Biogeochemistry (2009) 95:77–94
DOI 10.1007/s10533-009-9288-x

Storage and release of solutes from a subalpine seasonal snowpack: soil and stream water response, Niwot Ridge, Colorado

Mark W. Williams · Christine Seibold · Kurt Chowanski

Received: 22 July 2008 / Accepted: 15 January 2009 / Published online: 12 February 2009

Abstract Much of the research on the chemistry of snow and surface waters of the western US, Europe, and Asia has been conducted in high-elevation catchments above treeline. Here we provide information on the solute content of the seasonal snowpack at the Soddie site on Niwot Ridge, Colorado, a subalpine site near treeline. We focus on the storage and release of both inorganic and organic solutes to the soils underneath the snowpack, and subsequent effects on the chemical and nutrient content of the underlying soil solution and the adjacent headwater stream. The concentration of inorganic nitrogen (N) stored in the seasonal snowpack at the Soddie site of about 11 μeq L^{-1} was on the upper end of values reported for the northern hemisphere when compared to most areas of the Alps, Himalayas, and Tien Shan mountain ranges, but consistent with other reports of snowpacks in the Rocky Mountains. The storage of inorganic N in the snowpack at maximum accumulation averaged about 17 meq m^{-2}, or 170 eq ha^{-1} (on the order of 2 kg-N ha^{-1}). Solutes were released from storage in the form of an ionic pulse, with a maximum concentration factor of about four. In contrast to the seasonal snowpack, the dominant form of N in the soil solution was dissolved organic N. Thus, soils underlying the seasonal snowpack appear to assimilate inorganic N released from storage in the snowpack and convert it to organic N. A two component mixing model suggests that the majority of streamflow was this year's snowmelt that had infiltrated the subsurface and undergone subsequent biological and geochemical reactions. The inorganic N in surface waters at the headwaters of Como creek were always near or below detection limits, suggesting that this area at treeline is still N-limited.

Keywords Snow · Chemistry · Meltwater · Lysimeter · Isotopes · Soil solution · Surface water

Introduction

Snowpacks can accumulate significant amounts of particulates and solutes from atmospheric deposition. In much of western North America and mountainous regions of Europe and Asia, deep snowpacks form through the late autumn, winter and early spring (Kuhn 2001). The montane snowpack accumulates wet and dry atmospheric deposition, which may be held in storage until release during a melt period. At Niwot Ridge in Colorado as much as 80% of the

---

M. W. Williams · C. Seibold · K. Chowanski
Institute of Arctic and Alpine Research, University of Colorado at Boulder, UCB 450, Boulder, CO 80309, USA

M. W. Williams (✉)
Department of Geography, University of Colorado at Boulder, UCB 360, Boulder, CO 80309, USA
e-mail: markw@snobear.colorado.edu

annual water input and more than 50% of the annual inorganic N deposition can be stored in the snowpack and released during snowmelt episodes (Brooks and Williams 1999).

Snowmelt is the dominant hydrologic event on an annual basis in high-elevation areas (Williams et al. 1991; Caine 1996). Liquid water, particulates, and solutes stored over the winter period are released in a relatively short time period, usually on the scale of several weeks. Field and laboratory experiments have demonstrated that initial stages of snowmelt often have ionic concentrations many times higher than averages for the whole snowpack, an ionic pulse (Johannessen and Henriksen 1978; Colbeck 1981). Physical and chemical processes that determine the occurrence, magnitude and extent of an ionic pulse are not sufficiently understood to predict the ionic concentrations of snowpack meltwater at a point in time (Williams and Melack 1991a, b).

The rapid release of water and solutes from the seasonal snowpack has the potential to exert a significant impact on terrestrial and aquatic ecosystems (Williams and Melack 1991b; Williams et al. 1996a; Lepori et al. 2003; Edwards et al. 2007). The soil may function either as a source or sink of nutrients depending on the species involved and the extent to which snowmelt infiltrates (Williams et al. 1995; Brooks and Williams 1999). Frozen soils may reduce infiltration and thus provide the potential for solutes in snowmelt to reach a stream directly. In contrast, unfrozen soil encourages infiltration and provides the opportunity for the chemical content of snowmelt to be modified by soil processes prior to reaching the stream. Complicating matters even more, in some ecosystems snowmelt infiltrates frozen soil and does not travel to streams via surface flow (Shanley and Chalmers 1999). In the absence of plant uptake during the winter, nutrients such as nitrate may accumulate in the soil environment under the snow (Williams et al. 1996a, 1998). The degree to which any snowmelt infiltrates soils may be a source of the great variability in the chemical content of stream water at this time (Edwards et al. 2007). Thus, export of nitrate and other nutrients to streams may originate from some combination of solutes stored in the seasonal snowpack and released in melting waters or leaching from soil produced by under-snow mineralization processes (Rascher et al. 1987; Stottlemyer and Toczydlowski 1996; Stottlemyer 2001).

Much of the research on the chemistry of snow and surface waters has been conducted in high-elevation catchments above treeline (e.g. Edwards et al. 2007). In alpine streams of the Colorado Front Range of Colorado, several investigations have shown that nitrate in surface waters is elevated above background concentrations, suggesting that these areas are approaching N saturation (Williams et al. 1996b; Williams and Tonnessen 2000). Elevated amounts of ammonium and nitrate in wetfall are considered a major reason for the excess nitrate in surface waters (Burns 2004; Baron 2006). In contrast to these alpine areas, streams draining predominately forested areas in the Colorado Front Range appear to be N-limited (Hood et al. 2003a). A major unknown for this region is how the storage and release of solutes from the seasonal snowpack may affect the chemical and nutrient content of stream waters at treeline, which is the transition zone from alpine ecosystems to subalpine forests.

The presence of a forest canopy may generate a source of nutrients to the seasonal snowpack that is much less apparent in alpine areas. Litterfall from coniferous vegetation has the potential to add organic nutrients to the seasonal snowpack in subalpine areas. Moreover, the presence or absence of a forest canopy may alter the melt rate of the seasonal snowpack (Marks et al. 2008), affecting the delivery of solutes from the seasonal snowpack to underlying soils. Here we provide information on the solute content of the seasonal snowpack at the Soddie site on Niwot Ridge, a subalpine site near treeline. We focus on the storage and release of both inorganic and organic solutes to the soils underneath the snowpack, and subsequent effects on the chemical and nutrient content of the underlying soil solution and the adjacent headwater stream.

Site description

This study was conducted in a forest clearing near tree line at the high-elevation Soddie site, within the Niwot Ridge, Colorado, long-term ecological research (LTER) area (40°03′ N, 105°35′ W, 3,340 m). Here we report the chemical and isotopic content of the snowpack at maximum accumulation from 2002 to 2007, along with snowmelt and soil lysimeters and stream chemistry in 2006. This site has an underground laboratory 10′ × 30′ × 8′ in size, line power, with an array of snow lysimeters (Erickson 2004) and zero-tension soil lysimeters (Fig. 1). Adjacent to the soil lysimeters is a suite of meteorological instruments sufficient to close the energy balance. The national atmospheric deposition program (NADP) operates two nearby sites on Niwot Ridge in cooperation with the NWT LTER program and the University of Colorado Mountain Research Station (MRS): the Saddle site at 3,500 m (CO02) and the C1 site (CO90) at 3,005 m (http://nadp.sws.uiuc.edu/). Snowpits were sampled about weekly for physical and chemical parameters about 100 m from this experimental site (Fig. 1) so as not to disturb the natural snow cover over the snow and soil lysimeters. The location of the snowpit site was an open meadow carefully selected to present the same characteristics as the experimental site (e.g. same snow depth, distance from trees of soil lysimeters). Snow cover at the site generally lasts from October into June. The continental, high mountain climate of Niwot Ridge has been recorded continuously at the D-1 meteorological station on Niwot Ridge since the early 1950s. Mean annual temperature at D-1 is −3.7°C (Williams et al. 1996c). Almost 80% of the ~1,000 mm of annual precipitation falls as snow (Caine 1996). Redistribution of snow by the westerly winds is common (Erickson et al. 2005). The bulk snow pack temperature generally remains below 0°C until late spring, introducing a lag in the hydrological cycle by concentrating the release of melt water in a short, intense period of runoff (Caine 1996).

The high-elevation meadow is bounded by ribbon forest that serves to isolate the meadow snowpack from lateral inflow. Ribbon forests are an intriguing example of the interaction of snow and wind (Barbour and Billings 2000). These alternating and parallel strips of forest and "snow glades" form subalpine meadows that have been described from the subalpine regions of Wyoming, Montana, and Colorado (Billings 1969; Buckner 1977; Holtmeier 1982). The ribbon forest apparently functions as a natural snow fence, with snow accumulation inhibiting seedling establishment on the leeward side and forming a natural meadow. The ribbon forest at Niwot Ridge is a mixture of spruce (*Picea engelmannii*) and fir (*Abies lasiocarpa*), with some limber pine (*Pinus flexilis*). The meadow faces the southwest and is sloped ~7° to 10°. The montane meadow is covered by a mixture of grasses and forbs. Soil is classified as a mixed Typic Humicryepts, sandy-skeletal in texture. The Oe horizon (0–7 cm) overlays a well-developed A horizon (7–34 cm) on top of a B horizon that extends to a depth of 99 cm. Weathered regolith extends below a depth of 3.5 m. Parent material is colluvium, eolian material, and possibly glacial till or similar coarse-grained deposit. Coarse grains and sands are evident, possibly indicating freeze–thaw mechanisms due to cryoperturbation sorting of the soil matrix. Texture is a loamy sand to gravel with little clay content. The area is moderately well-drained.

The research site is located in the headwaters of the Como Creek drainage, a tributary stream draining the SE flank of Niwot Ridge. Extensive research on the chemical and nutrient content of Como Creek has been conducted near the MRS since the mid-1970s (Lewis and Grant 1980; Hood et al. 2003a, b). Stream samples for those and related studies were collected at an elevation of 2,900 m; the watershed area above the sampling site at the MRS is 664 ha. The headwaters of Como Creek extend slightly above tree line to 3,560 m in elevation. Greater than 80% of the watershed is mixed conifer forest with some aspen (*Populus tremuloides*). Como Creek watershed has similar climatology and snowfall amount as the adjacent Green Lakes Valley in the North Boulder Creek catchment (Hood et al. 2003a, b). However, Como Creek differs from Green Lakes Valley in two important respects: (1) There are no lakes in the catchment, and (2) there is no talus, exposed bedrock, steep cliffs, or periglacial features such as rock glaciers. The headwaters of Como Creek begin flowing in a seasonal stream about 100 m from the Soddie research site; basin area is about 8 ha and is predominately alpine tundra. Our sampling site for surface waters at the headwaters of Como Creek was about 300 m down-gradient from the Soddie experimental site (Fig. 1).

Methods

The snowpack was sampled approximately weekly for chemical content, physical properties, and oxygen isotopes of water from 2002 to 2007 following the protocols of Williams and Melack (1991a, b) and Williams et al. (1996a, 1999). Here we report values

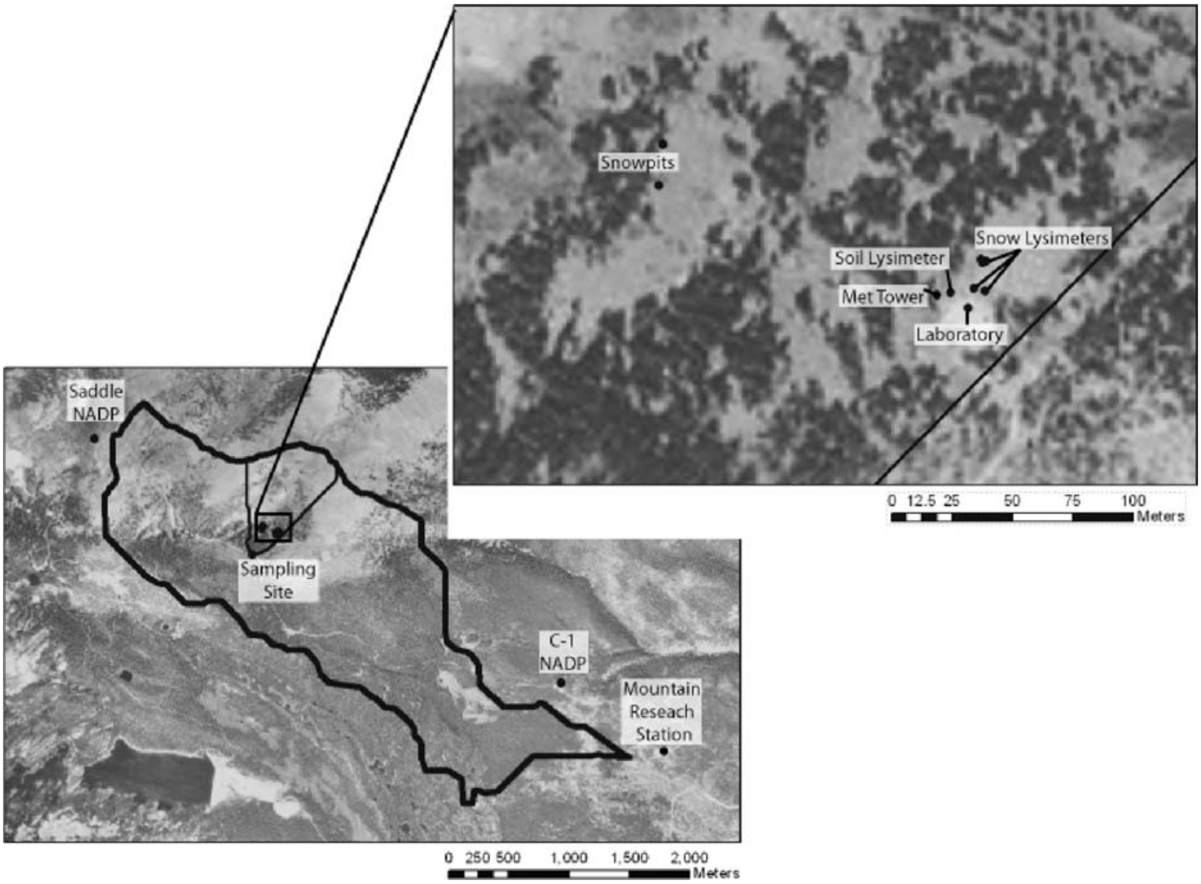

Fig. 1 Location and site map of the Soddie site, Niwot Ridge. Colorado. Sampling sites are shown for the meteorological station, snow, snow melt, soil lysimeters, and surface waters. Delineations indicate the Como Creek watershed and the headwater basin boundaries

for each year from 2002 to 2007 sampled at the time of maximum snow depth and prior to snowmelt, when maximum loading of solutes stored in the seasonal snowpack occurs. Snowpits were dug from the snow surface to the ground. The north-facing wall was the working wall where samples were collected. The north-facing wall of the snowpit was located on the south side of the snowpit and hence was shaded from direct sunlight, which can quickly change snow properties. During construction of the snowpit the excavated snow was placed only on the north side of the pit; snow was never placed on the south side of the snowpit so that area remained untrammeled and could be sampled in the future. To minimize contamination and other problems caused by destructive sampling of the snow, each snowpit was carefully refilled with snow from the north side of the pit after each sampling episode. The southwestern edge of the refilled snowpit was marked with a pole. The next weekly snowpit was always constructed to the south of the last snowpit in undisturbed snow. The new snowpit was located at a distance from the pole on the SW corner of the previous snowpit equal to the maximum snow depth of the previous snowpit, to avoid any possible disturbance to the snow pack from the previous snowpit.

Snow depth was measured with a hand-placed carpenter's rule from the snow surface to the snow-ground interface at the bottom of the snowpit. Snow density was measured in vertical increments of 10 cm from top to bottom of the snowpit using a 1-L (1,000 cm^3) stainless steel cutter and an electronic scale (±2 g). Temperature of the snowpack was measured every 10 cm using a 20-cm long dial stem thermometer, calibrated to ±0.2°C using a one-point calibration at 0°C. Grain type, size, and snowpack stratigraphy were also recorded but not reported here. Depth-weighted values were calculated for the density and temperature of the snowpack. Snow water equivalent (SWE) was then calculated as the height of the snowpack multiplied by the ratio of the depth-integrated snow density to that of liquid water (1,000 kg m^{-3}).

Snow samples were collected for chemical and oxygen isotopic analyses using beveled PVC tubes (50-mm diameter, 500-mm long), which had been soaked in 10% HCl and then rinsed at least five times with deionized water. Duplicate, vertical, contiguous cores in increments of 40-cm were collected from the snow-air interface to the snow-ground interface. Snow was transferred from the cores into new polyethylene bags and transported about 3 km to our analytical facilities the same day as collection. The depth-integrated concentrations of solutes in the snowpack for each duplicate core were determined by calculating the volume-weighted mean concentrations (VWM) as in Williams and Melack (1991a, b) and Williams et al. (1996a, 1999). Here we report the mean value of the two cores collected at maximum accumulation each year. This sampling protocol for snow properties is the same as previously reported in Williams and Melack (1991a, b), Williams et al. (1992, 1996a, 1999, 2001, 2006), Liu et al. (2004), and numerous other publications.

Release of solutes from the snowpack was investigated by collecting snowpack meltwater in 0.2-m^2 snow lysimeters before contact with the ground following the protocol of Williams et al. (1996a, 1999). Meltwater flowed by gravity from the snow lysimeters into the subnivian laboratory. Meltwater discharge for each snow lysimeter was measured continuously in individual tipping buckets at 10-min intervals (hand calibration showed that one tip was equal to 11 mL) and grab samples were collected about daily and analyzed for all major solutes and nutrients as well as $\delta^{18}O$. More emphasis was placed on collecting samples early in the melt cycle when concentration changes were expected to be larger compared to later in the melt cycle. Five snowpack lysimeters were sampled that represented two different snow regimes. Two snowpack lysimeters (Open-104 and Open-105) represented the open meadow and were situated 4-m apart in a clearing about 20 m from the nearest trees (Fig. 1). Three snowpack lysimeters (tree-17, tree-29, and tree-40) represented the forest area and were located in a row parallel to the ribbon forest, each 4 m apart, at the leeward (eastern) edge of ribbon forest.

Soil and surface water

Zero-tension soil lysimeters were installed about 2 m from the southwestern edge of the snow lysimeters in the open site in 1997 in a triplicated array at depths of 100, 300, and 500 mm, following the protocol of Litaor (1993). The nine zero-tension soil lysimeters were constructed of halved 400-mm sections of PVC pipe 250 mm in diameter, capped on one end, and plumbed to drain into a 1-L storage bottle connected to the surface with tygon tubing. After construction, lysimeters were rinsed copiously with deionized water, soaked in deionized water for 24 h, again rinsed, and then installed horizontally into the side wall of a soil pit which was immediately refilled; ammonium and nitrate concentrations in rinse water were below detection limits. Zero-tension soil lysimeters were sampled about weekly starting when the area became snow free; here we report the mean from all soil lysimeters that had water for that sampling date. Surface waters from the headwaters of Como Creek (about 300 m from the snow and soil lysimeter array) were collected as weekly grab samples starting when there was sufficient water for collection and ending when stream flow stopped; this section of Como Creek is a seasonal stream. Water samples were collected in polyethylene bottles soaked with deionized water overnight and then rinsed copiously five times; bottles were further rinsed three times with sample water at the time of collection. Samples were transported the same day as collection to our wet chemistry laboratory and treated the same as melted snow samples.

Laboratory methods

All surface water, soil, snow, and snowmelt samples were analyzed for pH, specific conductance, ANC, H^+, NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, K^+, Cl^-, NO_3^-, SO_4^{2-}, Si, DOC, DON, and $\delta^{18}O$. Samples for chemical and nutrient content were analyzed at the Kiowa wet chemistry laboratory run by the Niwot Ridge (NWT) LTER program, following the protocols presented in Williams et al. (2006). Specific conductivity, pH, and acid neutralizing capacity

(ANC) were measured on unfiltered samples within 1 week of collection. Conductivity and pH were measured with temperature-compensated meters and ANC was measured using the Gran Titration method. Waters analyzed for anions and cations were first filtered through a 47-mm Whatman Nuclepore membrane with an effective pore size of 1.0 μm. The base cations Na^+, Mg^{2+}, K^+, and Ca^{2+} were analyzed using a Perkin Elmer Analyst 100 Atomic Absorption Spectrometer with detection limits of 0.07, 0.04, 0.04, and 0.26 μeq L^{-1}, respectively. $NH_4{}^+$ and Si were measured on an OI Analytical Spectrophotometric Flow System IV Analyzer with a detection limit of 0.13 μeq L^{-1} for ammonium and 0.23 μmoles L^{-1} for silica. Nitrate, $SO_4{}^{2-}$, and Cl^- were measured on a Metrohm 761 Compact Ion Chromatograph with detection limits of 0.02, 0.04, and 0.14 μeq L^{-1}, respectively.

Total dissolved N (TDN) concentrations on filtered samples were determined by using potassium persulfate digestion to oxidize all forms of N into nitrate. The digested samples for TDN were then measured on an OI Analytical Spectrophotometric Flow System IV Analyzer with detection limit of 0.45 μmoles L^{-1} and precision of 1.39%. DON was calculated by subtracting measured total inorganic N from TDN. Samples for DOC were filtered through pre-combusted Whatman GF/F filters with a nominal pore size of 0.7 μm. DOC was determined by high-temperature catalytic oxidation using a Shimadzu Organic Carbon Analyzer at the Institute of Arctic and Alpine Research (INSTAAR) in Boulder, CO. Three replicate analyses yielded standard deviations of about 0.06 mg C L^{-1}, with a range of 0.01–0.22 mg C L^{-1}.

Analytical bias was assessed through charge balance calculations using calibrated standards. Split samples were analyzed in parallel with NADP/NTN Central Analytical Laboratory in an ongoing inter-laboratory comparison study effort. An ecosystem proficiency blind survey was performed June and July 2004 through environment Canada to assess the accuracy of the anion and cation methodologies. Analytical precision for all solutes was <2% and assessed with spikes, blanks, and replicates.

Samples for stable water isotopes were collected in 30-mL borosilicate vials with airtight caps. Isotopic analyses of ^{18}O were conducted using the CO_2–H_2O equilibration technique at the Stable Isotope Laboratory at the Institute of Arctic and Alpine Research in Boulder, CO. The ^{18}O values are expressed in conventional delta (δ) notation in units of per mil (‰) relative to Vienna standard mean ocean water (V-SMOW) with a precision of ±0.05‰:

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{VSMOW}}}{(^{18}O/^{16}O)_{\text{VSMOW}}} \times 1000$$

The new and old water components can be estimated using $\delta^{18}O$ by (e.g. Sklash et al. 1976; Hooper and Shoemaker 1986)

$$Q_{\text{stream}} \times C_{\text{stream}} = Q_{\text{new}} \times C_{\text{new}} + Q_{\text{old}} \times C_{\text{old}} \qquad (1)$$

with the water balance constraint that

$$Q_{\text{stream}} = Q_{\text{new}} + Q_{\text{old}} \qquad (2)$$

where Q is volume flow rate, C is $\delta^{18}O$ content, and the subscripts describe the water source. Hydrologic flowpaths were separated into reacted and unreacted components by substituting geochemical tracers for $\delta^{18}O$ and by substituting unreacted and reacted for the new and old components. Several conditions must be met for this two-component model, including (e.g. Sueker et al. 2000): (1) Tracer values of each component must be significantly different; (2) there are only two components contributing to streamflow; and (3) the tracer composition of each component is constant for the duration of the event, or variation is known from measurements.

Results

The primary form of N in the snowpack was nitrate (Table 1). The VWM concentration of nitrate at maximum snow accumulation in 2006 was 10.9 μeq L^{-1} and in 2007 was 12.1 μeq L^{-1}. Ammonium concentrations were 3.30 μeq L^{-1} in 2006 and 5.59 μeq L^{-1} in 2007, about half that of nitrate. Dissolved inorganic nitrogen ($DIN = NO_3{}^- + NH_4{}^+$) concentrations were thus 14.2 μeq L^{-1} in 2006 and 16.5 μeq L^{-1} in 2007. The concentration of DON in 2006 of 6.24 μmoles L^{-1} was four times the 1.40 μmoles L^{-1} in 2007. Dissolved organic carbon in the snowpack was about 1 mg L^{-1} in both years. The primary base cation was calcium; concentrations of 35.0 μeq L^{-1} in 2006 were about 3.5 times the concentration of 10.2 μeq L^{-1} in 2007. The low chloride values of <2 μeq L^{-1} suggest little seasalt influence in snowfall at this continental site. The snowpack was slightly acidic, with a hydrogen ion concentration of 1–5 μeq L^{-1}. The $\delta^{18}O$ of snow for both years at maximum snow accumulation was about −21‰.

The amount of SWE at maximum accumulation averaged 0.90 m from 2002 to 2007, ranging from a low of 0.54 m in 2002 to a high of 1.10 m in 2003 (Table 2). The SWE amounts for 2006 and 2007 were both a little more than 1 m, slightly above average for those 6 years. Inorganic inputs of N averaged about 17 meq m^{-2}, or 170 eq ha^{-1}. For 2006, loading in kg-N ha^{-1} was 0.46 for ammonium and 1.43 for nitrate, a DIN value of 1.90. In 2007, values were slightly higher with ammonium at 0.81 kg-N ha^{-1} and nitrate at 1.71 kg-N ha^{-1}, a DIN value of 2.53 kg-N ha^{-1}. Loading of DON averaged about 3.3 mmoles m^{-2} or 33 moles ha^{-1} over the 6 years, while the input of DOC averaged 0.82 g-C m^{-2} or 82 kg-C ha^{-1}.

For the chemistry and $\delta^{18}O$ values of snowpack meltwater before contact with the ground we report year 2006, because that is the year where we conducted the highest frequency of measurements. A total of 132 grab samples from the five snow lysimeters were collected with over 10,000 tipping bucket measurements of discharge from the five snow lysimeters. Snowmelt at snow lysimeter Open-104 started about day 106 (Fig. 2). Snowmelt the first 15 days or so was episodic and at low enough rates that there was no measured discharge after collecting enough water for chemical analyses. Starting on about day 135, snowmelt discharge showed a diurnal pattern typical of the Colorado Rockies, with a steep rising curve near noon and then a pronounced recession limb starting in the late afternoon as air temperature decreased below the freezing point and snowmelt stopped for the day (e.g. Williams et al. 1996c).

The $\delta^{18}O$ values in snowmelt ranged widely over time, with a consistent temporal pattern. Initial $\delta^{18}O$ values were near −24‰, compared to the average snowpack value at maximum accumulation (Table 1) of about −21‰. Values gradually become enriched with time, reaching −17.8‰ towards the end of melt. This pattern of more depleted $\delta^{18}O$ at the initiation of melt relative to bulk snowpack values, then enrichment with time, is consistent with previous reports from the alpine areas of Niwot Ridge. Both Taylor et al. (2002) and Liu et al. (2004) report the same magnitude of $\delta^{18}O$ values and same temporal pattern in the $\delta^{18}O$ values of snowmelt in the alpine area of Niwot Ridge and attribute this phenomenon to fractionation as meltwater generated at the top of the snowpack infiltrates to the bottom of the snowpack and into snowmelt lysimeters.

Nitrate values in snowmelt also varied consistently over time, highest at the initial stages of snowmelt and then decreasing as snowmelt progressed (Fig. 2). Maximum concentrations of nitrate of 34 μeq L^{-1} for snowpack lysimeter Open-104 occurred during the initial phase of snowmelt and then decreased with time. Concentrations of nitrate collected from multiple samples within a 24-h period were highest for samples collected overnight and lowest for samples collected in the early afternoon, an inverse relationship with discharge (e.g. Bales et al. 1993; Williams et al. 1996c). Concentrations of nitrate in meltwater generally decreased with time, reaching a low value of about 2 μeq L^{-1} near the end of snowmelt. The other major cations and anions behaved in a similar

Table 1 Chemical content of snow at maximum snow accumulation (μeq L^{-1} except DON in μmoles L^{-1} and DOC in mg L^{-1}) from Soddie site at Niwot Ridge compared to representative areas of the Northern Hemisphere (adapted from Edwards et al. 2007)

Reference	Location	H^+	NH_4^+	Ca^{2+}	Mg^+	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	DON	DOC	$\delta^{18}O$
This study, 2006	NWT	1.86	3.30	35.0	5.70	2.10	0.80	1.47	10.9	6.30	6.24	1.50	−21.92
This study, 2007	NWT	5.50	5.59	10.2	2.63	1.87	6.47	1.83	12.1	7.72	1.40	1.00	−21.05
Nickus et al. (1998)	Alps	5.5	0.7	0.5	0.2	0.2	0.0	0.6	2.8	1.7	NA	NA	NA
Kuhn (2001)	Alps	13.1	5.9	18.5	2.9	3.6	0.4	3.5	9.8	4.5	NA	NA	NA
Kang et al. (2004)	Himalayas	NA	0.0	0.1	0.1	0.0	0.0	0.7	0.2	0.5	NA	NA	NA
Kang et al. (2004)	China	2.9	1.7	6.1	0.4	1.7	0.4	1.7	5.7	1.6	NA	NA	NA
Barbaris and Betterton (1996)	Arizona	12.0	21.2	6.3	2.3	4.6	2.2	7.9	11.8	18.1	NA	NA	NA

Table 2 Chemical loading of snow (meq m^{-2} except DON in mmoles m^{-2} and DOC in g m^{-2}) at maximum snow accumulation at the Niwot Ridge Soddie site from 2002 to 2007

Year	SWE	H^+	NH_4^+	Ca^{2+}	Mg^+	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	DON	DOC
2002	0.54	4.82	4.29	7.52	1.67	1.11	0.95	1.10	11.97	4.31	1.30	0.18
2003	1.10	5.26	5.04	12.11	2.32	1.58	2.02	1.64	14.31	8.70	4.56	0.76
2004	0.77	3.13	8.90	5.49	1.01	0.94	0.94	1.41	9.33	4.66	2.76	0.50
2005	0.92	4.72	6.12	7.57	1.83	1.68	1.69	1.01	9.94	6.97	3.26	0.87
2006	1.01	1.88	3.34	35.41	5.77	2.12	0.81	1.48	11.05	6.37	6.31	1.52
2007	1.07	5.87	5.96	10.86	2.81	2.00	6.90	1.95	12.92	8.24	1.49	1.07
Mean	0.90	4.28	5.61	13.16	2.57	1.57	2.22	1.43	11.59	6.54	3.28	0.82
SD	0.21	1.42	2.14	12.42	1.87	0.47	0.54	0.27	1.96	1.79	1.89	0.50
CV	0.24	0.33	0.38	0.94	0.73	0.30	0.24	0.19	0.17	0.27	0.58	0.61

Snow water equivalence (SWE) in m

SD standard deviation; *CV* coefficient of variation

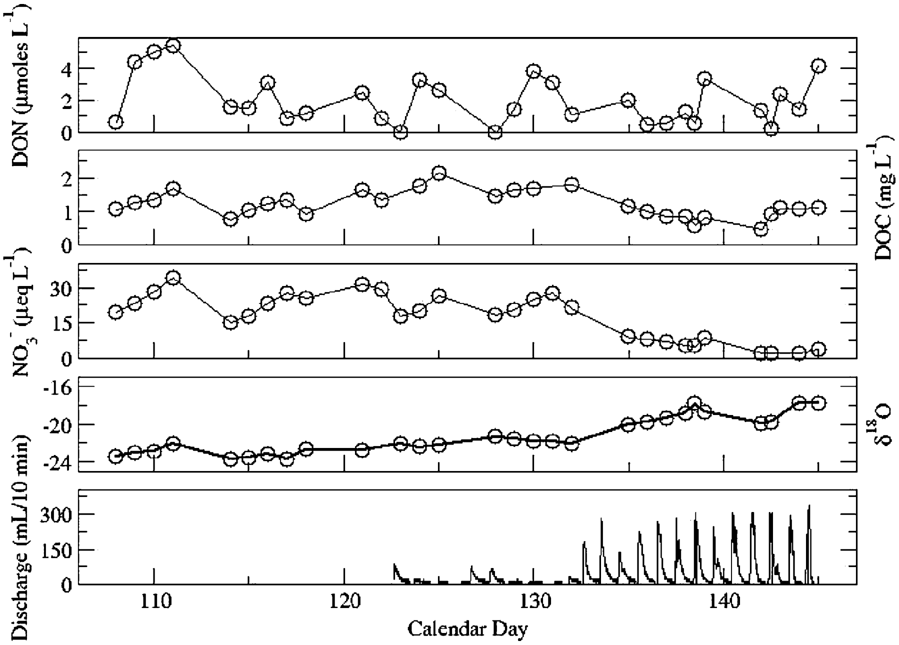

Fig. 2 Discharge, isotopic content and concentrations of selected solutes in snowpack meltwater before contact with the ground, Soddie lysimeter Open-104

fashion with time (data not shown). In contrast to $\delta^{18}O$ and nitrate, DOC and DON concentrations were highly variable with time and showed no consistent pattern with time (Fig. 2).

Dissolved inorganic solutes thus appear to be released from storage in the seasonal snowpack in the form of an ionic pulse. Here we evaluate the magnitude of a possible ionic pulse in snow lysimeter Open-104 by dividing the ionic concentration of a solute in meltwater at each time step (C_i) by the VWM concentration of that solute in the snowpack at the initiation of snowmelt (C_a); results are presented as a fraction of total snowmelt recorded by lysimeter Open-104 (Fig. 3). Both calcium and nitrate were concentrated by a factor of approximately four at the initiation of snowmelt, with the concentration factor declining below one as melt progressed. The concentration factor for the two solutes was similar, despite the fact that the concentration of calcium in the snowpack at maximum accumulation (C_a) in 2006 of 35 µeq L^{-1} was about 3 times greater than the 11 µeq L^{-1} of nitrate (Table 1). A simple regression analysis shows that concentrations of calcium and nitrate in meltwater before contact with the ground tracked each other over time ($R^2 = 0.88$, $p < 0.001$). For both nitrate and calcium, the concentration factor decreased below one when about 20% of snowmelt had occurred. The other major inorganic solutes were also released from storage in the seasonal snowpack in the form of an ionic pulse. Results from the other lysimeters are similar. In contrast to dissolved inorganic solutes, the organic solutes showed little consistent pattern over time. For this pattern to occur there must be additional sources of dissolved organic nutrients added to the snowpack after the initiation of snowmelt, as shown by Williams et al. (2001) for the alpine area of Niwot Ridge.

We evaluated the spatial variation in the release of solutes from storage in a seasonal snowpack in open versus forested areas by plotting concentration versus time for the five snowpack lysimeters (Fig. 4). Maximum snow depth in the clearing represented by snowpack lysimeters Open-104 and Open-105 was about 2 m. Water began flowing in both snow lysimeters on about day 106. In contrast, maximum snow depth near the leeward edge of the forest was closer to 5 m. All three snow lysimeters at the forest edge began flowing on about day 142, nearly 5 weeks after the lysimeters in the clearing. The range in δ^{18}O values of about −24 to −17‰ was similar among all five lysimeters. Nitrate values were similar among the five lysimeters as well. However, maximum concentrations of DOC and DON were much greater in meltwater collected at the three lysimeters near the forest edge compared to the two lysimeters in the clearing. Maximum DOC concentrations from the three snow lysimeters at the forest edge ranged from 12 to 25 mg L^{-1}, several-fold greater than the 2–7 mg L^{-1} from the snow lysimeters in the clearing. Similarly, maximum concentrations of DON near the forest edge of 12–20 μmoles L^{-1} were substantially higher than the 5–6 μmoles L^{-1} in snowpack meltwater from the clearing. Thus, the snowpack under the forest canopy appears to release a higher amount of dissolved organic matter to underlying soils compared to the snowpack located in a nearby open area.

However, note that the initial δ^{18}O values from snow lysimeters near the forest edge were about −16‰ (Fig. 4). Values then became more depleted and similar to the snow lysimeters in the open area at about −24‰, then became more enriched with time similar to the open areas. It is unclear why the initial δ^{18}O values from the forested area were enriched relative to later values. This process deserves more study.

Grab samples of stream water for chemical, nutrient, and oxygen isotopic content began on day 142 (the same day as when snowmelt was first recorded from snow lysimeters located at the forest

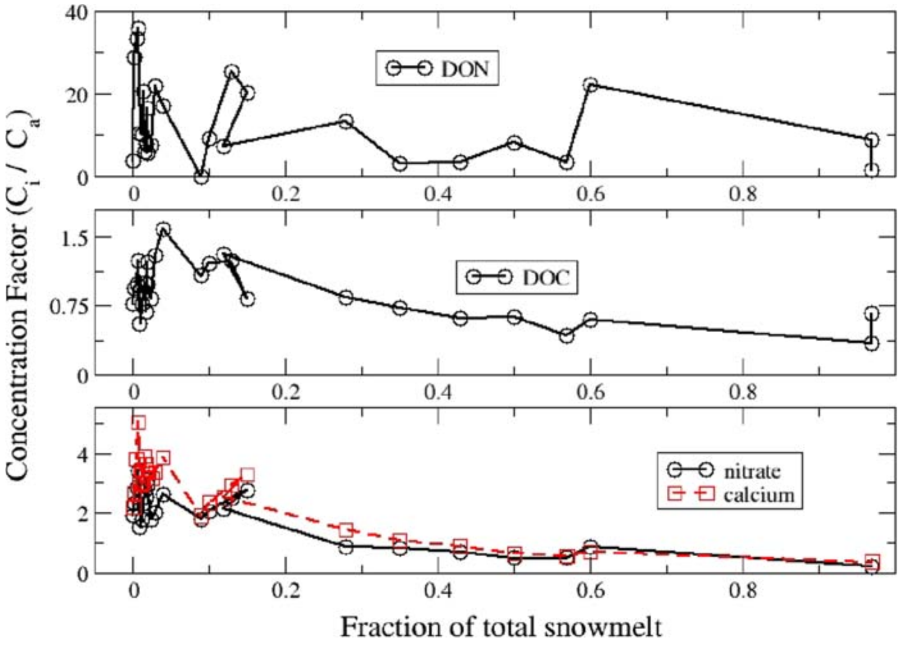

Fig. 3 The magnitude of the ionic pulse was evaluated for snow lysimeter Open-104 by dividing the ionic concentration of a solute in meltwater at each time step (C_i) by the VWM concentration of that solute in the snowpack at the initiation of snowmelt (C_a); results are presented as a fraction of total snowmelt recorded by the tipping bucket at the same time step

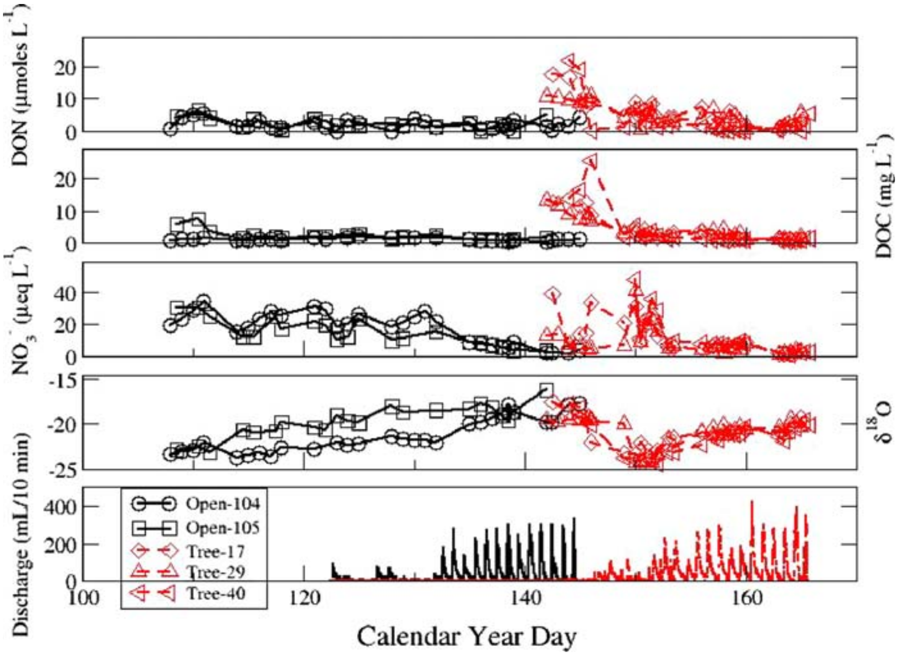

Fig. 4 Spatial variation in the release of solutes stored in the seasonal snowpack, comparing the solute content of open areas (snow lysimeters Open-104 and Open-105) to a forested area (snow lysimeters tree-17, tree-29, and tree-40)

edge) and continued at a frequency of about twice-weekly until flow ceased on about day 209, a total of 12 samples (Fig. 5). As with the δ^{18}O of snowmelt, the values of δ^{18}O in stream waters were most depleted at the initiation of sample collection and became more enriched with time. The δ^{18}O values were −19.4‰ on day 142 and then gradually became more enriched by about 3‰ to −16.4 on day 208. Calcium concentrations were around 50 μeq L^{-1} and showed little variation with time. Nitrate concentrations collected from the stream were always <1 μeq L^{-1} and often below the detection limit of 0.04 μeq L^{-1}. Similarly, there was little to no ammonium in surface waters (data not shown). Thus, DIN concentrations in surface water were negligible and much less than in either snow or snowpack meltwater before contact with the ground. The dominant form of nitrogen in surface waters was DON, with DON concentrations ranging from 4 to 9 μmoles L^{-1}. Concentrations of DOC were also much higher in stream waters than snow, ranging from 3 to 7 mg L^{-1}.

The soil solution was first sampled on day 157 when the area became snow free. After calendar day 208, water was only collected following summer rain events; there were a total of 6 days when water was collected from the soil lysimeters (Fig. 5). Because of the low volume of water collected from the soil lysimeters, we bulked the samples collected on each day. The δ^{18}O values were near −17‰ and then decreased over time to about −10‰, always less than the values in snowpack meltwater or surface waters. