THESIS

EFFECTS OF SNOW PERSISTENCE ON SOIL WATER NITROGEN ACROSS AN ELEVATION GRADIENT

Submitted by

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ABSTRACT

EFFECTS OF SNOW PERSISTENCE ON SOIL WATER NITROGEN ACROSS AN ELEVATION GRADIENT

In the western United States, the timing and magnitude of snowmelt is an important control on soil water and nutrient availability. Warming trends can alter the timing of snowmelt, directly impacting snow cover and soil freeze-thaw cycles, as well as available water for downstream use. While prior research relating snow to soil water nitrogen has focused on areas with persistent winter snow, the snow and soil water dynamics in lower elevation areas with intermittent snowpack are not as well documented. The broad goal of this study is to understand how the duration of snow persistence affects soil moisture and soil water nitrogen concentrations. The specific objectives are to address (1) how the duration of snow persistence affects soil moisture across an elevation gradient, from areas where the snowpack ranges from shallow and intermittent to deep and persistent throughout the winter and (2) how this gradient in snowpack affects soil water nitrogen.

Three study sites that span a 1500m elevation gradient were established in the Colorado Front Range to monitor snow, soil moisture, and soil water nitrogen. The highest elevation site, Michigan River, is located in the persistent snow zone; the middle elevation site, Dry Creek, is in the transitional snow zone; and the lowest elevation site, Mill Creek, lies in the intermittent snow zone. Each site was equipped with soil moisture probes at 5 and 20cm depth, soil temperature probes, snow depth poles monitored by time-lapse cameras, and ion exchange resin probes. The Mill Creek research site also contained nine snow manipulation chambers and twenty-seven tension lysimeters to sample soil water nitrogen.

Snow cover persisted for longer periods of time as elevation increased and soil temperatures decreased. Lower elevation sites were consistently warmer and drier than the higher elevation site. At the highest elevation site, soil moisture increased after a large pulse of snowmelt in the late spring, while the lower elevations experienced multiple smaller pulses of soil moisture following individual snow events. In the snow manipulation chambers, plots with increased snow depth experienced increased soil moisture, however plots with decreased snow depth did not always produce the lowest soil moisture. Additionally, soil moisture in the control snow plots and in plots with increased snow depth consistently increased throughout the melt season, whereas plots with decreased snow depth briefly increased after each snowmelt event then declined to pre-event levels. NO_3^- and NH_4^+ were correlated with soil moisture, and large increases in soil moisture were associated with a flushing signal of NO_3^-. This suggests that soil water nitrogen is regulated by the amount of soil water available, and that nitrogen can be impacted when changes in snow alter soil moisture timing and magnitude.

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Thank you all for this wonderful adventure.

DEDICATION

To my grandma for her dedication to hard work and perseverance.

Mama, gracias por todo. Por darme la inspiración para ser creativa y tenáz, y por enseñarme con tu ejemplo la importancia del esfuerzo y trabajo.

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1. INTRODUCTION

1.1 Snow and soil moisture

Over the past several decades, temperatures have increased, and snowpack has declined across the western United States (McCabe et al., 2009; Clow, 2010; Harpold et al., 2012). Snowpack changes have included decreases in both snow depth and snow water equivalent (SWE), a pattern that is projected to continue into the future (Regonda et al., 2005; Knowles et al., 2006; Fassnacht et al., 2015; Lute et al., 2015). Current warming trends have been associated with lower spring snow accumulation and an earlier onset of snowmelt (Mote et al., 2005; Adam et al., 2009; Fassnacht et al., 2018). Warming and drying trends in November have caused later onset of snow accumulation (Clow, 2010; Fassnacht et al., 2018), and increased warming and decreased precipitation have caused lower than average spring snow accumulation (Mote et al., 2005).

Prior research has shown strong links between snowpack loss and spatial and temporal soil moisture variability (Williams et al., 2009; Blankinship et al., 2014; Kampf et al., 2015; Harpold et al., 2015). Soil moisture is a critical component of the hydrologic cycle, impacting groundwater recharge, plant water use, and streamflow (Seyfried et al., 2009; Cavagnaro, 2016; Hammond et al., 2018). Snowmelt timing exerts significant influence on the seasonal availability of soil water; earlier snowmelt causes reduced average soil moisture and increased water stress in near-surface soils, and it impacts wetting and drying dynamics following snowmelt (Williams et al., 2009; Blankinship et al., 2014; Harpold and Molotch, 2015; Kampf et al., 2015; Webb et al., 2015; Harpold, 2016). Earlier snowmelt can shift the growing season forward, depleting late-summer soil moisture storage, and can alter soil moisture dynamics throughout the following growing season (Harpold and Molotch, 2015; Harpold, 2016; Potopova et al., 2016).

Soil moisture variability and connectivity directly impact annual streamflow in mountain watersheds and consequently water resources availability (Barnett et al., 2005; Hammond et al., 2018). Research in snow-dominated mountain watersheds has demonstrated that reductions in snowpack and the length of the snowmelt season limit natural water storage, producing lower average streamflow (Adam et al., 2009; Bode, 2016; Hammond et al., 2018). Reduced snowpack-derived streamflow poses a number of problems, affecting both water supply for regions depending on snowpack for water resources (Barnett et al., 2008; Nolin et al., 2012; Elias et al., 2016), and forest and fire management (Westerling et al., 2006; Gergel et al., 2017).

1.2 Snow and nitrogen

Nitrogen is a central nutrient for all life on Earth and is often the most limiting nutrient in ecosystem productivity (Gruber et al., 2008; Fay et al., 2015). Many studies have documented the importance of nitrogen for carbon sequestration, plant growth, and agricultural crop yields (Schrijver et al., 2007; De Vries et al., 2009; Du and de Vries, 2018; Lombardozzi et al., 2018). The flux of nitrogen through the environment is referred to as the nitrogen cycle, illustrated in Figure 1. Nitrogen enters natural terrestrial ecosystems through gaseous atmospheric conversion, atmospheric deposition, and decomposition of organic matter. Atmospheric nitrogen exists predominantly in the form of non-reactive N_2, which comprises about 78% of the atmosphere. This can be transformed into reactive nitrogen oxides (NO_x) such as nitrous oxide (N_2O), a greenhouse gas that contributes to global warming (Galloway et al., 2004; Ravishankara et al., 2009; U.S. EPA, 2010; Smith, 2010; Gregorich et al., 2015). Gaseous atmospheric nitrogen can be converted into a biologically useful form through nitrogen fixation (Söderlund and Rosswall, 1982). This process is facilitated by nitrogen-fixing bacteria that convert N_2 into bioavailable forms of nitrogen, such as ammonium (NH_4^+). The predominant inorganic forms of nitrogen are ammonium and nitrate (NO_3^-). NH_4^+ is a positively charged ion that often sorbs to negatively charged soil particles and organic matter, whereas NO_3^- is a negatively charged ion that is water soluble and prone to leaching out of the soil (Hinckley et al., 2014). Nitrogen can also enter the system through wet and dry nitrogen deposition in the form of NH_4^+, NO_3^-, and ammonia (NH_3). Nitrogen also exists in dead organic matter, which soil microbes decompose into dissolved organic nitrogen (DON) (Chapin et al., 2002). Additional microbes break down DON into NH_4^+ via mineralization and then into NO_2^- and NO_3^- via nitrification (Rosswall, 1981; Chapin et al., 2002). Inorganic nitrogen is taken up by plants or microbes via assimilation, converted back to atmospheric nitrogen through denitrification, or leached out of the soil (Tischner and Kaiser, 2007).

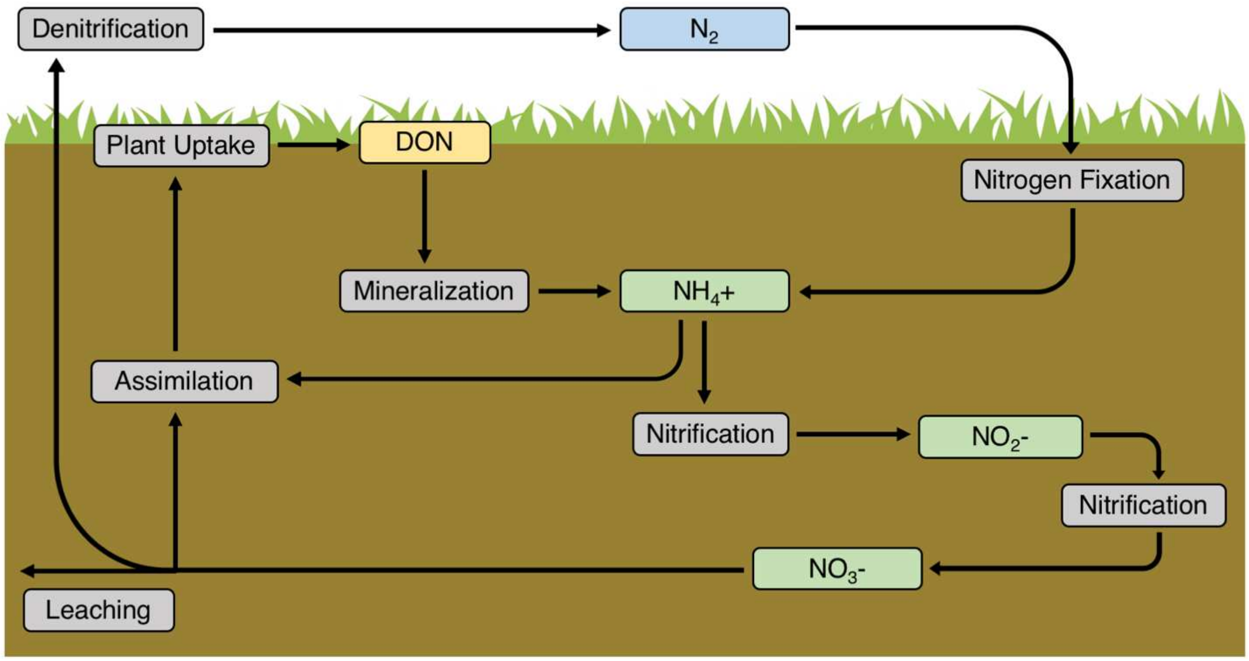

Figure 1. The nitrogen cycle is a biogeochemical process in which nitrogen is converted in and out of gaseous (blue), organic (yellow), and inorganic (green) forms through a variety of biological and physical pathways (grey).

Research in snow biogeochemistry has addressed questions about how varying snow cover affects nutrient cycling. A meta-analysis of winter nitrogen and carbon cycling studies found that the primary control on these cycles is the formation of consistent seasonal snow cover (Brooks et al., 2011). The depth and duration of overlying snowpack significantly affects the soil temperature and moisture that drive microbial activity and control the quantity of nitrogen that exists within each inorganic pool. The ongoing exchange of nitrogen between organic and inorganic forms and across ecosystems is essential for many biological and chemical processes. However, excess nitrogen export can lead to harmful environmental and ecological effects such as damage to aquatic systems, leaching of NO_3^- into groundwater, and loss of biodiversity, as well as negative implications for human health, water quality, and water resources (Galloway et al., 2008; Pardo et al., 2011; Suddick et al., 2013). Current research has shown that human activities have drastically increased levels of reactive nitrogen in the biosphere, dramatically impacting the nitrogen cycle (Vitousek et al., 1997; U.S. EPA, 2011). Altered snow melt timing in conjunction with increased nitrogen, often due to nitrogen deposition and the release of reactive nitrogen from glacier melting, increases nutrient loading in alpine lakes which leads to eutrophication and potentially harmful algal blooms (Baron et al., 2009). The coupled effects of anthropogenic change and climate warming on biogeochemical cycling has been linked to biodiversity loss, particularly due to nitrogen enrichment, which can enhance growth of fast growing, invasive species that outcompete native plant species (Porter et al., 2013). Additionally, nitrogen enrichment can make soils more acidic because as excess nitrogen leaches out of the soil, it takes additional nutrients, such as calcium and magnesium, along with it (Lucas et al., 2011; Tian et al., 2015). Acidic soils may be inhospitable for microbial communities and plant life (Fields, 2004).

1.3 Experimental Snow Manipulation

One common strategy for examining the effects of snow loss is snow manipulation. Prior studies have used manipulation experiments to either delay or advance snowmelt. To delay snowmelt, studies have utilized snow fences, reflective covers, and snow shoveling to increase quantities of snow and create conditions that preserve snow cover (Fahnestock et al., 2000; Brin et al, 2018). To advance snow melt, researchers have manually removed snow or increased the snowmelt rate using dark covers or warming treatments (Edmonds et al., 2006; Groffman et al., 2011; Zong et al., 2018). Research has emphasized the importance of snowmelt contributions to soil moisture and water storage. Methods that increased snow depth and delayed melt produced an increase in soil moisture and warmer soil temperatures (Walker et al., 1999). Methods that decreased snow depth and advanced snowmelt resulted in earlier peak soil moisture and decreased water storage, evident in reduced soil moisture by late spring / summer (Blankinship et al., 2014; Meromy et al., 2015).

Snow manipulation studies have produced consistent results in terms of the effect of snow depth on soil moisture, but the effects of snow manipulation on soil nitrogen have been more variable. Some studies that increased snow depth found a decrease in mobile nitrogen and rates of nitrogen leaching due to increased soil and plant nitrogen retention, as well as increased nitrogen mineralization (Blankinship et al., 2012; Li et al., 2016). In contrast studies found that the greater heat insulation and temperature caused by increased snow depth actually enhanced the mobility of inorganic nitrogen leading to an increase in NO_3^- and NH_4^+ in spring runoff (Kaste et al., 2008). Decreasing snow depth has caused increased soil frost and freeze-thaw cycling and decreased ecosystem nitrogen retention leading to increased nitrogen mobility and leaching (Joseph and Henry, 2008; Hentschel et al., 2009; Wipf and Rixen, 2010; Groffman et al., 2011; Blankinship et al., 2012). However, other studies have found that the effects of decreased snow depth on inorganic nitrogen and NO_3^- leaching were not significant (Kaste et al., 2008; Groffman et al., 2011). Synthesizing results from many multi-factor snow manipulation experiments is complicated due to the large variability in approaches, variables measured, and study regions (Wipf and Rixen, 2010; Shibata et al., 2016; Li et al., 2016). These varied results highlight the need for further research to clarify the complexities of over-winter nitrogen dynamics and how soil nitrogen processes will respond to hydrologic changes as a result of snowpack changes.

1.4 Key Knowledge Gaps

Decades of research has examined nitrogen dynamics under alpine snowpacks (Sievering et al., 1992; Brooks et al., 1996; Brooks et al., 2011) as well as nitrogen cycling and export during spring snowmelt (Williams and Melack, 1991; Heuer et al., 1999; Perrot et al., 2014; Hinckley et al., 2014). However, fewer studies have examined nitrogen dynamics in lower elevation forested montane catchments and how they vary throughout the year (Baron et al., 2009; Hinckley et al., 2014). It remains uncertain how these lower elevations will respond to snow loss and specifically how seasonal changes in hydrologic connectivity will affect nutrient cycling and transport. Additionally, we lack information on the effects of snow persistence on nutrient availability and export.

1.5 Research Goals

The goal of this research is to examine how varying snow persistence affects soil moisture and soil water nitrogen. The central questions motivating this research are (1) how does the duration of snow persistence affect soil moisture across an elevation gradient, from areas where the snowpack ranges from shallow and intermittent to deep and persistent throughout the winter? and (2) how does this gradient in snowpack affect soil water nitrogen? This research includes two components, the first compares snowpack dynamics across an elevation gradient and the second is a snow manipulation experiment at a low elevation site.

Based on background research, we propose the following conceptual model (Figure 2) as the hypothesis of this research. Prior research has shown that in regions with persistent snowpack (Figure 2, panel a_1), a deep snowpack insulates underlying soils, preventing soils from freezing (Edwards and Cresser, 1992; Brooks et al., 1998; Brooks and Williams, 1999a; Decker et al., 2003; Schimel et al., 2004). This allows biological processes within the soil to continue throughout the winter, gradually creating a pool of nitrogen available for plant uptake during the growing season (Brooks et al., 1998; Brooks et al., 2011). Under these conditions, studies have observed increased mineralization of DON into NH_4^+ and over-winter nitrification of NH_4^+ into NO_2^- and NO_3^- (Brooks et al., 1995; Williams et al., 1998b). At the initiation of snowmelt (a_2), inorganic N pools become depleted as NH_4^+ and NO_3^- are immobilized by microbial biomass and vegetation (Brooks et al., 1998; Templer and Socci, 2010). Although snow melt input is large, export of inorganic N to surface waters is low due to high nitrogen retention from plant and microbe uptake (Brooks et al., 1998; Brooks and Williams, 1999a; Blankinship et al., 2012).

In regions with intermittent snowpack (b_1), lower snow accumulation reduces thermal buffering, resulting in soil freezing and increased temperature variation within soils

(Hardy et al., 2001; Groffman et al., 2001b; Brown and DeGaetano, 2011). These regions may experience freeze-thaw events in which microbial cells burst as soils freeze, releasing pulses of DON released into the soil and decreasing rates of microbial activity (Sorensen et al., 2018). However, not all microbes burst, and as soils thaw and conditions become suitable for microbial activity, the labile DON supports a small burst of microbial activity, stimulating N mineralization and nitrification to produce NH_4^+ and NO_3^- (Brooks et al., 1995; Schimel and Clein, 1996, Chapin et al., 2002). Freeze-thaw events also damage plant roots and reduce root N uptake capacity (Tierney et al., 2001; Cleavitt et al., 2008; Templer and Socci, 2010; Sanders-DeMott et al., 2018). During the growing season (b_2), decreased soil moisture and microbial activity within these soils lead to lower decomposition of organic matter and decreased N mineralization rates (Brooks et al., 1995; Groffman et al., 2009; Duran, 2016). Overall, the combination of reduced microbial activity and decreased N immobilization leads to increased N losses from soils (Cleavitt et al., 2008; Christenson et al., 2010; Campbell et al., 2014). During snowmelt, studies have documented an initial "flush" of microbial N and higher levels of nitrate export (Schimel and Clein, 1996; Brooks et al., 1998; Joseph and Henry, 2008).

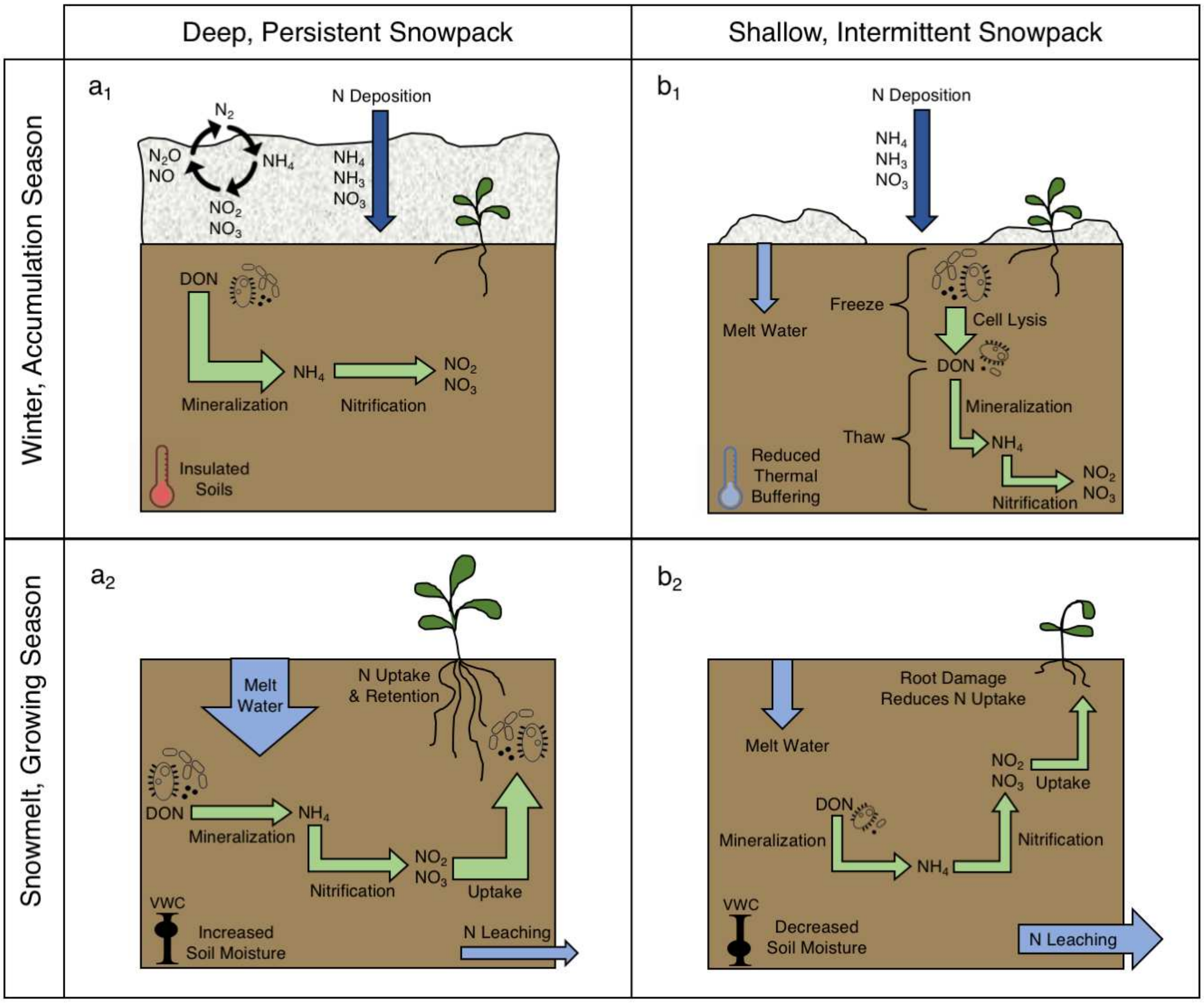

Figure 2. Conceptual model of hypothesized nitrogen cycling within soils in regions with persistent and intermittent snowpacks. Snow accumulation and persistence exerts a strong influence on soil nitrogen dynamics throughout the winter season (a_1/b_1) and spring snowmelt period (a_2/b_2). The width of each arrow indicates its magnitude, relative to the other arrows. Green arrows indicate biogeochemical pathways and blue arrows indicate input and output processes.

