environments. Avalanches occur in various forms and sizes and have the potential to quickly redistribute vast quantities of snow with speeds occasionally topping 100 meters per second. Avalanches require deep snowpacks, slopes generally over 25°, and are caused when slope parallel shear stresses overcome internal cohesion (Schaerer, 1981).

In general, wind redistribution has the greatest affect in alpine and tundra regions where wind fields are not as affected by surface roughness and vegetation. The two primary modes of snow transport are saltation and suspension. Saltation occurs nearest the surface and is the dominant mode at low wind speeds while suspension occurs to

heights of several tens of meters and dominates at high wind speeds (Pomeroy et al., 1991). The ability of the wind to transport snow is a function of wind speed, surface shear stress, air density, roughness height, shear velocity, and upwind fetch (Kind, 1981). A thorough description of the physics of blowing snow and snow transport can be found in Pomeroy et al. (1993). Although wind transport of snow can physically relocate snow from lee to non-lee areas, it also has the ability to reduce snowcover through enhanced sublimation of suspended or saltating snow. In contrast to stationary snow, blowing snow has a high surface area to mass ratio. This process subjects the blowing snow to intense atmospheric turbulence, increasing the potential for turbulent transfer of heat and water vapor (Pomeroy and Jones, 1996).

1.2.5 – *Sublimation*

Snow sublimation is driven by inputs of sensible and net-radiative heat which must be sufficient to drive the latent heat requirements of the sublimation process (Pomeroy and Jones, 1996). The fluxes of latent and sensible heat to the snow surface are, in general, controlled by the gradients of wind speed, air temperature, and vapor pressure in the atmosphere directly above the snow surface as well as the relevant turbulent diffusivities of momentum, heat, and water vapor for the given environment (Male, 1980). Thus, the importance of sublimation to the water balance of a mountain catchment depends on the relative amount of energy input available to drive the sublimation process. Several studies have reported sublimation to be episodic in nature due to the limited available energy of mountain catchments (Fassnacht, 2004; Hood et al.,

1999; Leydecker and Melack, 1999; Zhang et al., 2004). As vapor pressure deficits, temperature, and wind speed rise the ability of the atmosphere to drive sublimation increases (Hood et al., 1999). However, all of these studies rely on meteorological data to perform mass and energy balance equations to estimate sublimation and subsequently winter water balance. The equipment required to gauge the required meteorological measurements is expensive and cumbersome and therefore the number of mountain catchments with the required instrumentation is limited (Fassnacht, 2004).

1.2.6 – *Vegetation Interactions*

The effects of vegetation and canopy interception on snow distribution have been widely studied (Hardy et al., 1997; Hedstrom and Pomeroy, 1998; Link and Marks, 1999a; Marks et al., 1998; Molotch et al., 2007; Musselman et al., 2008). Forest cover is known to significantly affect the accumulation, redistribution, melt rate, and coverage duration of mountain snowpack, thus impacting the potential meltwater input. In addition snowpacks beneath forest cover are less variable than in open areas due to the forests ability to dampen the wind field (Pomeroy et al., 1998). However, the general belief regarding snow/vegetation interaction is that reduction of forest cover increases water yield (Hibert, 1967). This result is supported by findings that tree canopies can intercept up to 60% of falling snow and cause 25-45% of the total snowfall to be sublimated during suspension (Hedstrom and Pomeroy, 1998). Suspended snowfall is subjected to enhanced sublimation over snow on the ground as the surface to mass ratio increases during suspension. The complex mass and energy exchanges during suspension also

contribute to enhancing sublimation (Pomeroy et al., 1998). More recent work in northern New Mexico indicates snow depth can be optimized by optimal tree stand density (Veatch et al., 2008) and may have the ability to delay spring melt through reduction of incoming short-wave radiation (Musselman et al., 2008). Additionally, Rinehart et al. (2008) has implied canopy suspended snow can significantly alter the scattering of incoming shortwave radiation by changing the catchment albedo. The modeling results of this study showed the scattering of shortwave radiation through this process had significant effects on the amount, timing, and duration of snowcover.

1.2.7 – Periodic Melt Events

The general nature of continental snowpacks (very dry and cold) makes the influence of melting events prior to maximum accumulation limited, as they occur less frequently in continental environments. The Sierra Nevada and Cascade Mountains of California, Oregon, and Washington are located in maritime environments with more temperate climates. Snowpacks in these ranges are more susceptible to melt-freeze cycles, rain-on-snow events, and melt losses prior to max accumulation (Elder et al., 1991). Similar to sublimation the process of snowmelt is dictated by energy availability and snow albedo (Male and Gray, 1981). As the majority of available energy interacts with the snow pack at its surface, snow packs typically melt from the top down (Taylor et al., 2001), although a small amount of melt can occur at the base due to ground heat flux (Male and Gray, 1981). Melt losses in high-elevation catchments during accumulation are typically minimal as snowpacks rarely become isothermal prior to the melt period.

However, as previously mentioned radiation inputs may vary depending on aspect, indicating southern aspects may be more prone to melt during accumulation causing melt-freeze and potentially melt loss compared with other aspects.

1.3 FACTORS INFLUENCING SNOW CHEMISTRY AND SNOW WATER ISOTOPES

Several of the factors influencing snow chemical and isotopic signatures overlap with those affecting SWE distribution. These include wet deposition, elevation, wind redistribution, sublimation, and melt. Factors independent of those influencing SWE distribution include dry deposition, snow grain metamorphism and oxidation/ photochemical reactions.

1.3.1 - *Wet and Dry Deposition*

Chemical deposition to snowcover occurs in two ways, wet and dry deposition. Wet deposition to snow primarily occurs through snowfall and incorporates atmospheric chemicals via three main processes: (1) Imprisonment during ice crystal formation; (2) capture of gases, aerosols, and larger particulates within clouds; and (3) scavenging of these materials by snow crystals below the cloud layers during snowfall (Barrie, 1991). Below cloud scavenging is mainly caused by impaction, is dependant on snow crystal parameters such as grain type and size, and typically accounts for ~50% of the total chemical mass in snowfalls (Murakami et al., 1985). The major soluble species are

NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , Ca^{2+} , K^+ , Na^+ , and Mg^{2+} and are derived from natural and anthropogenic emissions including sea-salt aerosols, fossil-fuel burning, and volcanic activity (Pomeroy et al., 2005). Snowfall chemical composition depends on factors such as air mass origin, storm track, altitude, antecedent snowfalls, local pollutions sources, and meteorological conditions. Altitude can also play a key role as snowfall at higher elevation typically has lower concentrations due to the shorter air column for the snow crystals to scavenge from. However, the altitude affect can be solute specific as some catchments see more acidic conditions at higher elevations (Helliwell et al., 1998).

Water isotopes ($\delta^{18}\text{O}$, δD) are inherently part of the falling snow crystal and the isotopic content of falling snow can be affected by precipitation source, altitude, antecedent snowfalls, and temperature. Evaporation at the precipitation source dictates the initial content of atmospheric water vapor in storm masses. The latitude and altitude effects on water isotopes are well documented as higher latitudes and elevations are more depleted in the heavier ^{18}O and ^2H isotopes (Craig, 1961). This phenomenon is mainly due to temperature differences as equilibrium fractionation of water isotopes is temperature dependant (Clark and Fritz, 1997). Snowfall water isotopes exhibit seasonal trends with the most depleted ^{18}O and ^2H snowfalls occurring during the coldest month of the year (Motoyama and Hirasawa, 2005; Unnikrishna et al., 2002).

The spatial variability of snowfall chemistry can vary on length scales from meters to hundreds of meters. Tranter et al. (1986) viewed significant variation in Cl^- and NO_3^- of fresh snowfall chemistry over a 700m transect as one standard deviation was ~40% of the mean. Sulfate values showed considerably less variability with one standard

deviation less than 15% of the mean. A portion of the variability in snowfall chemistry was attributed to the 150m elevation change over the transect length. A Sierra Nevada study (Williams and Melack, 1991) reached different conclusions as differences in the VWM concentrations of snowfall were found to be insignificant using a one-way ANOVA over a catchment size of $\sim 1 \text{ km}^2$. The spatial and temporal variability of water isotopes is well documented and known as several isotope effects, however, the variability of isotopes within single precipitation events tends to be limited over short scales (Clark and Fritz, 1997).

Dry deposition to the snowpack typically occurs in the form of mineral dust and sea-salt aerosols, however, gaseous species may also be absorbed. Atmospheric deposition of dusts from as far away as Asia have been found in snowpacks in the western U.S. (Hidy, 2003). In general the deposition of sea-salt aerosols only has significant effects on snow chemistry in maritime environments (Helliwell et al., 1998; Tranter et al., 1986; Williams and Melack, 1991). Dry deposition to dry cold snow covers is also expected to be lower than maritime environments. The lack of liquid water in cold snow packs increases the surface resistance of snow which lessens the ability for dry deposition (Pomeroy et al., 1999). Recent research in the central and southern Rocky Mountains found dry deposition only significantly increased Ca^+ concentrations (Mast et al., 2001), while research in coastal Alaska found Na^+ and Cl^- concentrations were increased, most likely due to sea salt aerosols (Pomeroy et al., 1999).

1.3.2 – *Sublimation*

Sublimation and condensation generally have opposite effects on snow chemistry and water isotopes. Sublimation tends to increase the concentrations of conservative solutes as solute mass remains in the snow pack during the phase transition of water, while condensation lowers concentrations by depositing water volume without solute mass (Pomeroy et al., 1999). The fractionation of water isotopes caused by the phase transition from ice to water vapor also causes enrichment of the heavy isotopes (^{18}O and ^2H) (Stichler, 1986). The effects of condensation depend on the isotopic content of the condensing water, although studies have shown condensation tends to cancel the effects of sublimation in natural snow covers (Friedman et al., 1991; Moser and Stichler, 1975). Volatilization of organic (Leggett and Hogan, 1995) and inorganic solutes has also been observed under sublimation condition. Pomeroy and Jones (1996) found an increase in SO_4^{2-} and Cl^- concentrations, but no change in NO_3^- during sublimation under laboratory conditions, suggesting NO_3^- is volatilized proportional to sublimation. Similar results have been found in the field (Pomeroy et al., 1999).

1.3.3 – *Wind Transport and Redistribution*

The turbulent transport of snow can affect snow chemistry in three basic ways: (1) Chemicals incorporated within and on the surface of snow crystals are transported with the snow; (2) solutes can be concentrated within the snow crystal due to sublimation; and (3) blowing snow can perform additional scavenging of the environment during

suspension (Pomeroy and Jones, 1996). Process 1 increases chemical load at the deposition point, but can either increase or decrease concentration depending on the chemical content of the blowing snow compared with that at the deposition point. Processes 2 and 3 serve to increase chemical concentrations in the individual snow crystals and thus also increase chemical load at the deposition point. Pomeroy and Jones (1996) have also suggested that photochemical reactions could cause the loss of NO_3^- and potentially the concomitant oxidation of other reduced species (e.g. S^{4+}) during snow transport, although no direct evidence of this has been observed.

The main effects of blowing snow on the isotopic signature of snow cover are transport and sublimation, which has been previously discussed. Sublimation during transport enriches the individual snow crystals in the heavier water isotopes (^2H , ^{18}O) while transport alone changes the isotopic content of the snowcover at the deposition point. Therefore, in regions where blowing snow is of significant concern to the winter water balance, it can also significantly affect the distribution of snow chemical load and snow water isotopes.

1.3.4 – *Canopy Interception and Interaction*

The effects of canopy interception and interaction on snow chemistry and water isotopes are generally to increase chemical concentrations and enrich heavy isotopes. Suspended snow undergoes enhanced sublimation over snow on the ground (section 1.2.6), causing the aforementioned effects of sublimation on snow chemistry. Studies

have also hypothesized that dry deposition may be enhanced in canopy suspended snow, although physical and/or analytical evidence was not found (Pomeroy et al., 1999). Snow unloading from tree canopies can also scavenge nutrients from the branches and leaves of trees while leaf litter deposited in snowpacks beneath canopies can also contribute to snow pack chemical loads (Fahney, 1973; Pomeroy et al., 1999).

1.3.5 – *Snow Grain Metamorphism*

The influence of snow grain metamorphism on snow chemistry is still not fully understood. It is currently accepted that the solute becomes redistributed to, and concentrated on, the snow-grain surfaces or in snow particle bonds during dry snow metamorphism (Pomeroy et al., 2005). Direct observation of this process has not been made, however, it is the migration of solutes to the surfaces of ice crystals which is hypothesized as the primary driver of the ionic pulse (Bales et al., 1989; Brimblecombe et al., 1985; Cragin et al., 1996; Harrington et al., 1996; Hudson and Golding, 1998). Metamorphism effects of snow grains and their influence on water isotopes have been observed. The recrystallization caused by solar radiation, temperature, and wind variations has been shown to alter the original isotopic content of fresh snow (Moser and Stichler, 1975), while several laboratory and field studies have witnessed the enrichment of heavy isotopes during the formation of depth hoar at the base of the snowpack due to water vapor movement away from the snow pack base (Friedman et al., 1991; Sommerfeld et al., 1991; Unnikrishna et al., 2002).

1.3.6 – *Snowmelt*

The final process which will be covered which can influence snow chemistry and water isotopes is snow melt. Snowmelt causes the concentration of solutes in the meltwater, termed “ionic fractionation” or “ionic pulse”, such that 20-30% of the initial meltwater can release as much as 50-80% of the total solutes in the snowpack (Bales et al., 1989; Cragin et al., 1996; Harrington et al., 1996). Melt-freeze cycles have also been shown to increase or mitigate the potential of the ionic pulse depending on melt rate (Bales et al., 1989). Solutes have also been shown to exhibit a preferential elution sequence generally following $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ (Brimblecombe et al., 1985; Tranter et al., 1986) although studies have reached varying conclusions regarding this sequence (Bales et al., 1989; Cragin et al., 1996).

Snow grain metamorphism induced by snowpack temperature gradients as well as percolating meltwater have both been observed to cause the isotopic homogenization of snow packs (Taylor et al., 2001; Unnikrishna et al., 2002). Percolating meltwater is capable of incurring homogenization very quickly by comparison with metamorphism. Meltwater leaving the snowpack also serves to flush the snowpack in light isotopes, enriching the snowpack in the heavier isotopes (^2H , ^{18}O). Therefore, any melt occurring in the snowpack has the potential to rapidly alter the chemical (Hudson and Golding, 1998) and isotopic signature of the snow pack (Unnikrishna et al., 2002).

1.3.7 – *Spatial Variability of Snowpack Chemistry*

The majority of studies analyzing the spatial variability of snow chemistry have concluded Na^+ and Cl^- tend to be more variable in coastal regions due to sea-salt aerosols while Ca^{2+} and $\text{NO}_3^-/\text{SO}_4^{2-}$ are more variable in continental regions due to dust particulates and local anthropogenic emission sources respectively. In general, these studies employ statistical methods to distribute chemical and nutrient loads and clarify the processes influencing variability in snow chemistry (Rohrbough et al., 2003; Tranter et al., 1987; Turk et al., 2001; Williams and Melack, 1991; Williams et al., 1992). Work in California's Sierra Nevada found very low concentrations of major ions over four years (major anions 2.3-2.8 $\mu\text{eq/L}$, cations 0.6-1.7 $\mu\text{eq/L}$, pH ~5.3) with little spatial variation in any given year (Williams and Melack, 1991). Study of an alpine southern Wyoming snowpack showed significant spatial variability over less than 1 km^2 (Rohrbough et al., 2003). Sulfate, NO_3^- , and Cl^- all showed more than 3.8 $\mu\text{eq/L}$ difference over the study area. Rohrbough et al. attributes this heterogeneity to a variety of processes including dry deposition and volatile loss of the gaseous HNO_3 through equal temperature metamorphism of snow grains.

On a regional scale Turk et al. (2001) showed H^+ , Ca^{2+} , NH_4^+ , SO_4^{2-} , and NO_3^- concentrations in the Rocky Mountains were elevated over the Cascade and Sierra Nevada Mountains. Chloride concentrations had the opposite trend, which was attributed to sea-salt aerosols. Ion concentrations within the Rocky Mountains also increased geographically from North to South, with the highest overall concentrations and lowest pH values occurring in northern New Mexico. Turk et al. (2001) speculated that a

greater abundance of anthropogenic emission sources in southern Colorado and northern New Mexico may be increasing snowpack chemical concentrations in the southern Rocky Mountain region (SRMR). A concomitant study by Mast et al. (2001) utilized $\delta^{34}\text{S}$ values to infer the relative input of sulfur from anthropogenic and natural sources in the Rocky Mountains. The study concluded sulfur deposited in the SRMR was primarily derived from anthropogenic sources, as biogenic emissions, marine aerosols, and continental dust contributions were found to be negligible. The study also found sulfur in the SRMR was distinctly different than that deposited in Wyoming and Montana snowpacks.

While significant research has been conducted in the areas of SWE distribution and snow chemical/isotopic distribution, little research has been conducted exploring the linkages between the two. The purpose of this study was to establish how an energy gradient across study locations within a single elevation band may influence snow accumulation, distribution, and snow chemistry and water isotopes. The broad spectrum of environments in the snow studies reviewed in the introduction have shown local climatologic conditions significantly influence the snow pack in its water storage capacity, physical structure, and chemical/isotopic signature. Little work has been done in lower mid-latitude environments where the influences of cold air temperatures, high solar fluxes, mixed-conifer canopies, and moderate snowpacks may compile the relationships observed elsewhere. In addition, lower mid-latitude environments may be

at higher risk to the affects of global warming as yearly snowpacks show greater heterogeneity compared with more northern latitudes (NRCS, 2008b). The unique setting of this study allows us to explore the relationship between SWE and snow chemistry/water isotopes and how those relationships relate to the snow pack water balance. Hopefully with a broad overview of the factors which influence snow accumulation, ablation, chemistry, and water isotopes the readers of this thesis will be able to draw their own conclusions from the data presented.

1.4 STUDY SITE DESCRIPTION

The diverse landscape of New Mexico has unique and distinct effects on the hydrologic cycle of this semi-arid to arid terrain. The highlands of New Mexico experience seasonal snow covers which feed the perennially flowing Rio Grande River supporting a lush riparian corridor and rich agricultural industry along the rivers banks. The highest peaks in the state are found in northern New Mexico in the Sangre de Cristo, Sandia, and Jemez mountain ranges. Wheeler Peak is the highest in the state at 4012 meters in the Sangre de Cristo Range while each of these ranges lies at the southern margin of the Rocky Mountain ecoregion (Allen et al., 1991). Redondo Peak (3432m) and associate massif serve as the study area for this research and are located in the Valles Caldera National Preserve (VCNP), Jemez Mountains, northern New Mexico (106°33'23"W, 35°52'19"N) (Figure 1). The VCNP is a former land grant purchased by the U.S. government through the VCNP act of 2000 and comprises 89,000 acres of the caldera complex (Public Law 106-248, 2000). This area was once home to pre-Columbian Indian cultures (Paleo-Indian, Archaic, and ancestral Puebloan), Spanish land grants, homesteads and scattered ranches and still holds significant archeological value (Martin, 2003). Cattle grazing, timber harvesting, and mineral resource development all still occur in the surround national forest and private lands.

Redondo Peak, the largest topographic feature of the VCNP, is a resurgent dome centered within the ~1.25 Ma Valles Caldera complex (Phillips et al., 2007). The associated massif is comprised of Redondo and Redondito Peaks as well as two smaller un-named peaks with a prominence of 748m over the valles (valleys) below. The entire

resurgent caldera area is geologically complex due to the violent nature of its formation. Uplift and faulting of the resurgent domes have exposed large, rootless megabreccia blocks composed of pre-caldera rocks immersed in densely welded, intracaldera ash flow tuffs (Goff et al., 2005). The majority of these ash flow tuffs are rhyolitic and Tertiary to Quaternary in age. The largest bedrock member is the famous Upper Bandelier Tuff (Tshirege Member), which is densely welded on Redondo Peak (Goff et al., 2006). Contained within the tuffs is a large geothermal reservoir which was explored for geothermal potential in the 1960's and again in the 1980's. Meteoric waters penetrate deeply into the tuffs via fracturing where they are heated in excess of 300°C (Goff and Gardner, 1994). Geothermal alteration ranging from low to high grade has been observed producing altered and secondary forms of calcite, quartz, zeolite, chlorite, feldspar, pyrite, and bright-green epidote (Goff et al., 2006).

Elevation ranges from 2167m to 3432m within the VCNP and yields a variety of vegetation and soil conditions. Douglas fir, whit fir, blue spruce, Engelmann spruce, south-western white pine, and a few aspen stands comprise the primary mixed-conifer forest of the higher-elevations within the preserve (Muldavin and Tonne, 2003). The lower elevations (below ~2740m) see forested regions of ponderosa pine and Gambel oak scrubland (Muldavin and Tonne, 2003) with homogenous grasslands covering the multiple valleys which contain several riparian wetlands and bogs (Coop and Givnish, 2007).

The soils of the VCNP fall into two large groups: forest and grassland soils. Forest soils are primarily mountain soils (Andisols, Alfisol and Inceptisol soil orders), are

derived from the volcanic rocks and gravel (Muldavin and Tonne, 2003), and are shallower, frigid, well-drained sandy loams with high-permeability (NRCS, 2008a). The grassland soils are mostly Mollisols that have developed in the volcanic alluvium of the alluvial fans and piedmonts, or in recent water-deposited sediments of the valley bottoms. They are usually deeper and have rich organic material accumulations in the top layers along with fine textures and little rock accumulation (Muldavin and Tonne, 2003). These soils range from well-drained sandy loams to low permeability silty clay loams near streams (NRCS, 2008a).

The climate of the VCNP can be characterized as semi-arid and montane, with an average yearly precipitation of ~650mm over the last 4 years at micro-meteorological station 14 (3231m). Slightly less than half of the annual precipitation falls in the form of snow between November and April (winter months) with the majority of the remainder falling during the summer monsoon season (July-September). The Pacific Ocean and Gulf of California serve as the dominant precipitation sources. The nearby Quemazon SNOwpack TELemetry (SNOTEL) site has recorded SWE and temperature since 1989 and reports an annual maximum SWE of 257mm with an average temperature over the winter months of -2.2°C (NRCS, 2008b). Table 1 summarizes the winter snow accumulation and meteorological characteristics of our study area (Moore, 2008). Average relative humidity and wind speed are both low (60% and 2.0 m/s respectively) compared with other mountainous areas (Fassnacht, 2004) with a vectored mean wind direction from the west-northwest. Snowmelt typically begins in late March or early April as monthly temperatures transition from a March mean of -1°C to an April mean of

2.7°C (NRCS, 2008b). VCNP winters are significantly warmer than other Rocky Mountain environments with winter mean temperatures around -2.2°C. By comparison the University Camp SNOTEL site in Northern Colorado is at a similar elevation (3140M) yet records annual winter temperatures over the same time span of -5.5°C. The 2006-2007 winter can be described as average with the exception of temperature, as March 2007 was exceptionally warm leading to an earlier than normal maximum accumulation date (March 10th, 2007) and snowmelt.

My study area is contained within a broad, relatively flat area of the Redondo Massif with an average elevation of ~3015m. Small high elevation mountain clearings are interspersed within the mixed-conifer forest at this elevation. Average forest heights near our study domain range from 18.7 to 20.5m with a leaf area index (LAI) of 3.43 ± 0.5 (McDowell et al., 2008). The majority of snowmelt from the study area drains to the La Jara Creek catchment on the south side of the massif. La Jara Creek is the largest catchment on the Redondo massif and is instrumented with temperature sensors, pressure transducers, a recording stream gauge, a trapezoidal flume, and an automated water sampler. Seven smaller streams draining the catchment also are instrumented with flumes and temperature sensors (described in Lyon et al., 2008). An eddy covariance tower system along with instrumentation including snow depth sensors, alter-shielded heated rain-gauge, time-domain reflectometry (TDR) soil moisture sensors, and sap flow sensors are located at the northeast corner of our study domain at ~3050m.

1.5 THESIS FORMAT

The format of this thesis is defined by the University of Arizona Graduate College's *Manual for Theses and Dissertations* and is, therefore, subject to repetition. It includes an introductory chapter describing the uniqueness and relevance of this research, a chapter on the Present Study that briefly summarizes the findings of the manuscript included in Appendix A and discusses the conclusions and implications of these findings. Appendix A is a scientific manuscript on the spatial distribution of snow water equivalent, snow chemistry and water isotopes, and the processes inferred by the relationships between them. This manuscript is planned for submission to the journal *Water Resources Research*. The manuscript succinctly reiterates the introduction, conclusions, and implications presented in the body of this thesis, but it also includes chapters that describe the methods and discuss the results of my research. The manuscript addresses the following questions:

- 1) *What is the spatial variability of snow water equivalent and snow chemistry/water isotopes in our study domain?*
- 2) *Do differences in energy inputs caused by topography and vegetation shading influence the spatial variability of SWE and snow chemistry/water isotopes?*
- 3) *Can we use observed systematic differences in the chemical and isotopic signature of snow cover to imply the effects of energy gradient on snowpack water balance?*

2. PRESENT STUDY

The methods, results, and conclusions of this study are presented in the manuscript, “Quantifying spatial variability of snow water equivalent, chemistry, and water isotopes: Application to snowpack water balance.” Appendix A. The following is a summary of the most important findings in this paper.

2.1 PRESENT STUDY

In this research I attempt to evaluate the impact of an energy gradient on snow water equivalent (SWE), snow chemistry, and snow water isotopes. I compared measured values of SWE, analysis of major anions, major cations, biogeochemical nutrients, and water isotopes both with each other and with a solar forcing index. This approach allows me to gauge the behavior of SWE accumulation, variations of solutes and isotopes with SWE, and explore the potential for mass balance techniques within seasonal snowpacks. The principal goals of this study were three fold. First, my study seeks to establish the spatial variability of snow water equivalent and snow pack chemistry/water isotopes within 5 variable shading environments located in our study domain. Second, I analyze if differences in the energy inputs caused by topographic and vegetation shading relate to the spatial variability of SWE and snow pack chemistry/water isotopes. Third, I investigate if systematic differences in the chemical and isotopic signature of snow cover can be used to quantify energy gradient effects on snow pack water balance.

The locations of the five intensive snow pits were chosen to address the preceding study goals. Several basic criteria were used to select pit locations: (1) Each open snow pit location should have its own principal aspect or pits analyzing canopy shading should have no aspect, (2) all snowpits will be located in close elevation proximity, (3) snow pits should be located near other concurrent study sites/instrumentation, and (4) all snow pits should be located such that they are representative of the maximum SWE accumulation of the Redondo massif's upper elevations.

The general hypothesis was that the energy gradient between sites would directly relate to SWE and solute accumulation patterns over the winter season. In addition, an analysis of the potential of all solutes to act conservatively would yield one of two results. One, if solutes are conservative with SWE, then there would be potential to use mass balance techniques to estimate the partition of snowfall between sublimation and catchment water input. Two, if solutes were found to be conservative with the energy gradient then there may be potential to distribute catchment chemical inputs using measured concentrations and a solar forcing index.

2.2 CONCLUSIONS AND IMPLICATIONS

2.2.1 Context for Research

Mountain snowpacks in the western U.S. are the primary source of later spring and summer stream flow generation and their melt often causes the largest annual stream discharge event (Bales et al., 2006). The pathways taken by snowmelt to surface streams

has important implications for flood prediction, resource management, water budgets, and heat and chemical fluxes to rivers and riparian areas (Johannessen and Henriksen, 1978). Quantifying hydrologic flowpaths is also important for determining factors affecting water quality, mineral weathering, and hydrologic properties such as residence time and recharge. The influence of snowpacks in the southwest U.S. may be especially important for groundwater recharge as summer monsoon rains are characterized by high-intensity events, which produce a higher ratio of overland flow to infiltration (Wilson et al., 1980).

The unique ability of the snowpack to retain and accumulate chemical and pollution mass over the winter season makes the release of this mass potentially harmful to the aquatic and terrestrial ecosystems of high elevation areas, where the acid neutralizing capacity of soils is low (Huth et al., 2004). Therefore, gaining knowledge of the chemical composition of atmospheric deposition is critical for understanding regional and local air pollution and its effects on hydrologic systems (Turk et al., 2001).

Previous studies of snow chemistry and snow water isotopes have shown the spatial variability of snow chemistry can be highly variable (e.g. Rohrbough et al., 2003; Tranter et al., 1987; Turk et al., 2001; Unnikrishna et al., 2002). Variability can be attributed to physical redistribution (Pomeroy et al., 1991), dry deposition (Rohrbough et al., 2003), sublimation (Pomeroy et al., 1999), melt-freeze cycles and vegetation (Hudson and Golding, 1998), and surface-exchange of water vapor among other factors (Pomeroy et al., 2005). Despite the fact that many of these studies are performed in conjunction with SWE distribution studies, none of them have established links between snow

chemical concentrations and SWE accumulation; as the two are usually treated and distributed separately even though the processes affecting them are closely related.

The Valles Caldera National Preserve (VCNP) is located in the Jemez Mountains at the southern most extent of the Rocky Mountains in the arid high desert of northern New Mexico. The high-elevation environment of the VCNP contrasts the lower semi-arid desert from which it rises. The VCNP is also at the northern extent of the North American Monsoon, creating stark contrasts in precipitation inputs from the snow-dominated winter season (Nov.-Apr.) to the high-intensity precipitation characteristic of the monsoon season (Jul.-Sep.). The southerly latitude ($\sim 35^\circ$) of the VCNP results in higher solar energy inputs than mountain regions further north. The VCNP's environment may allow the influences of cold air temperatures, high vapor pressure deficits, elevated solar flux, mixed-conifer canopies, and moderate depth snowpacks to compile relationships between SWE and snow chemistry/isotopes. In addition, lower mid-latitude environments may be at higher risk to the affects of global warming as yearly snowpacks show greater heterogeneity compared with more northern latitudes (NRCS, 2008b). These characteristics create a unique study area to address the affects of solar energy input on the spatial variability of SWE, snow chemistry, snow water isotopes.

Two recent studies at our field site directly explored the influence of solar energy gradients on SWE accumulation and ablation. Musselmann (2008) analyzed the influence of vegetation shading on SWE accumulation and ablation at the plot scale of a single tree. Musselmann observed the relative timing of maximum SWE varied between

the exposed southern side of the tree and the shaded northern side, with maximum SWE occurring as much as 1 month later on the north side. The timing and duration of snowmelt was also influenced as the northern side of the tree ablated later and slower than the south side. In the second study, Rinehart et al. (2008) explored the impact light scattering and shading caused by high solar fluxes of lower latitude sites have on snow distribution. They concluded that snow or mixed snow-vegetation albedo has significant effects on scattering incoming short-wave radiation which in turn directly influences the amount, timing, and duration of maximum SWE. A third study by Kostrzewski et al. (2008) analyzed stream and spring water chemistry in the La Jara Creek drainage to gauge seasonal variability in flowpath, solute source, and nutrient modification. As applicable to this study, her results found higher than expected nitrogen concentrations during winter and snowmelt periods. The ratio of conservative solutes Cl:SO₄ in La Jara Creek also implied precipitation was the dominant solute source in this low residence time catchment.

The previous work indicated there was a need to explore the relationships between energy input and snow accumulation and chemistry/water isotopes over a greater range of energy environments. This study sought to address this need and to define the winter precipitation chemical input during a winter experiencing average snow accumulation. My approach during this study was to infer knowledge of the processes affecting snow accumulation and chemistry by establishing and repetitively visiting several intensive snow pit locations. The general hypothesis was that the energy gradient between sites would directly relate to SWE and solute accumulation patterns

over the winter season with the hope we could infer something about the partitioning of snowfall input between water loss and catchment water input.

2.2.2 Impacts of Solar Energy Gradient on Snow Accumulation

Observations of snow accumulation from mid-January through March 10th (maximum accumulation date) showed SWE differences between the topographically shaded open snow pits and the non-shaded open pits expand from <10mm to 103mm (Figure 5). The overall range of SWE observations at max accumulation stretched from 187mm at the dense vegetation (DV, under dense vegetation) pit to 340mm at the topographically shaded open snow pit 1 (TS1), a difference of 153mm or 45%. Snowfall from late November through mid-February was fairly consistent, however, after mid-February little deposition occurred resulting in a small accumulation change between the mid-February sampling campaign and max accumulation. In addition the topographically shaded open snowpits showed greater accumulation between all site visits than the non-shaded open sites and the DV site.

A comprehensive review of the principal factors affecting snow accumulation showed sublimation was the primary driver affecting variability in SWE between sites. Early in the winter season the zenith angle of the sun is low on the horizon. As the winter season progresses and solar zenith angles rise, the difference in energy inputs can metastasize between study locations. This may explain the increasing differences in SWE over the accumulation season, as increasing energy inputs provide enough energy

to drive the latent heat fluxes enhancing sublimation at the non-shaded open snow pit locations over the topographically shaded open snow pits.

The design of this study drove the need to develop a solar forcing index (SFI) to compare the relative influence of energy inputs between sites. A simple regression between observed SWE at maximum accumulation and SFI showed a strong relationship ($r^2=0.88$) between the open snow pit locations. This relationship provides more evidence that differences in energy inputs exist between sites and these differences are driving the variability in SWE at maximum accumulation. The dense vegetation pit is an exception in this relationship as it is strongly influenced by canopy interception. The SFI does not account for energy inputs during interception and suspension of snow, therefore, a direct relationship between SWE and SFI is not expected at the DV snow pit.

2.2.3 Impacts of Solar Energy Gradient on Snow Chemistry and Water Isotopes

Analyzing volume weighted mean (VWM) chemical concentrations and water isotope values from the snow samples showed a repetitive pattern in potentially conservative solutes/isotopes between sites. The topographically shaded-open snow pit locations contained the lowest concentrations of SO_4^{2-} , and Cl^- and were isotopically the lightest, while the dense vegetation pit had the highest concentrations and was isotopically the heaviest (Table 4). This relationship prompted an analysis of the relation of SWE with conservative solutes. Inverse regression relationships between SO_4^{2-} , Cl^- ,

$\delta^{18}\text{O}$, and δD with SWE showed strong correlations with r^2 values of 0.80, 0.62, 0.92, and 0.81 respectively. All but the Cl^- value is significant at the 95% confidence level.

The regression relationships of water isotopes and conservative solutes SO_4^{2-} and Cl^- with SWE (Figure 5) indicate the gradient of shading environments is not only affecting SWE accumulation and ablation, but also the isotopic and chemical signature of our snowpack. During the sublimation processes, the phase transition of water from ice to vapor causes fractionation in the water isotopes, preferentially enriching the heavier ^{18}O and ^2H isotopes in the snowpack as the lighter ^{16}O and ^1H isotopes enter the vapor phase (Stichler, 1986). The sublimation process also concentrates solutes by removing water mass while retaining chemical mass. Combined with the SWE data, results indicate sublimation is the primary driver causing variability both in SWE and solute/isotope concentrations at maximum accumulation.

An analysis of the elution trend of solutes was also performed to gauge the influence of SFI during the melt period. The differences in VWM SO_4^{2-} and NO_3^- concentration between March 10th and the March 31st sampling date are shown in Figure 6 plotted against SFI. This figure shows two results: (1) the VWM concentration change of SO_4^{2-} and NO_3^- between maximum accumulation and melt varied systematically with SFI and (2) the solutes appeared to follow the elution sequence $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ as similar to previous research (Brimblecombe et al., 1985; Tranter et al., 1986). While SO_4^{2-} showed preferential elution at all snow pits over NO_3^- , the full elution sequence of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ was only seen at the LR and T sites. The chloride sample at the SL site during the March 31st sampling date was potentially contaminated and is not depicted.

These results have important implications for estimating not only the solute load delivered to the catchment, but also the relative timing and concentration of the solutes released, which may impact catchment tracer studies ability to accurately quantify hydrologic flowpaths.

2.2.4 Snowpack Water Balance and Sublimation Estimates

Based on the aforementioned relationships between water isotopes, sulfate, chloride, and SWE, it was evident a mass balance calculation could be performed to partition snowfall between sublimation and water input. The range of sublimation estimates at each site varies (Figure 7), however, using sulfate mass balance as an overall indicator of sublimation I see sublimation estimates of the total snow water equivalent ranging from ~1% at the topographically shaded open sites (NL, LR) to ~16% at the non-shaded open sites (T, SL).

Studies using mass and energy balance approximations have found sublimation ranging from 4-13% of SWE in the Central Sierra Nevada (Leydecker and Melack, 1999) to 15% at Niwot Ridge, CO (Hood et al., 1999). The relative percentage of SWE sublimation estimated using mass balance techniques in this study agree well the aforementioned results. Sublimation estimates at the dense vegetation site are less conclusive for two main reasons: (1) Smaller snowfall events may be completely intercepted and sublimated during suspension, leaving no record in the snow pack below and (2) canopy interaction and leaf litter deposition clearly is affecting the chemical signature of the snow pack.

2.2.5 *Broader Implications*

The results of this study have direct applicability to catchment hydrology tracer studies and ecohydrology studies concerned with catchment availability of biogeochemical nutrients. Significant errors can arise in these studies from using single snow chemical samples to distribute chemical and isotopic inputs. Our study shows over 3‰ spatial variance in $\delta^{18}\text{O}$, indicating tracer studies may need to account for the spatial variation in the bulk snow composition prior to snowmelt. In addition, if our study were to estimate the nutrient budget in the seasonal snow pack using chemical data from 1 intense snow pit location, error would surpass 15%. Overall, the results of this study offer the possibility that solar forcing estimates may be useful for distributing SWE and snowpack chemical and isotopic signatures, both at maximum accumulation and during melt.

The second important implication of my research pertains to management. Hydrologic fluxes in mountain environments are commonly estimated using a series of meteorological measurements which require costly equipment and are difficult to install due to the remote nature of these sites (Bales et al., 2006; Hood et al., 1999; Leydecker and Melack, 1999; Molotch et al., 2007). The possibility of using mass balance applications to partition snow pack water balance may be useful for distributing water budgets in remote mountainous areas. Further analysis would be required to test the validity of our findings in other semi-arid montane catchments, but this technique could

be beneficial for water managers who needed an estimate of the hydrologic fluxes in mountain snowpacks.

Finally this study provides an initial assessment of the chemical signature of precipitation for an average winter snowpack within the Valles Caldera National Preserve. As per Public Law 106-248, all management of the Valles Caldera National Preserve must be based on scientific findings.

REFERENCES

- Allen, R.B., Peet, R.K. and Baker, W.L., 1991. Gradient Analysis of Latitudinal Variation in Southern Rocky-Mountain Forests. *Journal of Biogeography*, 18: 123-139.
- Bales, R.C., Davis, R.E. and Stanley, D.A., 1989. Ion Elution through Shallow Homogeneous Snow. *Water Resources Research*, 25(8): 1869-1877.
- Bales, R.C. et al., 2006. Mountain hydrology of the western United States. *Water Resources Research*, 42(8).
- Barrie, L.A., 1991. Snow formation and processes in the atmosphere that influence its chemical composition. In: T.D. Davies, Tranter M., and H.G. Jones, (Editor), *Proceedings of the NATO Advanced Workshop on Processes of Chemical Change in Snowpacks*. Springer-Verlag: Berlin, Maratea, Italy, pp. 1-20.
- Brimblecombe, P. et al., 1985. Relocation and preferential elution of acidic solute through the snowpack of a small, remote, high-altitude Scottish catchment. *Annals of Glaciology*, 7: 141-147.
- Brown-Mitic, C. et al., 2007. Seasonal water dynamics of a sky island subalpine forest in semi-arid southwestern United States. *Journal of Arid Environments*, 69(2): 237-258.
- Carroll, S.S. and Cressie, N., 1996. A comparison of geostatistical methodologies used to estimate snow water equivalent. *Water Resources Bulletin*, 32(2): 267-278.
- Clark, I. and Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. CRC Press, Boca Raton, 328 pp.
- Coop, J.D. and Givnish, T.J., 2007. Gradient analysis of reversed treelines and grasslands of the Valles Caldera, New Mexico. *Journal of Vegetation Science*, 18(1): 43-54.
- Cragin, J.H., Hewitt, A.D. and Colbeck, S.C., 1996. Grain-scale mechanisms influencing the elution of ions from snow. *Atmospheric Environment*, 30(1): 119-127.
- Craig, H., 1961. Isotopic Variations in Meteoric Waters. *Science*, 26: 1702 - 1703.
- Elder, K., Dozier, J. and Michaelsen, J., 1991. Snow Accumulation and Distribution in an Alpine Watershed. *Water Resources Research*, 27(7): 1541-1552.
- Fahney, T.J., 1973. Changes in Nutrient Content of Snow Water during Outflow from Rocky Mountain Coniferous Forest. *Oikos*, 32(3): 422-428.

- Fassnacht, S.R., 2004. Estimating Alter-shielded gauge snowfall undercatch, snowpack sublimation, and blowing snow transport at six sites in the coterminous USA. *Hydrological Processes*, 18(18): 3481-3492.
- Friedman, I., Benson, C. and Gleason, J., 1991. Isotopic Changes During Snow Metamorphism. In: H.P. Taylor (Editor), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. The Geochemical Society, San Antonio, pp. 211-221.
- Goff, F. and Gardner, J., 1994. Evolution of a mineralized geothermal system, Valles Caldera, NM. *Economic Geology*, 89(8): 1803-1832.
- Goff, F., Gardner, J., Reneau, S. and Goff, C.J., 2005. Geologic mapping of the Valles Caldera National Preserve, New Mexico. *Geologic Society of America Abstracts with Programs*, 37(7): 175, Paper No. 72-2.
- Goff, F., Gardner, J.N., Reneau, S.L. and Goff, C.J., 2006. Preliminary geologic map of the Valles San Antonio quadrangle, Sandoval County, New Mexico. New Mexico Bureau of Geology and Mineral Resources. Open-file Geologic Map OF-GM 132, scale 1:24,000.
- Goodison, B.E., Ferguson, H.L. and McKay, G.A., 1981. Measurement and Data Analysis. In: D.M. Gray (Editor), *Handbook of Snow*. Pergamon Press, New York, pp. 191-274.
- Hardy, J.P. et al., 1997. Snow ablation modeling at the stand scale in a boreal jack pine forest. *Journal of Geophysical Research-Atmospheres*, 102: 29397-29405.
- Harrington, R.F., Bales, R.C. and Wagnon, P., 1996. Variability of meltwater and solute fluxes from homogeneous melting snow at the laboratory scale. *Hydrological Processes*, 10(7): 945-953.
- Hedstrom, N.R. and Pomeroy, J.W., 1998. Measurements and modelling of snow interception in the boreal forest. *Hydrological Processes*, 12(10-11): 1611-1625.
- Helliwell, R.C., Soulsby, C., Ferrier, R.C., Jenkins, A. and Harriman, R., 1998. Influence of snow on the hydrology and hydrochemistry of the Allt a' Mharcaidh, Cairngorm mountains, Scotland. *Science of the Total Environment*, 217(1-2): 59-70.
- Hibert, A.R., 1967. Forest treatment effects on water yield. In: W.E. Sopper and H.W. Lull (Editor), *Int. Symp. For. Hydrol.* Pergamon Press, Oxford.
- Hidy, G.M., 2003. Snowpack and precipitation chemistry at high altitudes. *Atmospheric Environment*, 37(9-10): 1231-1242.

- Hood, E., Williams, M. and Cline, D., 1999. Sublimation from a seasonal snowpack at a continental, mid-latitude alpine site. *Hydrological Processes*, 13(12-13): 1781-1797.
- Hudson, R.O. and Golding, D.L., 1998. Snowpack chemistry during snow accumulation and melt in mature subalpine forest and regenerating clear-cut in the southern interior of BC. *Nordic Hydrology*, 29(3): 221-244.
- Huth, A.K., Leydecker, A., Sickman, J.O. and Bales, R.C., 2004. A two-component hydrograph separation for three high-elevation catchments in the Sierra Nevada, California. *Hydrological Processes*, 18(9): 1721-1733.
- Johannessen, M. and Henriksen, A., 1978. Chemistry of Snow Meltwater: Changes in Concentration During Melting. *Water Resources Research*, 14: 615-619.
- Kind, R.J., 1981. Snow Drifting. In: D.M. Gray (Editor), *Handbook of Snow*. Pergamon Press, New York.
- Kostrzewski, J., Brooks, P.D., Hogan, J. and Meixner, T., 2008. Quantifying seasonal variations in flowpath, solute source, and nutrient modification: a catchment comparison in Valles Caldera National Preserve, NM. *Ecohydrology*, In Review.
- Leggett, D.C. and Hogan, A.W., 1995. A Preliminary Experiment to Examine Chemical-Exchange at Soil Snow Interface. *Science of the Total Environment*, 161: 403-408.
- Leydecker, A. and Melack, J.M., 1999. Evaporation from snow in the central Sierra Nevada of California. *Nordic Hydrology*, 30(2): 81-108.
- Link, T.E. and Marks, D., 1999. Distributed simulation of snowcover mass and energy-balance in the boreal forest. *Hydrological Processes*, 13: 2439-2452.
- Lyon, S.W., Troch, P.A., Broxton, P.D., Molotch, N.P. and Brooks, P.D., 2008. Monitoring the timing of snow melt and the initiation of streamflow using a distributed network of temperature/light sensors. *Ecohydrology*, In Press.
- Male, D.H., 1980. The seasonal snowcover. In: S.C. Colbeck (Editor), *Dynamics of Snow and Ice Masses*. Academic Press, New York, pp. 305-395.
- Male, D.H. and Gray, D.M., 1981. Snowcover Ablation and Runoff. In: D.M. Gray and D.H. Male (Editor), *Handbook of Snow*. Pergamon Press, New York.
- Marks, D., Kimball, J., Tingey, D. and Link, T., 1998. The sensitivity of snowmelt processes to climate conditions and forest cover during rain-on-snow: a case study

- of the 1996 Pacific Northwest flood. *Hydrological Processes*, 12(10-11): 1569-1587.
- Martin, C., 2003. *Valle Grande: A history of the Baca Location No. 1. All Seasons Publishing, Los Alamos, New Mexico, 157 pp.*
- Mast, M.A., Turk, J.T., Ingersoll, G.P., Clow, D.W. and Kester, C.L., 2001. Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpacks. *Atmospheric Environment*, 35(19): 3303-3313.
- McDowell, N., White, S.A. and Pockman, W., 2008. Transpiration and stomatal conductance across a steep climate gradient in the southern Rocky Mountains. *Ecohydrology*, In Press.
- McKay, G.A. and Gray, D.M., 1981. The Distribution of Snow Cover. In: D.M. Gray and D.H. Male (Editor), *Handbook of Snow*. Pergamon Press, New York, pp. 153-190.
- Meiman, J.R., 1970. Snow accumulation related to elevation, aspect and forest canopy, *Proceedings of the Workshop Seminar on Snow Hydrology*. Queen's Printer of Canada, Ottawa, pp. 35-47.
- Molotch, N.P. et al., 2007. Estimating sublimation of intercepted and sub-canopy snow using eddy covariance systems. *Hydrological Processes*, 21(12): 1567-1575.
- Molotch, N.P., Painter, T.H., Bales, R.C. and Dozier, J., 2004. Incorporating remotely-sensed snow albedo into a spatially-distributed snowmelt model. *Geophysical Research letters*, 31.
- Moore, D., 2008. *Sevilleta Meteorological Data of the Valles Caldera National Preserve, 2003-2008*. Sevilleta LTER Database.
<http://sevilleta.unm.edu/research/local/climate/VCNP/>.
- Moser, H. and Stichler, W., 1975. Deuterium and Oxygen-18 contents as an index of the properties of snow covers, *Snow Mechanics; Proceedings of the Grindelwald Symposium*. IAHS Publication No. 114, pp. 122-135.
- Motoyama, H. and Hirasawa, N., 2005. Seasonal variations in oxygen isotope ratios of daily collected precipitation and wind drift samples and in the final snow cover at Dome Fuji Station, Antarctica. *Journal of Geophysical Research*, 110.
- Muldavin, E. and Tonne, P., 2003. *A Vegetation Survey and Preliminary Ecological Assessment of Valles Caldera National Preserve, New Mexico*. Natural Heritage New Mexico Publ. No. 06-GTR-302., Albuquerque, NM., 59 pp.

- Murakami, M., Kikuchi, K. and Magano, C., 1985. Experiments on aerosol scavenging by natural snow crystals. *Journal of the Meteorological Society of Japan*, 63: 130-135.
- Musselman, K., Molotch, N.P. and Brooks, P.D., 2008. Effects of vegetation on snow accumulation and ablation in a mid-latitude sub-alpine forest. *Hydrological Processes*, 22.
- NRCS, 2008a. <http://soils.usda.gov>.
- NRCS, 2008b. <http://www.wcc.nrcs.usda.gov/snotel/>.
- Phillips, E.H. et al., 2007. The Ar-40/Ar-39 age constraints on the duration of resurgence at the Valles caldera, New Mexico. *Journal of Geophysical Research-Solid Earth*, 112(B8).
- Pomeroy, J.W., Davies, R.E. and Tranter, M., 1991. The impact of blowing snow on snow chemistry, NATO Advanced Research Workshop on Processes of Chemical Change in Snowpacks, Maratea, Italy.
- Pomeroy, J.W. et al., 1999. Transformations of snow chemistry in the boreal forest: accumulation and volatilization. *Hydrological Processes*, 13(14-15): 2257-+.
- Pomeroy, J.W., Gray, D.M. and Landine, P.G., 1993. The Prairie Blowing Snow Model: characteristics, validation, operation. *Journal of Hydrology*, 144: 165-192.
- Pomeroy, J.W. and Jones, H.G., 1996. Wind-blown snow: Sublimation, transport, and changes to polar snow. In: E. Wolff and R.C. Bales (Editor), *Chemical exchange between the atmosphere and polar snow*. NATO ASI Series. Vol. 43. Springer-Verlag, Berlin, pp. 453-490.
- Pomeroy, J.W., Jones, H.G., Tranter, M. and Lilbæk, G., 2005. Hydrochemical Processes in Snow-Covered Basins. *Encyclopedia of Hydrological Sciences*, 14. John Wiley & Sons, Ltd.
- Pomeroy, J.W., Parviainen, J., Hedstrom, N.R. and Gray, D.M., 1998. Coupled modelling of forest snow interception and sublimation. *Hydrological Processes*, 12: 2317-2337.
- Public Law 106-248, 2000. The Valles Caldera National Preservation Act.
- Rinehart, A.J., Vivoni, E.R. and Brooks, P.D., 2008. Effects of vegetation, albedo, and radiation sheltering on the distribution of snow in the Valles Caldera, New Mexico. *Ecology*, In Review.

- Rohrbough, J.A., Davis, D.R. and Bales, R.C., 2003. Spatial variability of snow chemistry in an alpine snowpack, southern Wyoming. *Water Resources Research*, 39(7).
- Schaerer, P.A., 1981. Avalanches. In: D.M. Gray and D.H. Male (Editor), *Handbook of Snow*. Pergamon Press, New York, pp. 475-518.
- Sommerfeld, R.A., Clark, J. and Friedman, I., 1991. Isotopic changes during the formation of depth hoar in experimental snowpacks. In: H.P. Taylor (Editor), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. The Geochemical Society, San Antonio.
- Stichler, W., 1986. Snowcover and snowmelt processes studied by means of environmental isotopes. In: H.G. Jones (Editor), *Seasonal Snowcovers: Physics, Chemistry, and Hydrology*. NATO-ASI Series C, 211.
- Taylor, S. et al., 2001. Isotopic evolution of a seasonal snowpack and its melt. *Water Resources Research*, 37(3): 759-769.
- Tranter, M. et al., 1986. The composition of snowfall, snowpack, and meltwater in the Scottish Highlands-evidence for preferential elution. *Atmospheric Environment*, 20(3): 517-525.
- Tranter, M. et al., 1987. Spatial Variability in the Chemical-Composition of Snowcover in a Small, Remote, Scottish Catchment. *Atmospheric Environment*, 21(4): 853-862.
- Turk, J.T. et al., 2001. Major-ion chemistry of the Rocky Mountain snowpack, USA. *Atmospheric Environment*, 35(23): 3957-3966.
- U.S. Army Corps of Engineers, 1956. *Summary Report of the Snow Investigations*. U.S. Dept. of Commerce, Washington, D.C.
- Unnikrishna, P.V., McDonnell, J.J. and Kendall, C., 2002. Isotope variations in a Sierra Nevada snowpack and their relation to meltwater. *Journal of Hydrology*, 260(1-4): 38-57.
- Williams, M.W. and Melack, J.M., 1991. Precipitation Chemistry in and Ionic Loading to an Alpine Basin, Sierra-Nevada. *Water Resources Research*, 27(7): 1563-1574.
- Williams, M.W., Tonnessen, K., Melack, J.M. and Daqing, Y., 1992. Sources and spatial variation of the chemical composition of snow in the Tien Shan, China. *Annals of Glaciology*, 16: 25-31.

- Wilson, L.G., DeCook, K.J. and Neuman, S.P., 1980. Regional recharge research for Southwest alluvial basins, unnumbered report. Water Resources Research Center. Univ. of Arizona, Tucson.
- Wolford, R.A. and Bales, R.C., 1996. Hydrochemical modeling of Emerald Lake watershed, Sierra Nevada, California: Sensitivity of stream chemistry to changes in fluxes and model parameters. *Limnology and Oceanography*, 41(5): 947-954.
- Zhang, Y., Suzuki, K., Kadota, T. and Ohata, T., 2004. Sublimation from snow surface in southern mountain taiga of eastern Siberia. *Journal of Geophysical Research*, 109.

APPENDIX A – QUANTIFYING SPATIAL VARIABILITY OF SNOW WATER
EQUIVALENT, CHEMISTRY, AND WATER ISOTOPES: APPLICATION TO
SNOWPACK WATER BALANCE

**Quantifying spatial variability of snow water equivalent, chemistry, and water
isotopes: Application to snowpack water balance**

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ABSTRACT

The spatial variability of chemicals deposited in seasonal snow cover creates difficulty in estimating input of both nutrients and pollutants into terrestrial and aquatic environments. This study quantifies the spatial and temporal patterns in snow water equivalent (SWE), snow chemistry, and snow water isotopes associated with snowpack shading due to aspect and vegetation in the Valles Caldera National Preserve, located in the Jemez Mountains of northern New Mexico. Depth, density, stratigraphy, temperature, and snow chemistry samples were collected from five snow pit locations on approximate monthly intervals between January and April 2007. Snow pit locations contrast aspect and vegetation shading to gauge the affect of solar forcing without elevation or slope differences. Analysis of snow samples includes major anions (Cl^- , NO_3^- , SO_4^{2-}), major cations (Ca^{2+} , Na^+ , K^+), water isotopes, and biogeochemical nutrients (DOC, DN). Snow water equivalent (SWE) showed little spatial variability between sites early in the accumulation season ($\sim 10\text{mm}$) but differences expanded to 103mm (237 - 340mm, 30%) by the max accumulation date between open sites and to 153mm (187-340, 45%) between all sites. Sulfate concentrations varied by 22% (10.6 to 13.5 $\mu\text{eq/L}$), Cl^- by 35% (17.4 to 26.9 $\mu\text{eq/L}$), and $\delta^{18}\text{O}$ by 17% (-16.3 to -13.5‰), with SWE exhibiting strong inverse correlations with $\delta^{18}\text{O}$ ($r^2 = 0.96$), SO_4^{2-} ($r^2 = 0.80$), and Cl^- ($r^2 = 0.60$) values at max accumulation. Sulfate and Cl^- appear to act conservatively in the snowpack while water isotopes follow ideal fractionation behavior suggesting that variability in SWE and solutes/water isotopes is primarily driven by sublimation. A mass balance technique was employed to estimate the partitioning of snowfall between

sublimation and catchment water input. Sublimation of snowfall was estimated at 17% for the non-shaded open sites and 2% for the topographically shaded open sites.

INTRODUCTION

Spring snowmelt represents the majority of water available for spring stream flow generation and associated irrigation and municipal water supplies, providing water for over 60 million people in the western U.S. (Bales et al., 2006). The annual snowpack of the western United States is also a significant factor in the structure and function of high-elevation ecosystems. Snowmelt influences the availability of soil moisture which impacts biogeochemical fluxes, the establishment and survival of vegetation, and water availability for the vegetation growing season (Fagre et al., 2000). Consequently, our ability to quantify the distribution of snow water equivalent (SWE) and snowpack chemical loading in high-elevation, seasonally snow-covered basins is of utmost importance; both from the water resources perspective and for evaluation of the hydrologic and hydrochemical response of high-elevation catchments (Kattelman and Elder, 1991).

Processes affecting the accumulation and ablation of snowpacks are diverse and complex. Input and topographic factors such as variability in snowfall deposition, elevation, and slope can have both local and regional effects. The physical transport (wind and slope redistribution) of snow is known to significantly alter snow accumulation in alpine, boreal, and avalanche prone areas (McKay and Gray, 1981). Vegetation interactions (interception, suspension, unloading, and solar shading) have been shown to both reduce snow accumulation via interception/suspension mechanisms (Hedstrom and Pomeroy, 1998; Link and Marks, 1999b; Molotch et al., 2007; Pomeroy et al., 1998) yet increase SWE and delay melt through their insulation capacity (Musselman et al., 2008).

Sublimation and melt can alter snow accumulation with sublimation more prone in continental snowpacks while periodic melting occurs more frequently in maritime snowpacks. The relative influence of these processes on the spatial distribution of snow as well as the physical properties of the snowpack (e.g. density, temperature, and morphology) are highly dependant on local and regional climate and topography (McKay and Gray, 1981).

Seasonal snowcover also plays a unique role in high-elevation catchment hydrochemistry, as snowpacks accrue chemicals through wet and dry deposition over the snow accumulation season and then rapidly release them during melt (Pomeroy et al., 2005) via the snowmelt ion pulse (Bales et al., 1989; Cragin et al., 1996; Harrington et al., 1996). Studies on the chemical content of snow cover have sought to locate pollution sources (Mast et al., 2001; Pichlmayer et al., 1998), explored spatial and vertical variability of snow chemistry (e.g. Kuhn et al., 1998; Rohrbough et al., 2003; Tranter et al., 1987), and examined the relative influences of vegetation on snow chemistry (Hudson and Golding, 1998; Pomeroy et al., 1999). The majority of studies analyzing the spatial variability of snow chemistry employ statistical methods to distribute chemical and nutrient loads trying to clarify the factors influencing variability in snow chemistry (Rohrbough et al., 2003; Tranter et al., 1987; Williams and Melack, 1991; Williams et al., 1992).

Work in California's Sierra Nevada showed little spatial variation in major ion chemistry (Williams and Melack, 1991) while a study in southern Wyoming alpine snowpack showed more heterogeneity (Rohrbough et al., 2003). The Sierra Nevada are a

maritime environment with low vapor pressure deficits, deep seasonal snowpacks, and the influence of sublimation on water balance is minor. The Wyoming site is very cold, has intermittent wetfall, higher dry deposition, and due in part to higher vapor pressure deficits sublimation has a greater affect on the winter water budget. The differences in these two sites highlight the importance of the local environment on snow chemical concentrations and variability. This emphasizes the relative influence of snowfall, redistribution, and ablation on snow chemistry varies significantly between local environments.

On a regional scale Turk et al. (2001) showed major-ion concentrations in the Rocky Mountains were elevated over the Cascade and Sierra Nevada Mountains. Ion concentrations within the Rocky Mountains also increased geographically from North to South, with the highest overall concentrations occurring in northern New Mexico. Turk et al. (2001) speculated that a greater abundance of emission sources in southern Colorado and northern New Mexico may be increasing snowpack chemical concentrations in the Southern Rocky Mountain Region (SRMR). A concomitant study by Mast et al. (2001) utilized $\delta^{34}\text{S}$ of SO_4^{2-} . The study concluded sulfur deposited in the SRMR was primarily derived from anthropogenic sources, as biogenic emissions, marine aerosols, and continental dust contributions were found to be negligible. The study also found sulfur in the SRMR was distinctly different than that deposited in Wyoming and Montana snowpacks.

A significant amount of work has been performed on the water isotope content of snowpacks (e.g. Friedman et al., 1991; Judy et al., 1970; Moser and Stichler, 1975;

Sommerfeld et al., 1991; Sommerfeld et al., 1987; Stichler, 1986), especially in relation to meltwater fluxes and isotope hydrograph separation (Laudon et al., 2004; Taylor et al., 2002; Taylor et al., 2001; Unnikrishna et al., 2002). Moser and Stichler (1975) explored the effects of sublimation on water isotopes in experimental snowpacks and concluded that sublimation was capable of enriching the snowpack in the heavier isotopes (^2H and ^{18}O). Sommerfeld et al. (1987) found similar results and showed that isotope fractionation, driven by high vapor pressure deficits, could be a sensitive tool for determining relative mass change in a column of snow. This finding has been of significant debate in field studies, as subsequent research failed to demonstrate the ability of water isotopes to gauge mass change due to sublimation because of the two-dimensional movement of water vapor out of and into the snowpack (Friedman et al., 1991; Moser and Stichler, 1975). Recent field research by Earman et al. (2006) has shown promise for this technique in southwestern snowpacks, as progressive isotopic enrichment of snow during sublimation from snow lysimeter pans was seen.

Our ability to estimate the sublimation component of winter water balance is crucial to assist water and forest managers who rely on accurate predictions of snowpack water availability. Current methods of estimating sublimation in high-elevation catchments utilize a series of meteorological measurements derived from sensitive and expensive equipment. Three such methods, the mean-profile method (Leydecker and Melack, 1999), the aerodynamic profile method (Hood et al., 1999) and the eddy covariance (EC) method (Molotch et al., 2007), require continuous measurements of air temperature, snow surface temperature, humidity, wind speed, solar radiation, and surface roughness among

others to calculate the latent heat flux; converting it directly into millimeters of SWE loss or gain. While mass and energy balance methods similar to these are useful, they are limited to instrumented catchments which may or may not be representative of varying environments or even the entire catchment. Each of these studies have been successful in showing sublimation is often episodic in nature and increases toward peak accumulation, as sublimation rates increase as vapor pressure deficits rise, temperatures warm, turbulent fluxes increase, and solar radiation intensifies.

Two recent studies at our field site (Valles Caldera National Preserve, New Mexico) directly explored the influence of solar radiation and energy gradients on SWE accumulation and ablation. Musselmann et al. (2008) analyzed the influence of vegetation shading on SWE accumulation and ablation at the plot scale of a single tree. Musselmann observed the relative timing of maximum SWE varied between the non-shaded southern side of the tree and the shaded northern side, with maximum SWE occurring as much as 1 month later on the shaded side. The timing and duration of snowmelt was also influenced, as the shaded side of the tree ablated later and slower than the non-shaded side. In the second study, Rinehart et al. (2008) explored the impact light scattering, caused by high solar fluxes of lower latitude sites, and aspect shading have on snow distribution. He concluded that snow or mixed snow-vegetation albedo has significant effects on scattering incoming short-wave radiation, which in turn directly influences the amount, timing, and duration of maximum SWE.

In this paper we seek to investigate three primary objectives. First, this study seeks to establish the spatial variability of snow water equivalent and snowpack chemistry/water

isotopes within 5 variable shading environments located in our study domain. Second, we evaluate if differences in the energy inputs caused by topographic and vegetation shading relate to the spatial variability of SWE and snowpack chemistry/water isotopes. Third, we investigate if systematic differences in the chemical and isotopic signature of snow cover can be used to quantify energy gradient effects on snowpack water balance.

STUDY AREA

The field setting for this research is the Redondo Peak massif within the Valles Caldera National Preserve (VCNP), Jemez Mountains northern New Mexico (106°33'23"W, 35°52'19"N) (Figure 1). The VCNP is an 89,000 acre former land grant purchased by the U.S. government through the VCNP act of 2000. The Redondo Peak massif, the largest topographic feature of the VCNP, is centered within the ~1.25 Ma Valles Caldera complex (Phillips et al., 2007) and is comprised of Redondo and Redondito Peaks as well as two smaller un-named Peaks. The caldera complex is geologically complex with a primary bedrock composition of rhyolitic ash flow tuffs, the largest of which is the Upper Bandelier Tuff (Tshirege Member) (Goff et al., 2006). The VCNP is drained by the Jemez River which is a tributary of the Rio Grande River.

Elevation ranges from 2167m to 3432m (Redondo Peak) within the VCNP and yields a variety of vegetation and soil conditions. Douglas fir, whit fir, blue spruce, Engelmann spruce, south-western white pine, and a few aspen stands comprise the primary mixed-conifer forest of the higher-elevations within the preserve (Muldavin and Tonne, 2003). The lower elevations (below ~2740m) see forested regions of ponderosa

pine and Gambel oak scrubland (Muldavin and Tonne, 2003) with homogenous grasslands covering the multiple valleys which contain several riparian wetlands and bogs (Coop and Givnish, 2007). The resurgent domes including Redondo Peak have deep, well-drained sandy loams with high-permeability while the valley bottoms include a variety of soil types, from deep-well drained sandy loams to low permeability silty clay loams near streams (NRCS, 2008a).

The climate of the VCNP can be characterized as semi-arid and montane, with an average yearly precipitation of ~650mm over the last 4 years in the higher elevations. Slightly less than half of the annual precipitation falls in the form of snow between November and April (winter months) with the majority of the remainder falling during the summer monsoon season (July-September). The nearby Quemazon SNOwpack TELEmetry (SNOTEL) site has recorded SWE and temperature since 1989 and reports an annual average maximum SWE of 257mm with an average ambient air temperature over the winter months of -2.2°C (NRCS, 2008b). Table 1 summarizes the winter snow accumulation and meteorological characteristics of our study area (Moore, 2008). Average relative humidity and wind speed are both low (60% and 2.0 m/s respectively) compared with other mountainous areas and the overall vectored-mean wind direction is from the west-northwest (290°). Snowmelt typically begins in late March or early April as monthly temperatures transition from a March mean of -1°C to an April mean of 2.7°C (NRCS, 2008b). VCNP winters are significantly warmer than other Rocky Mountain environments with winter mean temperatures around -2.2°C . By comparison the University Camp SNOTEL site in Northern Colorado is at a similar elevation (3140m)

yet records annual winter temperatures over the same time span of -5.5°C . The 2006-2007 winter can be described as average with the exception of temperature, as March 2007 was exceptionally warm leading to an earlier than normal maximum accumulation date (March 10th) and snowmelt.

Our study area is contained within a broad, relatively flat area of the Redondo Massif with an average elevation of $\sim 3015\text{m}$. Small high elevation mountain clearings are interspersed within the mixed-conifer forest at this elevation. Average forest heights near our study domain range from 18.7 to 20.5m with a leaf area index (LAI) of 3.43 ± 0.5 (McDowell et al., 2008). The majority of snowmelt from the study area drains to the La Jara Creek catchment on the south side of the massif. La Jara Creek is the largest catchment on the Redondo massif and is instrumented with temperature sensors, pressure transducers, a recording stream gauge, a trapezoidal flume, and an automated water sampler. Additionally, seven smaller streams draining the catchment are instrumented with flumes and temperature sensors (described in Lyon et al., 2008). An eddy covariance tower system along with instrumentation including snow depth sensors, alter-shielded heated rain-gauge, time-domain reflectometry (TDR) soil moisture sensors, and sap flow sensors are located near the northeast corner of our study domain at $\sim 3050\text{m}$.

METHODS

Experimental Design

Five snow pit locations were established across our study domain varying aspect (as a proxy for topographic shading) and vegetation shading environments while limiting

potential impacts of elevation and slope between sites (Table 2). Snow pits were named in relation to the energy environment in which they are designated to represent. Four of the pits were located in open areas without nearby canopy cover and were selected to vary aspects as a proxy for solar input. The two snow pits with western aspects experience significant topographic shading and are designated as topographically shade pits 1 and 2 (TS1 and TS2). Two snow pits do not receive significant topographic shading and are designated non-shaded pits 1 and 2 (NS1 and NS2). TS1 and NS2 are located on the south side of the Redondo massif while TS2 and NS1 are located on the northern side. The fifth snow pit was chosen to reflect influences of dense canopy cover by establishing it directly underneath a grove of closely spaced trees (Dense Vegetation Pit, DV). . The two south massif pits (TS1 and NS2) are co-located with snow melt lysimeters while NS1 is located near an eddy covariance system. The collective goal of these snow pits was to establish a gradient of shading and vegetation cover environments which may incur systematic differences in both the amount of water and the solute and isotope contents of each snow pit.

Solar Forcing Index

The Solar Forcing Index (SFI) was developed using ArcGIS Solar Analyst (Fu and Rich, 2000) and was created in two sections—topographic SFI and vegetation SFI. The topographic SFI utilized a 10m digital elevation model (DEM) (USGS, 2003) of the VCNP executing Solar Analyst between November 1st, 2006 (start of snow accumulation) and March 10th, 2007 (max accumulation). The topographic solar index values generated

by Solar Analyst at each pit location were normalized to a flat, open control DEM developed at the mean site elevation (3015m) and geographical coordinates. To develop the vegetation SFI aerial photography was utilized to plot locations of trees within 30m of each cardinal direction at each snow pit location. Based on vegetations surveys within the VCNP, trees were conservatively estimated as 15m tall opaque right cones with a 3m base radius and placed onto the control DEM. Solar Analyst was executed on each vegetated control DEM for each snow pit between November 1st, 2006 and March 10th, 2007 and solar index values were normalized to the control DEM without vegetation. The vegetation SFI was estimated at 0.30 for the dense canopy pit based on reported values of solar transmissivity under dense canopy (Hardy et al., 2004; Zou et al., 2007). It was not possible to accurately represent vegetation SFI at the DV site as trees were modeled as opaque cones which yield zero solar transmissivity within the radius of the tree. The overall SFI is the product of the topographic and vegetation SFI's.

Data Collection and Sample Analysis

Locations were visited approximately monthly between mid-January and late March 2007. During each visit vertically faced snow pits were excavated to the ground and snowpack stratigraphy and morphology were recorded while snow density and temperature measurements were made every 10cm along the pit face. The bottom 5-10cm of each snowpit was excluded from density and snow chemistry sampling to avoid inclusion of leaf litter and soil. After measurements and samples were collected pits were backfilled and fresh snow pits were dug upslope of previous excavations during

successive visits. All snow pits were excavated at a time of day avoiding direct exposure of pit faces to sunlight. Snow samples were collected while wearing nitrile gloves and using one-liter snow cutters collecting samples for chemical and isotopic analysis from major stratum within the snowpack, and also across major ice layers along the vertical face of each snowpit. After collection samples were placed in pre-rinsed plastic bags.

A limited number of fresh snow samples were collected for chemical and isotopic analysis at each of the snow pit locations. Fresh snow can be characterized as snowfall sampled within 24 hours of deposition from the surface of the snowpit location. Two specific dates collected distributed fresh snow samples from the majority of the study sites (February 17th and March 31st). The March 31st snowfall event was the only event sampled at all 5 sites.

Snow samples were transported frozen to the University of Arizona, where they were melted in fridges at 4°C and filtered for analysis using pre-combusted, 0.70-µm GF/F grade glass fiber filters before being stored in pre-rinsed/combusted amber glass bottles. Major anion (Cl^- , NO_3^- , SO_4^{2-}) concentrations were determined on a Dionex Ion Chromatograph. Samples were separated through an AS17 analytical column using a KOH eluent which was removed using an ASRS suppressor column allowing anion concentrations to be quantified with a CD25 conductivity detector. Water isotope (δD , $\delta^{18}\text{O}$) values were analyzed on a Los Gatos Research liquid-water isotope analyzer. All isotope values are expressed in per mil notation (‰) relative to the Vienna standard mean ocean water (VSMOW). Major cation concentrations (Ca^{2+} , K^+ , Na^+ , Mg^{2+}) were determined using a Perkin-Elmer Optima 5100DV Inductively Coupled Plasma - Optical

Emission Spectrometer (ICP-OES) on nitric acid acidified sample aliquots. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations were analyzed using a Shimadzu TOC-V_{CPN}. Detection limits for major anions and cations were less than or equal to 0.025 mg/l, DOC detection limit was 50 µg/l, and TDN was 5 µg/l. Quality control techniques involved analysis of deionized-water blanks, external and internal reference standards, and comparing results from duplicate sample analysis. Replicate analysis of anions, cations, and biogeochemical nutrient samples and standards typically agree within 5% or better for concentrations greater than 1 mg/L and 10% or better from samples less than 1 mg/L, while $\delta^{18}\text{O}$ values were within 0.2‰ and $\delta\text{D} < 1\text{‰}$. All laboratory analyses were conducted at the University of Arizona. Individual snowpit chemical and isotopic samples were converted to volume-weighted means (VWM) using concentration, depth, and density following the methodology of Pomeroy et al. (1995) for each pit location and sampling date.

Meteorological Data and Mass Balance Equations

Meteorological data from five micrometeorological stations and the eddy covariance tower site within the VCNP as well as data from the Quemazon SNOTEL site (~13km NW from VCNP) was summarized from hourly records to daily and monthly means. Data from within the VCNP included temperature, precipitation, relative humidity, solar flux, wind speed, and vectored-mean wind direction. Data from the Quemazon SNOTEL site included precipitation, temperature, SWE, and snow depth measurements. Due to the distortion of the wind field through the displacement and

acceleration of wind flow over the top of precipitation gauges wind is the most dominant environmental factor contributing to the under measurement of solid precipitation, requiring precipitation data to be corrected for undercatch. The World Meteorological Organization (WMO) Solid Precipitation Measurement Intercomparison report outlines an undercatch correction method for an alter-shielded NWS standard recording gauge (Goodison et al., 1998) as used within our study site. Wind speed is first corrected from wind gauge height to precipitation gauge entrance height. Gauge heights were obtained from Moore (2008). The WMO report suggest correcting precipitation to the double fence international reference (DFIR) as it is the most widely used and applicable for international comparison (Goodison et al., 1998).

Mass balance calculations to partition snowfall between sublimation and catchment water input are shown here. The solute mass balance equation can be expressed as:

$$C_i V_i = C_o V_o \quad (1)$$

where C_i and V_i represent the cumulative snowfall VWM solute concentration and snowfall volume per unit area, respectively, while C_o and V_o are the observed VWM solute concentration and SWE (expressed as volume per unit area) at max accumulation respectively.

Oxygen isotope mass balance can be performed using the following equations, which are similar for deuterium (Clark and Fritz, 1997). Equation 2 dictates the equilibrium fractionation enrichment factor expressed as per mil (‰) due to the transition of water from the solid to vapor phase.

$$\varepsilon^{18}O_{l-s} = (1 - \alpha) * 10^3 \quad (2)$$

where $\varepsilon^{18}O_{l-s}$ is the per mil (‰) fractionation and α is the fractionation factor ($\alpha = 1.015$) (O'Neil (1968) cited in Clark and Fritz (1997)). Kinetic fractionation is governed by equation 3, where h is the humidity at the snow-atmosphere boundary.

$$\Delta\varepsilon^{18}O_{l-s} = 14.2 * (1 - h) \quad (3)$$

An analysis of the deuterium excess of the LMWL and snowpit isotopic values (outlined in Clark and Fritz, 1997) showed a humidity of approximately 73% at the snow-atmosphere boundary would be consistent to create the observed differences. The total fractionation of ^{18}O ($\varepsilon^{18}O_T$) due to sublimation is expressed:

$$\varepsilon^{18}O_T = \varepsilon^{18}O_{l-s} + \Delta\varepsilon^{18}O_{l-s} \quad (4)$$

The fractional water loss f due to sublimation enrichment can then be calculated at each snowpit according to Rayleigh distillation:

$$\delta^{18}O_{Obs.} - \delta^{18}O_{Snowfall} = \varepsilon^{18}O_T \cdot \ln(f) \quad (5)$$

where $\delta^{18}O_{Obs.}$ is the observed VWM isotopic value of each snowpit and $\delta^{18}O_{Snowfall}$ is the cumulative VWM isotopic value of snowfall.

RESULTS

Snowfall

Snowfall over the accumulation period was continuous and consistent across the entire preserve from late November through mid-February (Figure 2). No substantial deposition events occurred after mid-February and an exceedingly warm March led to an

early maximum accumulation date (March 10th, 2007). As the precipitation gauges are spread over a range of elevations (2598-3231m) and the data was consistent between storm events, an elevation based precipitation lapse rate (linear) was created with a regression fit $r^2=0.92$ and p value of 0.026. The linear lapse rate was chosen due to the sharp elevation contrasts within the site (Rinehart, 2008) and the regression equation for the winter precipitation period (Oct. 23rd – March 10th, 2007) is:

$$\text{Precipitation (mm)} = 0.22 * \text{Elevation(m)} - 331.$$

As elevation was limited as a function of study design, the elevation-precipitation lapse rate estimate of snowfall is not variable between sites (Table 3). Snowfall is influenced by regional climate, latitude, and elevation, however, due to the relatively small area encompassed by the study ($\sim 0.6 \text{ km}^2$) and the lack of elevation difference, snowfall may not be expected to vary significantly between sites (McKay and Gray, 1981).

Snow Water Equivalent Variability

During the first sampling campaign (Jan. 21, 2007) three snowpits were established with SWE showing less than 10mm of variation between the topographically shaded (TS1) and topographically open (NS1, NS2) sites (Figure 3). Subsequent campaigns saw the variability between these three sites expand from 10mm to 84mm of SWE by mid-February and up to 103mm (30%) of SWE by maximum accumulation (March 10th). Two additional snowpits (TS2, DV) were established in mid-February and SWE varied between all five sites by 153mm (45%) on March 10th. The topographically shaded pits (TS1, TS2) were similar in both February and March containing the highest SWE (340

and 338mm respectively) at maximum accumulation (March 10th) while the vegetation shaded pit (DV) contained the lowest (187mm), presumably due to canopy interception. The south facing of the two non-shaded open sites (NS2, 237mm) had less SWE than the northwest facing pit (NS1, 275mm) at max accumulation (March 10th).

Figure 3 also shows SWE accumulation is greater at all sites between January and February than between February and March, which is indicative of the snowfall pattern depicted in Figure 2. The topographically shaded-open pits (TS1, TS2) show greater SWE accumulation between each sampling campaign than the non-shaded open (NS1, NS2) and vegetation shaded (DV) sites. Differences between the precipitation lapse rate estimate of snowfall and observed SWE at maximum accumulation range from 3 to 151mm (Table 3). The snowmelt period began immediately after the maximum accumulation date (March 10th) and lasted into mid-April. The final sampling campaign (March 31st) showed the topographically open sites experience the highest percentage of melt (65% and 45% at NS1 and NS2 respectively), while the topographically and vegetation shaded pits (TS1, TS2, and DV) all experienced less than 40%, with the TS2 snow pit only experiencing 5% loss between March 10th and March 31st.

The observed SWE at maximum accumulation (March 10th) at the four open snowpit sites (TS1, TS2, NS1, NS2) shows that topographically shaded sites (TS1, TS2) have the highest SWE accumulation and the lowest SFI while the non-shaded sites (NS1, NS2) have the lowest SWE and greatest SFI. The relative influence of variability in shading environments and their relation to the spatial distribution of SWE is clearly shown, indicating energy input is a principal driver in SWE variability across our sites.

Quantifying the SFI at the dense vegetation pit is difficult as falling snow is intercepted and subsequently unloaded to the pit location, thus the energy experienced by the snow while it is suspended is not accounted for in the SFI. The SFI only estimates the energy input underneath the canopy where measurement and samples were obtained.

Isotopic and Chemical Variability

Volume weighted mean (VWM) $\delta^{18}\text{O}$ ranged from -16.3‰ to -13.5‰ at maximum accumulation while δD values ranged from -111‰ to -93‰ (Table 4). VWM sulfate concentrations varied from 10.6 to 13.5 $\mu\text{eq/L}$ while chloride concentrations appear affected by vegetation and range from 17.4 to 19.2 $\mu\text{eq/L}$ at the four open snow pit locations (TS1, TS2, NS1, NS2) with a concentration of 26.9 $\mu\text{eq/L}$ at the DV pit. Nitrate ranged from 9.4 to 15.6 $\mu\text{eq/L}$. Calcium and sodium exhibited a similar range from ~8.0 to 16.0 $\mu\text{eq/L}$ while potassium ranged also appears effected by canopy cover with a range of 2.0-2.2 $\mu\text{eq/L}$ between open sites and a concentration of 5.9 $\mu\text{eq/L}$ at the DV site. Similarly, DOC ranged from 0.57 to 1.03 mg/L at the open snow pit locations but is elevated to 1.37 mg/L at the DV pit. TDN ranged from 0.28 to 0.37 mg/L across our sites. The observed ranges in solutes (Table 4) are similar and or slightly higher than previous snow chemistry studies with observations in Northern New Mexico (Hidy, 2003; Ingersoll, 2000; Mast et al., 2001; Turk et al., 2001). Elevated concentrations may be expected due to the VCNP's location relative to the four corners area, which contains several anthropogenic emissions sources (Mast et al., 2001).

Volume weighted mean (VWM) water isotopes, SO_4^{2-} , and Cl^- follow a similar pattern between sites. The topographically shaded TS1 and TS2 pits have the lowest isotope values and contain the lowest chemical concentrations, the non-shaded open pits (NS1, NS2) are intermediate, while the dense vegetation pit (DV) is the heaviest isotopically with the highest SO_4^{2-} and Cl^- concentrations (Table 4). DOC exhibited an inverse pattern to that of $\delta^{18}\text{O}$, SO_4^{2-} and Cl^- at the four open sites (TS1, TS2, NS1, NS2) as DOC is lowest at the non-shaded NS1 and NS2 sites and highest at the topographically shaded TS1 and TS2 sites. The exception is the DV pit where vegetation and leaf litter in the snowpack appear to increase the DOC concentration. Nitrate, major cations, and TDN did not exhibit a clear association with aspect or vegetation (Table 4). Figure 5 details regression relationships between SWE and chemistry/water isotopes. $\delta^{18}\text{O}$ (5A) and δD (not shown) showed the strongest correlation with SWE with r^2 values of 0.93 and 0.86 respectively. Sulfate (5B) had the highest correlation with SWE of the solutes with an $r^2 = 0.80$, while Cl^- (5C) had an $r^2 = 0.62$. Each regression, with the exception of chloride, is statistically significant at the 95% confidence level. An analysis of the conservative potential of each ion was performed by analyzing chemical values of repetitively sampled snow strata. Concentrations of individual strata within the snowpack which showed little variation between sampling dates were given the highest conservative potential. In general SO_4^{2-} and Cl^- showed the highest potential while NO_3^- and the major cations showed the least.

Fresh snow samples demonstrated limited spatial variability in chemistry and isotopes (Table 5) as the standard deviation between sites of SO_4^{2-} , Cl^- , and water isotopes was

less than 20% of the mean for both events. The March 31st snowfall event showed standard deviations ranging from 3.2% to 14.4% of the mean for SO_4^{2-} , Cl^- , NO_3^- , and water isotopes. Chemical and isotopic variability between storms was high, however, water source, storm track, and antecedent meteorological conditions are known to affect precipitation chemistry (Losleben et al., 2000). Using all fresh snow samples collected a mean snowfall chemical and isotopic composition for the winter season was estimated for major anions and water isotopes (Table 5).

Differences in volume weighted mean SO_4^{2-} and NO_3^- concentration between March 10th and March 31st showed a strong relation to SFI (Figure 6). Figure 6 shows two results: (1) the VWM concentration change of SO_4^{2-} and NO_3^- between maximum accumulation and melt varied systematically with SFI and (2) the solutes appeared to follow the elution sequence $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ as similar to previous research (Brimblecombe et al., 1985; Tranter et al., 1986). While SO_4^{2-} showed preferential elution at all snow pits over NO_3^- , the full elution sequence of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ was only seen at the TS2 and NS1 sites. The chloride sample at the SL site during the March 31st sampling date was potentially contaminated and is not depicted.

Snowpack Mass Balance

Based on the observed correlation between water isotopes, SO_4^{2-} , Cl^- , and SWE each potential tracer appears to behave ideally for partitioning water within the snowpack (Figure 5). Under the assumption differences in SWE at max accumulation are due to sublimation (see discussion) the ideal behavior of these potential tracers allows for a

mass balance calculation—similar to open stream channels (e.g. Laudon et al., 2004; Sueker et al., 2000)—to estimate snowfall input. This approach allows for the partitioning of snowfall between sublimation loss and catchment water input (or observed SWE), as sublimation would be the difference between the mass balance calculated snowfall and observed SWE. Chemical and isotopic snowfall values (C_i from equation 1 and $\delta^{18}O_{Snowfall}$ from equation 5, respectively) were estimated using the mean analytical values from fresh snow samples (Table 5). Due to the weaker correlation between Cl^- and SWE, only SO_4^{2-} and water isotopes were used to gauge water flux from the snowpack.

The two topographically shaded open pits (TS1, TS2) show the least difference between the observed SWE and the mass balance calculated snowfall (Figure 7). The non-shaded open pits (NS1, NS2) show a larger difference. This implies the non-shaded open pits experienced greater amounts of sublimation loss from the snowpack. The average results of all mass balance calculations (SO_4^{2-} , $\delta^{18}O$, δD) expressed as flux (Table 6) show TS1 experienced net condensation gain of ~6mm while TS2 experienced sublimation loss (~16mm). The two non-shaded open pits (NS1, NS2) appear to experience similar average sublimation losses of ~34 and 30mm respectively. Utilizing SO_4^{2-} as the best estimate of sublimation loss and expressing loss as a percentage of the snowfall input shows the topographically shaded open sites lose little to sublimation (-2.8% to 5.8%) while the non-shaded open pits lose ~17%. Comparing the mass balance calculated snowfall with the elevation- precipitation lapse rate shows the mass balance

estimates are within the 95% confidence interval of the lapse rate prediction for all open sites except NS2.

DISCUSSION

Variability in SWE

Several processes are known to affect SWE leading up to maximum accumulation, promoting SWE variability catchment wide. Several of the major factors include: snowfall variability, terrain slope and elevation, wind redistribution, rain on snow events, periodic melt, canopy interception, and sublimation (Elder et al., 1991). Initially, the small-scale of the study catchment along with the precipitation lapse rate data (Table 3) seem to indicate variability in snowfall is a minor component of variability in SWE at max accumulation. Study design controlled for potential effects of slope and elevation limiting the influence of these factors. The presence of multiple distinct sun crusts in each pit separating layers of dendrite and round crystals in various stages of decomposition, the lack of physical melt indicators (i.e. flowpaths or “fingers”), and snow temperatures below 0°C throughout the vertical profile of the snowpit are strong indicators melt had not begun (please see Veatch et al., 2008 for a thorough description of physical characteristics). A layer analysis of snow chemical concentrations affirms this indication, as solutes are consistently distributed throughout the snow pit vertical profile. If snowmelt had occurred without melt water leaving the snowpack, a redistribution of solute mass would have been expected leaving a profile of increasing concentrations from the top down (Bales et al., 1989).

Wind direction within the study area is consistently from the west-northwest (Table 2) with a mean wind speed of 1.9 m/s and a mean maximum hourly speed of 4.4 m/s. As the typical boundary condition to induce saltation of snow is between 5-10 m/s (McClung and Schaerer, 2000), sustained redistribution of snow may not be expected. In addition, Veatch et al.(2008) compared depth measurements between variable lee and non-lee areas within the study domain. As wind direction is from the west, redistribution would be expected to scavenge from the western (lee) side of clearings to deposit on the eastern (non-lee) side. Significant difference between lee and non-lee areas was not observed leading to the conclusion wind redistribution was not a significant factor affecting snow depth during the study winter.

The effect of canopy cover on snow accumulation at the DV site is clear, as SWE is ~45% less than the topographically shaded open sites and ~25% less than the non-shaded open sites. Canopy interception is known to significantly affect snow accumulation and ablation and has been widely studied (e.g. Hedstrom and Pomeroy, 1998; Link and Marks, 1999a; Molotch et al., 2007; Montesi et al., 2004; Musselman et al., 2008; Sicart et al., 2004). Canopy interception of the total annual snowfall ranges depending on environment, but has been estimated to be ~60% for a dense coniferous forest (Hedstrom and Pomeroy, 1998) with associated sublimation losses of suspended snow exceeding 30% (Montesi et al., 2004). However, as the open snow pit locations are devoid of any effects of canopy interception this cannot be a major factor affecting observed variability between the open sites.

Early in the accumulation season (January 2007) little variance in SWE was observed between open sites yet at max accumulation variance was 30% (Figure 3). As the accumulation season progresses and solar azimuth angles rise, the difference in energy inputs can metastasize between study locations. The combination of high positive net-all-wave radiation, large vapor pressure difference between the snowpack and atmosphere, and apparent limited ability of other processes to affect accumulation implies sublimation is the primary driver influencing variability between open snowpit locations at max accumulation. The regression between SFI and SWE at maximum accumulation (Figure 4) implies the difference in energy inputs is driving variable sublimation rates between sites.

Variability in Water Isotopes and Chemistry

The covariance of water isotopes with SWE (Figure 5) indicate the gradient of shading environments is not only affecting SWE accumulation and ablation, but also the isotopic signature of the snowpack. Water isotope values vary inversely with SWE (Figure 5A) implying isotopic fractionation may be enriching the snowpack in the heavy isotopes (^{18}O and ^2H). Within snowpacks isotope fractionation can occur either during melt or sublimation, enriching ^{18}O and ^2H isotopes in the ice phase as ^{16}O and ^1H isotopes preferentially enter the liquid or vapor phase respectively. The snowpack shows no sign of melting prior to max accumulation (March 10th), implying sublimation is driving isotope fractionation. The kinetic effects of sublimation on snow water isotopes have been under debate for some time. The two-dimensional

interaction of water vapor at the snow-atmosphere boundary can cause both sublimation and condensation, altering the isotopic signature of the snowpack (Earman et al., 2006; Stichler, 1986). However, Moser and Stichler (1975) indicated kinetic fractionation effects on snow water isotopes can occur with high vapor pressure gradients despite the high relative humidity in the snowpack. Strong vapor pressure gradients at the snow-atmosphere boundary are plausible at our study site, indicating the majority of water vapor may move unidirectional, out of the snowpack. Pressure pumping effects have also been shown to increase the diffusive transfer of gaseous species out of the snowpack and may aid in causing the observed variations (Massman et al., 1997). Therefore, this study indicates isotopic fractionation of snow during sublimation, at least in a low-latitude semi-arid environment, may be useful for determining water mass flux from snowpacks.

Previous laboratory research of experimental snowpacks found similar results showing that isotope fractionation via sublimation could be a sensitive tool for determining relative mass change in a snow column. The study concluded that the mass loss or gain at any given location within the snowpack is determined by the snowpack equilibrium vapor pressure profile (Sommerfeld et al., 1987). Separate field studies have concluded the isotopic fractionation of snow during sublimation is not an important process over the winter season due to the two-dimensional interaction of water vapor. Moser and Stichler (1975) found isotopic enrichment occurred during the daytime hours (0800-1600) in the surface layers of snowpacks but condensation during nighttime hours (1600-0800) restored equilibrium. Similarly, Friedman et al.

(1991) concluded the presence of atmospheric and soil water vapor in natural snowpacks, negated the potential to use water isotopes to gauge water mass flux in a Fairbanks, Alaska snowpack. Recent research by Earman et al. (2006) has shown isotope enrichment can occur in southwestern snowpacks, however, fresh snow inputs prevented mass balance closure preventing the use of mass balance calculations to gauge sublimation loss. These studies highlight the importance atmospheric water vapor plays in the isotopic signature of natural snowpacks. Although some condensation undoubtedly occurs in our snowpack, which may dilute our ability to calculate mass flux, the net affect of sublimation on isotopic fractionation is not equaled by condensation as seen in previous research. The lack of significant fresh snowfalls between mid-February and late March also may have aided the net sublimation signature seen in the snowpack.

Similar to the water isotopes, the correlation between SWE and SO_4^{2-} and SWE and Cl^- indicates that sublimation processes have altered the concentrations of solutes at our study locations by max accumulation (March 10th) (Figure 5). During sublimation conservative solutes should concentrate within the snowpack, as water mass is removed from the snowpack and solute mass remains (see following paragraph). The consistency of this observation with the water isotopes continues to imply energy inputs and sublimation are principal drivers influencing the snowpack. There are, however, several other processes which can influence chemistry in mountain snowpacks including: wet and dry deposition, wind redistribution, volatilization, melt, vegetation/leaf litter, and biologically mediated oxidation

(Pomeroy et al., 2005). The chemistry in new snowfall has limited spatial variability (Table 5) and no distinct repetitive pattern across storms, which agrees with other studies (Williams and Melack, 1991). As the VCNP is located in a continental climate dry deposition of sea-salt aerosols is not expected to significantly influence Cl^- concentrations. Based on SO_4^{2-} values within the snowpack and previous research in the southern Rocky Mountains dry deposition is not expected to influence sulfate concentrations; however, it may influence Ca^{2+} and other major cation concentrations (Clow et al., 2002; Mast et al., 2001; Turk et al., 2001). Wind redistribution and melt have been previously addressed in relation to SWE and therefore are not expected to significantly influence chemical concentrations. Sulfate and Cl^- show no significant change in concentrations, although Cl^- concentrations are affected by vegetation at the DV site. Similar to SWE, variability in sublimation rates driven by differences in energy environment at max accumulation appears to be the primary driver affecting SO_4^{2-} concentrations at all sites and Cl^- concentrations at the open snow pit locations.

Investigations into the conservative potential of snowpack chemical species have shown some variability. A lab study found SO_4^{2-} mass was lost preferentially over Cl^- and NO_3^- during sublimation but found no direct justification for the differences between solutes (Cragin and McGilvary, 1995). Pomeroy et al. (1999) found NO_3^- to be conservative in the intense cold of the northern boreal forest near Inuvik, Northern Territories, Canada while SO_4^{2-} and Cl^- were more conservative in the warmer dry southern boreal forest near Waskesui, Saskatchewan. The variability was attributed to

sea salt aerosols in the Inuvik region and to volatilization of NO_3^- in the net all wave positive radiation environment of Waskesui during sublimation. Results of this study agree with the Waskesui site as SO_4^{2-} and Cl^- appear more conservative than NO_3^- .

The elevated concentrations of DOC within the DV pit at max accumulation are unsurprising (Fahney, 1973; Johnson et al., 2001); however, DOC may show signs of volatilization at the open study pits, as concentrations vary positively with SWE contrary to SO_4^{2-} and Cl^- . Organic species have been shown to diffuse through and be lost from snow (Leggett and Hogan, 1995) thus loss of DOC within the snowpack may be expected during sublimation. Nitrate and TDN are not elevated in vegetation and show no association with SWE and/or SFI. Variability in nitrate is complex as this species has been shown to volatilize in positive net all-wave radiation environments (Pomeroy et al., 1999), is prone to photochemical/biological reactions (Pomeroy et al., 2005), and may be influenced by canopy/leaf litter interaction despite little evidence for it in our study. A sub-goal of this project was to establish a precipitation input baseline for biogeochemical nutrients as follow up to the work of Kostrzewski et al. (2008).

The gradient of energy environments also appears to affect the relative timing of water and solute release from the snowpack (Figures 3 and 6). Snow pits with higher SFI's (NS1, NS2) appear to melt sooner and release more solute mass due to ion fractionation and elution (Bales et al., 1989) prior to snowpits with lower SFI's (TS1, TS2).

Implications of Energy Environment on Snowpack Water Balance

Combined, all of the results indicate energy inputs and subsequently sublimation is the primary driver causing variability both in SWE and isotope/solute values at max accumulation. Because the correlations between isotopes/solutes and SWE are strong, it enables us to partition the relative water mass flux between sublimation loss and catchment water availability. The range of sublimation estimates at each site vary, however, using SO_4^{2-} mass balance as an overall indicator of sublimation we see sublimation of snowfall ranging from ~6mm (2%) at the topographically shaded open sites (TS1, TS2) to ~50mm (17%) at the non-shaded open sites (NS1, NS2). The difference in sublimation between sites shows there is significant heterogeneity in sublimation across the study area, and that the amount of sublimation is closely linked with localized energy inputs at each site. The NS2 site was the only open site to fall outside of the precipitation lapse rate estimate 95% confidence interval. This result may imply there is some spatial heterogeneity in snowfall across our study catchment.

Studies using mass and energy balance approximations have estimated catchment wide sublimation from 4-13% of snowfall in the Central Sierra Nevada (Leydecker and Melack, 1999) and 15% at Niwot Ridge, CO (Hood et al., 1999). Molotch et al. (2007) used an eddy covariance method in a forested region of Niwot Ridge to estimate sublimation from above- and sub-canopy areas indicating that sublimation losses from above-canopy are similar to the alpine estimates of Hood et al. (1999) while sub-canopy sublimation was highly depended on the partitioning of sensible and latent heat fluxes in the canopy above. Sublimation estimates using mass balance

techniques in this study agree well with the aforementioned results. Sublimation estimates at the dense vegetation site are less conclusive for two main reasons: (1) Smaller snowfall events may be completely intercepted and sublimated during suspension, leaving no record of snowfall in the snowpack below and (2) canopy interaction and leaf litter deposition clearly are affecting the chemical signature of the snowpack.

Implications for Catchment Hydrology and Biogeochemistry

The results of this study have direct applicability to catchment hydrology tracer studies and ecohydrology studies concerned with catchment availability of biogeochemical nutrients. Research in these fields commonly use a combination of snow course data and a single point sample of the chemical/isotopic signature of the snowpack to distribute chemical loads and tracer inputs (Huth et al., 2004; McGuire et al., 2005). The variability in SWE and chemical and isotopic signatures of the snowpack at the VCNP indicate using this technique could result in significant error. Taylor et al. (2002) explored how variability in the temporally changing isotopic signature of snowmelt can cause uncertainty in hydrograph separation. Based on the typically observed 3 to 5‰ $\delta^{18}\text{O}$ variation during snowmelt, up to 25% error in the new water estimates can be observed. Our study shows over 3‰ spatial variance in $\delta^{18}\text{O}$ of the snowpack, indicating tracer studies may need to account not only for variations in water isotopes during melt, but also the spatial variation in the bulk snow composition prior to snowmelt. As the timing of snowmelt also varies between sites,

there is potential the fractionation due to snowpacks at various stages of melt combined with variability in the bulk snow composition prior to melt could metastasize error in quantifying new water. In addition, if our study were to distribute the chemical/nutrient loads using values from a snow pit which experienced evapoconcentration/organic volatilization due to sublimation, overestimation of chemical loads at shaded sites would surpass 18% and underestimation of nutrient loads would exceed 40%.

Original study design called for distributed snowpack sampling to test the validity of observations made at the intensive snow pit sites, however, the early onset of snowmelt prevented distributed sampling from occurring. Further research is needed to test the validity of this study in a greater diversity of solar forcing environments. Due to the high equipment and labor costs associated with meteorological instrumentation in remote mountainous areas, the possibility of using mass balance applications to partition snowpack water balance may be beneficial. The applicability of isotope mass balance is potentially limited to semi-arid and arid snowpacks due to atmospheric water vapor-snowpack interaction, however, chemical mass balance may be applicable in a variety of environments. The results of this study also offer the possibility that solar forcing estimates may be useful for distributing not only SWE but also snowpack chemical and isotopic signatures, both at maximum accumulation and during melt.

CONCLUSIONS

SWE values at max accumulation varied by 30% in the open snow pit sites, and 45% between open and dense canopy cover sites without elevation or slope differences. Major volume weighted mean anion concentrations of SO_4^{2-} , NO_3^- , Cl^- , and water isotopes ($\delta^{18}\text{O}$, δD) showed significant spatial variability, which combined with differences in SWE, leads to considerable variability in chemical loading and the isotopic signature of the snowpack. Consistent strong correlations between solutes and SWE, water isotopes and SWE, Solar forcing index (SFI) values and SWE, and SFI values and solutes leads to the conclusion that differences in energy inputs are driving variable sublimation rates between snow pits. This appears to be the simplest and most likely explanation for the observed variability in SWE and the chemical/isotopic signature of the snowpack. Because chemical solutes (SO_4^{2-} , Cl^-) and water isotopes ($\delta^{18}\text{O}$, δD) behave ideally to partition water within the snowpack, simple mass balance calculations can account for the hydrologic partitioning of snowfall between sublimation and catchment water availability. Sublimation estimates range from ~6mm (2%) (topographically shaded open) to 50mm (17%) (non-shaded open). The chemical and isotopic signature of seasonal snowpacks may provide a possible tool to assess snowpack water budgets and spatial variability in SWE as demonstrated in this study. Further research is needed to test the validity of these relationships across a greater range of energy environments, however, the spatial variance of SWE, chemistry, and isotopes in the snowpack in relation to solar forcing may have direct application for biogeochemical and hydrologic tracer studies needing to distribute SWE and snow chemical/isotopic values catchment wide.

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REFERENCES

- Bales, R.C., Davis, R.E. and Stanley, D.A., 1989. Ion Elution through Shallow Homogeneous Snow. *Water Resources Research*, 25(8): 1869-1877.
- Bales, R.C. et al., 2006. Mountain hydrology of the western United States. *Water Resources Research*, 42(8).
- Brimblecombe, P. et al., 1985. Relocation and preferential elution of acidic solute through the snowpack of a small, remote, high-altitude Scottish catchment. *Annals of Glaciology*, 7: 141-147.
- Clark, I. and Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. CRC Press, Boca Raton, 328 pp.
- Clow, D.W., Ingersoll, G.P., Mast, M.A., Turk, J.T. and Campbell, D.H., 2002. Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: implications for winter dry deposition. 36(14): 2337-2348.
- Coop, J.D. and Givnish, T.J., 2007. Gradient analysis of reversed treelines and grasslands of the Valles Caldera, New Mexico. *Journal of Vegetation Science*, 18(1): 43-54.
- Cragin, J.H., Hewitt, A.D. and Colbeck, S.C., 1996. Grain-scale mechanisms influencing the elution of ions from snow. *Atmospheric Environment*, 30(1): 119-127.
- Cragin, J.H. and McGilvary, R., 1995. Can inorganic chemical species volatilize from snow?, *Biogeochemistry of Seasonally Snow Covered Catchments*. Proceedings of Boulder Symposium. IAHS Publ. No. 228. IAHA Press: Wallingford, UK, pp. 11-16.
- Earman, S., Campbell, A.R., Phillips, F.M. and Newman, B.D., 2006. Isotopic exchange between snow and atmospheric water vapor: Estimation of the snowmelt component of groundwater recharge in the southwestern United States. *Journal of Geophysical Research-Atmospheres*, 111(D9).
- Elder, K., Dozier, J. and Michaelsen, J., 1991. Snow Accumulation and Distribution in an Alpine Watershed. *Water Resources Research*, 27(7): 1541-1552.
- Fagre, D. et al., 2000. An Elevational Gradient in Snowpack Chemical Loading at Glacier National Park, Montana: Implications for Ecosystem Processes, International Snow Science Workshop., Big Sky, Montana.
- Fahney, T.J., 1973. Changes in Nutrient Content of Snow Water during Outflow from Rocky Mountain Coniferous Forest. *Oikos*, 32(3): 422-428.

- Friedman, I., Benson, C. and Gleason, J., 1991. Isotopic Changes During Snow Metamorphism. In: H.P. Taylor (Editor), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. The Geochemical Society, San Antonio, pp. 211-221.
- Fu, P. and Rich, P.M., 2000. *The Solar Analyst 1.0 Manual*. Helios Environmental Modeling Institute (HEMI), USA.
- Goff, F., Gardner, J.N., Reneau, S.L. and Goff, C.J., 2006. Preliminary geologic map of the Valles San Antonio quadrangle, Sandoval County, New Mexico. New Mexico Bureau of Geology and Mineral Resources. Open-file Geologic Map OF-GM 132, scale 1:24,000.
- Goodison, B.E., Louie, P.Y.T. and Yang, D., 1998. WMO solid precipitation measurement intercomparison final report. WMO Instruments and Observing Methods Report, 67. WMO/TD No. 872.
- Hardy, J.P. et al., 2004. Solar radiation transmission through conifer canopies. *Agricultural and Forest Meteorology*, 126(3-4): 257-270.
- Harrington, R.F., Bales, R.C. and Wagnon, P., 1996. Variability of meltwater and solute fluxes from homogeneous melting snow at the laboratory scale. *Hydrological Processes*, 10(7): 945-953.
- Hedstrom, N.R. and Pomeroy, J.W., 1998. Measurements and modelling of snow interception in the boreal forest. *Hydrological Processes*, 12(10-11): 1611-1625.
- Hidy, G.M., 2003. Snowpack and precipitation chemistry at high altitudes. *Atmospheric Environment*, 37(9-10): 1231-1242.
- Hood, E., Williams, M. and Cline, D., 1999. Sublimation from a seasonal snowpack at a continental, mid-latitude alpine site. *Hydrological Processes*, 13(12-13): 1781-1797.
- Hudson, R.O. and Golding, D.L., 1998. Snowpack chemistry during snow accumulation and melt in mature subalpine forest and regenerating clear-cut in the southern interior of BC. *Nordic Hydrology*, 29(3): 221-244.
- Huth, A.K., Leydecker, A., Sickman, J.O. and Bales, R.C., 2004. A two-component hydrograph separation for three high-elevation catchments in the Sierra Nevada, California. *Hydrological Processes*, 18(9): 1721-1733.
- Ingersoll, G.P., 2000. *Snowpack Chemistry at Selected Sites in Colorado and New Mexico During Winter 1999-2000*. U.S. Geologic Survey Open File Report, 00-394: 9.

- Johnson, D.W., Susfalk, R.B., Dahlgren, R.A., Caldwell, T.G. and Miller, W.W., 2001. Nutrient fluxes in a snow-dominated, semi-arid forest: Spatial and temporal patterns. *Biogeochemistry*, 55(3): 219-245.
- Judy, C., Meiman, J.R. and Friedman, I., 1970. Deuterium variations in an annual snowpack. *Water Resources Research*, 6: 125-129.
- Kattelman, R. and Elder, K., 1991. Hydrologic Characteristics and Water-Balance of an Alpine Basin in the Sierra-Nevada. *Water Resources Research*, 27(7): 1553-1562.
- Kostrzewski, J., Brooks, P.D., Hogan, J. and Meixner, T., 2008. Quantifying seasonal variations in flowpath, solute source, and nutrient modification: a catchment comparison in Valles Caldera National Preserve, NM. *Ecohydrology*, In Press.
- Kuhn, M., Haslhofer, J., Nickus, U. and Schellander, H., 1998. Seasonal development of ion concentration in a high alpine snow pack. *Atmospheric Environment*, 32(23): 4041-4051.
- Laudon, H., Seibert, J., Kohler, S. and Bishop, K., 2004. Hydrological Flow Paths During Snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soilwater, and runoff. *Water Resources Research*, 40: 9.
- Leggett, D.C. and Hogan, A.W., 1995. A Preliminary Experiment to Examine Chemical-Exchange at Soil Snow Interface. *Science of the Total Environment*, 161: 403-408.
- Leydecker, A. and Melack, J.M., 1999. Evaporation from snow in the central Sierra Nevada of California. *Nordic Hydrology*, 30(2): 81-108.
- Link, T.E. and Marks, D., 1999a. Distributed simulation of snowcover mass and energy-balance in the boreal forest. *Hydrological Processes*, 13: 2439-2452.
- Link, T.E. and Marks, D., 1999b. Point simulation of seasonal snow cover dynamics beneath boreal forest canopies. *Journal of Geophysical Research-Atmospheres*, 104: 27841-27857.
- Losleben, M., Pepin, N. and Pedrick, S., 2000. Relationships of precipitation chemistry, atmospheric circulation, and elevation at two sites on the Colorado front range. *Atmospheric Environment*, 34(11): 1723-1737.
- Lyon, S.W., Troch, P.A., Broxton, P.D., Molotch, N.P. and Brooks, P.D., 2008. Monitoring the timing of snow melt and the initiation of streamflow using a distributed network of temperature/light sensors. *Ecohydrology*, In Press.

- Massman, W.J. et al., 1997. A model investigation of turbulence-driven pressure-pumping effects on the rate of diffusion of CO₂, N₂O, and CH₄ through layered snowpacks. *Journal of Geophysical Research-Atmospheres*, 102(D15): 18851-18863.
- Mast, M.A., Turk, J.T., Ingersoll, G.P., Clow, D.W. and Kester, C.L., 2001. Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpacks. *Atmospheric Environment*, 35(19): 3303-3313.
- McClung, K.N. and Schaerer, P.A., 2000. *The Avalanche Handbook*. The Mountaineers, Seattle, WA, 271 pp.
- McDowell, N., White, S.A. and Pockman, W., 2008. Transpiration and stomatal conductance across a steep climate gradient in the southern Rocky Mountains. *Ecohydrology*, In Press.
- McGuire, K.J. et al., 2005. The role of topography on catchment-scale water residence time. *Water Resources Research*, 41(5).
- McKay, G.A. and Gray, D.M., 1981. The Distribution of Snow Cover. In: D.M. Gray and D.H. Male (Editor), *Handbook of Snow*. Pergamon Press, New York, pp. 153-190.
- Molotch, N.P. et al., 2007. Estimating sublimation of intercepted and sub-canopy snow using eddy covariance systems. *Hydrological Processes*, 21(12): 1567-1575.
- Montesi, J., Elder, K., Schmidt, R.A. and Davis, R.E., 2004. Sublimation of intercepted snow within a subalpine forest canopy at two elevations. *Journal of Hydrometeorology*, 5(5): 763-773.
- Moore, D., 2008. Sevilleta Meteorological Data of the Valles Caldera National Preserve, 2003-2008. Sevilleta LTER Database. <http://sevilleta.unm.edu/research/local/climate/VCNP/>.
- Moser, H. and Stichler, W., 1975. Deuterium and Oxygen-18 contents as an index of the properties of snow covers, *Snow Mechanics; Proceedings of the Grindelwald Symposium*. IAHS Publication No. 114, pp. 122-135.
- Muldavin, E. and Tonne, P., 2003. *A Vegetation Survey and Preliminary Ecological Assessment of Valles Caldera National Preserve, New Mexico*. Natural Heritage New Mexico Publ. No. 06-GTR-302., Albuquerque, NM., 59 pp.
- Musselman, K., Molotch, N.P. and Brooks, P.D., 2008. Effects of vegetation on snow accumulation and ablation in a mid-latitude sub-alpine forest. *Hydrological Processes*, 22.

- NRCS, 2008a. <http://soils.usda.gov>.
- NRCS, 2008b. <http://www.wcc.nrcs.usda.gov/snotel/>.
- O'Neil, J.R., 1968. Hydrogen and oxygen isotope fractionation between ice and water. *Journal of Physical Chemistry*, 72: 3683-3684.
- Phillips, E.H. et al., 2007. The Ar-40/Ar-39 age constraints on the duration of resurgence at the Valles caldera, New Mexico. *Journal of Geophysical Research-Solid Earth*, 112(B8).
- Pichlmayer, F., Schoner, W., Seibert, P., Stichler, W. and Wagenbach, D., 1998. Stable isotope analysis for characterization of pollutants at high elevation alpine sites. *Atmospheric Environment*, 32(23): 4075-4085.
- Pomeroy, J.W. et al., 1999. Transformations of snow chemistry in the boreal forest: accumulation and volatilization. *Hydrological Processes*, 13(14-15): 2257-+.
- Pomeroy, J.W., Jones, H.G., Tranter, M. and Lilbæk, G., 2005. Hydrochemical Processes in Snow-Covered Basins. *Encyclopedia of Hydrological Sciences*, 14. John Wiley & Sons, Ltd.
- Pomeroy, J.W., Marsh, P., Jones, H.G. and Davies, T.D., 1995. Spatial distribution of snow chemical load at the tundra-taiga transition, Biogeochemistry of Seasonally Snow Covered Catchments. *Proceedings of Boulder Symposium*. IAHS Publ. No. 228. IAHA Press: Wallingford, UK, pp. 191-203.
- Pomeroy, J.W., Parviainen, J., Hedstrom, N.R. and Gray, D.M., 1998. Coupled modelling of forest snow interception and sublimation. *Hydrological Processes*, 12: 2317-2337.
- Rinehart, A.J., Vivoni, E.R. and Brooks, P.D., 2008. Effects of vegetation, albedo, and radiation sheltering on the distribution of snow in the Valles Caldera, New Mexico. *Ecology*, In Press.
- Rohrbough, J.A., Davis, D.R. and Bales, R.C., 2003. Spatial variability of snow chemistry in an alpine snowpack, southern Wyoming. *Water Resources Research*, 39(7).
- Sicart, J.E. et al., 2004. A sensitivity study of daytime net radiation during snowmelt to forest canopy and atmospheric conditions. *Journal of Hydrometeorology*, 5(5): 774-784.
- Sommerfeld, R.A., Clark, J. and Friedman, I., 1991. Isotopic changes during the formation of depth hoar in experimental snowpacks. In: H.P. Taylor (Editor),

Stable Isotope Geochemistry: A Tribute to Samuel Epstein. The Geochemical Society, San Antonio.

- Sommerfeld, R.A., Friedman, I. and Nilles, M., 1987. The fractionation of natural isotopes during temperature gradient metamorphism of snow. In: H.G. Jones (Editor), Seasonal Snowcovers: Physics, Chemistry and Hydrology. NATO-ASI series C, 211, pp. 95-106.
- Stichler, W., 1986. Snowcover and snowmelt processes studied by means of environmental isotopes. In: H.G. Jones (Editor), Seasonal Snowcovers: Physics, Chemistry, and Hydrology. NATO-ASI Series C, 211.
- Sueker, J.K., Ryan, J.N., Kendall, C. and Jarrett, R.D., 2000. Determination of hydrologic pathways during snowmelt for alpine/subalpine basins, Rocky Mountain National Park, Colorado. Water Resources Research, 36(1): 63-75.
- Taylor, S., Feng, X., Williams, M. and McNamara, J., 2002. How isotopic fractionation of snowmelt affects hydrograph separation. Hydrological Processes, 16: 3683-3690.
- Taylor, S. et al., 2001. Isotopic evolution of a seasonal snowpack and its melt. Water Resources Research, 37(3): 759-769.
- Tranter, M. et al., 1986. The composition of snowfall, snowpack, and meltwater in the Scottish Highlands-evidence for preferential elution. Atmospheric Environment, 20(3): 517-525.
- Tranter, M. et al., 1987. Spatial Variability in the Chemical-Composition of Snowcover in a Small, Remote, Scottish Catchment. Atmospheric Environment, 21(4): 853-862.
- Turk, J.T. et al., 2001. Major-ion chemistry of the Rocky Mountain snowpack, USA. Atmospheric Environment, 35(23): 3957-3966.
- Unnikrishna, P.V., McDonnell, J.J. and Kendall, C., 2002. Isotope variations in a Sierra Nevada snowpack and their relation to meltwater. Journal of Hydrology, 260(1-4): 38-57.
- USGS, 2003. Valles Caldera National Preserve 10m Digital Elevation Model. University of New Mexico Earth Data Analysis Center.
- Veatch, W.V., Brooks, P.D., Gustafson, J.R. and Molotch, N.P., 2008. Quantifying the Effects of Forest Canopy Cover on Net Snow Accumulation at a Continental, Mid-Latitude Site. Ecohydrology, In Press.

- Williams, M.W. and Melack, J.M., 1991. Precipitation Chemistry in and Ionic Loading to an Alpine Basin, Sierra-Nevada. *Water Resources Research*, 27(7): 1563-1574.
- Williams, M.W., Tonnessen, K., Melack, J.M. and Daqing, Y., 1992. Sources and spatial variation of the chemical composition of snow in the Tien Shan, China. *Annals of Glaciology*, 16: 25-31.
- Zou, C.B., Barron-Gafford, G.A. and Breshears, D.D., 2007. Effects of topography and woody plant canopy cover on near-ground solar radiation: Relevant energy inputs for ecohydrology and hydrogeology. *Geophysical Research Letters*, 34(24).

TABLES

Table 1: Snow pit location characteristics. Each site was selected to vary aspect and vegetation cover independent of elevation. A topographic and vegetation solar index were developed for each snow pit. Two snow pits are topographically shaded open (TS1, TS2), two are non-shaded open (NS1, NS2), on one is located directly under dense canopy (DV).

Snow Pit Name	Elevation (m)	Field Aspect	Relative Solar Forcing		
			Topographic	Vegetation	Overall
Topo-Shaded 1 (TS1)	3006	72° (ESE)	0.81	0.93	0.75
Topo-Shaded 2 (TS2)	3060	22° (NNW)	0.64	0.90	0.57
Non-Shaded 1 (NS1)	3014	298° (NNE)	0.95	0.95	0.90
Non-Shaded 2 (NS2)	3012	135° (SE)	1.07	0.97	1.04
Dense Vegetation (DV)	3010	N/A	0.95	0.30	0.28

Table 2: Summary of Meteorological Characteristics from Nov. 1 through Apr. 30. Snow accumulation period typically begins near November 1st with maximum SWE typically occurring during the last week of March.

November - April	Quemazon SnoTel Data		Field Data (VCNP Micro-Met Station 14 and Mixed Conifer Site Snow Pingers)			Vectored Mean Wind Direction (degrees)
	Max SWE (mm)	Mean Temp (°C)	Max Depth (cm)	Mean RH (%)	Mean Wind Speed (m/s)	
1980-2006	257	-2.2	--	--	--	--
2003-2006	209	-2.0	64	60	2.0	279
2006-2007	274	-0.2	72	58	1.9	290

Table 3: Summary of observed SWE at peak accumulation and precipitation-elevation lapse rate predicted SWE for each pit location. Differences between observed SWE and precipitation input range from 3 to 151 mm of water.

Snow Pit	Observed SWE	Lapse Rate Precipitation (mm)	
	(mm)	Prediction	95% Confidence Range
Topo-Shaded 1 (TS1)	340	337	311 – 363
Topo-Shaded 2 (TS2)	338	349	320 – 378
Non-Shaded 1 (NS1)	275	339	312 – 366
Non-Shaded 2 (NS2)	237	339	312 – 365
Dense Vegetation	187	338	312 – 365

Table 4: Volume weighted mean water isotopes, major anions, major cations, and biogeochemical nutrients. Water isotopes, SO_4^{2-} , and Cl^- vary inversely with SWE while NO_3^- , major anions, and TDN have little correlation. Cl^- and DOC are strongly influenced by canopy cover as both are elevated in the DV pit.

Snow Pit	$\delta^{18}\text{O}$ (‰)	δD (‰)	SO_4^{2-} ($\mu\text{eq L}^{-1}$)	Cl^- ($\mu\text{eq L}^{-1}$)	NO_3^- ($\mu\text{eq L}^{-1}$)	Ca^{2+} ($\mu\text{eq L}^{-1}$)	Na^+ ($\mu\text{eq L}^{-1}$)	K^+ ($\mu\text{eq L}^{-1}$)	DOC mg L^{-1}	TDN mg L^{-1}
TS1	-16.3	-111	10.6	17.4	10.8	7.8	10.3	2.1	1.03	0.28
TS2	-15.4	-104	11.6	19.7	15.6	15.9	12.5	2.2	0.95	0.37
NS1	-14.7	-99	13.1	19.0	12.2	10.2	12.0	2.0	0.57	0.34
NS2	-14.1	-96	12.5	19.6	9.4	11.4	15.6	2.2	0.60	0.29
DV	-13.5	-93	13.5	26.9	14.5	15.8	11.9	5.9	1.37	0.32

Table 5: Mean new snowfall chemistry and water isotope composition for two new snowfall events. Standard deviations are represented in parentheses. The February event was sampled in three locations distributed across our study domain while the March event was sampled at five locations. Overall chemical and isotopic variability within an individual storm is low. Additional non-distributed new snowfall samples were collected and used to calculate the average new snow values.

Date	SO ₄ ²⁻ (μeq/L)	Cl ⁻ (μeq/L)	NO ₃ ⁻ (μeq/L)	δ ¹⁸ O ‰	δD ‰
17-Feb-07	5.2 (1.1)	13.8 (0.9)	7.3 (2.1)	-17.4 (0.1)	-126 (2.6)
31-Mar-07	12.6 (0.9)	25.1 (3.6)	24.1 (0.7)	-13.5 (1.1)	-95 (5.5)
Average New Snow	10.9 (4.6)	17.9 (5.8)	13.7 (7.7)	-16.0 (3.0)	-113 (23.7)

Table 6: Mass balance calculated sublimation flux from each snow pit (expressed as millimeters of SWE).

Method	TS1 (mm)	TS2 (mm)	NS1 (mm)	NS2 (mm)	DV (mm)
SO_4^{2-}	-9.3	20.9	54.9	44.1	43.9
$\delta^{18}\text{O}$	-4.3	11.9	21.8	23.3	29.3
δD	-4.9	15.4	25.9	23.2	27.9
Mean	-6.2	16.1	34.2	30.2	33.7

FIGURES

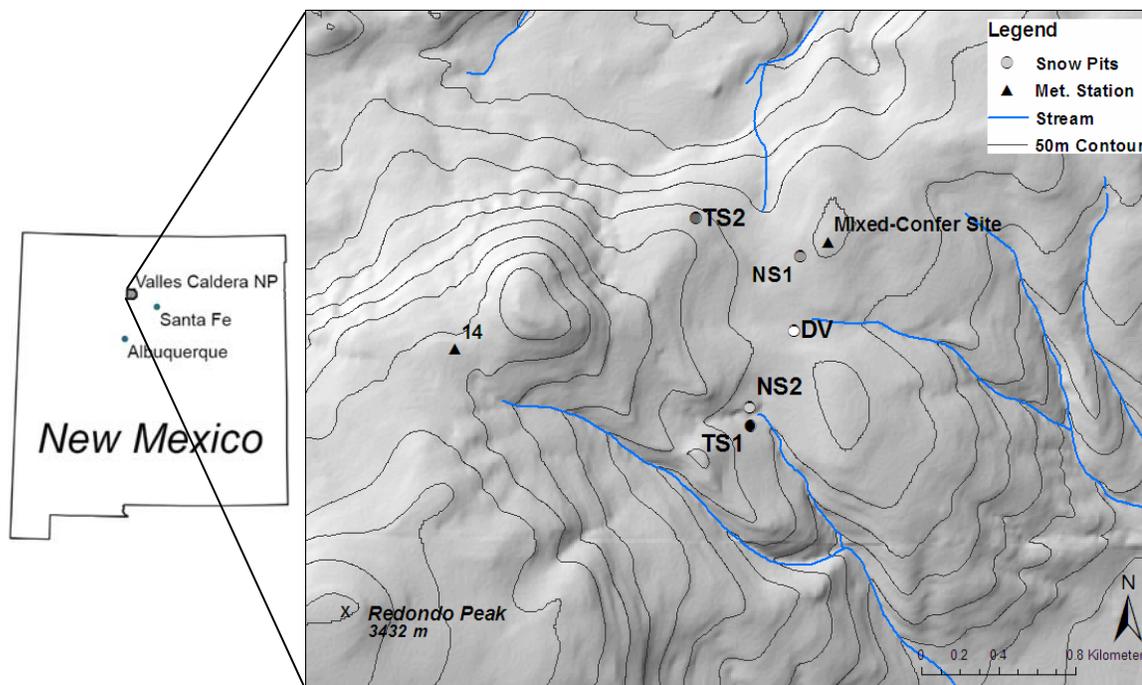


Figure 1: Site figure depicting the relative location of the VCNP within New Mexico, and our five study sites on the Redondo Peak Massif (TS1, TS2, NS1, NS2, DV). One of the five VCNP micro-meteorological stations is shown on the map (Stations 14) as well as the mixed conifer instrumentation site with eddy covariance tower.

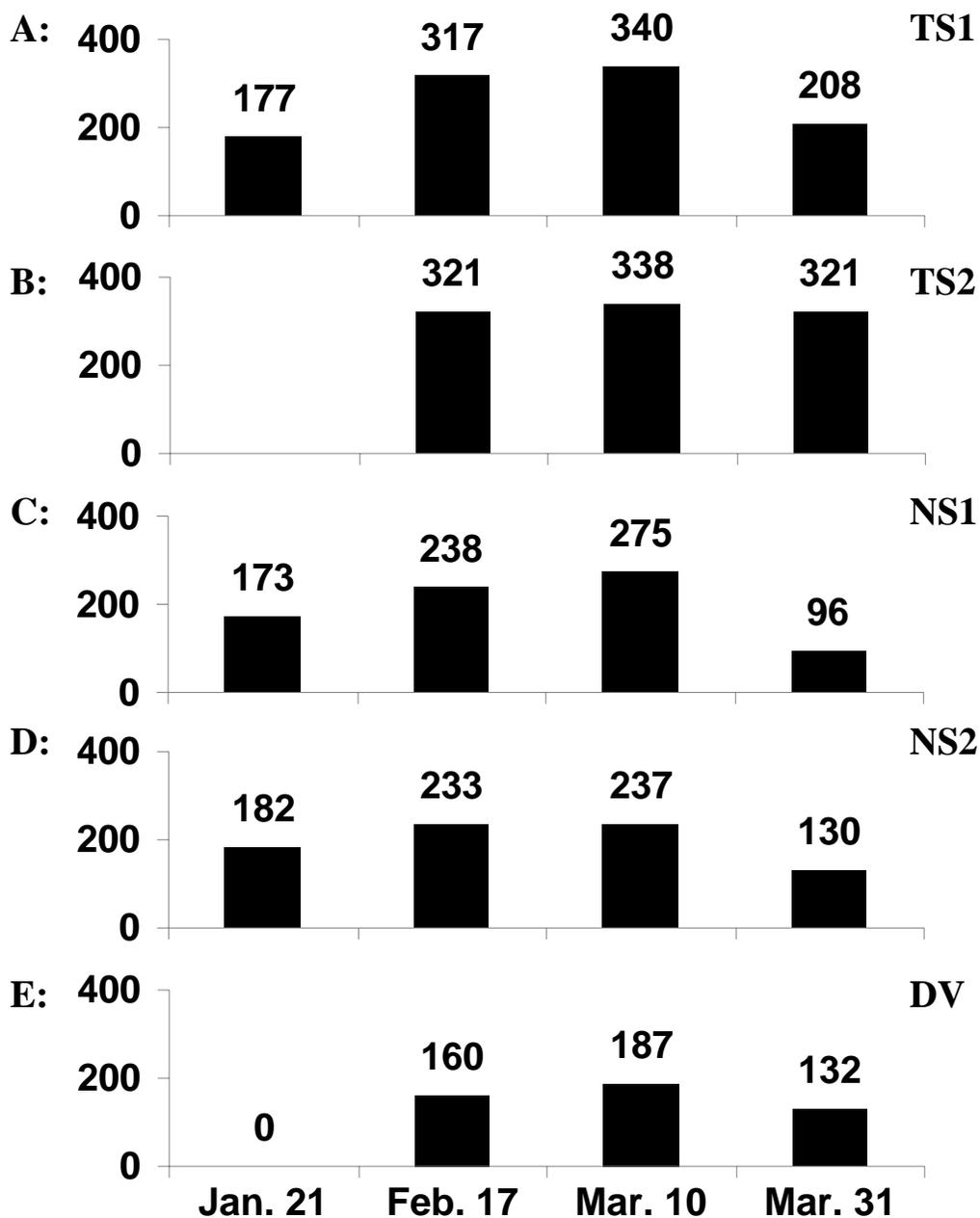


Figure 3: Snow water equivalent (SWE) variability up to max accumulation (Mar. 10th) and into snowmelt (Mar. 31st) at the five study sites. On Jan. 21 the variability between the three established pits (TS1, NS1, NS2) is less than 10mm SWE but at max accumulation increases to 103mm (30%) between open sites TS1 and NS2 and to 153mm between all sites (45%). The relative time of melt and subsequent loss of SWE varies between sites as well.

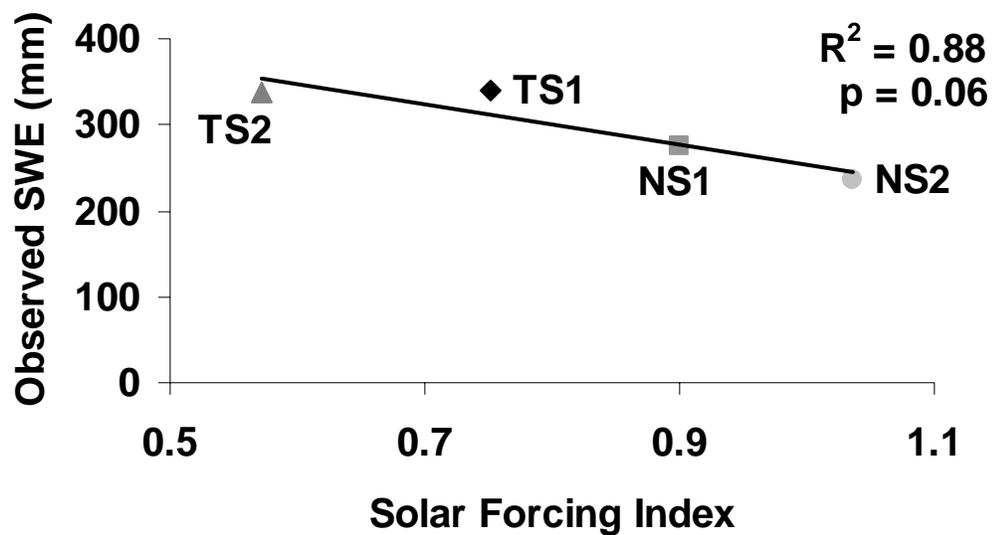


Figure 4: Influence of relative solar index across our five study sites. The observed SWE correlates well with solar forcing index despite the lack of data points while the DV pit is excluded from the comparison due to canopy effects.

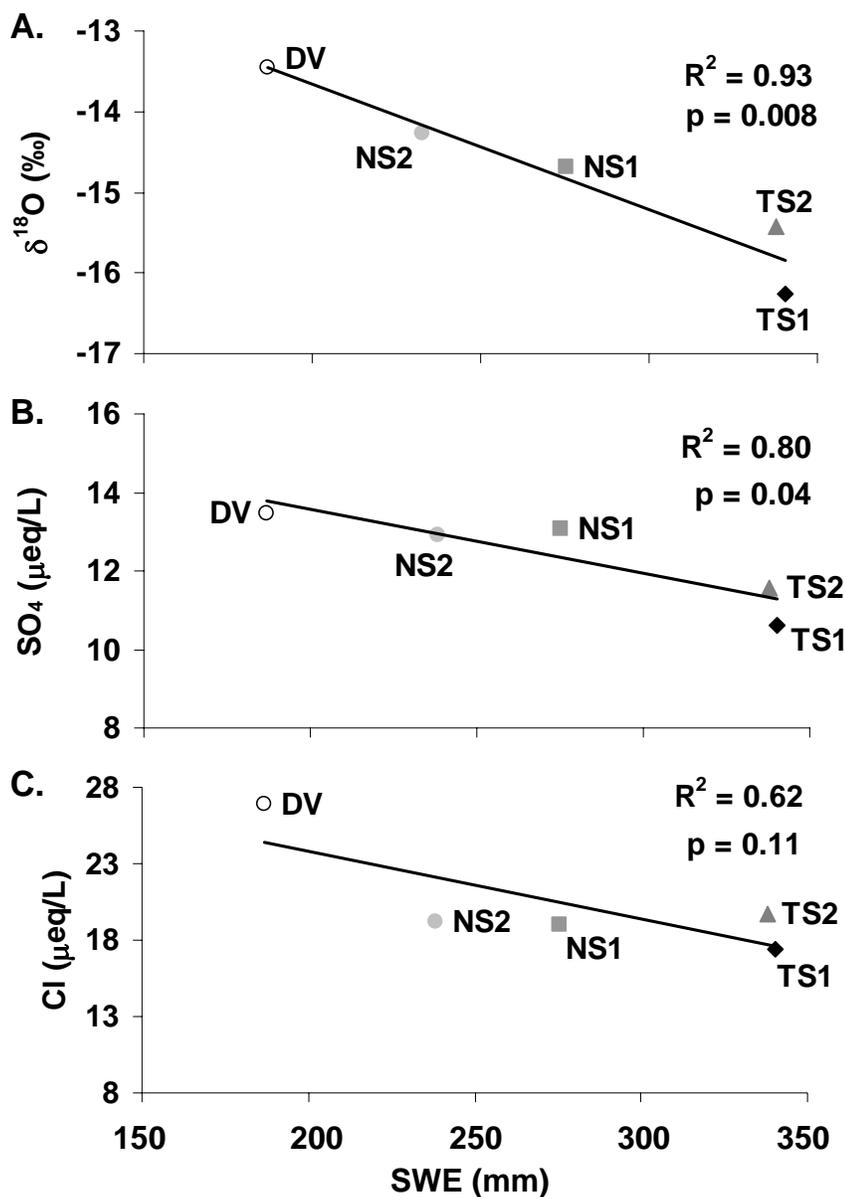


Figure 5: Max accumulation volume weighted mean water isotope ($\delta^{18}\text{O}$, 5A) and anion concentrations (SO_4^{2-} and Cl^- , 5B and 5C respectively) varying with SWE at each of the five study pits. The correlation between concentration and SWE is strong for each, as concentration increases with decreasing SWE. These trends may be indicative of sublimation water loss within our study domain.

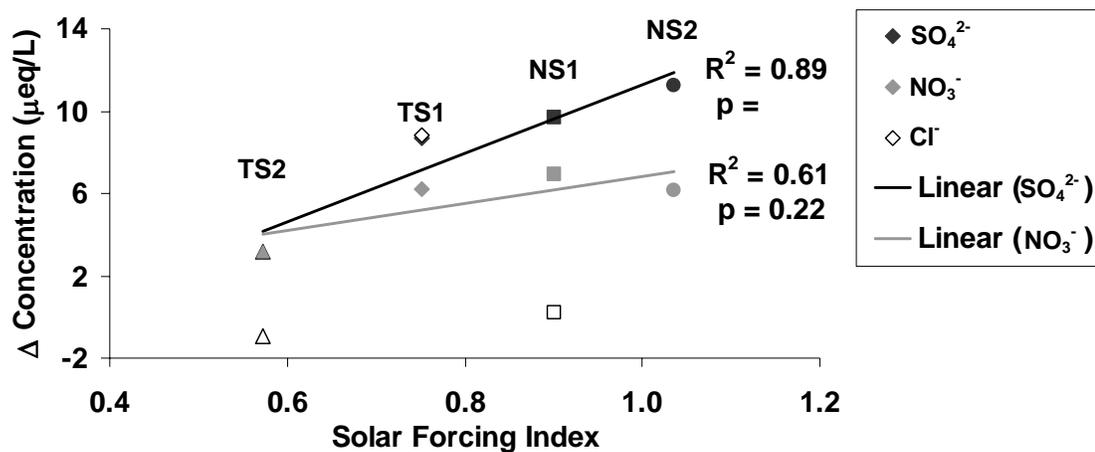


Figure 6: Depicts change in concentration between March 10th (max accumulation) and March 31st (melt season). Concentration changes for sulfate and nitrate show the open pits with the highest solar forcing index (SFI) (NS1 and NS2) experience the largest differences, while the open pit with the lowest SFI (TS2 pit) experiences the smallest change. Generally the samples show a preferential elution sequence following Tranter et al. (1986) and Brimblecomb et al. (1985) of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$.

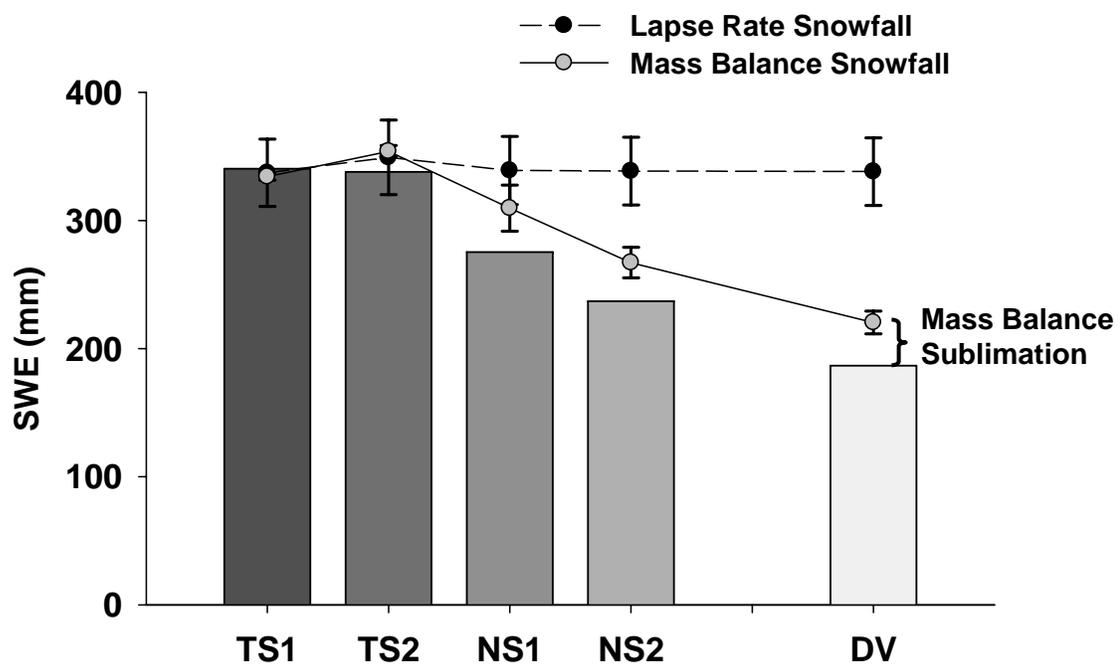


Figure 7: Depiction of observed SWE at max accumulation, mean mass balance calculated snowfall, and lapse rate predicted snowfall. The observed SWE is displayed as bars. The mean mass balance calculated snowfall using SO_4^{2-} , $\delta^{18}\text{O}$, and δD is shown with standard deviation bars. The elevation-precipitation lapse rate is shown with 95% confidence interval bars. The DV site SWE accumulation and chemistry is influenced by canopy interception/interaction and thus does not reflect all depositional events. Mass balance calculated sublimation is the difference between observed SWE and mass balance calculated snowfall.

APPENDIX B: SNOWPIT SAMPLE PHYSICAL AND CHEMICAL DATA FOR THE
2006-2007 WINTER.

This appendix contains all the physical and chemical data for the snowpit sites collected during the 2006-2007 winter in the Valles Caldera National Preserve. Snowpit physical data including sample name, depth, morphology, temperature, and density measurements are included in Tables B1-B6. Chemical anion concentrations (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) for all samples and anions analyzed are included in Table B7. Chemical cation data (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Si^{4+} , Al^{3+} , Zn^{2+}) for all samples and cations analyzed are included in Table B8 while water isotopes (δD and $\delta^{18}O$) and biogeochemical nutrients (dissolved organic carbon (DOC) and total dissolved nitrogen (TDN)) of every sample are included in Table B9. Volume weighted mean concentrations of major anions (Cl^- , NO_3^- , SO_4^{2-}) and major cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Si^{4+}) are reported in Table B10. Volume weighted mean water isotope values (δD and $\delta^{18}O$) and biogeochemical nutrient (DOC and TDN) concentrations are reported in Table B11. A brief description of the method used to calculate volume weighted mean concentrations is included following the tables at the end of this appendix.

TABLES

Table B1: Snow pit sampling name, date, sample depth, morphology, and approximate deposition date. The deposition dates were derived following the snow calendar method (Schoner et al., 1993).

Snow Pit	Sample Name	Date	Sample Depth (cm)	Snow Type	Approximate Deposition Date(s)
Topo Shaded 1	VCNL-1-01	19-Jan	70-57	Past Storm	1/13 th 1/14
	VCNL-1-02	19-Jan	57-28	Rounds	mid 12/28 th 12/29
	VCNL-1-03	19-Jan	28-11	Rounds	12/19 th 12/21
	VCNL-1-04	19-Jan	11-0	Depth hoar	mix small early storms
Non-Shaded 2	VCSL-1-01	21-Jan	78-68	New Snow	1/19 th 1/20
	VCSL-1-04	21-Jan	68-58	Past Storm	1/13 th 1/14
	VCSL-1-02	21-Jan	48-38	Rounds	top 12/28 th 12/29
	VCSL-1-03	21-Jan	28-18	Rounds	12/19 th 12/21
Non-Shaded 1	VCT-1-01	20-Jan	71-61	New Snow	1/19 th 1/20 and below
	VCT-1-02	20-Jan	61-51	Past Storm	1/13 th 1/14 and below
	VCT-1-03	20-Jan	51-31	Rounds	bottom 12/28 th 12/29 & maybe below
	VCT-1-04	20-Jan	31-13	Rounds	12/19 th 12/21 and maybe above
Topo Shaded 1	VCNL-2-05	16-Feb	115-105	New Snow	2/11 th 2/12
	VCNL-2-06	16-Feb	95-85	Rounds/Ice	Across Ice 2-11 & 2/1
	VCNL-2-07	16-Feb	75-65	Rounds	Suncrest 1/13-14 & 1/19
	VCNL-2-08	16-Feb	65-55	Rounds	1/13 th 1/14
	VCNL-2-09	16-Feb	35-25	Rounds	12/28 th 12/29 th suncrest
Non-Shaded 2	VCSL-2-05	16-Feb	85-75	New Snow	2/11 th 2/12
	VCSL-2-06	16-Feb	75-65	New/ Previous Snow	Across Ice 2-11 & 2/1
	VCSL-2-07	16-Feb	55-45	Rounds	1/13 th 1/14
	VCSL-2-08	16-Feb	35-25	Rounds	bottom of 12/28 th 12/29
	VCSL-2-09	16-Feb	25-15	Rounds	12/19 th 12/21

Snow Pit	Sample Name	Date	Sample Depth	Snow Type	Approximate Deposition Date(s)
Non-Shaded 1	VCT-2-06	16-Feb	71-61	New Snow/ Rounds/Ice	Across Ice 2-11 & 2/1
	VCT-2-07	16-Feb	51-41	Rounds	top of 12/28 th 12/29
	VCT-2-08	16-Feb	31-21	Mixed Rounds	lower of 12/28 th 12/29
	VCT-2-09	16-Feb	21-11	Mixed Rounds	12/19 th 12/21
Topo-Shaded 2	VCNW-2-01	17-Feb	115-105	New Snow	2/17 and 2/11 th 2/12
	VCNW-2-02	17-Feb	95-85	Prev. Storm	1/31 th 2/1
	VCNW-2-03	17-Feb	75-65	Rounds w/ small suncrest	suncrest 1/20 and 1/14
	VCNW-2-04	17-Feb	45-35	Mixed Rounds	lower of 12/28 th 12/29
	VCNW-2-05	17-Feb	25-15	Mixed Rounds	12/19 th 12/21
Small Clearing	VCC-2-01	17-Feb	70-60	New /Ice /Prev.	2/11-12 (maj) and 1/31-2/1
	VCC-2-02	17-Feb	60-50	Prev Storm/ Suncrest	1/31 th 2/1
	VCC-2-03	17-Feb	50-40	Rounds	1/13 th 1/14
	VCC-2-04	17-Feb	40-30	Rounds/ Suncrest	even mix 1/12-14 & 12/28-29 across sun
	VCC-2-05	17-Feb	20-10	Rounds	12/19 th 12/21
Dense Vegetation	VCV-2-01	17-Feb	63-53	New Snow	2/17 and 2/11 th 2/12
	VCV-2-02	17-Feb	53-43	Broken Rounds	1/31 th 2/1
	VCV-2-03	17-Feb	43-33	Rounds	1/13 th 1/14
	VCV-2-04	17-Feb	33-23	Rounds	top of 12/28 th 12/29
	VCV-2-05	17-Feb	23-13	Mixed Rounds	12/28-29 and 12/19-20
Topo Shaded 1	VCNL-3-10	10-Mar	105-95	Surface Hoar/ Ice/ Rounds	across ice 3/8 & 3/1 & 2/24 & 2/12
	VCNL-3-11	10-Mar	85-75	Rounds	1/31 th 2/1
	VCNL-3-12	10-Mar	65-55	Rounds	1/13 th 1/14
	VCNL-3-13	10-Mar	45-35	Rounds	mid 12/28 th 12/29
	VCNL-3-14	10-Mar	25-15	Rounds	12/19 th 12/21

Snow Pit	Sample Name	Date	Sample Depth	Snow Type	Approximate Deposition Date(s)
Non-Shaded 2	VCSL-3-10	10-Mar	65-45	Surface Hoar/ Rounds	across ice 3/8 & 3/1 & 2/24 & 2/12 & 2/1
	VCSL-3-11	10-Mar	45-25	Rounds	Mix 1/13-14 & 12/28-29
	VCSL-3-12	10-Mar	15-0	Facets	12/19 th 12/21
Non-Shaded 1	VCT-3-10	10-Mar	79-69	Surface Hoar/ Rounds	Mix 3/8, 3/1, 2/24
	VCT-3-11	10-Mar	69-59	Rounds	Ice acrs 2/11-12 (maj) & 2/1
	VCT-3-12	10-Mar	49-29	Rounds	Mix 1/13-14 & 12/28-29
	VCT-3-13	10-Mar	19-9	Rounds/Facets	12/19 th 12/21
Topo-Shaded 2	VCNW-3-06	10-Mar	108-98	Surface Hoar/ Rounds Rounds with Thick Ice	3/8, ice, 2/24-5
	VCNW-3-07	10-Mar	88-78	Layer	Ice acrs 2/11-12 & 2/1 even
	VCNW-3-08	10-Mar	58-48	Rounds	1/13 th 1/14
	VCNW-3-09	10-Mar	38-28	Rounds	12/28 th 12/29 and maybe below
	VCNW-3-10	10-Mar	18-08	Rounds and Depth Hoar	12/19 th 12/21
Small Clearing Pit	VCC-3-06	10-Mar	62-52	Surface Hoar/ Rounds	Mix 3/8, 3/1, 2/24
	VCC-3-07	10-Mar	52-42	Rounds across Suncrest	Across Ice 2-11 & 2/1
	VCC-3-08	10-Mar	42-32	Rounds	1/13 th 1/14
	VCC-3-09	10-Mar	32-22	Rounds	mid 12/28 th 12/29
Dense Vegetation	VCC-3-10	10-Mar	22-12	Rounded & Broken Grains	12/28-29 and 12/19-20
	VCV-3-06	10-Mar	65-55	Surface Hoar/ Rounds	--
	VCV-3-07	10-Mar	55-45	Homogenous Rounds	--
	VCV-3-08	10-Mar	45-35	Homogenous Rounds	--
Plot 3	VCV-3-09	10-Mar	35-25	Homogenous Rounds	--
	VC3-3-01	11-Mar	51-25	Surface Hoar/ Rounds	--
Plot 3d	VC3-3-02	11-Mar	25-0	Rounds	--
	VC3d-3-01	11-Mar	64-32	Surface Hoar/ Rounds	--
	VC3d-3-02	11-Mar	32-0	Rounds	--

Snow Pit	Sample Name	Date	Sample Depth	Snow Type	Approximate Deposition Date(s)
Plot 1e	VC1e-3-01	11-Mar	74-37	Surface Hoar/ Rounds	--
	VC1e-3-02	11-Mar	36-0	Rounds	--
Plot 2c	VC2c-3-01	11-Mar	65-33	Surface Hoar/ Rounds	--
	VC2c-3-02	11-Mar	33-0	Rounds	--
Topo Shaded 1	VCNL-3-15	11-Mar	94-69	Surface Hoar/ Rounds	--
	VCNL-3-16	11-Mar	69-40	Integrated Rounds	--
	VCNL-3-17	11-Mar	40-0	Integrated Rounds	--
Non-Shaded 2	VCSL-3-13	11-Mar	72-50	Surface Hoar/Rounds	--
	VCSL-3-14	11-Mar	50-25	Integrated Rounds	--
	VCSL-3-15	11-Mar	25-0	Integrated Rounds	--
Topo Shaded 1	VCNL-4-18	31-Mar	63-58	New Snow	--
	VCNL-4-19	31-Mar	58-0	Homogenous Rounds	--
Non-Shaded 2	VCSL-4-16	31-Mar	40-36	New Snow	--
	VCSL-4-17	31-Mar	36-7	Homogenous Rounds	--
Non-Shaded 1	VCT-4-14	31-Mar	28-27	New Snow	--
	VCT-4-15	31-Mar	27-5	Homogenous Rounds	--
Topo-Shaded 2	VCNW-4-11	31-Mar	85-80	New Snow	--
	VCNW-4-12	31-Mar	80-61	Rounds	--
	VCNW-4-13	31-Mar	61-43	Rounds	--
	VCNW-4-14	31-Mar	43-24	Rounds	--
	VCNW-4-15	31-Mar	24-7	Mixed Rounds/Facets	--
Small Clearing	VCC-4-11	31-Mar	38-28	Homogenous Rounds	--
	VCC-4-12	31-Mar	28-18	Homogenous Rounds	--
Dense Vegetation	VCV-4-10	31-Mar	39-37	New Snow	--
	VCV-4-11	31-Mar	37-9	Homogenous Rounds	--

Table B2: Topographically Shaded 1 (TS1) snow pit temperature and density measurements. Bold and shaded cells indicate samples were brought back to the University of Arizona for chemical and isotopic analysis.

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)				Stratigraphy Notes
January 19, 2007	Surface	-10	--	--	--	--	70-57 - New Snow
	70-60	-10	178	186	176	169	57-28 - Rounds
	60-50	-10	233	237	--	--	28-11 - Mixed Rounds
	50-40	-9	252	266	--	--	11-0 - Facets
	40-30	-8	271	275	--	--	
	30-20	-5	283	286	--	--	
	20-10	-3	274	304	--	--	
	15-5	-3	274	233	--	--	
	5-0	-2	--	--	--	--	
February 16, 2007	Surface	-3	--	--	--	--	Wind hardened layer at surface
	115-105	-6	173	174	169	--	Significant ice layer at 91 cm
	105-95	-7.5	210	205	--	--	115-92 - New Snow
	95-85	-7	261	270	268	--	92-91 - Ice Layer
	85-75	-5.5	266	242	296	265	91-75 - Rounds .5-1mm
	75-65	-5	286	290	285	--	72-71 - Suncrest
	65-55	-4	322	291	270	302	71-13 - Rounds
	55-45	-3.5	302	300	--	--	13-0 - Depth Hoar
	45-35	-3	312	305	--	--	
	35-25	-3	336	339	--	--	
	25-15	-2.5	313	302	308	--	
	15-5	-2.5	300	301	--	--	
	5-0	-2	--	--	--	--	

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)				Stratigraphy Notes
March 10, 2007	Surface	0.3	--	--	--	--	105-100 Surface Hoar
	105-95	-1.5	315	323	--	--	100 - Thick Ice layer
	95-85	-2	283	297	274	--	100-86 Rounds
	85-75	-1	329	324	311	--	86-85 thick ice layer
	75-65	-1	311	268	280	--	85-68 Rounds
	65-55	-1	344	288	324	286	68 - Suncrest
	55-45	-1	296	270	325	--	68-48 Rounds
	45-35	-1.5	286	294	287	302	48 - Suncrest
	35-25	-1.5	347	362	338	--	48-29 Rounds
	25-15	-1	357	352		--	29 Suncrest
	15-5	-1.5	302	362	340	--	29 -13 Rounds
	5-0	-1.5	--	--	--	--	13-0 Depth Hoar

Table B3: Topographically-Shaded 2 (TS2) snow pit temperature and density measurements. Bold and shaded cells indicate samples were brought back to the University of Arizona for chemical and isotopic analysis.

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)				Stratigraphy Notes
February 17, 2007	Surface	-7	--	--	--	--	115-97 - New Snow
	115-105	-10.3	197	195	--	--	97-95 - Distinct Thick Ice Layer
	105-95	-8.3	249	247	--	--	95-78 - Previous Storm
	95-85	-7	259	261	--	--	78-77 - Suncrest
	85-75	-6	271	275	--	--	77-70 - Rounds
	75-65	-5.3	297	297	--	--	70 - Mild Suncrest
	65-55	-5	315	294	309	--	70-51 - Rounds
	55-45	-4.5	305	309	--	--	51-50 - Suncrest
	45-35	-4	353	327	340	330	50-33 - Mixed Rounds
	35-25	-3.5	345	350	--	--	33-32 - Suncrest
	25-15	-2.7	341	337	--	--	32-16 - Mixed Rounds
	15-5	-2.5	305	323	329	--	16-0 - Depth Hoar (Facets)
5-0	-2.3	--	--	--	--		
March 10, 2007	Surface	0	--	--	--	--	108 Surface hoar w/ ice
	108-98	-0.5	277	274	254	290	104 - Thin Ice
	98-88	-2.5	261	273	264	--	104-96 - Rounds
	88-78	-3	312	305	--	--	96 - Ice layer
	78-68	-3.5	308	380	312	--	96-85 Rounds
	68-58	-3	300	322	322	--	85-83 Thick Ice layer
	58-48	-3	326	312	353	323	83-68 Rounds
	48-38	-3	325	319	--	--	68 Thin ice
	38-28	-2	325	336	--	--	68-48 Rounds
	28-18	-2	354	348	--	--	48 - Thin Ice
	18-8	-1.5	297	313	--	--	48-13 Rounds
8-0	-1	--	--	--	--	13-0 Depth Hoar	

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)			Stratigraphy Notes
March 31, 2007	Surface	--	--	--	--	85-80 New Snow
	85-80	--	176*	136*	122*	85-84 Thick Ice Layer
	80-61	--	412	404	--	84-61 Large Rounds
	61-43	--	375	378	--	61-60 Thick Ice Layer
	43-24	--	389	401	--	60-43 Rounds
	24-7	--	382	404	--	43 - Suncrest 43-24 Rounds 24 - Suncrest 24-7 Mixed rounds and facets 7-0 Depth Hoar

Table B4: Non-Shaded 1 (NS1) snow pit temperature and density measurements. Bold and shaded cells indicate samples were brought back to the University of Arizona for chemical and isotopic analysis.

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)			Stratigraphy Notes
January 20, 2007	Surface	-6	--	--	--	71-63 - New Snow
	71-61	-7	126	130	147	63-56 - Previous Storm
	61-51	-8	233	226	--	36-13 - Rounds
	51-41	-7	244	248	--	13-0 - Facets (Depth Hoar)
	41-31	-7	281	277	--	
	31-21	-5.5	291	265	--	
	21-11	-5.5	276	248	--	
11-0	-2.5	--	--	--		

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)			Stratigraphy Notes
February 16, 2007	Surface	-3.5	--	--	--	81-66 - New Snow
	81-71	-5.5	190	210	198	66-65 - Ice Layer seen elsewhere
	71-61	-6	238	240	232	65-51 - Rounds
	61-51	-5.5	270	271	--	51 - Suncrest
	51-41	-5	313	281	290	51-36 - Mixed Rounds/Fused grains
	41-31	-4	300	302	--	36-18 - Rounds (larger then 51-36)
	31-21	-3	317	313	--	
	21-11	-3	340	299	304	
	11-0	-2	297	245	--	
March 10, 2007	Surface	--	--	--	--	79 - 61 Surface crystallization w/ soft crust
	79-69	-2	373	293	307	61-59 Ice Layer thick
	69-59	-1.5	357	311	--	59-41 Rounds
	59-49	-1.5	319	379	--	41-40 Ice Lense
	49-39	-2	335	345	--	40-12 Rounds
	39-29	-2	326	331	--	12 - Bottom Rounded Facets
	29-19	-2	311	329	--	
	19-9	-2	360	388	386	
	9-0	--	311	--	--	

Table B5: Non-Shaded 2 (NS2) snow pit temperature and density measurements. Bold and shaded cells indicate samples were brought back to the University of Arizona for chemical and isotopic analysis.

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)			Stratigraphy Notes
January 21, 2007	Surface	-10	--	--	--	Two distinct suncrests at 51 and 29 cm
	78-68	-11	87	90		80-75 - New Snow
	68-58	-8.5	208	194	172	75-66 - Prev. Storm
	58-48	-7	233	241	--	66-51 - Rounds
	48-38	-6	253	249	--	51 - Suncrest
	38-28	-5	289	283	--	51-29 - Rounds
	28-18	-4	297	300	--	29 - Suncrest
	18-8	-4	304	288	--	29-15 - Rounds
	8-0	-2.5	--	--	--	15-0 - Fassets (Depth Hoar)
February 16, 2007	Surface	-4	--	--	--	85-71 - New Snow
	85-75	-4.5	173	171		70-69 - Distinct Ice Layer as seen elsewhere
	75-65	-5.5	251	255		69-62 - Previous Storm
	65-55	-5	278	293	275	62-61 - Suncrest
	55-45	-4.5	295	291		61-43 - Rounds
	45-35	-3.5	297	291		43-42 - Suncrest
	35-25	-3	315	310		42-24 - Mixed Rounds
	25-15	-3	320	318	326	24-23 - Suncrest
	15-5	-2	311	319		23-10 - Mixed Rounds
5-0	-2	--	--	--		
March 10, 2007	Surface	-1	--	--		60 light crust
	65-55	-2	349	343		51-50 Solid Crust
	55-45	-1.5	331	336		19 - decomposing layer
	45-35	-2.5	389	376		8 - 0 Facted layer
	35-25	-2	346	363		
	25-15	-1.5	447	356		
	15-5	-1	384	346		
5-0	-0.5					

Table B6: Dense vegetation (DV) snowpit temperature and density measurements. Bold and shaded cells indicate samples were brought back to the University of Arizona for chemical and isotopic analysis.

Sample Date	Depth	T (°C)	Repeat Density Measurements (kg/m ³)				Stratigraphy Notes
February 17, 2007	Surface	-7	--	--	--	--	63-53 - New Snow
	63-53	-7	189	190	--	--	53 - Ice Layer
	53-43	-6	230	229	--	--	53-45 - Previous Storm
	43-33	-5	293	273	250	265	45-33 - Fused Facets
	33-23	-4	275	280	--	--	33-15 - Facets (Cups?)
	23-13	-4	279	285	--	--	15-5 - Prisms
	13-0	-4	264	279	271	--	5-0 - Depth Hoar
March 10, 2007	Surface	--	--	--	--	--	Tichk Surface Ice Layer at 5 cm
	65-55	--	237	250	259	--	Homogenous below (rounds)
	55-45	--	256	260	--	--	Log across the bottom 10-15 cm
	45-35	--	290	285	291	--	
	35-25	--	305	311	--	--	
	25-15	--	--	--	--	--	
	15-5	--	--	--	--	--	

Table B7: Anion data for all samples collected over the 2007-2008 winter.

Sample Name	2007 Sample Date	Sample Depth	Analysis ($\mu\text{eq/L}$)						
			F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻
VCNL-1-01	19-Jan	70-57	10.24	62.28	0.13	0.04	14.45	19.58	2.73
VCNL-1-02	19-Jan	57-28	4.33	12.28	0.07	0.01	4.43	1.79	0.32
VCNL-1-03	19-Jan	28-11	4.28	10.28	0.09	0.01	8.08	8.80	1.36
VCNL-1-04	19-Jan	11-0	1.82	17.31	0.06	0.02	13.46	19.50	1.22
VCSL-1-01	21-Jan	78-68	11.62	20.93	0.11	0.01	7.61	12.42	0.84
VCSL-1-04	21-Jan	68-58	4.16	40.49	0.10	0.04	13.60	16.61	2.96
VCSL-1-02	21-Jan	48-38	5.41	12.65	0.06	0.01	3.92	1.18	0.42
VCSL-1-03	21-Jan	28-18	5.63	17.44	0.09	0.01	11.05	29.10	0.21
VCT-1-01	20-Jan	71-61	11.59	34.65	0.07	0.00	7.46	6.44	2.15
VCT-1-02	20-Jan	61-51	7.81	30.18	0.12	0.03	11.44	17.68	2.89
VCT-1-03	20-Jan	51-31	4.22	11.12	0.06	0.01	5.74	3.52	0.50
VCT-1-04	20-Jan	31-13	7.16	22.51	0.10	0.02	9.82	18.20	0.50
VCNL-2-05	16-Feb	115-105	6.38	20.91	0.10	0.01	15.00	10.40	0.28
VCNL-2-06	16-Feb	95-85	6.04	17.69	0.06	0.02	22.30	8.71	0.63
VCNL-2-07	16-Feb	75-65	2.65	11.02	0.03	0.01	9.80	7.13	0.18
VCNL-2-08	16-Feb	65-55	2.88	19.38	0.07	0.04	12.45	16.30	0.18
VCNL-2-09	16-Feb	35-25	5.12	13.66	0.07	0.02	9.94	8.32	0.32
VCSL-2-05	16-Feb	85-75	3.24	14.10	0.03	0.01	5.81	4.42	0.07
VCSL-2-06	16-Feb	75-65	4.16	13.13	0.02	0.02	9.31	6.72	0.23
VCSL-2-07	16-Feb	55-45	8.75	35.57	0.17	0.05	13.77	19.27	0.32
VCSL-2-08	16-Feb	35-25	5.57	12.16	0.08	0.02	5.16	2.15	0.21
VCSL-2-09	16-Feb	25-15	3.62	13.63	0.08	0.02	9.03	17.06	0.11
VCT-2-05	16-Feb	81-71	3.98	12.73	0.08	0.01	6.37	4.75	0.10
VCT-2-06	16-Feb	71-61	2.81	15.52	0.03	0.02	16.40	9.02	0.16
VCT-2-07	16-Feb	51-41	2.26	26.47	0.04	0.04	13.03	16.42	ND
VCT-2-08	16-Feb	31-21	2.87	9.81	0.06	0.02	4.55	1.39	0.06
VCT-2-09	16-Feb	21-11	3.82	12.00	0.17	0.02	9.93	17.91	0.23

Sample Name	2007 Sample Date	Sample Depth	Analysis (µeq/L)						
			F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻
VCNW-2-01	17-Feb	115-105	4.32	14.46	0.12	0.01	9.77	6.53	0.27
VCNW-2-02	17-Feb	95-85	3.76	13.18	0.07	0.01	10.96	6.31	0.09
VCNW-2-03	17-Feb	75-65	5.19	21.37	0.11	0.03	11.08	11.21	0.37
VCNW-2-04	17-Feb	45-35	2.03	7.25	0.06	0.01	4.74	1.59	0.40
VCNW-2-05	17-Feb	25-15	3.44	12.03	0.11	0.02	9.00	23.55	0.74
VCC-2-01	17-Feb	70-60	3.67	14.46	0.08	0.02	11.97	8.07	0.11
VCC-2-02	17-Feb	60-50	3.94	10.22	0.05	0.01	10.53	8.68	0.10
VCC-2-03	17-Feb	50-40	3.71	23.60	0.02	0.04	11.14	13.08	0.15
VCC-2-04	17-Feb	40-30	3.17	15.59	0.03	0.03	10.89	11.62	0.09
VCC-2-05	17-Feb	20-10	3.99	10.81	0.05	0.01	7.46	8.30	0.12
VCV-2-01	17-Feb	63-53	3.46	19.09	0.04	0.02	14.15	9.65	0.12
VCV-2-02	17-Feb	53-43	3.82	15.41	0.00	0.02	11.58	10.46	0.21
VCV-2-03	17-Feb	43-33	3.38	25.96	0.04	0.04	14.04	16.34	ND
VCV-2-04	17-Feb	33-23	3.72	22.36	0.02	0.03	12.25	13.87	ND
VCV-2-05	17-Feb	23-13	2.44	11.47	0.02	0.01	9.27	10.90	0.08
VCNL-3-10	10-Mar	105-95	4.64	15.14	0.03	0.02	19.60	11.53	5.02
VCNL-3-11	10-Mar	85-75	3.42	12.62	0.03	0.02	12.19	6.21	0.94
VCNL-3-12	10-Mar	65-55	1.61	35.61	0.02	0.01	7.02	3.16	1.10
VCNL-3-13	10-Mar	45-35	2.31	12.95	0.03	0.01	5.40	1.29	0.33
VCNL-3-14	10-Mar	25-15	1.71	12.51	0.02	0.03	9.88	21.96	0.03
VCSL-3-10	10-Mar	65-45	1.41	13.93	0.02	0.01	8.01	4.17	0.85
VCSL-3-11	10-Mar	45-25	1.37	25.08	0.02	0.02	9.45	5.74	0.70
VCSL-3-12	10-Mar	15-0	1.54	17.70	0.02	0.02	11.33	20.07	0.39
VCT-3-10	10-Mar	79-69	1.45	12.66	0.03	0.01	13.06	5.89	0.33
VCT-3-11	10-Mar	69-59	1.30	16.06	0.02	0.03	8.41	5.19	0.22
VCT-3-12	10-Mar	49-29	2.45	20.62	0.04	0.02	8.86	6.90	0.79
VCT-3-13	10-Mar	19-9	2.85	20.29	0.03	0.02	16.13	23.41	0.05
VCNW-3-06	10-Mar	108-98	3.49	29.79	0.01	0.02	19.06	12.51	2.88
VCNW-3-07	10-Mar	88-78	1.91	23.92	0.04	0.02	19.18	8.25	0.55

Sample Name	2007 Sample Date	Sample Depth	Analysis (µeq/L)						
			F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻
VCNW-3-08	10-Mar	58-48	2.07	19.59	0.16	0.16	14.21	13.99	1.32
VCNW-3-09	10-Mar	38-28	1.33	10.65	0.04	0.02	11.53	7.71	1.31
VCNW-3-10	10-Mar	18-08	1.92	24.08	0.03	0.02	16.67	20.88	0.03
VCC-3-06	10-Mar	62-52	1.63	22.90	0.02	0.02	15.04	9.34	0.78
VCC-3-07	10-Mar	52-42	1.92	28.43	0.02	0.02	15.12	11.56	4.00
VCC-3-08	10-Mar	42-32	2.47	27.20	0.04	0.04	15.73	17.08	6.61
VCC-3-09	10-Mar	32-22	1.74	9.32	0.04	0.01	5.21	1.58	0.44
VCC-3-10	10-Mar	22-12	1.39	10.94	0.04	0.01	12.38	9.44	ND
VCV-3-06	10-Mar	65-55	1.94	14.73	0.03	0.02	18.58	11.23	1.83
VCV-3-07	10-Mar	55-45	2.59	55.39	0.06	0.04	16.91	16.20	1.57
VCV-3-08	10-Mar	45-35	4.04	26.12	0.04	0.03	15.14	14.92	5.14
VCV-3-09	10-Mar	35-25	2.36	23.09	0.00	0.03	12.81	12.93	2.20
VC3-3-01	11-Mar	51-25	2.07	22.97	0.03	0.02	16.64	12.30	0.53
VC3-3-02	11-Mar	25-0	2.39	54.91	0.00	0.03	13.35	13.66	0.00
VC3d-3-01	11-Mar	64-32	3.07	28.03	0.04	0.02	21.74	14.99	4.17
VC3d-3-02	11-Mar	32-0	2.52	22.30	0.05	0.02	20.28	22.94	3.92
VC1e-3-01	11-Mar	74-37	1.49	20.60	0.07	0.02	13.50	8.58	0.01
VC1e-3-02	11-Mar	36-0	1.34	21.56	0.05	0.01	8.65	12.54	0.18
VC2c-3-01	11-Mar	65-33	2.03	29.12	0.05	0.03	17.56	14.84	2.93
VC2c-3-02	11-Mar	33-0	1.40	21.91	0.05	0.05	10.99	16.63	0.40
VCNL-3-15	11-Mar	94-69	1.95	32.48	0.03	0.01	11.53	6.90	0.81
VCNL-3-16	11-Mar	69-40	2.43	19.00	0.05	0.02	11.83	10.56	2.96
VCNL-3-17	11-Mar	40-0	1.84	15.44	0.07	0.02	13.58	18.06	1.24
VCSL-3-13	11-Mar	72-50	1.61	49.50	0.02	0.02	9.96	5.44	1.38
VCSL-3-14	11-Mar	50-25	1.47	13.71	0.08	0.01	9.35	6.26	1.82
VCSL-3-15	11-Mar	25-0	2.57	23.91	0.06	0.02	12.14	16.44	0.70
VCNL-4-18	31-Mar	63-58	0.82	19.58	0.14	0.01	23.69	12.80	0.20
VCNL-4-19	31-Mar	58-0	0.47	8.57	0.04	0.01	4.58	1.89	0.20
VCSL-4-16	31-Mar	40-36	0.88	28.11	0.30	0.00	22.36	11.21	0.17

Sample Name	2007 Sample Date	Sample Depth	Analysis ($\mu\text{eq/L}$)						
			F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻
VCSL-4-17	31-Mar	36-7	0.94	27.68	0.03	0.00	3.44	1.71	0.10
VCT-4-14	31-Mar	28-27	1.13	23.48	0.11	0.01	22.12	10.91	0.10
VCT-4-15	31-Mar	27-5	0.69	18.76	0.06	0.02	5.26	3.37	0.05
VCNW-4-11	31-Mar	85-80	0.87	27.98	0.19	0.01	23.19	12.51	0.05
VCNW-4-12	31-Mar	80-61	0.95	13.63	0.04	0.01	6.89	3.08	0.27
VCNW-4-13	31-Mar	61-43	0.82	31.12	0.17	0.02	9.01	8.80	0.08
VCNW-4-14	31-Mar	43-24	0.59	17.44	0.03	0.00	5.22	2.40	0.03
VCNW-4-15	31-Mar	24-7	0.68	20.96	0.06	0.00	8.81	17.13	0.06
VCC-4-11	31-Mar	38-28	0.73	17.37	0.06	0.00	5.29	1.18	0.02
VCC-4-12	31-Mar	28-18	0.86	12.56	0.05	0.00	5.43	5.31	0.59
VCV-4-10	31-Mar	39-37	ND	26.40	0.12	1.01	28.90	15.41	1.62
VCV-4-11	31-Mar	37-9	2.34	64.14	0.06	0.02	1.26	2.54	0.40

Table B8: Cation data for all samples collected over the 2007-2008 winter.

Sample Name	2007 Sample Date	Sample Depth	Analysis ($\mu\text{eq/L}$)						
			Ca^{2+}	K^+	Mg^{2+}	Na^+	Si^{4+}	Al^{3+}	Zn^{2+}
VCNL-1-01	19-Jan	70-57	25.45	2.15	5.59	23.76	14.38	0.53	0.39
VCNL-1-02	19-Jan	57-28	4.71	3.51	1.09	17.82	7.31	1.31	0.27
VCNL-1-03	19-Jan	28-11	9.35	2.06	1.71	17.80	9.63	0.34	0.42
VCNL-1-04	19-Jan	11-0	16.82	3.28	3.26	18.15	6.28	0.00	0.26
VCSL-1-01	21-Jan	78-68	6.95	2.06	1.25	20.83	6.93	0.07	0.73
VCSL-1-04	21-Jan	68-58	10.94	1.76	1.94	17.47	4.87	0.01	0.44
VCSL-1-02	21-Jan	48-38	24.49	2.70	5.39	24.94	11.79	0.55	0.37
VCSL-1-03	21-Jan	28-18	3.74	1.46	0.93	17.02	7.96	0.03	0.41
VCT-1-01	20-Jan	71-61	11.99	4.13	2.95	23.03	6.57	0.21	0.59
VCT-1-02	20-Jan	61-51	24.75	2.82	4.57	18.12	5.49	1.00	0.52
VCT-1-03	20-Jan	51-31	6.88	1.69	1.51	15.61	5.23	0.00	0.25
VCT-1-04	20-Jan	31-13	14.94	3.28	2.25	22.14	8.28	0.15	0.49
VCNL-2-05	16-Feb	115-105	9.23	3.20	1.93	19.14	5.28	0.04	0.82
VCNL-2-06	16-Feb	95-85	13.12	4.54	3.03	17.88	3.59	0.15	0.45
VCNL-2-07	16-Feb	75-65	6.26	1.59	1.33	15.52	4.98	0.00	0.21
VCNL-2-08	16-Feb	65-55	20.27	2.02	4.11	16.16	6.14	0.70	0.17
VCNL-2-09	16-Feb	35-25	10.53	2.32	1.18	12.09	2.65	0.25	0.44
VCSL-2-05	16-Feb	85-75	3.59	3.08	0.50	16.86	3.92	0.09	0.39
VCSL-2-06	16-Feb	75-65	3.56	1.88	0.63	9.69	1.48	0.03	0.53
VCSL-2-07	16-Feb	55-45	25.38	2.36	5.17	21.45	8.87	0.60	0.39
VCSL-2-08	16-Feb	35-25	2.88	1.44	0.25	11.15	1.99	0.15	0.35
VCSL-2-09	16-Feb	25-15	9.91	2.36	1.54	15.43	2.88	0.00	0.39
VCT-2-05	16-Feb	81-71	3.20	1.79	0.67	17.09	4.11	0.00	0.60
VCT-2-06	16-Feb	71-61	5.85	2.52	1.42	16.64	4.70	0.29	0.31
VCT-2-07	16-Feb	51-41	19.67	1.95	4.45	18.01	4.74	0.65	0.21
VCT-2-08	16-Feb	31-21	2.48	1.09	0.39	12.60	6.88	0.10	0.22
VCT-2-09	16-Feb	21-11	10.78	2.06	1.23	10.69	5.43	0.69	0.40
VCNW-2-01	17-Feb	115-105	6.30	2.83	1.35	17.37	4.81	0.07	0.62
VCNW-2-02	17-Feb	95-85	3.37	1.67	0.69	16.10	3.80	0.00	0.42

Sample Name	2007 Sample Date	Sample Depth	Analysis ($\mu\text{eq/L}$)						
			Ca^{2+}	K^+	Mg^{2+}	Na^+	Si^{4+}	Al^{3+}	Zn^{2+}
VCNW-2-03	17-Feb	75-65	11.94	2.63	2.98	17.81	8.61	1.39	0.42
VCNW-2-04	17-Feb	45-35	2.92	2.79	0.49	14.44	3.99	0.08	0.29
VCNW-2-05	17-Feb	25-15	7.17	1.95	1.25	16.53	3.79	0.00	0.37
VCC-2-01	17-Feb	70-60	7.75	2.04	0.92	15.65	5.73	0.26	0.32
VCC-2-02	17-Feb	60-50	9.71	1.60	1.19	12.37	4.18	0.45	0.29
VCC-2-03	17-Feb	50-40	20.09	3.25	4.83	17.96	9.12	0.97	0.20
VCC-2-04	17-Feb	40-30	17.19	3.10	3.43	16.75	5.45	0.31	0.24
VCC-2-05	17-Feb	20-10	5.36	1.65	0.98	12.97	5.14	0.09	0.19
VCV-2-01	17-Feb	63-53	8.19	2.34	1.70	16.93	4.29	0.03	0.39
VCV-2-02	17-Feb	53-43	10.79	2.62	2.27	16.87	4.82	0.02	0.49
VCV-2-03	17-Feb	43-33	26.66	19.61	8.47	19.47	9.88	0.64	0.31
VCV-2-04	17-Feb	33-23	21.79	6.28	5.69	18.13	6.38	0.78	0.32
VCV-2-05	17-Feb	23-13	11.87	4.55	2.77	16.47	6.04	0.59	0.32
VCNL-3-10	10-Mar	105-95	19.99	3.77	3.96	11.05	4.89	1.56	0.31
VCNL-3-11	10-Mar	85-75	4.51	2.46	1.05	9.31	1.34	0.57	0.30
VCNL-3-12	10-Mar	65-55	4.98	2.40	1.55	13.04	1.28	0.59	0.25
VCNL-3-13	10-Mar	45-35	2.54	1.31	0.36	9.09	0.98	0.15	0.27
VCNL-3-14	10-Mar	25-15	6.56	1.09	1.14	9.30	1.07	0.54	0.26
VCSL-3-10	10-Mar	65-45	6.75	1.64	1.24	10.15	4.49	1.05	0.23
VCSL-3-11	10-Mar	45-25	11.95	2.40	2.26	11.00	4.10	0.93	0.21
VCSL-3-12	10-Mar	15-0	9.30	2.07	1.50	8.90	1.21	0.21	0.24
VCT-3-10	10-Mar	79-69	6.05	1.64	1.04	11.58	2.52	0.66	0.28
VCT-3-11	10-Mar	69-59	4.62	1.98	0.99	9.14	0.50	1.57	0.23
VCT-3-12	10-Mar	49-29	8.66	1.01	1.96	9.48	1.34	0.65	0.16
VCT-3-13	10-Mar	19-9	14.65	2.94	2.73	15.25	2.71	0.55	0.45
VCNW-3-06	10-Mar	108-98	41.03	4.63	7.52	14.09	6.82	1.82	0.47
VCNW-3-07	10-Mar	88-78	7.49	2.16	1.54	10.88	1.20	0.86	0.27
VCNW-3-08	10-Mar	58-48	23.44	1.89	4.75	19.52	41.12	2.01	0.28
VCNW-3-09	10-Mar	38-28	10.38	1.32	1.66	9.07	2.31	0.53	0.26

Sample Name	2007 Sample Date	Sample Depth	Analysis ($\mu\text{eq/L}$)						
			Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Si ⁴⁺	Al ³⁺	Zn ²⁺
VCNW-3-10	10-Mar	18-08	18.46	3.05	3.76	12.21	4.56	0.97	0.47
VCC-3-06	10-Mar	62-52	6.89	1.45	1.25	9.43	1.58	0.29	0.23
VCC-3-07	10-Mar	52-42	15.08	2.35	3.13	14.96	4.57	1.11	0.32
VCC-3-08	10-Mar	42-32	24.10	3.47	4.57	13.10	4.98	1.65	0.25
VCC-3-09	10-Mar	32-22	1.46	0.78	0.38	8.92	2.15	0.35	0.26
VCC-3-10	10-Mar	22-12	10.92	1.50	1.55	9.55	2.02	0.60	0.23
VCV-3-06	10-Mar	65-55	15.19	2.08	2.37	10.17	2.90	0.63	0.28
VCV-3-07	10-Mar	55-45	22.63	7.99	5.03	15.08	3.65	0.64	0.31
VCV-3-08	10-Mar	45-35	25.15	9.93	6.57	14.54	3.82	0.77	0.32
VCV-3-09	10-Mar	35-25	11.84	5.24	2.60	10.80	2.11	0.72	0.28
VC3-3-01	11-Mar	51-25	15.32	4.18	4.22	10.17	2.53	0.88	0.27
VC3-3-02	11-Mar	25-0	15.03	8.01	5.54	16.50	2.91	0.54	0.26
VC3d-3-01	11-Mar	64-32	20.59	6.02	4.35	12.13	2.39	0.60	0.49
VC3d-3-02	11-Mar	32-0	17.85	6.48	3.83	10.42	1.53	0.45	0.27
VC1e-3-01	11-Mar	74-37	11.72	1.88	2.27	10.65	2.41	0.94	0.24
VC1e-3-02	11-Mar	36-0	6.48	1.45	1.05	8.86	0.76	1.25	0.22
VC2c-3-01	11-Mar	65-33	19.01	3.14	3.73	17.27	4.05	1.24	0.50
VC2c-3-02	11-Mar	33-0	6.94	1.78	1.22	10.99	1.27	1.89	0.52
VCNL-3-15	11-Mar	94-69	10.10	2.73	1.56	13.74	2.83	0.95	0.47
VCNL-3-16	11-Mar	69-40	13.08	2.71	2.78	11.53	2.63	0.98	0.24
VCNL-3-17	11-Mar	40-0	10.47	1.35	1.73	10.34	1.38	0.84	0.27
VCSL-3-13	11-Mar	72-50	8.33	1.86	1.65	10.73	3.87	1.13	0.44
VCSL-3-14	11-Mar	50-25	9.70	1.50	1.81	9.24	2.06	0.65	0.25
VCSL-3-15	11-Mar	25-0	9.04	1.53	1.42	9.00	2.15	0.29	0.40
VCNL-4-18	31-Mar	63-58	31.72	3.28	5.50	14.87	6.69	0.98	0.41
VCNL-4-19	31-Mar	58-0	4.54	1.55	0.68	11.29	2.32	0.37	0.28
VCSL-4-16	31-Mar	40-36	27.91	3.74	4.42	16.74	8.50	1.48	0.49
VCSL-4-17	31-Mar	36-7	4.72	1.04	1.13	19.21	7.27	1.58	0.23
VCT-4-14	31-Mar	28-27	48.74	2.63	8.38	15.98	11.32	1.53	0.50

Sample Name	2007 Sample Date	Sample Depth	Analysis ($\mu\text{eq/L}$)						
			Ca^{2+}	K^+	Mg^{2+}	Na^+	Si^{4+}	Al^{3+}	Zn^{2+}
VCT-4-15	31-Mar	27-5	5.58	2.49	1.19	13.83	3.74	0.51	0.36
VCNW-4-11	31-Mar	85-80	36.35	2.57	5.42	18.03	7.40	1.10	0.48
VCNW-4-12	31-Mar	80-61	4.58	1.62	1.15	12.98	5.13	1.29	0.40
VCNW-4-13	31-Mar	61-43	12.25	1.85	2.81	17.89	5.08	0.89	0.34
VCNW-4-14	31-Mar	43-24	4.23	1.87	0.82	14.83	3.18	0.29	0.37
VCNW-4-15	31-Mar	24-7	9.47	2.86	1.74	15.30	3.91	0.33	0.52
VCC-4-11	31-Mar	38-28	11.36	1.55	2.56	14.54	8.31	1.93	0.38
VCC-4-12	31-Mar	28-18	4.93	1.23	1.23	13.77	2.15	0.34	0.46
VCV-4-10	31-Mar	39-37	45.18	8.53	9.21	18.10	10.64	1.59	0.58
VCV-4-11	31-Mar	37-9	19.74	9.59	5.51	43.55	24.80	3.51	0.82

Table B9: Water isotope (δD and $\delta^{18}\text{O}$) and biogeochemical nutrient (DOC and TDN) data for all samples.

Sample Name	2007 Sample Date	Sample Depth	$\delta^{18}\text{O}$ (‰)	δD (‰)	DOC mg L^{-1}	TDN mg L^{-1}
VCNL-1-01	19-Jan	70-57	-10.13	-59.0	1.14	0.47
VCNL-1-02	19-Jan	57-28	-21.88	-164.7	0.67	0.17
VCNL-1-03	19-Jan	28-11	-14.35	-97.5	0.87	0.23
VCNL-1-04	19-Jan	11-0	-9.51	-59.6	1.05	0.45
VCSL-1-01	21-Jan	78-68	-23.17	-170.8	0.61	0.21
VCSL-1-04	21-Jan	68-58	-8.95	-52.0	0.65	0.45
VCSL-1-02	21-Jan	48-38	-11.50	-72.4	0.60	0.44
VCSL-1-03	21-Jan	28-18	-21.69	-158.7	0.28	0.11
VCT-1-01	20-Jan	71-61	-19.44	-141.0	1.52	0.27
VCT-1-02	20-Jan	61-51	-10.68	-67.2	1.56	0.50
VCT-1-03	20-Jan	51-31	-19.29	-138.6	0.52	0.17
VCT-1-04	20-Jan	31-13	-10.86	-67.2	0.76	0.37
VCNL-2-05	16-Feb	115-105	-17.84	-125.6	0.89	0.41
VCNL-2-06	16-Feb	95-85	-19.33	-137.0	2.12	0.44
VCNL-2-07	16-Feb	75-65	-19.31	-138.4	0.63	0.23
VCNL-2-08	16-Feb	65-55	-13.83	-91.9	0.86	0.42
VCNL-2-09	16-Feb	35-25	-16.15	-111.1	0.82	0.32
VCSL-2-05	16-Feb	85-75	-17.56	-128.6	0.38	0.22
VCSL-2-06	16-Feb	75-65	-16.19	-113.4	0.81	0.26
VCSL-2-07	16-Feb	55-45	-12.14	-80.2	0.77	0.48
VCSL-2-08	16-Feb	35-25	-18.33	-130.5	0.34	0.16
VCSL-2-09	16-Feb	25-15	-11.58	-74.9	0.53	0.32
VCT-2-05	16-Feb	81-71	-17.41	-123.6	0.39	0.19
VCT-2-06	16-Feb	71-61	-16.91	-121.1	0.62	0.40
VCT-2-07	16-Feb	51-41	-11.96	-78.0	0.66	0.42
VCT-2-08	16-Feb	31-21	-18.43	-133.5	0.27	0.12
VCT-2-09	16-Feb	21-11	-11.36	-71.2	0.52	0.33
VCNW-2-01	17-Feb	115-105	-17.33	-124.6	0.77	0.29
VCNW-2-02	17-Feb	95-85	-16.91	-118.4	0.41	0.28
VCNW-2-03	17-Feb	75-65	-18.11	-123.7	1.15	0.33
VCNW-2-04	17-Feb	45-35	-18.79	-130.5	0.50	0.13
VCNW-2-05	17-Feb	25-15	-10.05	-60.7	0.46	0.36
VCC-2-01	17-Feb	70-60	-15.91	-114.8	0.47	0.31
VCC-2-02	17-Feb	60-50	-16.86	-118.8	0.57	0.25
VCC-2-03	17-Feb	50-40	-13.73	-92.7	0.92	0.36
VCC-2-04	17-Feb	40-30	-15.90	-113.9	1.11	0.35
VCC-2-05	17-Feb	20-10	-13.58	-93.0	0.51	0.22
VCV-2-01	17-Feb	63-53	-15.50	-112.0	0.78	0.35
VCV-2-02	17-Feb	53-43	-14.96	-107.4	0.95	0.32

Sample Name	2007 Sample Date	Sample Depth	$\delta^{18}\text{O}$ (‰)	δD (‰)	DOC mg L^{-1}	TDN mg L^{-1}
VCV-2-03	17-Feb	43-33	-13.30	-93.4	3.32	0.35
VCV-2-04	17-Feb	33-23	-13.95	-98.7	1.84	0.31
VCV-2-05	17-Feb	23-13	-14.86	-102.4	1.42	0.22
VCNL-3-10	10-Mar	105-95	-15.65	-108.7	2.14	0.44
VCNL-3-11	10-Mar	85-75	-17.88	-123.0	1.14	0.25
VCNL-3-12	10-Mar	65-55	-20.08	-145.5	1.38	0.17
VCNL-3-13	10-Mar	45-35	-19.77	-141.3	0.38	0.13
VCNL-3-14	10-Mar	25-15	-11.56	-69.8	0.41	0.34
VCSL-3-10	10-Mar	65-45	-15.83	-112.1	0.52	0.21
VCSL-3-11	10-Mar	45-25	-16.14	-112.6	0.59	0.26
VCSL-3-12	10-Mar	15-0	-10.14	-68.7	0.72	0.41
VCT-3-10	10-Mar	79-69	-16.38	-117.0	0.43	0.30
VCT-3-11	10-Mar	69-59	-16.66	-115.3	0.50	0.22
VCT-3-12	10-Mar	49-29	-18.11	-128.1	0.41	0.23
VCT-3-13	10-Mar	19-9	-10.41	-60.4	0.77	0.49
VCNW-3-06	10-Mar	108-98	-14.49	-98.0	2.45	0.36
VCNW-3-07	10-Mar	88-78	-18.22	-125.7	0.73	0.38
VCNW-3-08	10-Mar	58-48	-16.02	-110.4	0.78	0.38
VCNW-3-09	10-Mar	38-28	-15.62	-105.9	0.63	0.27
VCNW-3-10	10-Mar	18-08	-10.17	-60.3	1.31	0.50
VCC-3-06	10-Mar	62-52	-16.15	-112.9	0.63	0.31
VCC-3-07	10-Mar	52-42	-16.25	-114.5	0.88	0.33
VCC-3-08	10-Mar	42-32	-15.13	-103.2	1.07	0.42
VCC-3-09	10-Mar	32-22	-18.69	-129.7	0.41	0.13
VCC-3-10	10-Mar	22-12	-15.12	-103.2	0.55	0.27
VCV-3-06	10-Mar	65-55	-15.11	-107.4	0.98	0.38
VCV-3-07	10-Mar	55-45	-13.95	-94.5	1.59	0.36
VCV-3-08	10-Mar	45-35	-13.41	-91.7	2.52	0.32
VCV-3-09	10-Mar	35-25	-12.98	-88.9	1.10	0.29
VC3-3-01	11-Mar	51-25	-14.54	-103.0	1.34	0.47
VC3-3-02	11-Mar	25-0	-14.29	-99.9	1.76	0.76
VC3d-3-01	11-Mar	64-32	-15.43	-111.5	1.78	0.42
VC3d-3-02	11-Mar	32-0	-13.22	-91.4	1.50	0.63
VC1e-3-01	11-Mar	74-37	-15.51	-108.3	0.67	0.34
VC1e-3-02	11-Mar	36-0	-14.61	-99.8	0.48	0.27
VC2c-3-01	11-Mar	65-33	-14.56	-103.8	0.89	0.43
VC2c-3-02	11-Mar	33-0	-14.12	-100.0	0.52	0.33
VCNL-3-15	11-Mar	94-69	-15.82	-112.8	0.55	0.29
VCNL-3-16	11-Mar	69-40	-16.57	-114.8	0.83	0.31
VCNL-3-17	11-Mar	40-0	-11.91	-76.7	0.59	0.37
VCSL-3-13	11-Mar	72-50	-15.71	-111.8	0.62	0.26

Sample Name	2007 Sample Date	Sample Depth	$\delta^{18}\text{O}$ (‰)	δD (‰)	DOC mg L⁻¹	TDN mg L⁻¹
VCSL-3-14	11-Mar	50-25	-17.49	-124.9	0.53	0.24
VCSL-3-15	11-Mar	25-0	-12.58	-82.9	0.56	0.38
VCNL-4-18	31-Mar	63-58	-13.94	-95.4	1.21	0.51
VCNL-4-19	31-Mar	58-0	-14.61	-101.0	0.30	0.16
VCSL-4-16	31-Mar	40-36	-14.98	-103.4	1.20	0.64
VCSL-4-17	31-Mar	36-7	-13.04	-90.6	0.57	0.18
VCT-4-14	31-Mar	28-27	-12.08	-89.6	2.90	0.62
VCT-4-15	31-Mar	27-5	-12.54	-84.4	0.54	0.28
VCNW-4-11	31-Mar	85-80	-13.79	-94.5	1.08	0.54
VCNW-4-12	31-Mar	80-61	-16.07	-110.2	0.55	0.22
VCNW-4-13	31-Mar	61-43	-13.95	-94.1	0.59	0.35
VCNW-4-14	31-Mar	43-24	-16.82	-121.5	0.37	0.25
VCNW-4-15	31-Mar	24-7	-11.64	-73.2	0.91	0.46
VCC-4-11	31-Mar	38-28	-12.28	-87.7	1.16	0.15
VCC-4-12	31-Mar	28-18	-14.26	-101.1	0.54	0.17
VCV-4-10	31-Mar	39-37	-12.69	-90.3	7.39	0.15
VCV-4-11	31-Mar	37-9	-12.35	-89.7	2.15	0.54

Table B10: Volume weighted mean chemical concentrations for major anions (Cl^- , NO_3^- , SO_4^{2-}) and cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Si^{4+}) for each snowpit and corresponding sampling date.

Snowpit	2007 Sample Date	Volume Weighted Mean Concentration ($\mu\text{eq/L}$)							
		Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}	Na^+	Si^{4+}
Topo-Shaded 1	21-Jan	19.08	8.90	10.15	10.82	2.88	2.24	18.70	8.77
	17-Feb	15.02	12.18	10.67	12.62	2.38	2.27	15.12	4.43
	10-Mar	17.38	10.82	10.60	7.80	2.10	1.60	10.29	1.85
	12-Mar	21.07	12.49	12.78	11.18	2.14	2.01	11.61	2.15
	31-Mar	8.83	5.04	2.15	5.19	1.59	0.80	11.38	2.42
Non-Shaded 2	21-Jan	19.54	8.01	12.98	14.44	2.08	3.08	20.65	8.73
	17-Feb	19.19	9.39	9.55	11.41	2.17	2.07	15.57	4.21
	10-Mar	19.63	9.59	12.93	9.64	2.08	1.74	10.13	3.35
	12-Mar	28.19	10.51	9.55	9.05	1.62	1.63	9.61	2.65
	31-Mar	27.69	4.03	2.00	5.43	1.13	1.23	19.13	7.31
Non-Shaded 1	21-Jan	19.57	8.60	12.86	13.56	2.80	2.39	19.69	6.85
	17-Feb	16.26	10.34	11.33	9.15	1.89	1.73	14.52	5.34
	10-Mar	18.97	12.18	13.07	10.21	1.96	2.03	11.96	1.92
	31-Mar	18.81	5.43	3.45	6.03	2.49	1.27	13.85	3.82
Topo-Shaded 2	17-Feb	14.44	9.22	12.05	7.32	2.36	1.58	16.59	5.39
	10-Mar	19.71	15.58	11.57	15.87	2.21	3.03	12.46	10.06
	31-Mar	20.64	7.82	8.44	8.15	2.11	1.68	15.23	4.35
Dense Veg.	17-Feb	17.26	11.50	12.12	15.49	6.85	4.04	17.38	6.36
	10-Mar	26.93	14.49	13.47	15.82	5.93	3.52	11.88	2.69
	31-Mar	63.56	1.68	2.74	20.13	9.58	5.57	43.16	24.59

Table B11: Volume weighted mean water isotope (δD and $\delta^{18}\text{O}$) and biogeochemical nutrients (DOC and TDN) for each snowpit and corresponding sampling date.

Snowpit	2007 Sample Date	$\delta^{18}\text{O}$ (‰)	δD (‰)	DOC mg L⁻¹	TDN mg L⁻¹
Topo Shaded 1	21-Jan	-16.19	-114.7	0.88	0.29
	17-Feb	-16.48	-114.1	0.91	0.35
	10-Mar	-16.27	-111.4	1.03	0.28
	12-Mar	-14.39	-98.1	0.66	0.33
	31-Mar	-14.59	-100.9	0.32	0.17
Non-Shaded 2	21-Jan	-14.24	-96.0	0.51	0.33
	17-Feb	-14.07	-96.0	0.58	0.32
	10-Mar	-14.26	-99.4	0.60	0.29
	12-Mar	-15.24	-106.3	0.57	0.29
	31-Mar	-13.10	-91.0	0.59	0.20
Non-Shaded 1	21-Jan	-14.07	-94.7	0.80	0.32
	17-Feb	-14.79	-101.8	0.51	0.31
	10-Mar	-14.69	-98.5	0.57	0.34
	31-Mar	-12.54	-84.5	0.56	0.29
Topo-Shaded 2	17-Feb	-15.63	-105.9	0.70	0.29
	10-Mar	-15.43	-104.1	0.95	0.37
	31-Mar	-14.45	-98.3	0.63	0.33
Dense Veg.	17-Feb	-14.53	-102.1	1.67	0.29
	10-Mar	-13.46	-92.5	1.37	0.32
	31-Mar	-12.36	-89.7	2.23	0.53

CALCULATION OF VOLUME-WEIGHTED-MEAN CONCENTRATIONS

Volume-weighted mean (VWM) concentrations of major anions (Cl^- , NO_3^- , SO_4^{2-}), major cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Si^{4+}), water isotopes (δD , $\delta^{18}\text{O}$), and biogeochemical nutrients (DOC, TDN) were calculated using the following method.

$$VWM = \frac{\sum(C_{i,L} \times V_L)}{V_T} = \frac{\sum[C_{i,L} \times (H_L \times \rho_L)]}{\sum(\rho_n \times d_n)}$$

Where each variable represents the following:

$C_{i,L}$ = Concentration of ion i , in layer L

H_L = Height of layer L represented by $C_{i,L}$. This is actually a volume of snow, as it is normalized to a unit area.

ρ_L = average density for layer L represented by $C_{i,L}$

ρ_n = average density of n density measurements recorded with each sample

d_n = depth of density cut n (always equals 10 cm = 0.10 m).

DISCUSSION:

The underlying assumption is that each sample represents a homogenous stratigraphic unit within the snowpack. Stratigraphy observations combined with precipitation and mean temperature measurements from nearby meteorological stations allows for the reconstruction of snowpack depositional history (Appendix C) (Schoner et al., 1993). This depositional history aids in identifying the amount of the snowpack each sample represents in conjunction with the field methods which were originally used to select

samples. While variability does occur, especially near the edges of stratigraphic layers, the overall point chemistry is encompassed through this method.

REFERENCES

- Schoner, W., Staudinger, M., Winiwarter, W. and Pichlmayer, F., 1993. Dating of snow samples from snow pits at Sonnblick, Austria Alps, as a tool for interpretation of chemical analysis. In: P.B. PM Borrell, T. Cvitas, W. Seiler (Editor), Proceedings of the EUROTRAC Symposium 1992. SPB Academic Publishing, Hague, pp. 753-756.

APPENDIX C: DOMINANT WIND DIRECTION INFLUENCE ON CHEMICAL
VARIABILITY

Appendix C contains an analysis of the influence of dominant wind direction during storm events on snow chemistry. The overarching justification for this analysis was to determine if storms with westerly wind directions contained elevated chemical concentrations over those from other directions. This may have implicated fossil fuel burning in the 4-corners region is influencing hydrochemistry in the VCNP. Results indicate it is possible this may be occurring and warrants further research.

ADDITIONAL METHODS

Outside of the methods outlined in the manuscript portion of this thesis (appendix A) an additional method was employed for the analysis of dominant wind direction on snow chemistry. The snow calendar method uses physical observations of the snow pack and meteorological data to assign depositional dates to specific snow layers. Figure C1 is an example figure showing how SWE deposition recorded at a SNOw TELemetry (SNOTEL) site can aid this method. Once snow pack layers have been dated, specific chemical samples obtained from those layers can be related both to the deposition date and the meteorological characteristics at the time of deposition. This method has been used successfully to relate pollution sources to their relative influence on snow chemistry (Pichlmayer et al., 1998). A detailed description of the snow calendar method can be found in Schöner et al. (1993). The snow calendar method relies on the assumption that chemical mass deposited in the snow pack is immobile. In maritime snow packs or snowpacks in very temperate regions this assumption may fail as these snow packs commonly experience a number of melt-freeze cycles which can cause the relocation of

chemical mass in the snow pack (Pomeroy et al., 2005). Chemical mass in snow packs from cold, continental or alpine sites are generally more conservative allowing for more reliable use of the snow calendar method.

RESULTS AND DISCUSSION

Once snow stratigraphy was related to a depositional timeframe all snow samples were assigned to specific time frames of deposition. Storm dates were surveyed to find storms which were sampled across our study area. Four specific storms were identified as having been sampled in at least four of the six original snow pits. The storm dates were December 19th, 2006; December 28th, 2006; January 13th, 2007; and February 12th, 2007. The average wind direction of each of these storms as recorded by VCNP micro-meteorological station 14 (average over the duration of the precipitation period) is plotted against sulfate concentration in Figure C2. In general storms with a westerly component have higher SO_4^{2-} concentrations than the one storm with a southeastern wind direction. The two storms with southwestern wind directions have the highest sulfate concentrations.

Sulfate to chloride ratios of these storms are shown in Figure C3 compared with dominant wind direction. Chemical ratios often are more useful than specific concentrations. This may be especially true when trying to relate pollution sources to snow chemistry, as biomass often contains unique chemical ratios that can be preserved when burning. While not entirely conservative, chloride concentrations varied significantly less than SO_4^{2-} . The $\text{SO}_4^{2-}/\text{Cl}$ ratios are dominated by the SO_4^{2-}

concentration as a result, as westerly wind directions have higher ratios. The ratio break signifying a westerly storm appears to occur around 0.5, with ratios less than 0.5 representing easterly.

Higher sulfate concentrations from western storms may be indicating air masses and snowfall are scavenging a more sulfate rich atmosphere west of the VCNP. However, the wind direction at the time of snowfall does not necessarily indicate the air mass continually traveled from that direction. Take for instance the 12/19/06 depositional event, which had a dominant wind direction of 243° . The air mass delivering this precipitation may have come farther from the north or south and changed course shortly before releasing its moisture at our site. This indicates the air mass most likely came with some westerly trajectory, but to state the absolute direction the air mass traveled from is 243° would not be precise. Thus, we can conclude snowfall events from air masses with westerly components are delivering more sulfate mass than those with easterly components, but to be more specific without calculating or modeling the back trajectories of the air masses would most likely be a faltering assumption.

Further research would be required to assess the validity of our conclusions. One way would be to use the HYSPLIT model (Draxler and Rolph, 2003), which is a simple way of viewing modeled back trajectories based on a large database of meteorological data. For a more complete analysis a statistical method analyzing storm direction (N-S and E-W respectively), vigor of flow, and vorticity as outlined by Losleben et al. (2000); could be used. An initial analysis using the HYSPLIT model may

useful to gauge if a more thorough analysis would be justified, however, analyzing the back trajectories was outside the scope of my study.

FIGURES

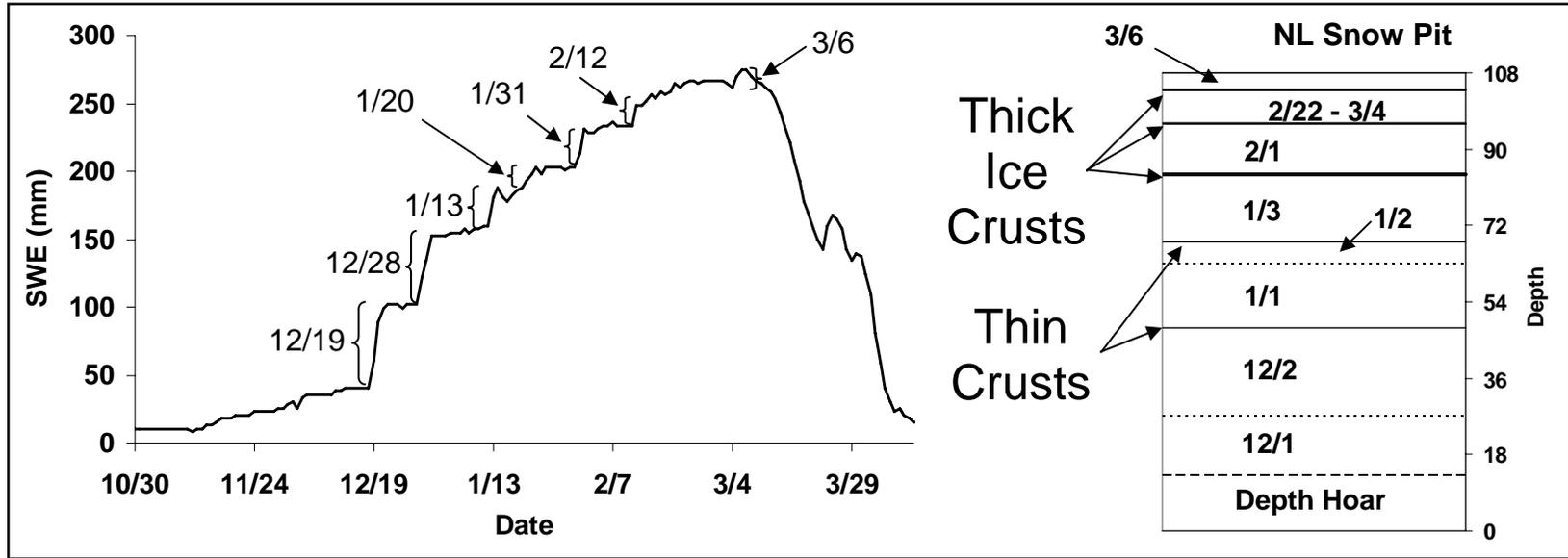


Figure C1: A brief example of information used to construct a snow calendar. The left side of the panel depicts SWE accumulation during the 2006-2007 winter at the Quemazon Snotel site #708 (NRCS, 2008b), while the right side depicts stratigraphy and morphology observations in the NL snow pit. Meteorological records from the VCNP micro-meteorological station 14 were also used (Moore, 2008). Relating SWE, temperature, and precipitation measurements with stratigraphy/morphology observations allows for the relative dating of stratigraphic layers in the snowpack similar to above. Chemical samples from the layers can then be related to deposition date and meteorological characteristics (Schoner et al., 1993).

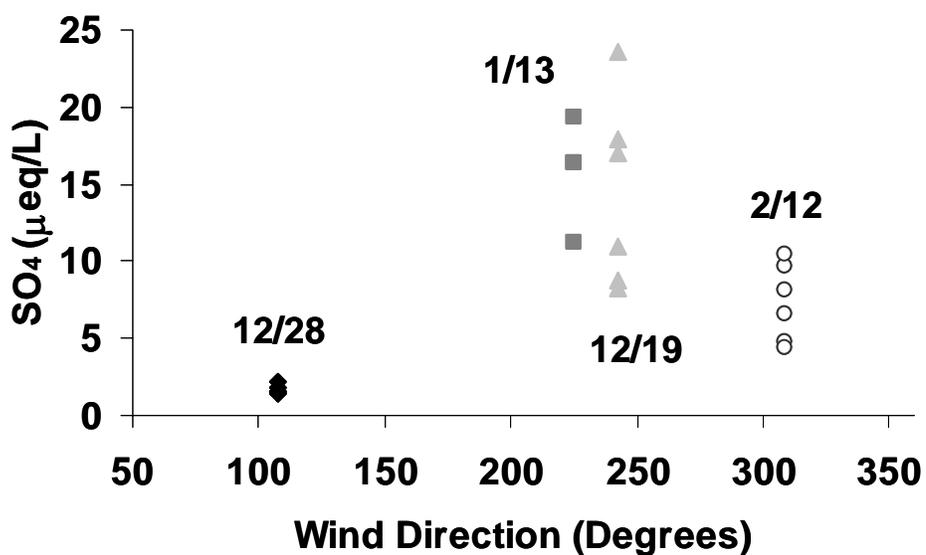


Figure C2: Sulfate concentrations of snow layers pertaining to specific deposition events. Between four and six snowpit sites provided layers that were functional in relating chemical concentrations with deposition date. Storms with dominantly western wind directions (225-250) appear to contain higher relative sulfate concentrations than storms with more northern or eastern wind directions. This may indicate the four corners region with several coal fired powered plants are affecting SO_4^{2-} concentrations at the VCNP.

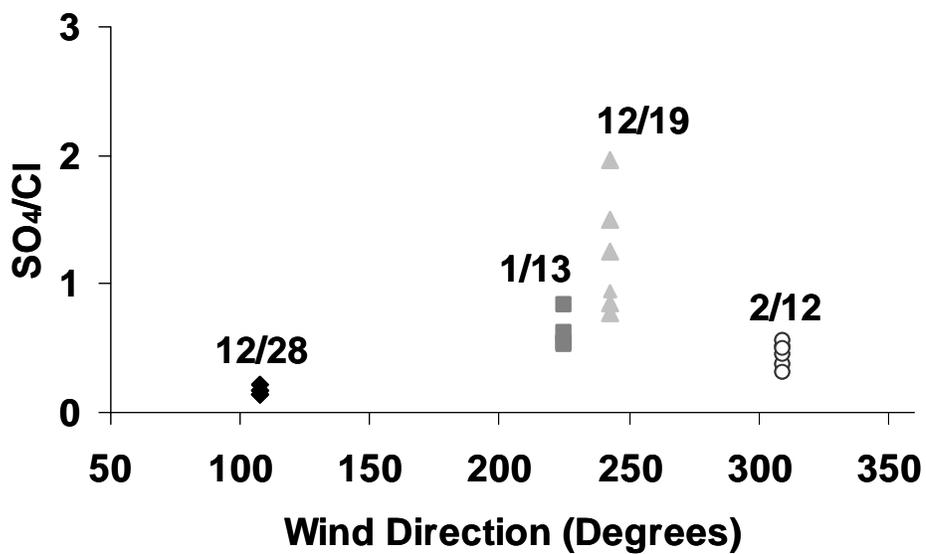


Figure C3: Chemical ratios can often be better indicators of pollution sources as we see a tighter grouping of ratios than pure SO_4^{2-} concentrations. Sulfate to chloride ratios above 0.5 appear to be indicative of dominant westerly storm directions at the time of deposition.

REFERENCES

- Draxler, R.R. and Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model. NOAA Air Resour. Lab, Silver Spring, Md. (Available at <http://www.arl.noaa.gov/ready/hysplit4.html>).
- Losleben, M., Pepin, N. and Pedrick, S., 2000. Relationships of precipitation chemistry, atmospheric circulation, and elevation at two sites on the Colorado front range. *Atmospheric Environment*, 34(11): 1723-1737.
- Moore, D., 2008. Sevilleta Meteorological Data of the Valles Caldera National Preserve, 2003-2008. Sevilleta LTER Database. <http://sevilleta.unm.edu/research/local/climate/VCNP/>.
- NRCS, 2008b. <http://www.wcc.nrcs.usda.gov/snotel/>.
- Pichlmayer, F., Schonert, W., Seibert, P., Stichler, W. and Wagenbach, D., 1998. Stable isotope analysis for characterization of pollutants at high elevation alpine sites. *Atmospheric Environment*, 32(23): 4075-4085.
- Pomeroy, J.W., Jones, H.G., Tranter, M. and Lilbæk, G., 2005. Hydrochemical Processes in Snow-Covered Basins. *Encyclopedia of Hydrological Sciences*, 14. John Wiley & Sons, Ltd.
- Schonert, W., Staudinger, M., Winiwarter, W. and Pichlmayer, F., 1993. Dating of snow samples from snow pits at Sonnblick, Austria Alps, as a tool for interpretation of chemical analysis. In: P.B. PM Borrell, T. Cvitas, W. Seiler (Editor), *Proceedings of the EUROTRAC Symposium 1992*. SPB Academic Publishing, Hague, pp. 753-756.

APPENDIX D: ISOTOPIC HOMOGENIZATION OF SNOWPITS

Appendix D contains additional analysis briefly mentioned in the manuscript in appendix A. This appendix compares simple statistical analysis of snow samples collected for isotopic analysis at each pit location over the accumulation and ablation seasons and compares each collection date. The results indicate isotopic homogenization occurs over the accumulation season at each pit location.

RESULTS AND DISCUSSION

Extensive research has been conducted on the influence of water vapor movement both internally and from external sources to the snow pack on snow pack water isotopes (e.g. Friedman et al., 1991; Koeniger et al., 2008; Moser and Stichler, 1975; Motoyama and Hirasawa, 2005; Sommerfeld et al., 1991; Sommerfeld et al., 1987; Stichler, 1986; Taylor et al., 2001; Unnikrishna et al., 2002). Studies have indicated that early in the snow pack accumulation stage, snow pack stratigraphy and corresponding isotopic values are representative of the distinct isotopic signatures of the individual precipitation events which can have a broad range of values (Judy et al., 1970; Krouse and Smith, 1972). Laboratory and field studies have shown isotopic fractionation associated with vapor movement from the bottom of the snow pack into upper snow pack layers, resulting in enrichment of the oxygen-18 isotope over that of oxygen-16 in depth hoar formation at the base of the snow pack (Friedman et al., 1991; Sommerfeld et al., 1991; Sommerfeld et al., 1987). Unnikrishna et al. (2002) recorded snow pack homogenization over the course of snowmelt due to the enhanced mixing conditions brought on by continuous

water vapor and liquid water exchange. Taylor et al. (2001) found homogenization occurred over the accumulation season as well as during snowmelt.

Water vapor exchange within the snow pack is promoted by temperature gradient driven metamorphism of snow grains where crystal edges are sublimated due to small vapor pressure differences between concave and convex points in the crystal structure (Colbeck, 1987). The continuous movement of water vapor within the humid snow pack promotes homogenization of water isotopes within the center of the snow pack. The high relative humidity and relative frequency of liquid water appearing in maritime snowpacks during humidity and during melt enhances this affect (Unnikrishna et al., 2002). Tables D1 and D2 show mean and standard deviations of water isotope values analyzed over the 2006-2007 winter at each of our study locations. Standard deviations reduce significantly between January and February at the NL, T, and SL sites while remaining fairly constant between February and maximum accumulation (March 10th). Standard deviations again reduce between the 10th and 12th of March at the NL and SL sites, which were the only two sites sampled on this date, as melt had begun by March 11th. A similar reduction in the standard deviation is recorded at the LR site between March 10th and March 31st, which experienced the lowest melt rate between the dates and enabled us to collect several samples compared with only two at every other site.

While these results were not a focus of the manuscript in appendix A, the results indicated our sites experience isotopic homogenization over the winter season. The homogenization seen early in the season may be a reflection of either consistent input lowering variability or water vapor fluxes or most likely both processes. As we do not

have direct measurements of precipitation it is difficult to gauge the variability between snowfall events. The DV snowpit showed the least variance among all sites. This may be attributed to canopy suspension prior to deposition, as snow at this site would have experienced enhanced sublimation due to the dramatic increase in exposed surface area of snow grains during canopy suspension (Hedstrom and Pomeroy, 1998).

TABLES

Table D1: Statistical analysis of $\delta^{18}\text{O}$ values for each snowpit over the 2006-2007 winter accumulation and ablation seasons. Standard deviations reduce from January to March within each snowpit indicating isotopic homogenization is occurring due to water vapor fluxes within the snow pack.

Pit	Measure	21-Jan	17-Feb	10-Mar	12-Mar	31-Mar
NL	Mean (‰)*	-16.19	-16.48	-16.27	-14.39	--
	St. Dev.	5.70	2.34	3.51	2.50	--
LR	Mean (‰)	--	-15.63	-15.43	--	-14.45
	St. Dev.	--	3.53	2.97	--	2.05
T	Mean (‰)	-14.07	-14.79	-14.69	--	--
	St. Dev.	4.96	3.30	3.41	--	--
SL	Mean (‰)	-14.24	-14.07	-14.26	-15.24	--
	St. Dev.	7.15	3.11	3.38	2.48	--
DV	Mean (‰)	--	-14.96	-13.46	--	--
	St. Dev.	--	0.88	0.92	--	--

Table D2: Statistical analysis of δD values for each snowpit over the winter 2006-2007 accumulation and ablation seasons. Similar to Table D1 the standard deviations reduce from January to March within each snowpit indicating isotopic homogenization is occurring.

Pit	Measure	21-Jan	17-Feb	10-Mar	12-Mar	31-Mar
NL	Mean (‰)*	-114.67	-114.09	-111.39	-98.08	--
	St. Dev.	49.74	19.52	30.56	21.44	--
LR	Mean (‰)	--	-105.89	-104.12	--	-98.27
	St. Dev.	--	28.75	24.39	--	18.29
T	Mean (‰)	-94.68	-101.84	-98.55	--	--
	St. Dev.	41.94	28.66	30.37	--	--
SL	Mean (‰)	-95.95	-96.01	-99.40	-106.31	--
	St. Dev.	59.96	26.47	25.19	21.52	--
DV	Mean (‰)	--	-104.83	-92.53	--	--
	St. Dev.	--	7.25	8.20	--	--

* - The mean values shown in Tables C1 and C2 are not equivalent to volume weighted mean values, however, statistical analysis of volume weighted means is not possible on volume weighted mean values.

REFERENCES

- Colbeck, S.C., 1987. Snow metamorphism and classification In: H.G. Jones (Editor), Seasonal Snowcovers: Physics, Chemistry and Hydrology. NATO-ASI series C, 211, pp. 1-35.
- Friedman, I., Benson, C. and Gleason, J., 1991. Isotopic Changes During Snow Metamorphism. In: H.P. Taylor (Editor), Stable Isotope Geochemistry: A Tribute to Samuel Epstein. The Geochemical Society, San Antonio, pp. 211-221.
- Hedstrom, N.R. and Pomeroy, J.W., 1998. Measurements and modelling of snow interception in the boreal forest. *Hydrological Processes*, 12(10-11): 1611-1625.
- Judy, C., Meiman, J.R. and Friedman, I., 1970. Deuterium variations in an annual snowpack. *Water Resources Research*, 6: 125-129.
- Koeniger, P., Hubbart, J.A., Link, T. and Marshall, J.D., 2008. Isotopic variation of snow cover and streamflow in response to changes in canopy structure in a snow-dominated mountain catchment. *Hydrological Processes*, 22(4): 557-566.
- Krouse, H.R. and Smith, J.L., 1972. $^{18}\text{O}/^{16}\text{O}$ abundance variations in Sierra Nevada seasonal snowpacks and their use in hydrological research, Proceedings of the Banff Symposia. UNESCO-WMO-IASH, Geneva, Switzerland, pp. 24-38.
- Moser, H. and Stichler, W., 1975. Deuterium and Oxygen-18 contents as an index of the properties of snow covers, *Snow Mechanics*; Proceedings of the Grindelwald Symposium. IAHS Publication No. 114, pp. 122-135.
- Motoyama, H. and Hirasawa, N., 2005. Seasonal variations in oxygen isotope ratios of daily collected precipitation and wind drift samples and in the final snow cover at Dome Fuji Station, Antarctica. *Journal of Geophysical Research*, 110.
- Schoner, W., Staudinger, M., Winiwarter, W. and Pichlmayer, F., 1993. Dating of snow samples from snow pits at Sonnblick, Austria Alps, as a tool for interpretation of chemical analysis. In: P.B. PM Borrell, T. Cvitas, W. Seiler (Editor), Proceedings of the EUROTRAC Symposium 1992. SPB Academic Publishing, Hague, pp. 753-756.
- Sommerfeld, R.A., Clark, J. and Friedman, I., 1991. Isotopic changes during the formation of depth hoar in experimental snowpacks. In: H.P. Taylor (Editor), Stable Isotope Geochemistry: A Tribute to Samuel Epstein. The Geochemical Society, San Antonio.
- Sommerfeld, R.A., Friedman, I. and Nilles, M., 1987. The fractionation of natural isotopes during temperature gradient metamorphism of snow. In: H.G. Jones

(Editor), *Seasonal Snowcovers: Physics, Chemistry and Hydrology*. NATO-ASI series C, 211, pp. 95-106.

Stichler, W., 1986. Snowcover and snowmelt processes studied by means of environmental isotopes. In: H.G. Jones (Editor), *Seasonal Snowcovers: Physics, Chemistry, and Hydrology*. NATO-ASI Series C, 211.

Taylor, S. et al., 2001. Isotopic evolution of a seasonal snowpack and its melt. *Water Resources Research*, 37(3): 759-769.

Unnikrishna, P.V., McDonnell, J.J. and Kendall, C., 2002. Isotope variations in a Sierra Nevada snowpack and their relation to meltwater. *Journal of Hydrology*, 260(1-4): 38-57.