2. RESEARCH METHODS

2.1 Site Description

2.1.1 Physical Setting

Three research sites were established along an elevation gradient in the Colorado Front Range (Figure 3). Elevation is a major factor that influences the climate, precipitation, and temperature in this region. The sites span a 1500m elevation gradient, each located in one of the following snow zones: persistent, transitional, and intermittent. Sites were established in locations with minimal incline and canopy interception. The highest elevation site, Michigan River, is located at 3248m; the middle elevation site, Dry Creek, is located at 2361m, and the lowest elevation site, Mill Creek, is located at 1793m (Table 1).

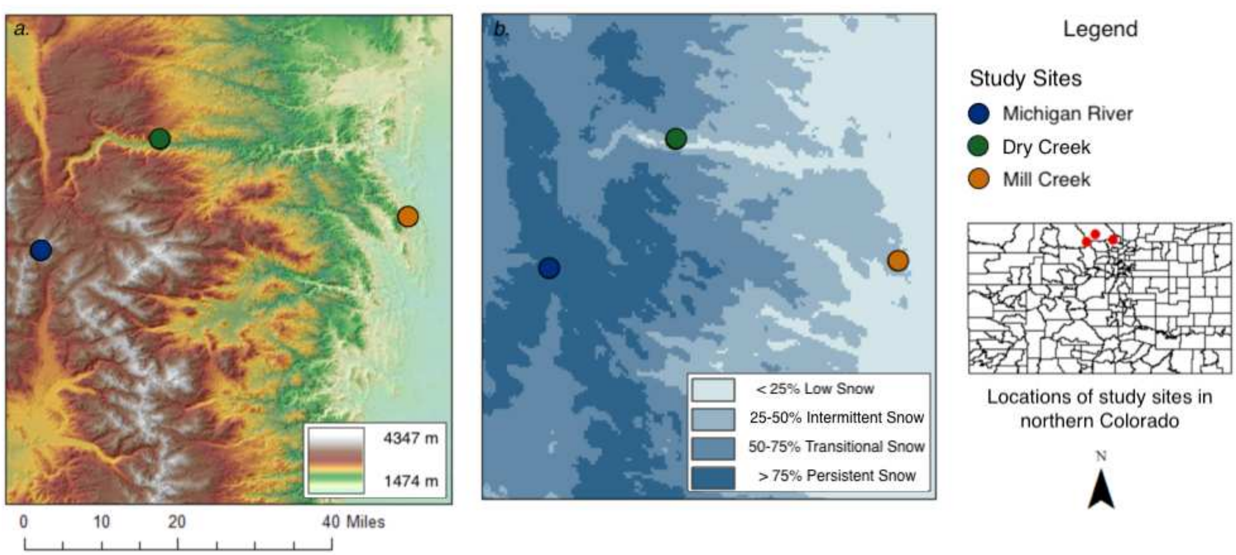

Figure 3. Location of study sites in northern Colorado displayed over (a) elevation from USGS (U.S. Geological Survey, 2015), and (b) snow zones from MODIS (Hammond et al., 2017). Snow zones are determined from mean annual snow persistence values from January 1 to July 3 and defined as the following: low snow (< 25%), intermittent SP (25% < SP< 50%), transitional (50% < SP < 75%), and persistent (> 75%).

Table 1. Characteristics of research sites. Snow zone information from Moore et al., 2015. Mean annual precipitation (P_{MA}) and mean annual temperature (T_{MA}) obtained from PRISM 4km 30-year normals from 1981 to 2010 (PRISM Climate Group, 2019)

Catchment	Snow Zone	Drainage Basin	Elevation (m)	P_{MA} (mm)	T_{MA} (°C)
Michigan River	Persistent	North Platte	3248	1172	0.2
Dry Creek	Transitional	Cache la Poudre	2361	419	5.2
Mill Creek	Intermittent	Cache la Poudre	1793	495	9.0

2.1.2 Climate

Study sites are located in three snow zones: persistent, transitional, and intermittent. These zones are determined by the extent of snow persistence, defined by Moore et al. (2015) as the mean annual fraction of time with snow present from January 1 to July 3. The persistent snow zone maintains a deep snowpack throughout the winter, with snow cover present for 75-100% of the time from January 1 to July 3 (Richer et al., 2013). The mean annual temperature is 0.2°C and mean annual precipitation is 1172mm (PRISM Climate Group, 2019). Mean monthly temperatures vary from -9.5°C to 11.1°C and monthly total precipitation from 60mm to 133mm (Figure 4). The transitional snow zone is defined as areas with 50-75% snow persistence. This zone maintains seasonal snow cover with snow cover duration varying by elevation. This region experiences slightly warmer average temperatures, with a mean annual temperature of 5.2°C and mean monthly temperature ranging from -4.2°C to 16.4°C. The mean annual precipitation is 419mm, with monthly total precipitation varying from 14mm to 53mm. The intermittent snow zone usually does not maintain snow cover throughout the winter, with snow persisting 25-50% of the time. In this zone, snow typically melts relatively soon after snow events. Mean annual temperature is 9.0°C and mean monthly temperatures range from -1.7°C to 21.2°C. Mean annual precipitation is 495mm and monthly total precipitation ranges from 13mm to 79mm.

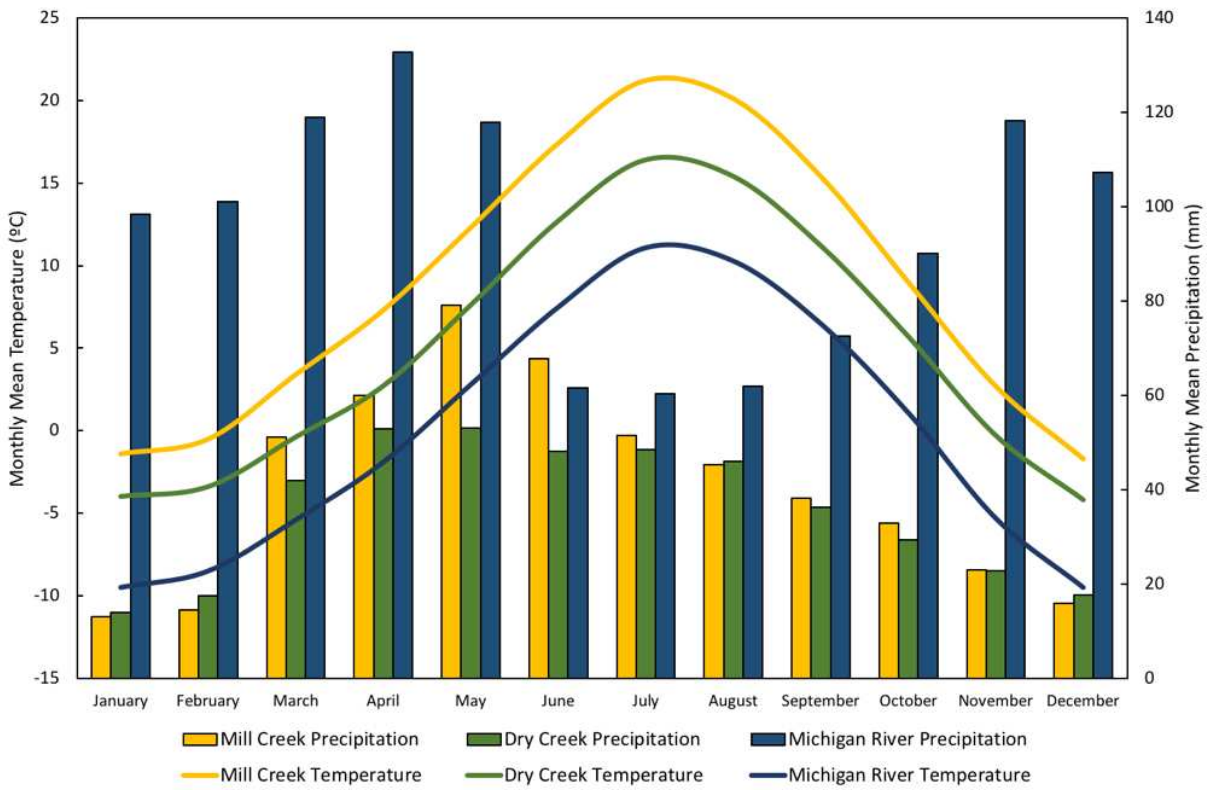

Figure 4. Monthly mean temperature and precipitation averaged from 1981 to 2010, data obtained from PRISM 4km 30-year normals (PRISM Climate Group, 2019)

2.1.3 Soil and Vegetation

Michigan River is located in an alpine meadow, where sandy loam soils with a rich organic layer supports vibrant wildflowers (*Mertensia ciliata, Castilleja rhexifolia)* and semi-woody shrubs throughout the summer growing season. The site is surrounded by dense subalpine spruce-fir forests (*Abies lasiocarpa, Picea engelmannii)*. The soil is mainly Pinkham sandy loam, a deep, well-draining soil formed from glacial till (Web Soil

Survey, 2019). Dry Creek is situated in a small valley bottom between north and south facing slopes with sandy loam soils that promote herbaceous vegetation during the spring and summer months. This woodland site is surrounded by Douglas fir (*Pseudotsuga menziesii*), lodgepole pine (*Pinus contorta)*, and aspen trees (*Populus tremuloides)*, as well as true mountain mahogany (*Cercocarpus montanus)* and Rocky Mountain juniper (*Juniperus scopulorum*). The dominant soil type is Typic Haplustolls, which consists of colluvium derived from igneous and metamorphic rock (Web Soil Survey, 2019). Mill Creek is located in a valley bottom with tall grasses in the spring and cacti year-round. The soil is a loamy sand, specifically Wetmore soil derived from material weathered from granite that promote high runoff (Web Soil Survey, 2019). The site is in a largely open area; however, Ponderosa pine trees (*Pinus ponderosa)* cover the surrounding grassland hillsides producing a dense layer of pine needle litter. To determine soil texture for each site, three soil samples were collected from both 5cm and 20cm depth and analyzed in the lab using the hydrometer method (Table 2). Michigan River and Dry Creek both have sandy loam soils, and Mill Creek has loamy fine sand.

Table 2. Average soil particle size distributions from samples collected at 5 and 20 cm depth. Values given are the average of six soil samples.

Site	% sand	% clay	% silt	Texture
Michigan River	0.58	0.12	0.30	Sandy Loam
Dry Creek	0.77	0.07	0.16	Sandy Loam
Mill Creek	0.81	0.08	0.12	Loamy Fine Sand

2.2 Materials and Methods

2.2.1 Elevation comparison

The first component of the study involved comparing snow, soil moisture, and soil water nitrogen between the three elevations of study sites. At each site, three replicate 1.5m x 1.5m plots were established. Browning time-lapse trail cameras were installed facing fixed snow poles marked with 5cm increments. Pictures were taken hourly to document snow depth. Each plot was equipped with two soil moisture probes (CR616/SM150/SM300, at 5- and 20-cm depth) and one temperature probe (CR 109, at 5cm). Soil moisture and temperature probes were wired to three Campbell Scientific CR200 data loggers. Measurements were taken in 15-min intervals for soil moisture and temperature. Daily precipitation and air temperature were downloaded from the PRISM database and snow water equivalent (SWE) was computed from snow depth pictures and snow density measurements from field snow surveys. To distinguish precipitation input between rain and snow, the following principles were applied: (1) if PRISM reported precipitation and SWE was greater than SWE from the previous day, then the input was categorized as snow; (2) if PRISM reported precipitation and SWE was less than SWE from the previous day or was zero, then the input was categorized as rain.

Plant Root Simulator (PRS) Probes (Western Ag. Innovations, Saskatoon, SK) were utilized to compare soil water nitrogen between the three study sites. PRS probes consist of an ion exchange resin membrane held in a plastic support that simulate the nutrient exchange between plant roots and the surrounding soil water. Anion probes have a positively charged membrane that adsorb negatively charged ions from the soil, while cation probes have a negatively charged membrane that adsorb positively charged ions from the soil. This exchange provides a measure of nutrient supply rate, dependent on the ion availability and activity in the soil. Together an anion and cation probe produce a pair, and four pairs produce a pooled sample of nitrogen supply. Probes were refrigerated in the dark until deployment to prevent premature ion exchange.

Four pairs of probes were installed in each of three plots at each of the three sites, Michigan, Dry, and Mill. Probes were inserted vertically into the soil, in the 0-10cm soil layer where nutrient exchange and root activity is greatest. Probes were installed in October and November, before snow accumulation, and replaced monthly following snow melt. The monthly collection time period was recommended by Western Ag. Innovations to allow sufficient time for ion exchange. Once a probe was removed, a new probe of the same type (cation or anion) was reinserted into the same location. Removed probes were cleaned with deionized (DI) water to remove residual soil and prevent further ion exchange, then refrigerated until shipment to Western Ag. Innovations for analyses. Nutrient contents were eluted from the PRS probes with 0.5M HCl and analyzed for NO_3– N and NH_4– N by colorimetry using an automated flow injection analysis system. The resulting nutrient supply rate is expressed as the weight of nutrient adsorbed per surface area over time (e.g. μg nutrient / $10cm^2$ / burial period). The limit of detection (LOD) for both NO_3^- and NH_4^+ analyses given by Western Ag. was 2 μg N / $10cm^2$.

2.2.2 Snow manipulation

To examine the effects of changing snow depth on soil moisture and soil water nitrogen at a specific site, a snow manipulation was conducted at the lowest elevation site, Mill Creek. Nine plots, each 1.5m x 1.5m x 1m, were constructed at the Mill Creek intermittent snow zone site (Figure 5). Three plots were controls, with no changes to snow, while the treatments for the remaining six plots were designed to increase and decrease snow depth. These plots will be referred to as control, high snow, and low snow plots. The snow chambers were constructed with 1-inch PVC pipe frames secured on 1m rebar posts and wrapped in either white or black canvas on three sides (Figure 6). The fourth side had a clear plastic sheet with visible depth increments facing a Browning time-lapse trail camera used to document snow depth within the chambers. The white canvas was intended to delay snowmelt by increasing the albedo of the confined snow, while the black canvas was intended to accelerate snowmelt by decreasing the albedo. Following snow events, snow was shoveled from the three low snow plots to the corresponding three high snow plots to amplify the difference in snow between plots.

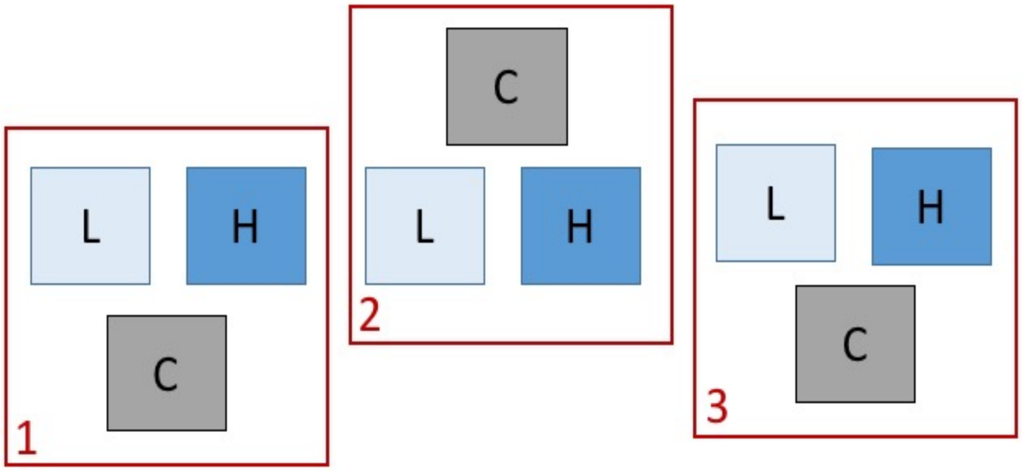

Figure 5. High snow (H), low snow (L), and control (C) plot setups for Groups 1-3 at the Mill Creek research site

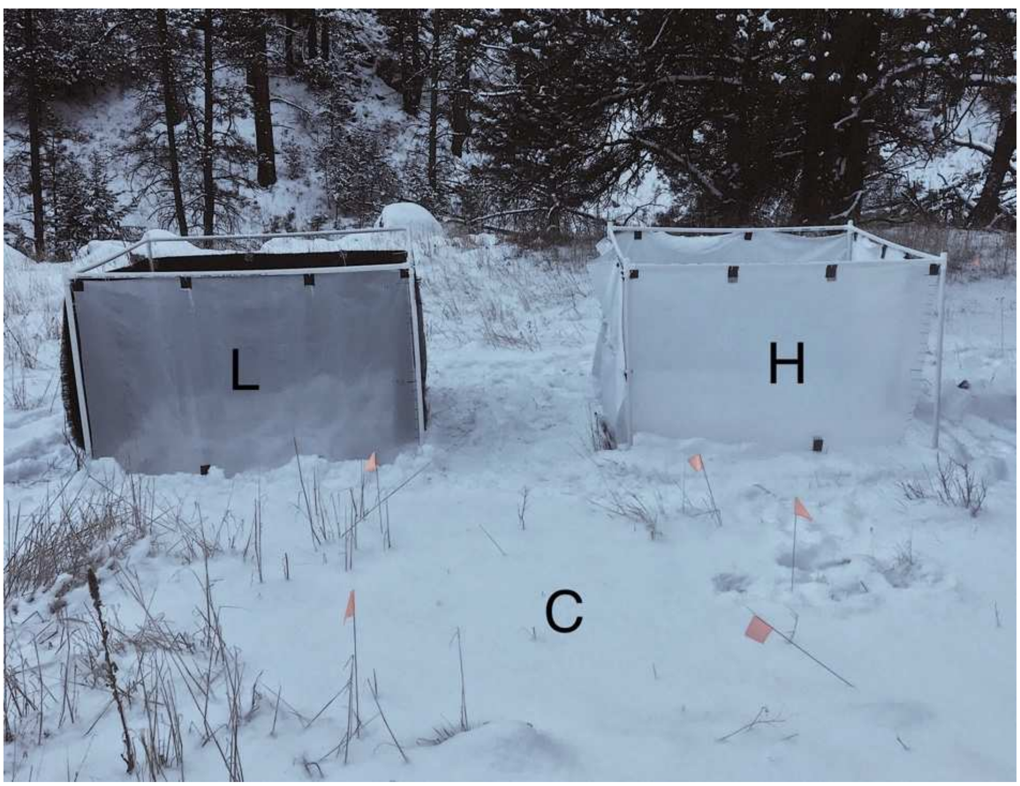

Figure 6. Group 1 high snow (H), low snow (L), and control (C) snow plots at Mill Creek

Twenty-seven suction lysimeters, three in each of the nine plots, were installed to collect soil water following snowmelt events. To avoid selection bias, each plot was visually divided into a 3 x 3 grid, and the locations of the three lysimeters within the grid were randomly determined. The lysimeters consist of a 1-foot cylindrical tube with a porous ceramic cap at the base and rubber stopper on the top. The stopper has a hole to set vacuums and withdraw samples. To install the lysimeters, an auger was used to dig a precise hole, the same dimensions as the lysimeter. After inserting the lysimeter, any space between the body and the soil was filled with a soil-DI water slurry. Lysimeters were left for six months before sampling. High-density polyethylene (HDPE) sample bottles were washed with DI water, soaked in a 10% HCl acid bath for at least 48 hours, and rinsed again with DI water in preparation for sample collections. Following snow events, a vacuum was set to approximately 50 centibars on each lysimeter using a hand pump, clamped, and left for 24-hours. During this time, suction pulls soil water into the lysimeter through the porous cap. After the collection period, the vacuums were released and the lysimeters were connected to the collection apparatus (Figure 7). This apparatus consists of a flexible nylon tube inserted into the lysimeter's rubber stopper on one end and a side arm flask on the other. The vacuum pump was connected to the side arm flask and pumped until all of the soil water entered the flask. The sample was then poured into a labeled HDPE sample bottle, capped, and stored in a cooler on ice until transfer to the lab for analysis. The collection apparatus was then rinsed with DI water following each lysimeter collection. Samples were processed at the EcoCore Analytical Facility, at Colorado State University, using flow injection analysis on the

Alpkem Flow Solution IV (O.I. Analytical, College Station, Texas). Solution concentrations of nitrate and ammonium were measured using EPA Method #353.2 for the determination of nitrate-nitrogen and DIN Method #38406 for ammonia-nitrogen. The LOD for both nitrogen analyses was 0.02 mg/L.

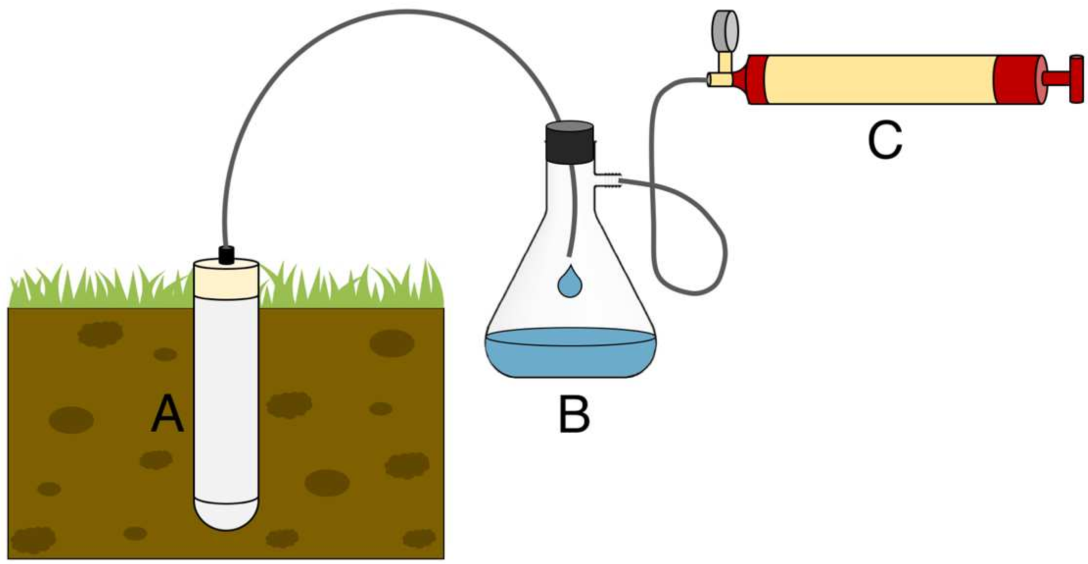

Figure 7. The lysimeter sampling apparatus. The lysimeter (A) is inserted into the soil, with only the cap accessible. A flexible rubber tube is then inserted into the lysimeter on one end and a side arm flask (B) on the other. A second tube connects the side arm flask to the hand pump (C).

2.3 Approaches to Data Analysis

Both correlation analysis and multivariate regressions were used to identify which environmental variables relate to soil water nitrogen. For the elevational comparison, time series of daily data were compiled for each site. To evaluate effects of independent variables on soil water nitrogen, soil temperature, snow depth, and soil moisture were averaged over the corresponding burial period for each PRS probe collection. For the nitrogen measurements from lysimeter samples, soil temperature, snow depth, and soil moisture were daily values from the corresponding lysimeter collection day. Correlations were then computed between each independent variable (snow depth, soil temperature, soil moisture) and nitrogen values from PRS probes and lysimeters. These values were computed for each individual site and for all sites combined.

Multivariate regression equations were computed using JMP (version 13.0) to predict the concentrations of NO_3^- and NH_4^+ based on soil temperature, snow depth, and soil moisture. The regression equations are in the following form:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots \beta_n x_n$$

where y is the predicted value, x values are predictor variables, and β values are coefficients. Regression models were developed for the prediction of NO_3^- and NH_4^+ (1) with and without first sample collections for all sites combined and (2) for PRS and lysimeter nitrogen for the Mill Creek snow manipulation study.

3. RESULTS

3.1 Elevational Study

3.1.1 Michigan River

At Michigan River, snow was present from early October through late June in water year 2017, with peak snow depth of 2450mm on May 1, 2017. In water year 2018, snow was present from late September to mid-June, with peak snow depth of 2950mm on April 9, 2018 (Figure 8). Snow depth was higher during the second year, water year 2018, with a difference between peak snow depths of 500mm.

Annual soil temperature (T) at this site was 2.8°C (s = 4.1°C) with the highest monthly temperature in July (10.9°C) and the lowest in December (0.2°C). Soil temperatures were higher during water year 2017 (3.3°C, s = 4.6°C) than 2018 (2.3°C, s = 3.6°C). Soil temperature dipped below freezing (0°C) during water year 2017, from November 7 to December 16, but overall winter soil temperatures at 5cm depth were at or slightly above freezing (Figure 9). Minimum temperature was -2.1°C in water year 2017 and 0°C in water year 2018.

Average volumetric water content (VWC) was greater at 20cm depth (0.31 ± 0.002) than at 5cm (0.25 ± 0.001) (Figure 8). Monthly average VWC ranged from 0.23 to 0.38 at 20cm depth and from 0.22 to 0.32 at 5cm depth. In water year 2017, peak VWC was 0.38 and occurred in June, 25 days after the start of snow melt. In water year 2018, peak VWC was 0.43 and occurred in June, 51 days after the start of snow melt. Total precipitation was 7086mm for the two-water year study period, where 83% input was from snow melt and 17% from rain (Figure 9).

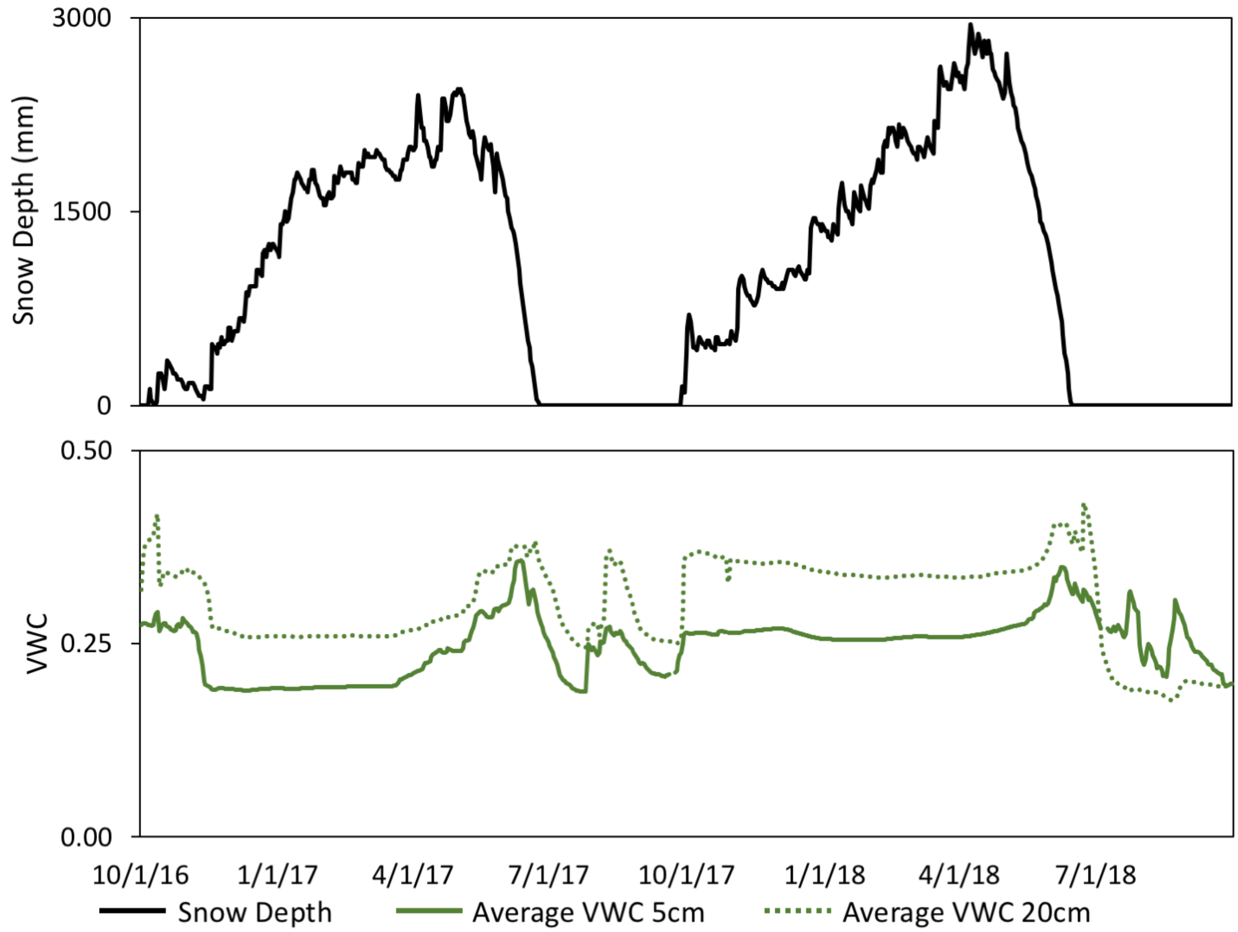

Figure 8. Snow depth and average soil moisture as volumetric water content (VWC) at Michigan River for water years 2017 and 2018

PRS resin probes recorded the highest N values in June during peak snowmelt when soil moisture was highest. NO_3^- values were much higher than NH_4^+ for every sample (Figure 9). For water year 2017, peak NO_3^- was 158.7 μg/10cm^2 (41.9 $\pm$ 15.3 μg/10cm^2), and peak NH_4^+ was 6.1 μg/10cm^2 (3.0 $\pm$ 0.6 μg/10cm^2). For water year 2018, peak NO_3^- was 450.5 μg/10cm^2 (70.9 $\pm$ 48.0 μg/10cm^2) and peak NH_4^+ was

3.6 $\mu g/10cm^2$ (1.8 ± 0.3 $\mu g/10cm^2$). NO_3^- and NH_4^+ values were often highest during the first collection then decreased over the following two collections. All NO_3^- values were above the LOD however half of the NH_4^+ values were below it.

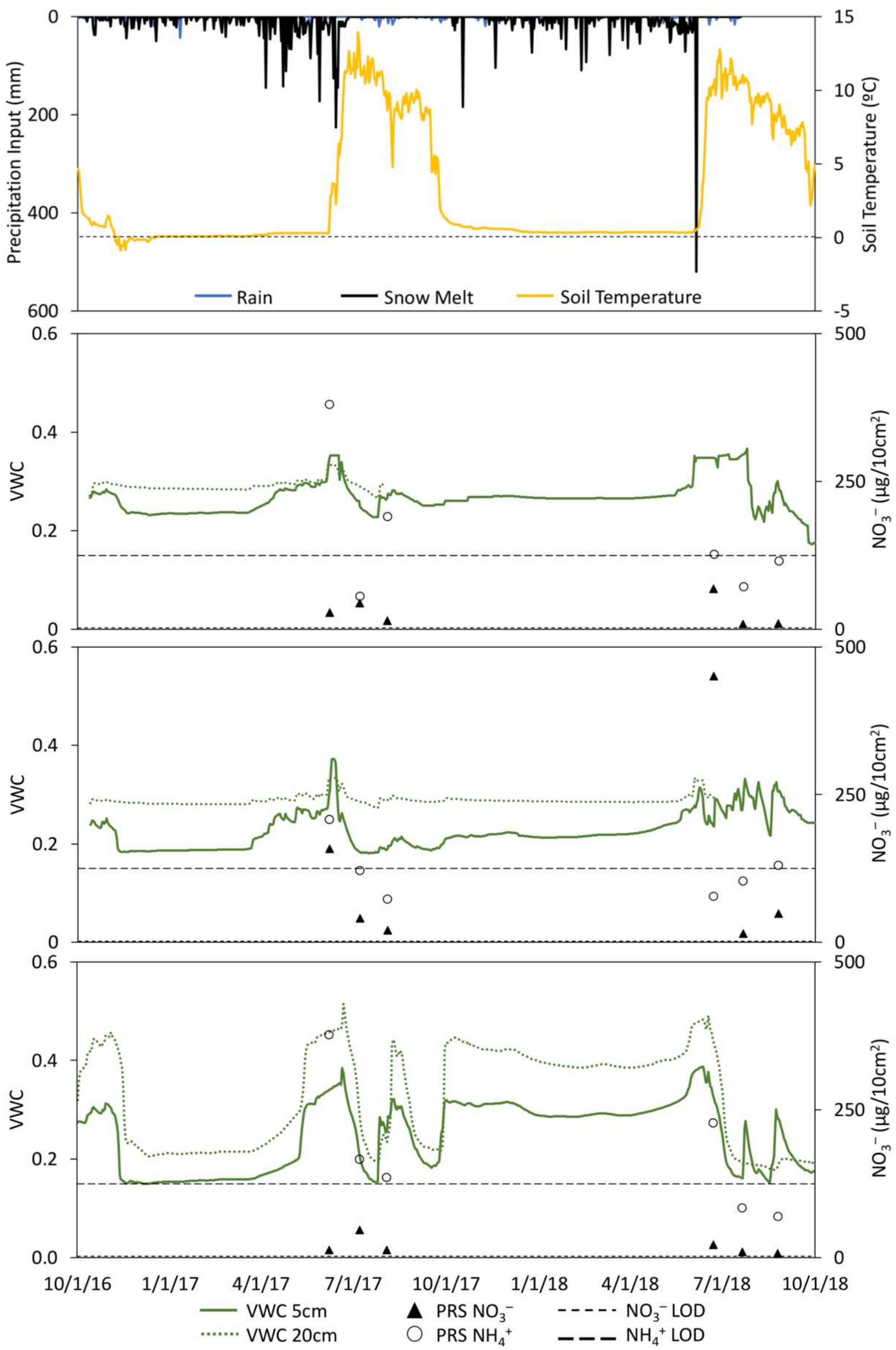

Figure 9. Precipitation input and soil temperature at 5cm depth, and daily soil moisture and PRS-Nitrogen for plot 1, plot 2, and plot 3 at Michigan River. Horizontal dashed lines indicate the limit of detection (LOD) for both NO_3^- and NH_4^+ of 2 μg N/10cm².

Cross-correlations between variables (r) were computed for average temperature ($T_{average}$), minimum temperature ($T_{minimum}$), VWC at 5cm, NO_3^-, and NH_4^+ for the month-long PRS burial periods (Figure 10). NO_3^- values were not significantly correlated with either temperature or VWC. NH_4^+ values were not correlated with minimum temperature or VWC at 5cm but had a significant negative correlation with average temperature (r = -0.64**). NO_3^- and NH_4^+ values from the first collection of PRS probes of each season were sometimes outliers as probes were left in situ overwinter; these are denoted as triangles in Figure 10. First collection points were removed from the dataset, and correlations (r_R) for the same variables were again computed. The correlation between NH_4^+ and average temperature (r_R = -0.03) decreased in strength as well as statistical significance. However, the correlation between NO_3^- and VWC at 5cm (r_R = 0.73**) increased in both strength and significance.

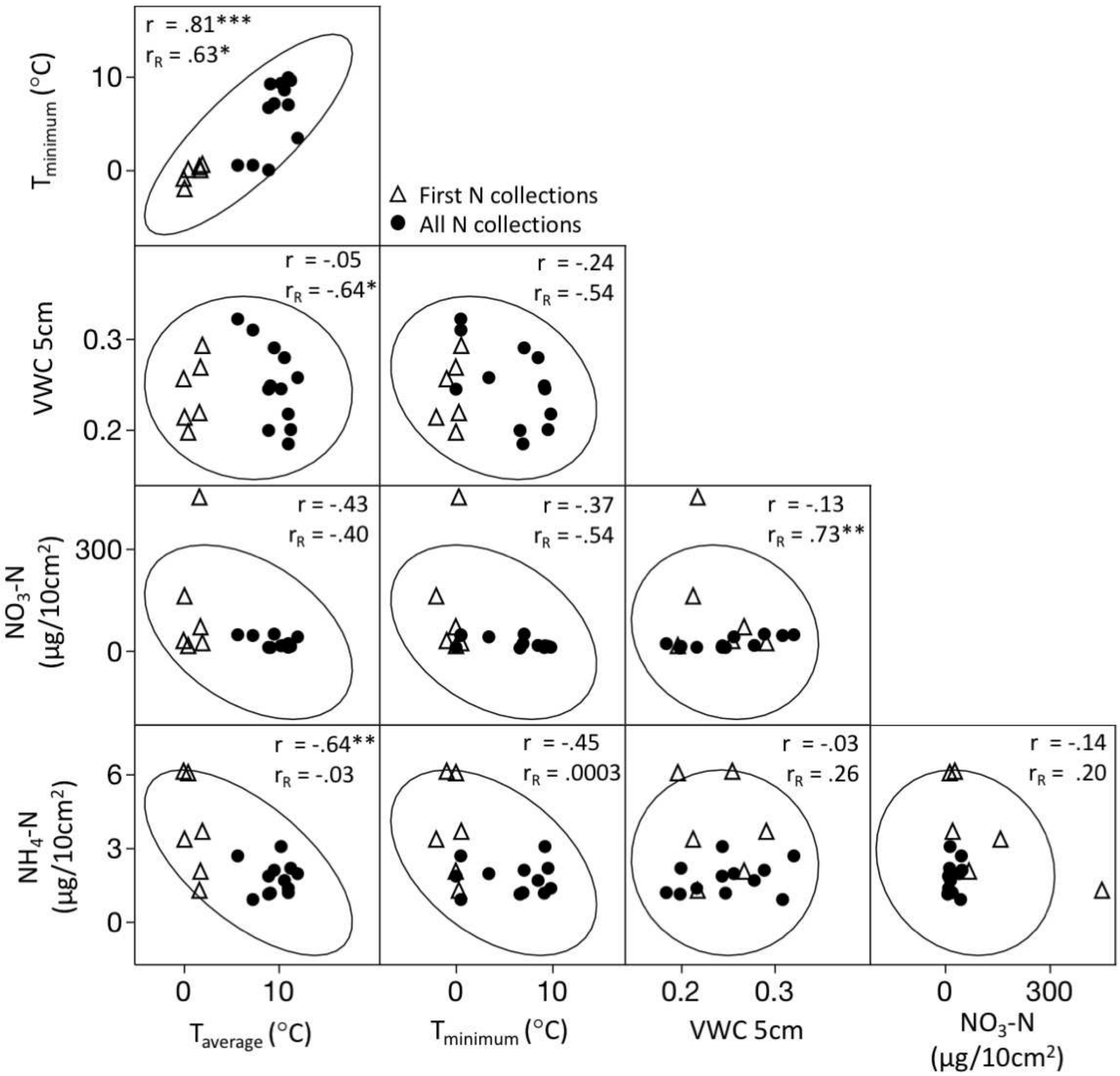

Figure 10. Cross-correlation chart for Michigan River for month-long PRS burial periods. First nitrogen collections are denoted by triangles, and 95% density ellipses are shown around points. Pairwise correlations for all sites (r) as well as correlations with the removal of the first nitrogen collection points (r_R) are shown. Statistical significance is indicated for each correlation (n = 18) where * = p-value $\leq$ 0.05, ** = p-value $\leq$ 0.01, and *** = p-value $\leq$ 0.001.

3.1.2 Dry Creek

At Dry Creek, snow was present intermittently from mid-November through late May in water year 2017 and from early October to early May in water year 2018 (Figure 11). Peak snow depth for water year 2017 was 750mm on May 19, 2017, and for water year 2018 was 200mm on October 9, 2017. On average, January exhibited the highest snow depths. Peak snow depth was 550mm higher in water year 2017 than in water year 2018.

Annual soil temperature was 6.6°C (s = 6.8°C), with the highest monthly temperatures in July (17.6°C) and the lowest in December (-0.7°C) (Figure 12). Average soil temperature was greater in water year 2017 (7.4°C, s = 7.0°C) than water year 2018 (5.7°C, s = 6.4°C). Soil temperature reached below freezing from November 27 to February 17 during water year 2017 and again from December 7 to March 13 in water year 2018 (Figure 12). Minimum temperature was -5.6°C in water year 2017 and -3.2°C in water year 2018.

In water year 2017, peak soil moisture of 0.39 occurred in May, 7 days after the start of snow melt. In water year 2018, peak soil moisture of 0.28 also occurred in May, only one day after the loss of snow cover. Deeper soils (20 cm) had higher average soil moisture of 0.21 ± 0.001 compared to average soil moisture in shallow soils (5 cm) of 0.19 ± 0.001 (Figure 11). Average soil moisture ranged from 0.15 to 0.27 at 20cm depth and from 0.13 to 0.24 at 5cm depth. Total precipitation was 1338mm for the two-water year study period, where 41% input was from rain and 59% from snow melt (Figure 12).

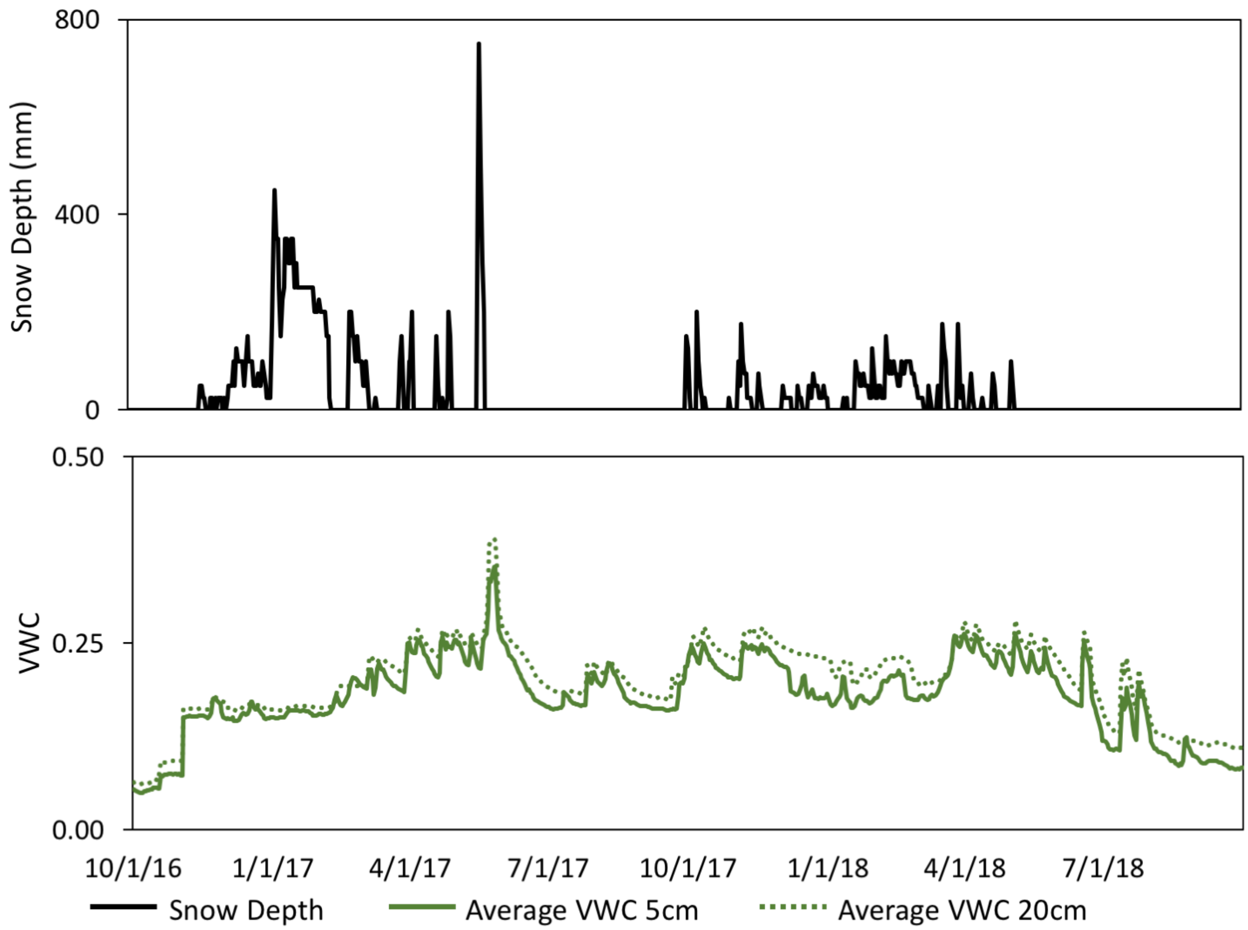

Figure 11. Snow depth and average soil moisture as volumetric water content (VWC) at Dry Creek

NO_3^- was present in higher values than NH_4^+ for all samples. For water year 2017 peak NO_3^- was 36.9 μg/10cm^2 (10.4 ± 3.1 μg/10cm^2) and peak NH_4^+ was 4.7 μg/10cm^2 (1.3 ± 0.4 μg/10cm^2), occurring in July and June. For water year 2018, peak NO_3^- was 41.5 μg/10cm^2 (9.0 ± 2.7 μg/10cm^2) and peak NH_4^+ was 8.1 μg/10cm^2 (1.9 ± 0.5 μg/10cm^2), both occurring in April. Following peak N, values decreased throughout the sampling season. Only two NO_3^- values were below the LOD while two-thirds of NH_4^+ values were below the limit.

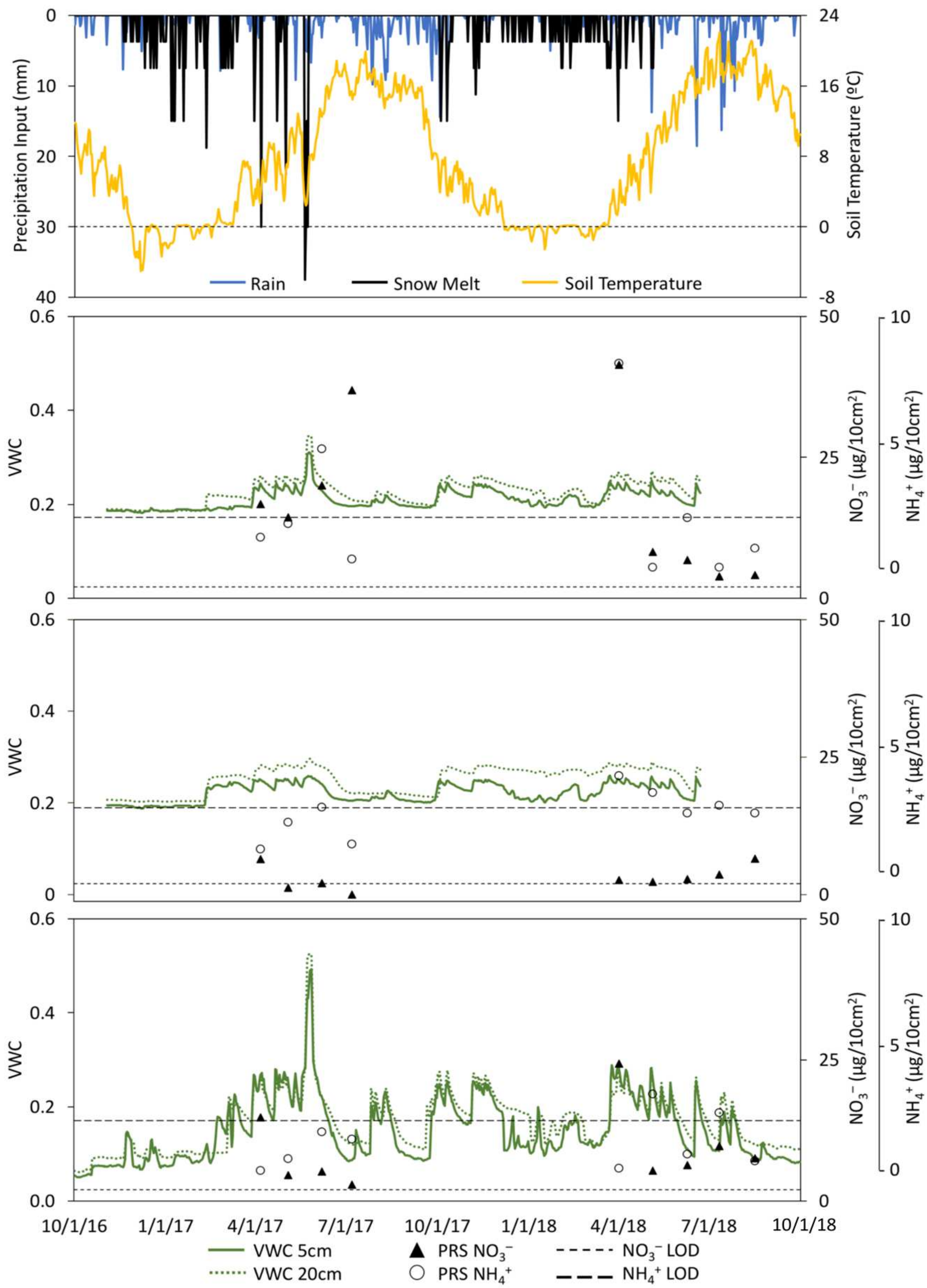

Figure 12. Rain and snowmelt input, soil temperature, and daily soil moisture and PRS-Nitrogen for plot 1, plot 2, and plot 3 at Dry Creek. Horizontal dashed lines indicate the limit of detection (LOD) for both NO_3^- and NH_4^+ of 2 μg N/10cm^2.

NO_3^- and NH_4^+ had a significant positive correlation with each other (r = 0.39*) but were not significantly correlated with any other variables (Figure 13). Values from the first collection of PRS probes of each season were sometimes outliers in NO_3^- and NH_4^+ values; when these points were removed, correlation strength and significance decreased for both NH_4^+ and NO_3^- ($r_R = 0.07$), and the significance of any other correlations with NO_3^- or NH_4^+ did not improve.

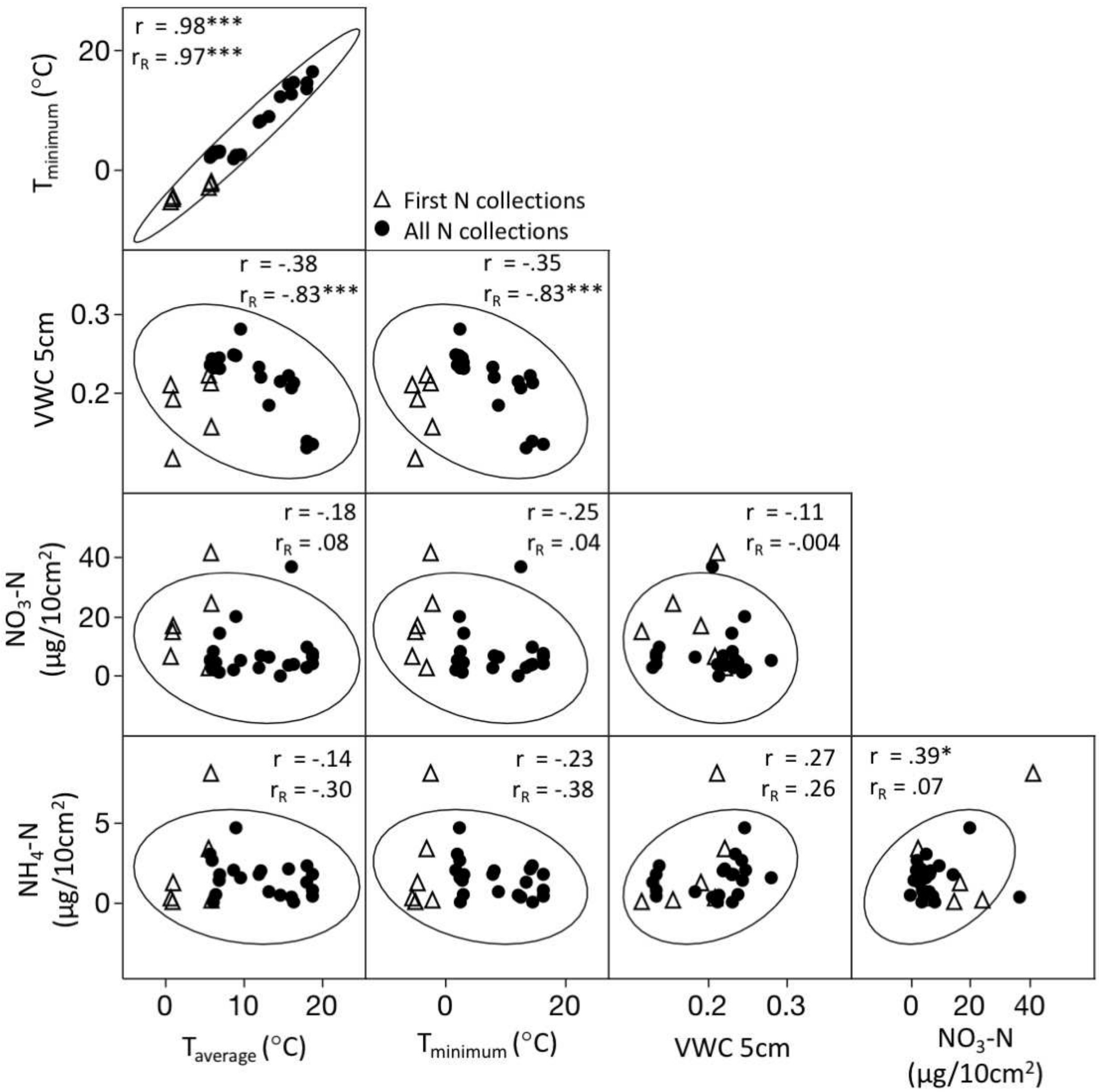

Figure 13. Cross-correlation chart for Dry Creek for month-long PRS burial periods. First nitrogen collections are denoted by triangles and 95% density ellipses are shown around points. Pairwise correlations for all sites (r) as well as correlations with the removal of the first nitrogen collection points (r_R) are shown. Statistical significance is indicated for each correlation (n = 27) where * = p-value $\leq$ 0.05, ** = p-value $\leq$ 0.01, and *** = p-value $\leq$ 0.001.

3.1.3 Mill Creek

At Mill Creek, snow was present intermittently from mid-November to mid-May in water year 2017 and from mid-October through late April in water year 2018 (Figure 14). Peak snow depth of 350mm occurred on January 5 for water year 2017 and 227mm on February 24 for water year 2018. Peak snow depth was greater in water year 2017 than water year 2018, with a difference of 123mm. On average, snow depth was greatest in January.

Annual soil temperature was 8.9°C (s = 7.5°C), with the highest monthly temperatures in July (20.3°C) and the lowest in January (0.4°C) (Figure 15). Soil temperatures were greater in water year 2018 (9.6°C, s = 7.7°C) than water year 2017 (8.1°C, s = 7.2°C). Soil temperature reached below freezing (0°C) from November 30 to January 14 during water year 2017 and on January 16, January 17, and February 26 during water year 2018 (Figure 15). Minimum temperature was -2.0°C in water year 2017 and -0.6°C in water year 2018.

Average soil moisture ranged from 0.11 to 0.24 at 5cm depth and from 0.14 to 0.24 at 20cm depth. Average soil moisture was greater at 5cm than 20cm during water year 2017 and greater at 20cm depth than 5cm during water year 2018 (Figure 14). In water year 2017, peak soil moisture of 0.24 occurred in April, 1 day after the loss of snow cover. In water year 2018, peak soil moisture of 0.32 occurred in May, also 1 day after the loss of snow cover. Total precipitation was 1172mm for the two-year study period, where 55% fell as rain and 45% as snow (Figure 15).

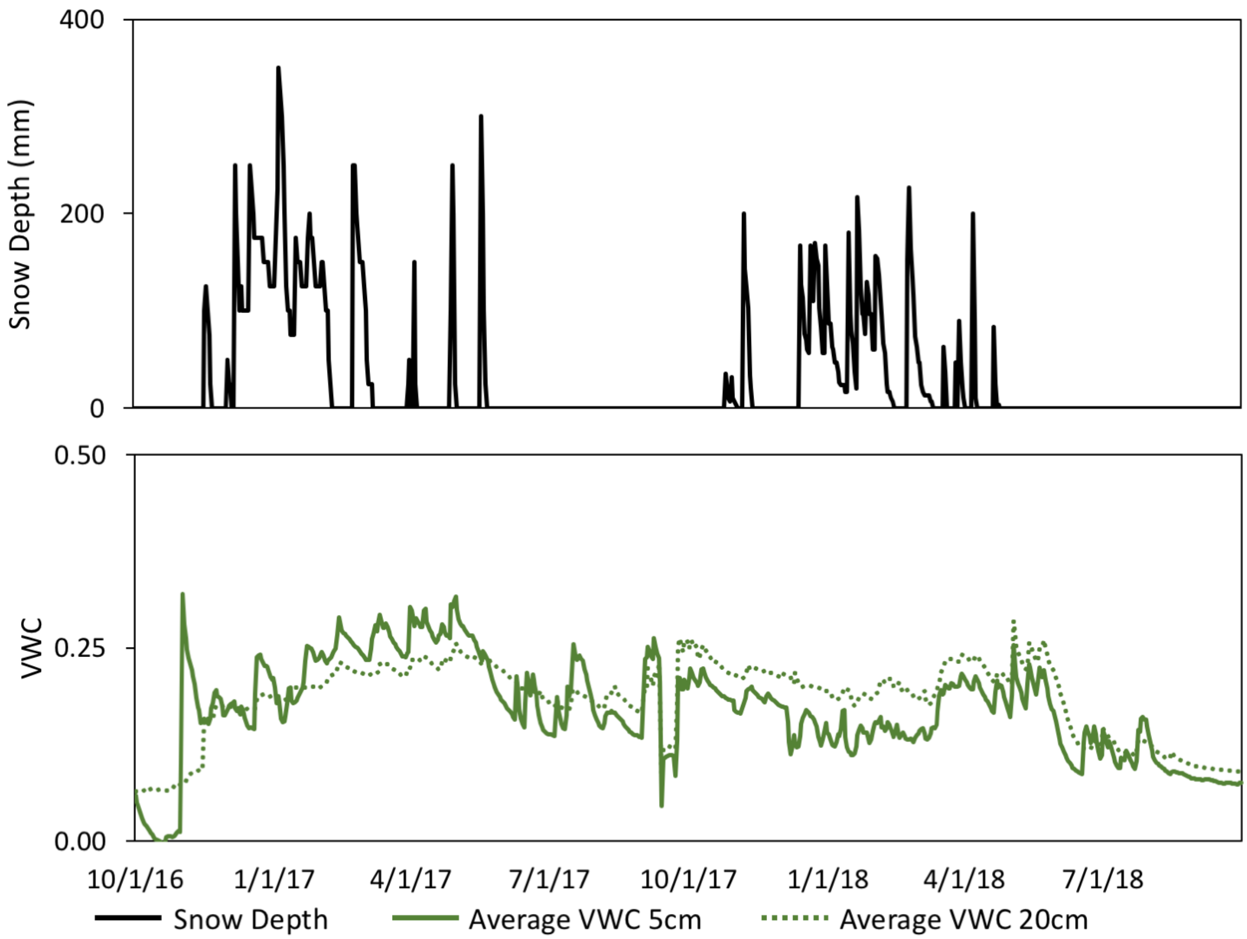

Figure 14. Snow depth and soil moisture as volumetric water content (VWC) at Mill Creek

NO_3^- values were higher than NH_4^+ for nearly all sampling dates. Average NO_3^- was higher in water year 2017 than 2018 while average NH_4^+ was higher in water year 2018 than 2017. The resin probes captured a pattern of decline in NO_3^- over time (Figure 15). This decline in concentrations over time correlates with a decrease in soil moisture. For water year 2017 peak NO_3^- was 332.7 μg/10cm^2 (56.0 ± 27.4 μg/10cm^2) in April and peak NH_4^+ was 7.2 μg/10cm^2 (4.4 ± 0.6 μg/10cm^2) in July. For water year 2018, peak NO_3^- was 91.7 μg/10cm^2 (20.1 ± 6.5 μg/10cm^2) and peak NH_4^+ was 15.1 μg/10cm^2 (5.0 ± 1.1 μg/10cm^2), both occurring in March. All NO_3^- values were above the LOD and only 15% of NH_4^+ values were below.

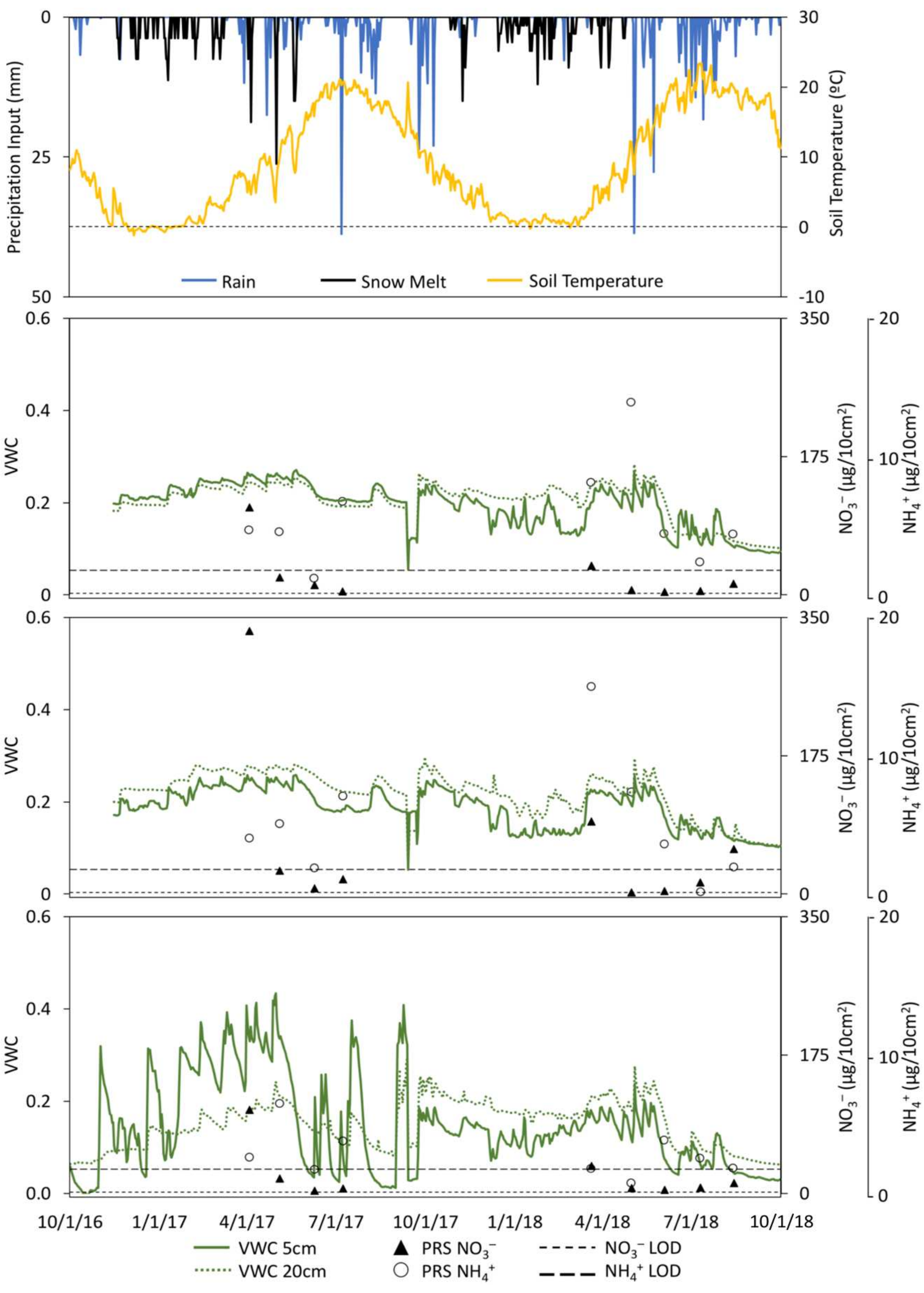

Figure 15. Precipitation input and soil temperature, and daily soil moisture and PRS-Nitrogen for plot 1, plot 2, and plot 3 at Mill Creek. Horizontal dashed lines indicate the limit of detection (LOD) for both NO_3^- and NH_4^+ of 2 μg N/10cm^2.

There were significant correlations between the following variables: NO_3^- and average temperature ($r = -0.53^{**}$), NO_3^- and minimum temperature ($r = -0.43^{*}$), and NH_4^+ and average temperature ($r = -0.39^{*}$) (Figure 16). Data points from the first collection of PRS probes of each season are denoted as triangles; after these points were removed the correlation between NH_4^+ and average temperature ($r_R = -0.45^{*}$) increased in strength and statistical significance but the correlations between NO_3^- and average temperature ($r_R = 0.03$) and NO_3^- and minimum temperature ($r_R = 0.14$) did not improve.

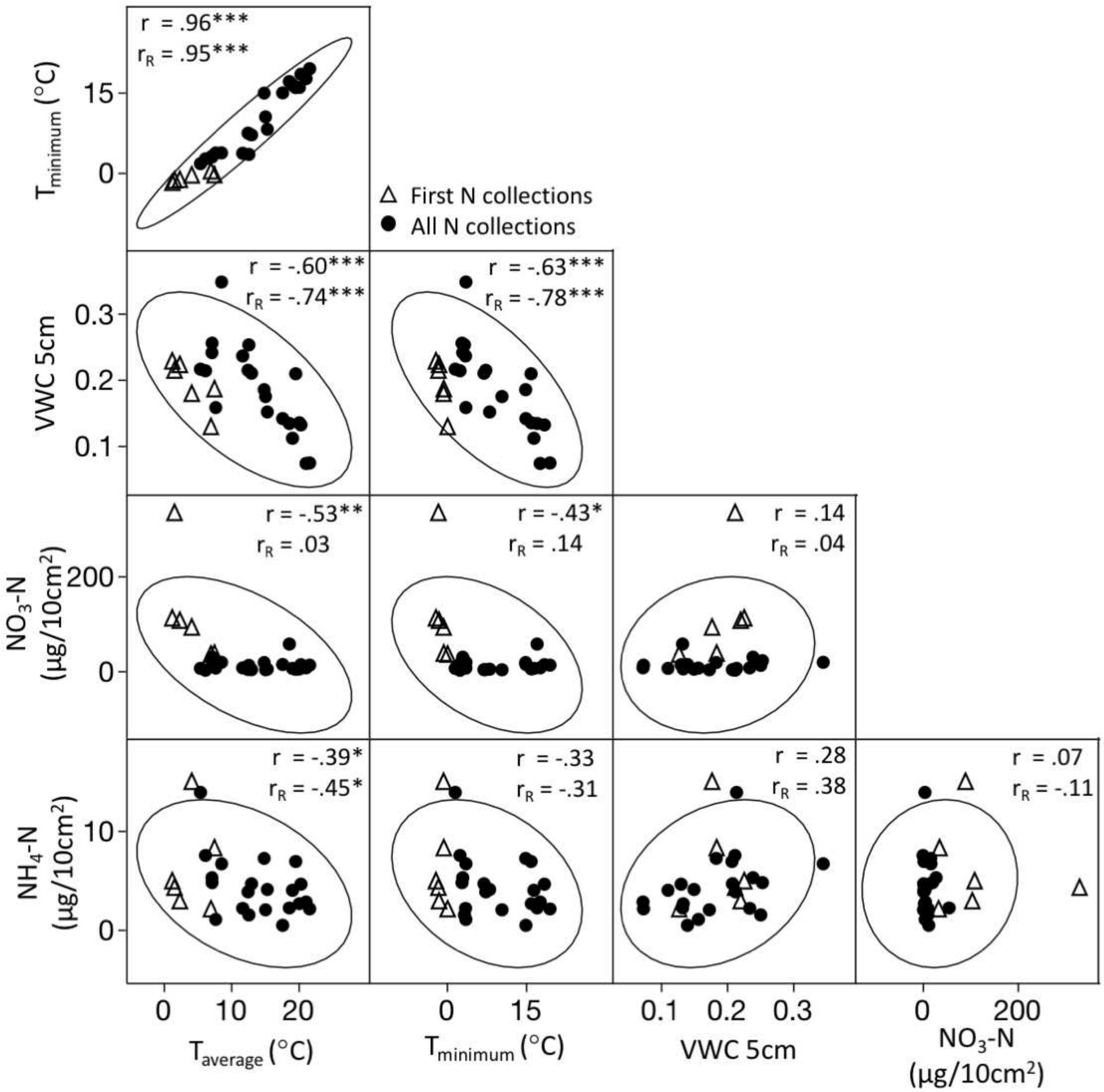

Figure 16. Cross-correlation chart for Mill Creek for month-long PRS burial periods. First nitrogen collections are denoted by triangles and 95% density ellipses are shown around points. Pairwise correlations for all sites (r) as well as correlations with the removal of the first nitrogen collection points (r_R) are shown. Statistical significance is indicated for each correlation (n = 27) where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

3.1.4 Comparison across sites

The three sites differed significantly in terms of snow depth and soil moisture (Figure 17). Snow persisted for longer periods of time as elevation increased and temperatures decreased. At Michigan River, snow depth steadily increased throughout the winter and spring, whereas at Dry Creek and Mill Creek, snow increased through the winter and began to decrease after January. By July, snow had melted out at all sites. Snow at Michigan River began to accumulate a month earlier and persisted about a month longer than at the lower two sites. Average snow depth from January 1 to July 3 was 1708mm at Michigan River, 52mm at Dry Creek, and 39mm at Mill Creek (Table 3). A Welch's analysis of variance (ANOVA) was conducted to compare the difference between snow depths among sites [$F = 436.04$, $p \leq 0.0001$]. Results indicated a significant difference between snow depth at Michigan River and Dry Creek as well as between Michigan River and Mill Creek. Michigan River exhibited peak snow depths that were nearly 6 times greater than at Dry Creek and 9 times greater than at Mill Creek. Comparing water years at each individual site, snow depths were greater in water year 2018 for Michigan River, but were greater in water year 2017 for both Dry Creek and Mill Creek (Table 3).

Soil moisture increased with elevation, and the timing of soil moisture input correlated with a decrease in snow depth. VWC increased to peak values in May for Mill Creek and Dry Creek, and June for Michigan River (Figure 17). At Michigan River, peak soil moisture occurred 1-2 months after the start of snow melt, while at Dry Creek and Mill

Creek peak soil moisture occurred 1-7 days after the start of snow melt, coinciding with increased snow melt. VWC subsequently decreased in the late summer months (July through September). Average soil moisture was greater at 20cm depth than at 5cm depth during both water years at Michigan River and Dry Creek but was greater at 20cm depth only in water year 2018 at Mill Creek. Average VWC from January 1 to July 3 was 0.28 (s = 0.07) at Michigan River, 0.21 (s = 0.05) at Dry Creek, and 0.20 (s = 0.06) at Mill Creek. Welch's ANOVA showed a significant difference for both VWC at 5cm and at 20cm between all three sites [$F = 450.86$, $p \leq 0.0001$; $F = 1378.80$, $p \leq 0.0001$]. Unlike snow depth, soil temperature was inversely correlated to elevation; as elevation increased, soil temperature decreased. Soil temperature was coldest in January and warmest in July. At the lower two sites, Dry Creek and Mill Creek, VWC decreased as soil temperature increased, this is particularly evident from April through July as soils dried out.

The three sites varied in terms of the timing and concentration of soil water nitrogen and did not follow a consistent pattern with elevation. Over the two-year period, Michigan River exhibited the highest NO_3^- concentration (56.4 $\pm$ 24.7 μg/10cm^2), followed by Mill Creek (36.1 $\pm$ 12.9 μg/10cm^2) then Dry Creek (9.7 $\pm$ 2.0 μg/10cm^2). Highest monthly average NO_3^- coincided with peak VWC in April for Mill Creek and in June for Michigan River (Figure 17). Monthly average NO_3^- then declined for both sites as VWC declined. Dry Creek did not follow this pattern and instead monthly average NO_3^- remained relatively constant. Welch's ANOVA showed a significant difference in NO_3^- between

Michigan River and Dry Creek [F = 2.33, p = 0.16] but not between Michigan River and Mill Creek or between Mill Creek and Dry Creek. Over the two-year period, Mill Creek exhibited the highest NH_4^+ concentration (4.7 ± 0.7 μg/10cm^2), followed by Michigan River (2.4 ± 0.4 μg/10cm^2) then Dry Creek (1.6 ± 0.3 μg/10cm^2). At Mill Creek, monthly average NH_4^+ steadily decreased from March to August. NH_4^+ values were significantly different between Mill Creek and Dry Creek [F = 6.09, p ≤ 0.05], where Mill Creek exhibited the highest monthly NH_4^+ values (with the exception of in June) while Dry Creek exhibited the lowest NH_4^+ values of all sites. At Dry Creek, average NH_4^+ fluctuated monthly, but overall slightly declined from April to August (Figure 17). At Michigan River, peak NH_4^+ occurred in June, coinciding with peak VWC, then decreased in July as VWC decreased.

Table 3. Peak and average values for snow depth (SD), volumetric water content (VWC), soil temperature (T), and PRS nitrogen for Michigan River, Dry Creek, and Mill Creek for the entire two-year record (n = 730). Standard error is shown for average VWC, soil temperature, and nitrogen. Values are separated into water year 2017 and water year 2018.

	Michigan River		Dry Creek		Mill Creek	
	WY 17	WY 18	WY 17	WY 18	WY 17	WY 18
Peak SD (mm) and Date	2450 05/01/17	2950 04/09/18	750 05/19/17	200 10/09/17	350 01/05/17	227 02/24/18
Avg SD (mm) (Jan 1–Jul 3)	1661	1755	81	24	49	28
Snow Input	81%	86%	61%	57%	51%	39%
Rain Input	19%	14%	39%	43%	49%	61%
Peak VWC and Date	0.38 06/21/17	0.43 06/17/18	0.39 05/25/17	0.28 05/04/18	0.32 04/30/17	0.24 04/22/18
Total Avg VWC	0.26 ± 0.001	0.29 ± 0.002	0.19 ± 0.001	0.21 ± 0.001	0.20 ± 0.002	0.17 ± 0.001
Avg VWC 5cm	0.23	0.26	0.19	0.20	0.20	0.15
Avg VWC 20cm	0.29	0.33	0.20	0.22	0.20	0.18
Soil $T_{average}$ (°C)	3.3 ± 0.1	2.3 ± 0.1	7.4 ± 0.2	5.7 ± 0.2	8.1 ± 0.2	9.6 ± 0.2
Soil $T_{minimum}$ (°C)	-2.1	0	-5.6	-3.2	-2.0	-0.6
Peak NO_3 (μg/10cm^2) and Date	158.7 06/07/17	450.5 06/22/18	36.9 07/07/17	41.5 04/01/18	332.7 04/03/17	91.7 03/20/18
Average NO_3 (μg/10cm^2)	41.9 ± 15.3	70.9 ± 48.0	10.4 ± 3.1	9.0 ± 2.7	56.0 ± 27.4	20.1 ± 6.5
Peak NH_4 (μg/10cm^2) and Date	6.1 06/07/17	3.6 06/22/18	4.7 06/07/17	8.1 04/01/18	7.2 07/08/17	15.1 03/20/18
Average NH_4 (μg/10cm^2)	3.0 ± 0.6	1.8 ± 0.3	1.3 ± 0.4	1.9 ± 0.5	4.4 ± 0.6	5.0 ± 1.1

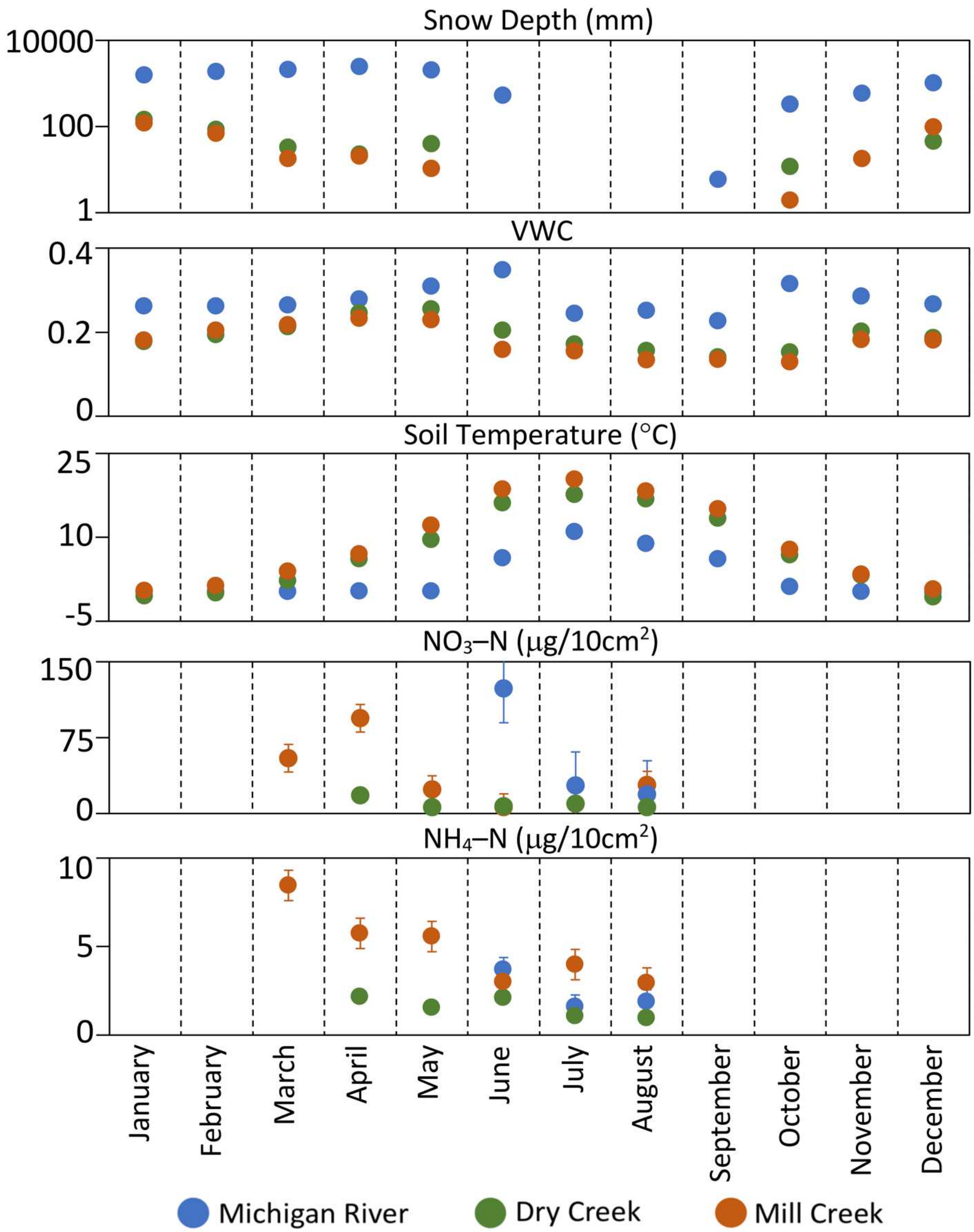

Figure 17. Monthly average values for snow depth, volumetric water content at 5cm, soil temperature at 5cm, PRS NO_3^-, and PRS NH_4^+ at each site from 10/1/2016 to 9/30/2018. Error bars represent standard errors of values from 6 probes in 3 plots for each month.

Correlations between variables were computed for average temperature ($T_{average}$), minimum temperature ($T_{minimum}$), VWC at 5cm, NO_3^-, and NH_4^+ (Figure 18). NO_3^- was significantly negatively correlated with both average temperature (r = -0.38**) and minimum temperature (r = -0.29*), while NH_4^+ did not have significant correlations with any other variables. Removing first collection points decreased both the strength and statistical significance of NO_3^- and average temperature (r_R = -0.11) and NO_3^- and minimum temperature (r_R = -0.10) but increased the strength and significance of NO_3^- and VWC at 5cm (r_R = 0.29*). While individually most sites had positive correlations between NO_3^- and NH_4^+ and VWC, and negative correlations between NO_3^- and NH_4^+ and soil temperature, these correlations weaken when all sites were analyzed collectively.

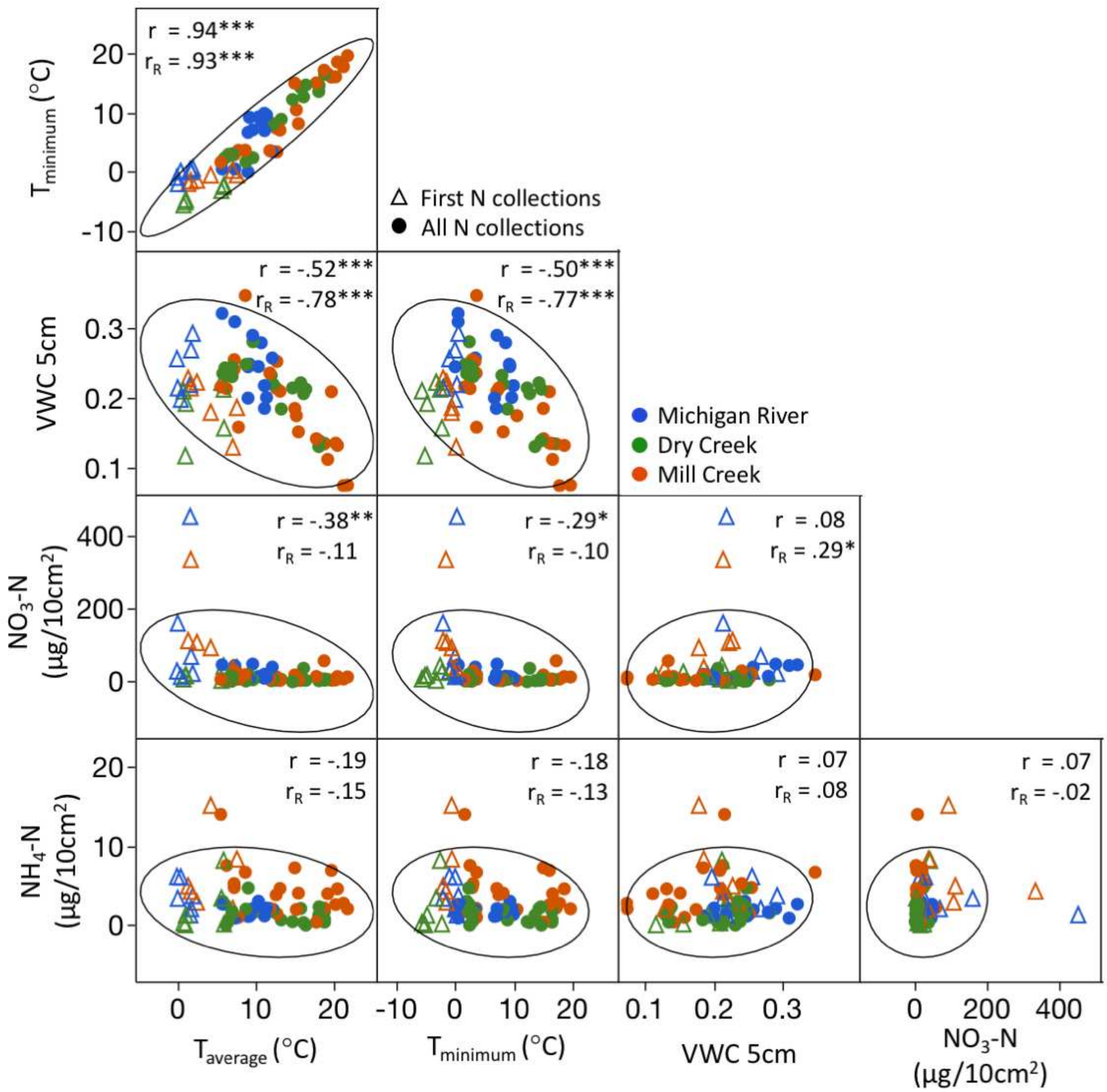

Figure 18. Cross-correlation chart (n = 72) at the watershed scale with 95% density ellipses shown. Points for Michigan River are shown in blue, Dry Creek in green, and Mill Creek in orange. Points from first nitrogen collections of each season are shown as triangles. Pairwise correlations for all sites (r) as well as correlations with the removal of the first nitrogen collection points (r_R) are shown. Statistical significance is indicated for each correlation where * = p-value $\leq$ 0.05, ** = p-value $\leq$ 0.01, and *** = p-value $\leq$ 0.001.

A multivariate regression model was constructed to predict the value of NO_3^- across all sites using average temperature (°C), minimum temperature (°C), and VWC at 5cm. The model produced the following regression equation:

$$NO_3^- = 143.45 – 10.97\ T_{avg} + 5.62\ T_{min} – 171.17\ VWC_{5cm}$$

This model [F(3,68) = 5.54, p = 0.0018] implies a negative relationship between NO_3^- and average temperature and VWC at 5cm, and a positive relationship between NO_3^- and minimum temperature. Values from the first sample collection of each season were removed and a new regression equation was produced:

$$NO_3^- = -20.91 + 0.45\ T_{avg} + 0.36\ T_{min} + 121.04\ VWC_{5cm}$$

Although this model better predicts the response of NO_3^- than the original model (indicated by a lower RMSE value), the removal of first collections also decreased the statistical significance and thus this model is not statistically significant (Table 4).

Table 4. Multiple regression equations for the prediction of NO_3 and NH_4 across all sites, for equations with all points and with the removal of first nitrogen collection points. Statistical significance is indicated where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

	R^2	RMSE	P-value	Intercept	$T_{average}$	$T_{minimum}$	VWC_{5cm}
$NO_3^-{}_{All}$	0.20	62.46	0.0018	143.45**	-10.97**	5.62	-171.17
$NO_3^-{}_{Removal}$	0.12	12.84	0.0928	-20.91	0.45	0.36	121.04*
$NH_4^+{}_{All}$	0.04	2.86	0.4658	4.26*	-0.09	-0.01	-1.65
$NH_4^+{}_{Removal}$	0.02	2.47	0.7440	4.67	-0.12	0.01	-3.29

A multivariate regression model for NH_4^+ was constructed, yielding the following regression equation:

$$NH_4^+ = 4.26 - 0.09\ T_{avg} – 0.01\ T_{min} – 1.65\ VWC_{5cm}$$

Here NH_4^+ has a negative relationship with average temperature, minimum temperature, and VWC at 5cm [$F(3,68) = 0.86$, $p = 0.47$]. Due to outliers, values from the first sample collection of the season were removed and produced the following updated regression equation:

$$NH_4^+ = 4.67 - 0.12\ T_{avg} + 0.01\ T_{min} - 3.29\ VWC_{5cm}$$

Removal of values from the first collection resulted in a lower RMSE value, indicating that this model better predicts the response of NH_4^+ than the original model (Table 4). Using these four equations, predicted values of NO_3^- and NH_4^+ were computed and plotted against the actual values of NO_3^- (Figure 19) and NH_4^+ (Figure 20), with a 1:1 line shown. The models show a mixture of underpredictions (below 1:1 line) and overpredictions (above 1:1 line). The predictions for the first sample collections were consistently high even those the first sample collection values had a wide range of actual values. In Figure 19, Dry Creek was nearly always overpredicted while Mill Creek was mostly underpredicted. After removing first sample collection points, the NO_3^- model continued to overpredict Dry Creek while points for Mill Creek and Michigan River were equally distributed above and below the 1:1 line (Figure 20). For NH_4^+, values for Mill Creek were distributed below the 1:1 line, separating out from Dry Creek and Michigan River.

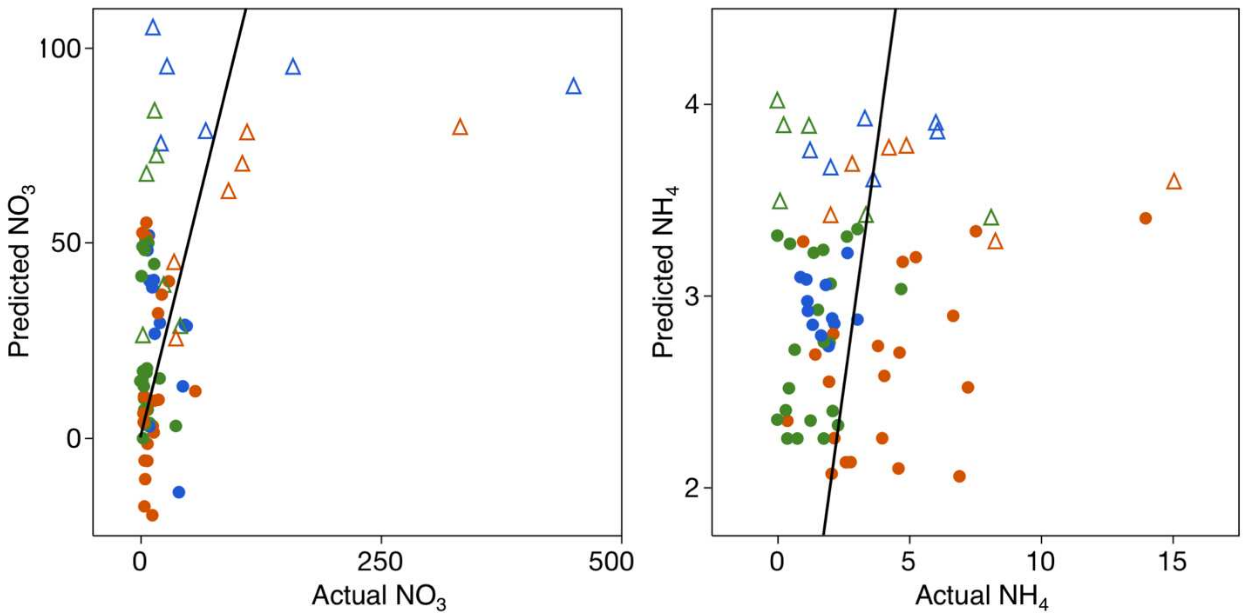

Figure 19. Actual vs predicted NO_3^- and NH_4^+ for all sites, with 1:1 line. Sites are differentiated by color: Michigan River in blue, Dry Creek in green, and Mill Creek in orange. First sample collections are denoted as triangles.

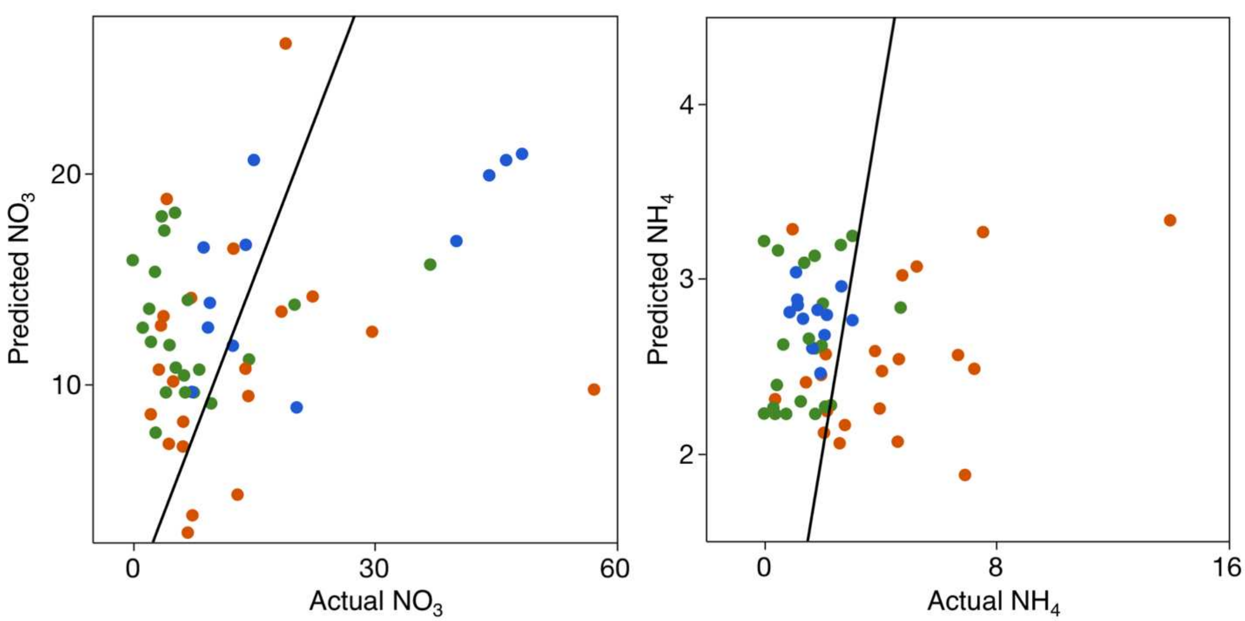

Figure 20. Actual vs predicted NO_3^- and NH_4^+ for all sites, with 1:1 line. Sites are differentiated by color: Michigan River in blue, Dry Creek in green, and Mill Creek in orange. First sample collections have been removed.

3.2 Intermittent Snow Manipulation

Snow manipulation plots were added to the Mill Creek site in water year 2018. On average the high snow plot received the greatest amount of snow, about 2x greater than the low snow plot and 1.5x greater than the control snow plot (Figure 21). The greatest snow depth was 280mm and occurred on February 24, 2018, in the high snow plot (Table 5). A Welch's analysis of variance (ANOVA) was conducted to compare the difference between snow depths among sites [$F = 10.50$, $p \leq .0001$]. There was a significant difference in snow depth between the high snow and low snow plots ($p = .0018$) but not between the high snow and control snow or low snow and control snow plots. Average volumetric water content (VWC) was greater at 20cm depth than at 5cm for all plots (Figure 21). High snow plots exhibited the highest average VWC at both depths, followed by low snow plots, then control snow plots. There was a significant difference in VWC at both 5cm and 20cm between the high snow and control snow plots ($p < .0001$) and the low snow and control snow plots ($p < .0001$), but not between the high snow and low snow plots. Peak VWC was 0.28 in the high snow plot, 0.29 in the low snow plot, and 0.28 in the control snow plot. Peak VWC occurred on May 3, in all plots, 68 days after peak snow depth. Soil temperatures ranged from -0.6°C to 25°C. Average soil temperature from November 1 to March 31 was 1.7°C in the high snow plot, 2.5°C in the low snow plot, and 2.1°C in the control plot (Table 5). Soil temperature dipped below freezing (0°C) on several incidences between January to March 2018 in both the high snow and low snow plots (Figure 22).

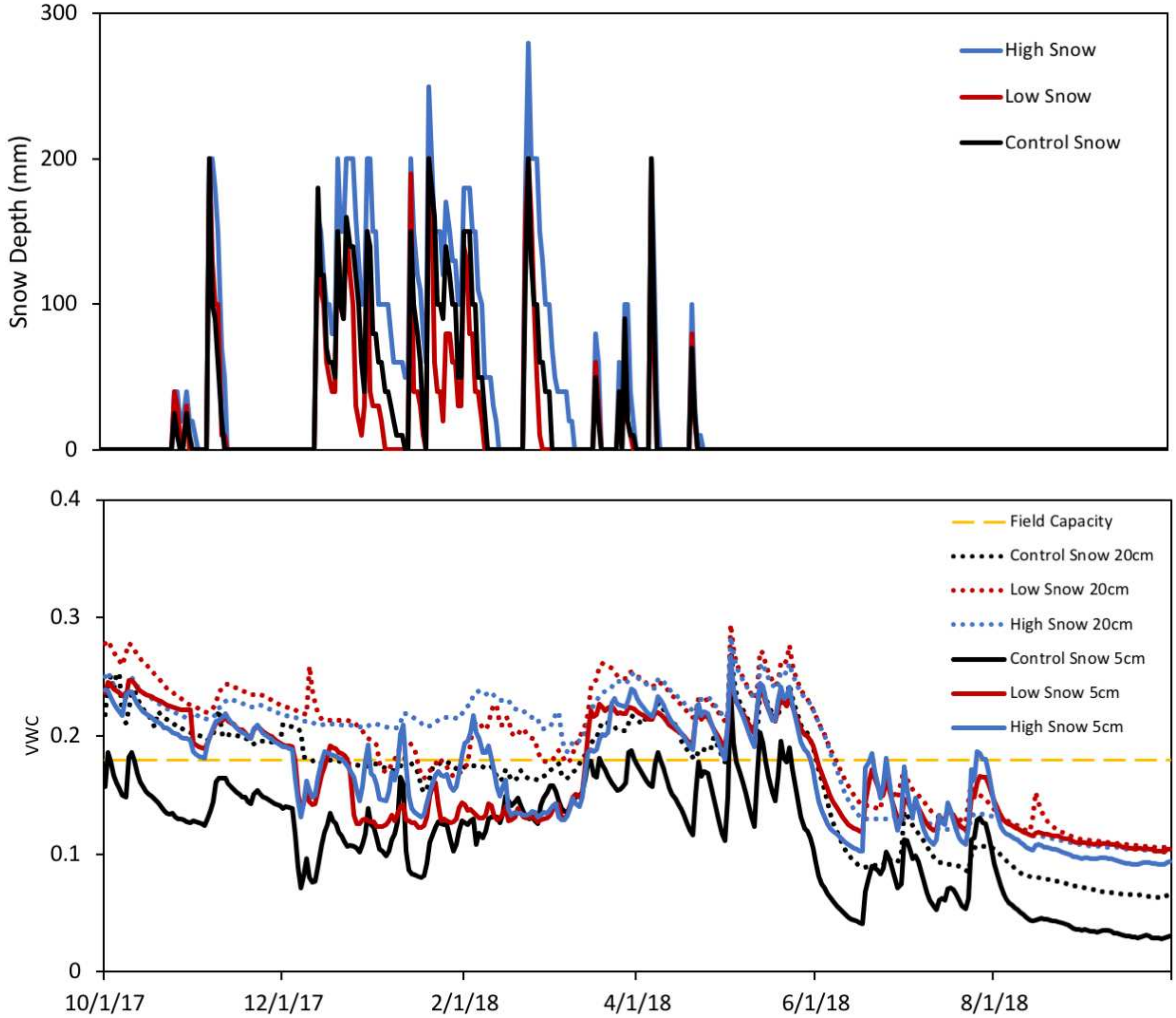

Figure 21. Snow depth and soil moisture for high snow, low snow, and control snow plots at Mill Creek

Table 5. Peak and average values for snow depth (SD), volumetric water content (VWC), and soil temperature (T) for high snow, low snow, and control snow plots. Average values for snow depth, VWC, and soil temperature are taken from November 1 through March 31. Standard error is shown for average VWC and soil temperature. Dates with an asterisk (*) indicate that peak values occurred on multiple dates.

	High Snow	Low Snow	Control Snow
Peak SD (mm) and Date	280 02/24/18	200 02/24/18*	200 02/24/18*
$SD_{average}$ (mm)	72	32	44
Peak VWC and Date	0.28 05/03/18	0.29 05/03/18	0.28 05/03/18
Average VWC 5cm	0.17 ± 0.002	0.16 ± 0.003	0.13 ± 0.002
Average VWC 20cm	0.22 ± 0.001	0.21 ± 0.002	0.18 ± 0.001
Soil $T_{average}$ (°C)	1.7 ± 0.1	2.5 ± 0.1	2.1 ± 0.2
Soil $T_{minimum}$ (°C)	-0.5	-0.6	0.2

Soil water nitrogen was sampled at Mill Creek during the spring and summer during water year 2018. PRS probes were collected from March to August while lysimeters were sampled from February through May. PRS nitrogen values reflect the amount of nitrogen adsorbed to the resins within month-long burial periods and is reported in terms of a supply rate, in units of micrograms of nitrogen per $10cm^2$. Lysimeter nitrogen values reflect the concentration in soil water samples collected from snow melt events. Lysimeter nitrogen is reported as a concentration, in units of milligrams per liter.

In the high snow and low snow plots, lysimeter NO_3^- increased as VWC increased from February to April then declined in May following peak VWC. In the control snow plot, lysimeter NO_3^- increased through March then declined in April, a month before the other two plots. The PRS probes captured a pattern of decline over time in NO_3^- from March to June for all three plots. PRS NO_3^- peaked as soil temperatures began to increase but before peak VWC occurred (Figure 22). By the time peak VWC occurred, PRS NO_3^- had drastically declined. PRS NO_3^- then increased from June to August, correlating with increased VWC from late summer thunderstorms. Additionally, soil temperature was higher and VWC was lower in the control plot than in the high snow and low snow plots.

Average PRS NO_3^- was highest in the low snow plots (33.8 ± 17.6 μg/10cm^2), on average about 2.5 times greater than the high snow (13.2 ± 6.2 μg/10cm^2) and control plots (13.4 ± 5.6 μg/10cm^2). Average lysimeter NO_3^- was highest in the high snow plots (0.8 ± 0.14 mg/L), followed by the low snow plots (0.2 ± 0.04 mg/L), and then the control plots (0.1 ± 0.02 mg/L) (Table 6). Peak PRS NO_3^- for all three plots were from the March 20 probe collection. The low snow plots had the highest peak value (91.7 μg/10cm^2), followed by the high snow plots (37.1 μg/10cm^2), and then the control snow plots (35.1 μg/10cm^2) (Figure 22). Peak lysimeter NO_3^- occurred on April 8 for both the high snow plots (1.4 mg/L) and the low snow plots (0.4 mg/L), and on March 30 for the control snow plots (0.2 mg/L).

Table 6. Average and peak values from PRS resin probes and lysimeter soil water samples for soil water NO_3^- at each snow manipulation plot type. PRS probes were collected five times from March 20 to August 13. Lysimeters were sampled six times from February 25 to May 21. Standard error is shown for average NO_3^-.

	PRS Resin Probes			Lysimeter Soil Water		
Plot Type	Average NO_3^- (μg/10cm^2)	Peak NO_3^- (μg/10cm^2)	Date of Peak	Average NO_3^- (mg/L)	Peak NO_3^- (mg/L)	Date of Peak
High Snow	13.2 ± 6.2	37.1	3/20/2018	0.8 ± 0.14	1.4	4/8/18
Low Snow	33.8 ± 17.6	91.7	3/20/2018	0.2 ± 0.04	0.4	4/8/18
Control	13.4 ± 5.6	35.1	3/20/2018	0.1 ± 0.02	0.2	3/30/18

Table 7. Average and peak values from PRS resin probes and lysimeter soil water samples for soil water NH_4^+ at each snow manipulation plot type. PRS probes were collected five times from March 20 to August 13. Lysimeters were sampled six times from February 25 to May 21. Standard error is shown for average NH_4^+.

	PRS Resin Probes			Lysimeter Soil Water		
Plot Type	Average NH_4^+ (μg/10cm^2)	Peak NH_4^+ (μg/10cm^2)	Date of Peak	Average NH_4^+ (mg/L)	Peak NH_4^+ (mg/L)	Date of Peak
High Snow	6.8 ± 2.0	14.0	4/30/2018	0.1± 0.01	0.1	4/8/18
Low Snow	5.8 ± 2.6	15.1	3/20/2018	0.1± 0.02	0.2	3/20/18
Control	2.4 ± 0.5	4.1	6/03/2018	0.1± 0.02	0.2	5/13/18

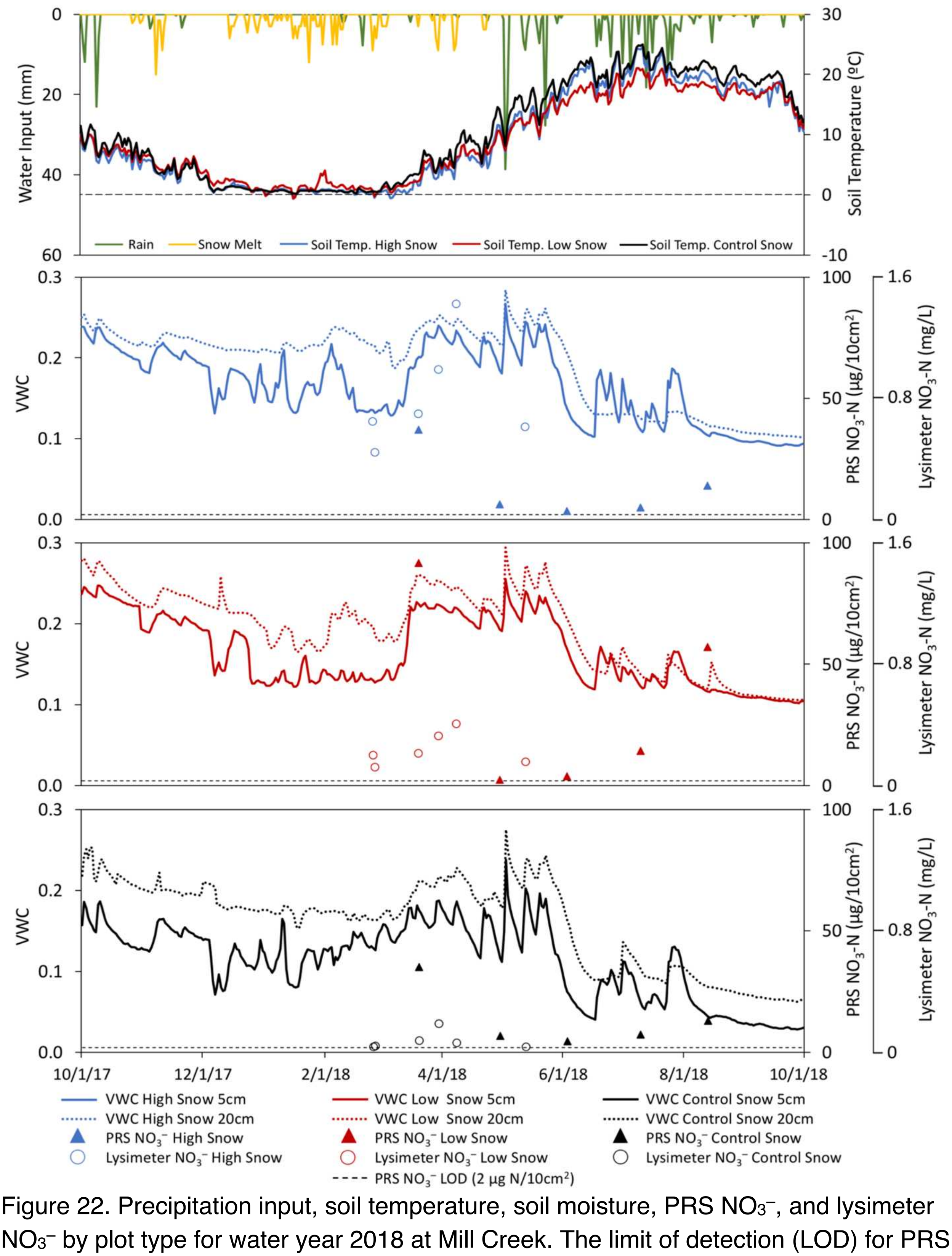

Figure 22. Precipitation input, soil temperature, soil moisture, PRS NO_3^-, and lysimeter NO_3^- by plot type for water year 2018 at Mill Creek. The limit of detection (LOD) for PRS NO_3^- (2 μg N/10cm^2) is indicated by a horizontal dashed line. The LOD for lysimeter NO_3^- (0.02 mg/L) is not shown as all samples were above the limit.

Average PRS NH_4^+ was highest at the high snow plots (6.8 ± 2.0 μg/10cm²) followed by the low snow plots (5.8 ± 2.6 μg/10cm²) and then the control snow plots (2.4 ± 0.5 μg/10cm²) (Table 7). Average lysimeter NH_4^+ was highest in the low snow plots (0.11 ± 0.02 mg/L), then the control snow plots (0.10 ± 0.02 mg/L), and lastly the high snow plots (0.09 ± 0.01 mg/L). Peak PRS NH_4^+ occurred on March 20 for the low snow plots (15.1μg/10cm²), April 30 for the high snow plots (14.0 μg/10cm²), and June 3 for the control snow plots (4.1 μg/10cm²). Peak lysimeter NH_4^+ occurred on March 20 in the low snow plot (0.2 mg/L), April 8 in the high snow plot (0.1 mg/L), and May 13 in the control snow plot (0.2 mg/L). In both the high snow and low snow plots, peak PRS NH_4^+ occurred before peak VWC then decreased following peak VWC. In the control snow plot, PRS NH_4^+ was at its lowest immediately before peak VWC occurred and then at its peak immediately after peak VWC occurred. PRS NH_4^+ showed a pattern of decline over time from April to July in the high snow plots, from March to July in the low snow plots, and from June to August in the control plots, correlating with increasing soil temperature (Figure 23). Lysimeter NH_4^+ exhibited a pattern of rising and falling, but in general increased in concentration from February to April in the high snow and control snow plots, as VWC increased. Peak lysimeter NH_4^+ occurred before peak VWC in the high snow and low snow plots, but after peak VWC in the control snow plots. Unlike the high snow and low snow plots, the control snow plots consistently increased in NH_4^+ concentration with each sampling event.

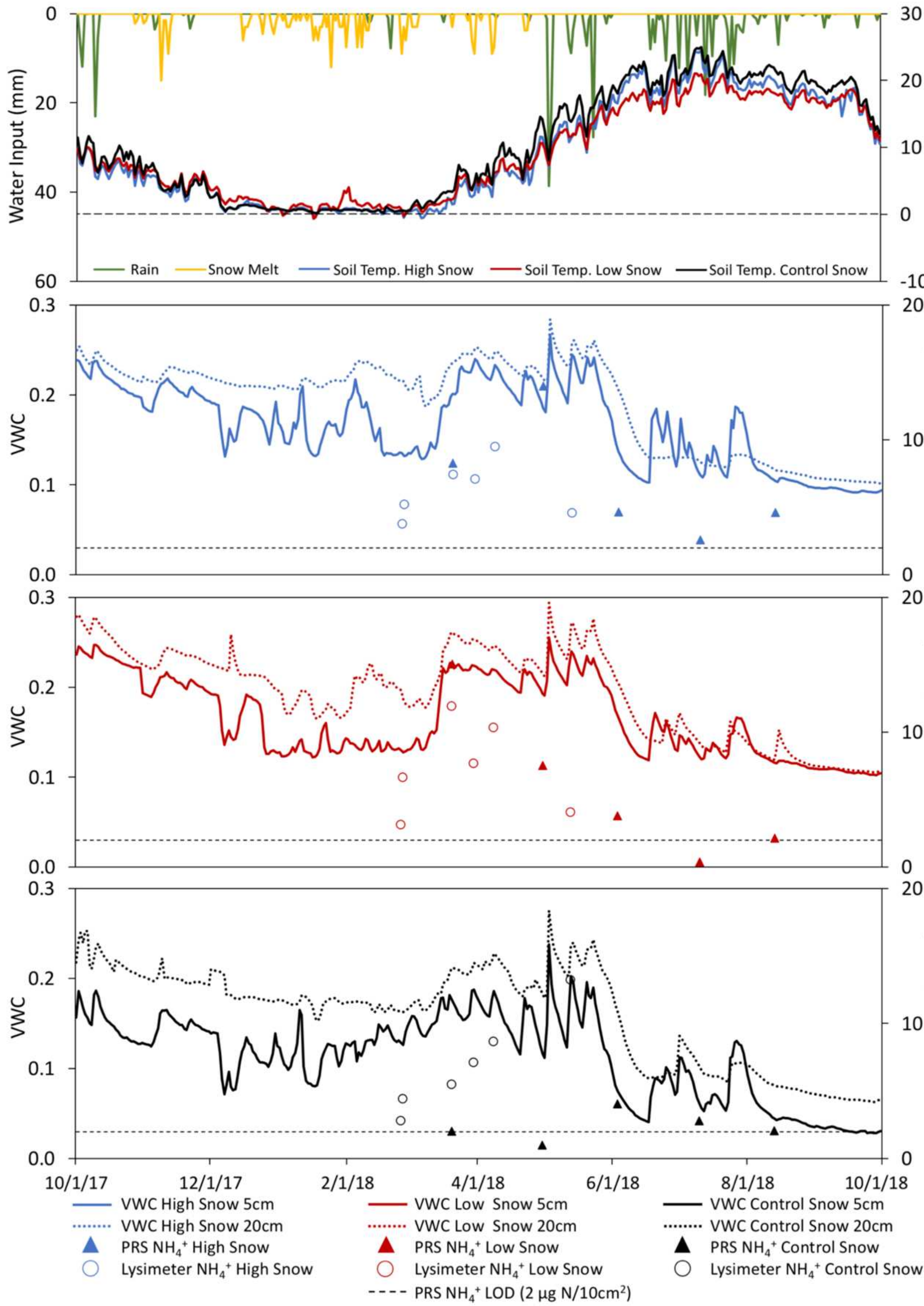

Figure 23. Precipitation input, soil temperature, soil moisture, PRS NH_4^+, and lysimeter NH_4^+ by plot type for water year 2018 at Mill Creek. The limit of detection (LOD) for PRS NH_4^+ (2 µg N/10cm^2) is indicated by a horizontal dashed line. The LOD for lysimeter NH_4^+ (0.02 mg/L) is not shown as all samples were above the limit.

Multivariate correlation matrices were computed for all plots collectively as well as for high snow plots, low snow plots, and control snow plots using snow depth, soil temperature, VWC, NO_3^-, and NH_4^+. The multivariate correlation matrix using PRS data utilized average and total snow depth, VWC at 5cm and 20cm, average and minimum temperature, and PRS NO_3^- and NH_4^+ from each month-long burial period (Figure 24). The correlation matrix using lysimeter data used daily averages from each sampling date for snow depth, VWC at 5cm and 20cm, temperature, and lysimeter NO_3^- and NH_4^+ (Figure 25). Correlation values and statistical significance are reported in Table 8 for PRS data and in Table 9 for lysimeter data. The only significant correlation involving NO_3^- was between PRS NO_3^- and total snow depth (r = 0.52*). NH_4^+ was significantly positively correlated with VWC at 5cm for both PRS NH_4^+ (r = 0.53*) and lysimeter NH_4^+ (r = 0.51*), and with VWC at 20cm for lysimeter NH_4^+ (r = 0.50*). PRS NH_4^+ showed significant negative correlations with average temperature (r = -0.60*) and with minimum temperature (r = -0.59*). Additional correlations were computed for relationships by plot type, with values reported in Table 8 and 9.

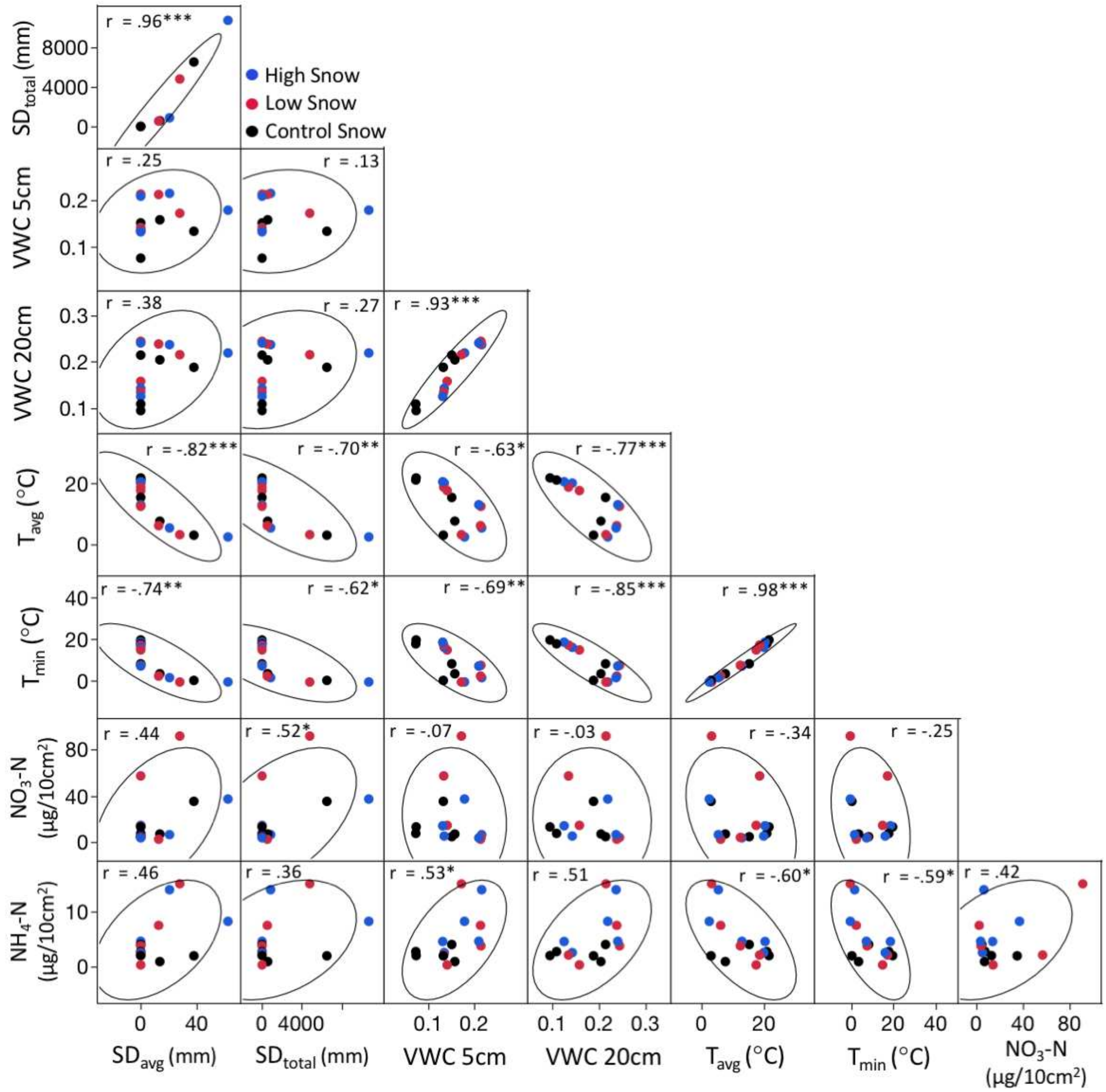

Figure 24. Cross-correlation matrix for Mill Creek using PRS nitrogen results from water year 2018, with 95% density ellipses shown. Values for average snow depth (SD_{avg}), total snow depth (SD_{total}), volumetric water content (VWC), average soil temperature (T_{avg}), and minimum soil temperature (T_{min}) are from month-long periods corresponding to each PRS burial period. Plot type is differentiated by color: high snow in blue, low snow in red, and control snow in black. Pairwise correlations for all points (r) are shown. Statistical significance is indicated for each correlation where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

Table 8. Pairwise correlations for variables at Mill Creek associated with PRS nitrogen samples, by plot type. Statistical significance is indicated for each correlation where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

Variable	By Variable	Correlation by Plot Type			
		All Plots	High Plots	Low Plots	Control Plots
Total Snow Depth	Average Snow Depth	.96***	.97**	.94*	.96**
VWC 5cm	Average Snow Depth	.25	.27	.22	.41
VWC 5cm	Total Snow Depth	.13	.11	.02	.26
VWC 20cm	Average Snow Depth	.38	.43	.41	.42
VWC 20cm	Total Snow Depth	.27	.31	.25	.30
VWC 20cm	VWC 5cm	.93***	.97**	.97**	.99**
Average Temp.	Average Snow Depth	-.82***	-.84	-.90*	-.90*
Average Temp.	Total Snow Depth	-.70**	-.72	-.75	-.78
Average Temp.	VWC 5cm	-.63*	-.73	-.62	-.75
Average Temp.	VWC 20cm	-.77***	-.81	-.75	-.75
Minimum Temp.	Average Snow Depth	-.74**	-.77	-.85	-.80
Minimum Temp.	Total Snow Depth	-.62*	-.64	-.70	-.68
Minimum Temp.	VWC 5cm	-.69**	-.81	-.70	-.87
Minimum Temp.	VWC 20cm	-.85***	-.90*	-.83	-.88
Minimum Temp.	Average Temp.	.98***	.99**	.99**	.97**
PRS NO_3^-	Average Snow Depth	.44	.89*	.62	.89*
PRS NO_3^-	Total Snow Depth	.52*	.95*	.79	.96**
PRS NO_3^-	VWC 5cm	-.07	-.10	-.48	.02
PRS NO_3^-	VWC 20cm	-.03	.07	-.31	.06
PRS NO_3^-	Average Temp.	-.34	-.55	-.27	-.61
PRS NO_3^-	Minimum Temp.	.25	-.44	-.18	-.47
PRS NH_4^+	Average Snow Depth	.46	.49	.98**	-.44
PRS NH_4^+	Total Snow Depth	.36	.26	.93*	-.24
PRS NH_4^+	VWC 5cm	.53*	.68	.33	-.05
PRS NH_4^+	VWC 20cm	.51	.62	.51	.08
PRS NH_4^+	Average Temp.	-.60*	-.78	-.92*	.41
PRS NH_4^+	Minimum Temp.	-.59*	-.75	-.89*	.25
PRS NH_4^+	PRS NO_3^-	.42	.16	.61	-.28

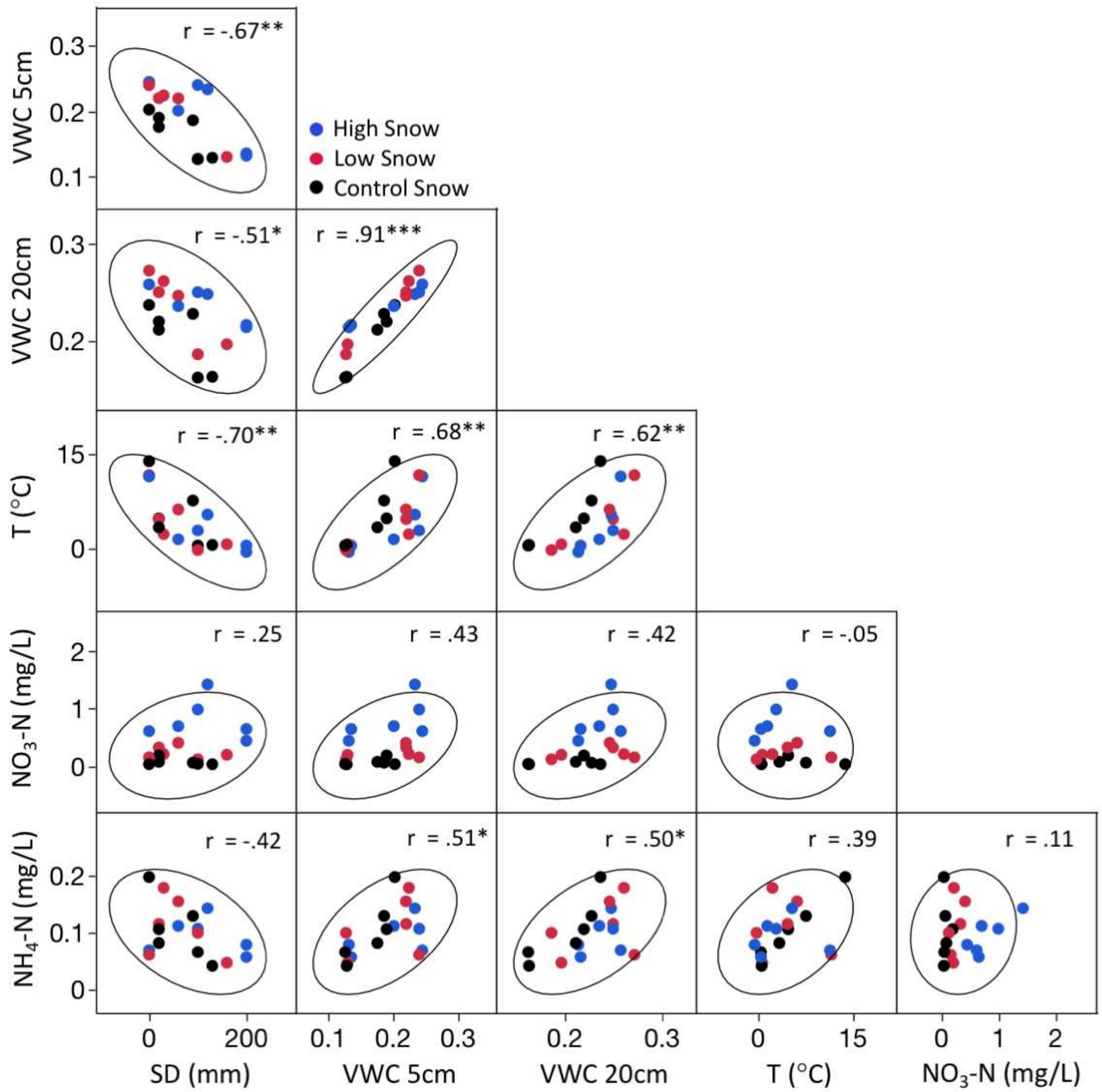

Figure 25. Cross-correlation matrix for Mill Creek using lysimeter nitrogen results from water year 2018, with 95% density ellipses shown. Snow depth (SD), volumetric water content (VWC), and soil temperature (T) are daily average values corresponding to each lysimeter sampling date. Plot type is differentiated by color: high snow in blue, low snow in red, and control snow in black. Pairwise correlations for all points (r) are shown. Statistical significance is indicated for each correlation where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

Table 9. Pairwise correlations between variables at Mill Creek associated with lysimeter samples, by plot type. Statistical significance is indicated for each correlation where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

Variable	By Variable	Correlation by Plot Type			
		All Plots	High Plots	Low Plots	Control Plots
VWC 5cm	Snow Depth	-.67**	-.83*	-.91*	-.82*
VWC 20cm	Snow Depth	-.51*	-.86*	-.89*	-.77
VWC 20cm	VWC 5cm	.91***	.99***	.99***	.99***
Temperature	Snow Depth	-.70**	-.80	-.72	-.65
Temperature	VWC 5cm	.68**	.76	.78	.84*
Temperature	VWC 20cm	.62**	.84*	.79	.86*
Lysimeter NO_3^-	Snow Depth	.25	-.11	-.19	-.44
Lysimeter NO_3^-	VWC 5cm	.43	.59	.44	.41
Lysimeter NO_3^-	VWC 20cm	.42	.52	.34	.34
Lysimeter NO_3^-	Temperature	-.05	.22	.20	-.05
Lysimeter NH_4^+	Snow Depth	-.42	-.20	-.40	-.68
Lysimeter NH_4^+	VWC 5cm	.51*	.54	.45	.84*
Lysimeter NH_4^+	VWC 20cm	.50*	.43	.39	.85*
Lysimeter NH_4^+	Temperature	.39	.03	-.12	.99***
Lysimeter NH_4^+	Lysimeter NO_3^-	.11	.83*	.50	-.003

A multivariate regression model was constructed using JMP software to predict the value of NO_3^- across all sites using snow depth (SD), temperature (T), VWC, and NH_4^+. Insignificant predictors were removed from subsequent iterations to generate a best fit model with only significant predictors. The scatterplot of predicted values versus residuals showed that the data met the assumptions of homogeneity of variance and linearity, and the residuals were approximately normally distributed. While PRS NO_3^- was not significantly correlated with VWC or temperature (Figure 24), it can be represented in a statistically significant multivariate model using snow depth (mm), VWC, and temperature (°C) as shown in the following regression equation:

$$NO_3^-{}_{(PRS)} = 230.63 - 4.68\ SD_{avg} + 0.02\ SD_{total} + 460.31\ VWC_{5cm} - 906.61\ VWC_{20cm} - 7.52\ T_{avg}$$

This model was a significant predictor of NO_3^- [$R^2 = 0.65$, $F(5,9) = 3.29$, $p = 0.05$] (Table 10). This model suggests that PRS NO_3^- is inversely related to average snow depth, VWC at 20cm, and average temperature, and positively related to total snow depth and VWC at 5cm. According to this equation, VWC is a strong predictor of NO_3^-. A separate multivariate regression model was used to predict lysimeter NO_3^-. Although lysimeter NO_3^- was not statistically correlated with any individual variables (Figure 25), it was highly significantly correlated with both snow depth (mm) and VWC in the following multivariate model:

$$NO_3^-{}_{(Lysimeter)} = -1.35 + 0.01\ SD + 13.42\ VWC_{5cm} - 5.66\ VWC_{20cm}$$

Using this model, 77% of the variance in the data can be explained by the predictor variables (Table 11). The results indicate that the model was a highly significant predictor of NO_3^- [$R^2 = 0.77$, $F(3,14) = 15.32$, $p = 0.0001$]. According to the modeled relationships, as snow depth and VWC at 5cm increase, and VWC at 20cm decrease,

NO_3^- increases. This equation also suggests that VWC is a strong driver of NO_3^-. Using these equations, predicted values of NO_3^- and were computed and plotted against the actual values of NO_3 for PRS NO_3^- (Figure 26) and lysimeter NO_3^- (Figure 27). Both models have good performance for predicting NO_3^- ($R^2_{(PRS)} = 0.65$, $R^2_{(Lysimeter)} = 0.77$), as most values fall close to the 1:1 line. However, unlike the PRS model, the lysimeter model showed a large separation by plot type. The high snow plots tend to be slightly underpredicted while the low snow plots tend to be overpredicted (Figure 27).

A multivariate model was set to predict NH_4^+ based on the following variables: average snow depth (mm), total snow depth (mm), VWC at 5cm, VWC at 20cm, average temperature (°C), and minimum temperature (°C). The initial model was reduced by removing variables with the highest p-values, producing the following regression equation:

$$NH_4^+{}_{(PRS)} = 30.27 + 232.65\ VWC_{5cm} - 324.41\ VWC_{20cm} + 2.16\ T_{avg} - 3.27\ T_{min}$$

This equation is the best fit model for the prediction of PRS NH_4^+ [$R^2 = 0.54$, $F(4,10) = 2.96$, $p = 0.07$] (Table 10). It suggests that PRS NH_4^+ is directly related to VWC at 5cm and average temperature, inversely related to VWC at 20cm and minimum temperature, and that VWC is a strong predictor in the determination of NH_4^+. This model does not fit as well as the NO_3^- models, and it both overpredicts and underpredicts PRS NH_4^+ (Figure 26). While PRS NH_4^+ in the high snow and low snow plots had a wide range of actual values, the model predicted values within a much smaller range. While lysimeter NH_4^+ had strong univariate correlations with VWC (Table 9), no significant multivariate model could be produced [$R^2 = 0.28$, $F(4,13) = 1.28$, $p = 0.33$].

Table 10. Model summary for the prediction of NO_3^- and NH_4^+ at Mill Creek using PRS nitrogen results. Variables include average snow depth ($SD_{average}$), total snow depth (SD_{total}), volumetric water content at 5cm and 20cm, average soil temperature ($T_{average}$), and minimum soil temperature ($T_{minimum}$). Significant predictors are indicated where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

	Intercept	$SD_{average}$	SD_{total}	VWC 5cm	VWC 20cm	$T_{average}$	$T_{minimum}$
NO_3^- (PRS)	230.63*	-4.68*	0.02*	460.31	-906.61*	-7.52*	
NH_4^+ (PRS)	30.27			232.65	-324.41	2.16	-3.27
	R^2		R^2_{adj}		RMSE		P-value
NO_3^- (PRS)	0.65		0.45		18.79		0.05
NH_4^+ (PRS)	0.54		0.36		3.55		0.07

Table 11. Model summary for the prediction of NO_3^- at Mill Creek using lysimeter nitrogen results. Variables include snow depth (SD) and VWC at 5cm and 20cm. Significant predictors are indicated where * = p-value ≤ 0.05, ** = p-value ≤ 0.01, and *** = p-value ≤ 0.001.

	R^2	R^2_{adj}	RMSE	P-value	Intercept	SD	VWC 5cm	VWC 20cm
NO_3^- (Lysimeter)	0.77	0.72	0.20	.0001	-1.35*	0.01***	13.42***	-5.66

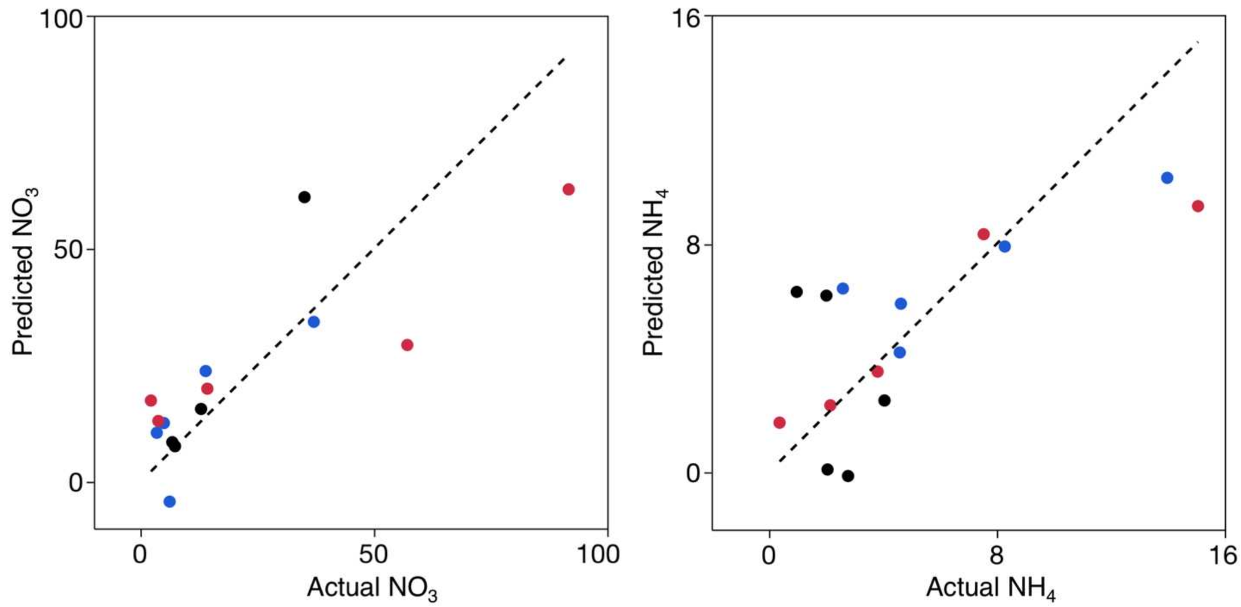

Figure 26. Actual vs predicted PRS NO_3^- and NH_4^+ with a 1:1 dashed line. Plot types are differentiated by color: high snow in blue, low snow in red, and control snow in black.

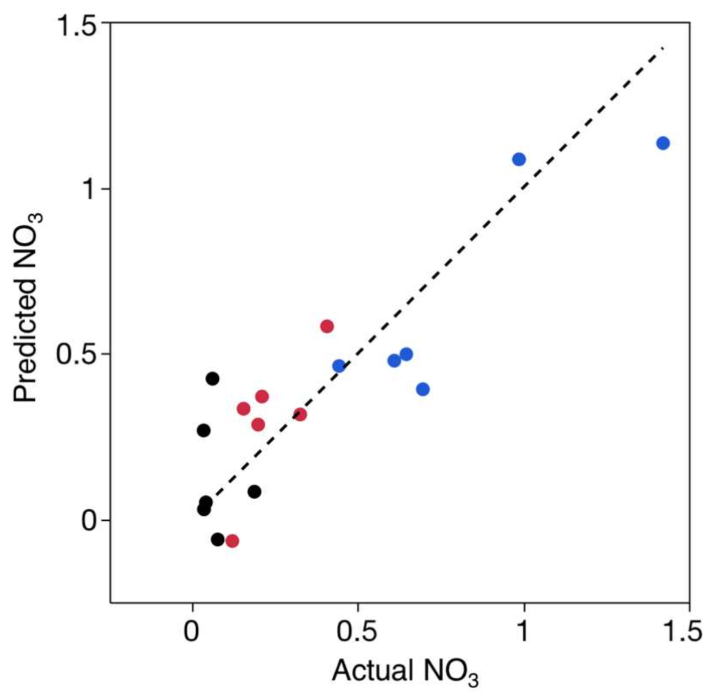

Figure 27. Actual vs predicted lysimeter NO_3^- with 1:1 dashed line. Plot types are differentiated by color: high snow in blue, low snow in red, and control snow in black. Lysimeter NH_4^+ is not shown in this figure because no statistically significant regression equation was identified.

4. DISCUSSION

4.1 Elevational Study

4.1.1 The temperature and soil moisture regime

Comparison of site metrics across snow zones demonstrates how the spatial and temporal variability of snow affects soil moisture dynamics. These results support previous findings that document increased snow persistence with increased elevation and decreased temperature, and later peak soil moisture at higher elevations (Williams et al., 2009; Blankinship et al., 2014; Kampf et al., 2015; Tennant et al., 2017). In the high elevation persistent snow zone, soil moisture rapidly increased after the seasonal snowpack melted while the lower elevation transitional and intermittent snow zones experienced episodic soil moisture inputs following mid-winter snowmelt events. As a result, soil moisture fluctuated more at the lower elevations. As expected, higher elevations experienced lower annual soil temperatures. However, as shown in previous studies, the presence of deep (>50 cm) and consistent seasonal snow cover can insulate soils throughout the winter (Zhang, 2005; Fuss et al., 2016). At Michigan River, soil temperatures remained above freezing throughout most of the period with snow cover, from November to May. Lower snow accumulation and inconsistent snow cover at Dry Creek and Mill Creek prevented insulation and induced soil freezing from November to March.

4.1.2 Connection to nitrogen

The development of consistent seasonal snow cover not only regulates soil temperature and soil water availability, but also the complex interactions between these variables, vegetation, and biogeochemical cycling. Climate trends have shown later onset of snow accumulation (Fassnacht et al., 2018) which can lead to soils freezing before snow cover can provide sufficient insulation. This can alter the ability for microbial processes to continue under winter snowpacks. At Michigan River, snow was removed to access sensors for maintenance in November 2016. This exposed soils and induced freezing, but during the following winter soils were not exposed, were insulated throughout the winter, and did not freeze. PRS probes revealed that average NO_3^- was lower, and average NH_4^+ was higher during the first year with below freezing soil temperatures than during the second year. Concurrent with our conceptual model, this indicates that soil freezing may have limited over-winter nitrification of NH_4^+ to NO_3^- during the first year. Conversely, during the following year insulated soils likely promoted microbial activity leading to enhanced nitrification and therefore an increased pool of NO_3^-. Additionally, during both water years, Dry Creek experienced both the coldest soil temperatures and the most days with freezing soil temperatures, and it had the lowest NO_3^- values of all three sites. To further understand the impacts of freezing on N pools, future studies could collect soil core samples before snow accumulation as well as during and after soil freezing and snowmelt and measure the total N to determine the relative quantities of organic and inorganic N pools.

In this study, we observed elevated N values from the first collections of the season that are likely an artifact of an extended burial period, as probes for these first collections were deployed over-winter instead of the standard month-long period. Furthermore, due to limited site access, over-winter probes were buried at Michigan River for 98 days longer during WY 2017 and 68 days longer during WY 2018 than at Mill Creek, which allowed a greater opportunity for the probes to adsorb N from the soil. Elevated NO_3^- in the first collection may also be attributed to over-winter nitrification, further stimulated by an increase in VWC during snowmelt, a pattern consistent with previous studies in snowmelt-driven systems (Creed et al.,1996; Brooks et al., 1996; Brooks et al., 1998; Yano et al., 2019). After the initial collection, all three sites exhibited a decrease in NO_3^-, although this occurred later in the season at Michigan River and was attenuated at Dry Creek.

At Michigan River, the first probes were collected prior to the growing season, but by the second collection the site had experienced a burst of herbaceous plant growth, coinciding with reduced NO_3^- likely as a result of uptake by plants. Simultaneously, NH_4^+ that had mineralized over-winter was present in lower quantities than NO_3^- likely due to preferential plant uptake and rapid nitrification to NO_3^-. At Dry Creek, while most plots also experienced peak NO_3^- during the first collection and a decline into the second, there were no further consistent patterns across plots. This site had hydrologic differences that may have complicated N results and contributed to values that were substantially lower than the other two sites. Daily time lapse photos documented overland flow during snowmelt that could have contributed to NO_3^- losses through increased denitrification and leaching, in addition to losses via plant uptake (Williams et al., 1998; Szukics et al., 2010).

At Mill Creek, the NO_3^- pool was smaller after winter than at Michigan River. Concurrent with the two higher sites, the first collection had the highest NO_3^- supply followed by a decrease as plants growth occurred. However, as VWC increased with summer storms, NO_3^- increased again, which may be because hydrologic connectivity reactivated nitrifying bacteria that were dormant in the dry soils due to cellular impairment or diffusional limitations (Stark and Firestone, 1995; Placella and Firestone, 2013). This finding is consistent with previous studies that observed increased NO_3^- due to stimulated mineralization and nitrification during rewetting (Kaste et al., 2002; Gu and Riley, 2010; Schaeffer et al., 2017). Results showed that NH_4^+ was also associated with VWC, although correlations were not as strong as with NO_3^-. However, this may be a result of limited NH_4^+ due to preferential biotic uptake by vegetation and microbes or rapid conversion of NH_4^+ to NO_3^- (Schmidt et al., 2007; Legay et al., 2013).

The reduction in NO_3^- and NH_4^+ after the initial collections may also be attributed to changes in soil temperature. Although some studies have found that increasing soil temperature is a strong driver of soil N availability (Binkley et al., 1994; Guntiñas et al., 2012) because warmer temperatures facilitate microbial activity, our findings are consistent with other research that has documented decreased NH_4^+ and NO_3^- with soil temperature (Groffman et al., 2009; Durán et al., 2014, 2016). These studies suggest that warmer temperatures may lead to drier soils that disrupt rather than promote microbial activity. In a natural system, it is difficult to separate the effects of temperature from soil moisture because the two covary. To further disentangle the effects of temperature and soil moisture on nitrogen dynamics, future studies could utilize soil cores and measure N pools under various controlled soil temperature and moisture conditions (Foerster et al., 2009).

4.2 Intermittent Snow Manipulation

4.2.1 The temperature and soil moisture regime

Mill Creek experienced small, episodic inputs of soil moisture following individual snow events. Increased snow depth in the high snow plots consistently led to increased soil moisture. However, the control snow plots, rather than the low snow plots, experienced the lowest average soil moisture. Inconsistencies between snow depth and soil moisture may be attributed to plot location variability. The snow manipulation chambers provide shading and wind protection to the high and low snow plots, which may explain why the unprotected control snow plots often had lower snow depths than the experimental plots. Additionally, plots were situated near a row of Ponderosa pine trees that may have contributed to snowfall interception as well as an inconsistent loss of soil moisture within the plots. Although the control snow plots had lower average soil moisture, soil moisture increased steadily with each snowmelt input from January to April, as soils approached field capacity. From December to March, soil moisture peaks following snow melt inputs were noticeably smaller in the low snow plots than the other two plots. During this same time period, the high snow plots had larger, more pronounced soil moisture peaks with slower declines. Similar to south facing slopes from studies such as Hinckley et al. (2014), the plots at Mill Creek experienced pronounced wetting and drying cycles, but with soil moisture passing through the soil matrix at different time scales. Soil moisture was retained for longer periods of time in the high snow plots following snow melt, but it was retained longer in the low snow plots following spring and summer rains. Continued climate warming may lead to earlier spring snowmelt which will likely shift soil moisture patterns, particularly in these lower elevation, intermittent snow zones. These water-limited systems that sit at the rain-snow transition are highly susceptible to the effects of decreased snowpack and earlier snowmelt, where soil moisture may shift towards patterns of decreased storage and rapid transport seen in the low snow plots and south facing slopes (Hinckley et al., 2014; Klos et al., 2014).

Conducting the snow manipulation at the intermittent snow site enabled easiest site access but there was not enough snow to create substantial differences in snow regimes between plots. Future studies could employ similar methods to understand the long-term effects of snow depth cover and duration on soil moisture dynamics while further enhancing the difference between manipulated snow plot types.

4.2.2 Patterns in nitrogen and differences between plot types

Soil moisture is necessary for the transport of NO_3^- and NH_4^+ through the soil profile, to stimulate plant growth and forest health, and to encourage the ongoing movement and dispersal of nutrients across ecosystems. One of the main controls over soil moisture mobility and biogeochemical processes is soil texture (Hook and Burke, 2000). At Mill Creek, water passed quickly through the well-drained, loamy sandy soils, often leaving these areas VWC-limited. These soils have low field capacity, where reduced amounts of water are held in the soil matrix for short residence times. This limits the opportunities for biogeochemical transformations such as mineralization and nitrification to occur (Hinckley et al., 2014). During periods of snow melt, these soils are susceptible to nutrient leaching losses as soil moisture quickly passes through the soil profile, rapidly transporting N. Unlike soils with high clay and organic matter contents, sandy soils tend to have low cation exchange capacity (CEC) which limits their ability to adsorb positive ions in the soil. This is why inorganic N increased with increased soil water content (Hook and Burke, 2000). Lysimeters captured a pattern of increasing mobile soil water nitrogen during the first large pulse of snow melt input (late March 2018), then declining mobile soil water nitrogen after peak VWC, a pattern indicative of flushing and consistent with results from previous studies (Williams et al., 1995; Baron and Campbell, 1997; Piatek et al., 2005; Campbell et al., 2014). PRS probes captured peak soil NO_3^- in the first collection before the soil moisture flush. However as soil moisture increased NO_3^- previously held in the soil matrix was likely flushed out (see increasing lysimeter soil water NO_3^-) resulting in decreased in PRS NO_3^-. While soil moisture continued to increase, low PRS NO_3^- may indicate that mobile NO_3^- was either flushed from the system or taken up by plants and microbial biomass (Kaste et al., 2002; Piatek et al., 2005; Campbell et al., 2014).

While prior research has shown the potential for increased NH_4^+ uptake with greater temperature (Baer et al., 2014; Yano et al., 2019), our results showed that only lysimeter NH_4^+ (and not PRS NH_4^+) was positively correlated with soil temperature. Similar to the elevational study, we observed decreased PRS NH_4^+ with increasing temperature. Potentially as soils warmed, available soil moisture decreased, disrupting microbial activity. However, because the timing of soil temperature increase occurred simultaneously with the timing of VWC rise, it is unclear whether this correlation may have been due to the timing of sampling rather than soil temperature affecting lysimeters and PRS probes differently. Additionally, according to our analysis, NO_3^- and soil temperature were not significantly correlated for either lysimeter or PRS NO_3^-. This suggests that nitrogen cycling may be more strongly influenced by soil moisture than temperature, as supported in previous research (Bonito et al., 2003; Griffiths et al., 2009).

The regression models from Mill Creek performed better than models from the elevational study, likely because nitrogen samples were from the same area and therefore were not subject to the challenges of comparing sites from a 1500m elevational gradient. The lysimeter model shows strong grouping by plot type (Figure

27), likely due to the differences in VWC by plot type and the dependency on VWC noted in the regression equation (Table 11). This is a strong indication that manipulating snow to increase soil moisture increased the flush of nitrate.

Overall, these findings showed that snow manipulation mediated the soil moisture dynamics that govern nutrient cycling. A loss of snow may lead to more limited soil water storage, which reduces nutrient transformations within soils because of longer time periods with insufficient water. Drier soil conditions led to more NO_3^- held in the soil rather than mobilized in the soil water, whereas wetter conditions allowed more NO_3^- to be mobilized in soil water. Although most natural ecosystems are N limited, studies have shown that atmospheric N deposition has increased over the last century and is expected to continue to increase due to current anthropogenic activities (Fenn et al., 2003; Galloway et al., 2008). Increased nitrogen availability can lead to increased nitrification and NO_3^- flushing from the soil profile, decreased soil buffering capacity, and acidification of soils and surface waters (Lieb et al., 2011). Studies in ecosystems similar to Mill Creek have observed that these soils have the potential to acidify quicker than soils with higher organic matter content in response to nitrogen additions, reducing plant species richness and altering soil microbial communities (Seastedt et al., 2001; Compton et al., 2004). Thus, the impacts of snowpack changes interact with those of spatiotemporal nitrogen cycling, leading to a complex set of changing processes.

4.3 Uncertainties

Comparing nitrogen responses to snow across an elevation gradient is challenging because many other factors in the system change besides snow persistence. Although temperature and moisture are important climatic drivers of nitrogen cycling, we must also take into account the chemical and microbial processes occurring within the snow and soil. Incorporating methods to monitor and sample active microbial communities, as well as other linked chemical cycles such as carbon, could provide a more thorough analysis of the controls on soil nitrogen responses. Additionally, PRS probe burial periods varied from one site to the other, due to time restraints on field visits. If I were to repeat this study, I would try to make the sampling dates more uniform and would also increase the sample size so that there were more than three points per sampling period.

Another challenge I faced during lysimeter sampling was that several lysimeters would constantly run dry. Lysimeter-based sampling is inherently restricted to wetter soil conditions; therefore, it would be helpful to have more baseline data to understand if some sites are by nature drier than others. A stronger, constant vacuum would also be necessary for soil water extraction from drier, sandy soils. Additionally, selecting a study site higher in elevation would allow for greater depths of snow to be moved around and would allow for more differentiation in snow depth and soil moisture by plot type.

5. CONCLUSIONS

The goal of this research was to investigate how snow persistence affects soil moisture and soil water nitrogen, and to understand how they are impacted by changes in elevation and snowpack. Snow depths and persistence changed substantially across the elevation gradient. At the highest elevation, soil moisture increased during a large pulse of snowmelt in the late spring, whereas the lower elevation experienced multiple smaller pulses of soil moisture following individual snow events. These pulses of soil moisture were associated with a flushing signal of NO_3^- and a correlation between soil moisture and NH_4^+. As a result of increased snow persistence and delayed snow loss, the timing of NO_3^- decline was delayed at the higher elevation site. At the lowest elevation site elevated soil moisture mobilized soil NO_3^- and resulted in a flushing of N during snowmelt. NH_4^+ was correlated with soil temperature in some cases, but this correlation appeared to be an artifact of sample collection timing rather than an actual temperature effect. This brought up the importance of looking at time series to avoid inferring relationships between variables that may actually just be a function of when they were measured.

As shown in this research, snow depth exerts considerable influence on soil water availability and in turn affects N in the soil profile. Seasonal patterns of NO_3^- and NH_4^+ in soil water were similar at all elevations studied, however the magnitude and timing of these patterns varied. Loss of snow may not dramatically change the seasonality of NO_3^-, but it can reduce NO_3^- export if soil moisture is also reduced. Snow persistence influences patterns not only during the winter and spring, but throughout the following growing season. Changes in snow persistence can have cascading effects on not only the soil moisture dynamics but also ecosystem responses. Therefore, it is necessary to utilize long term studies, over wet and dry years, from the winter snow accumulation period through the following growing season to further understand the effects of climate change on biogeochemical cycling in seasonally snow-covered regions.

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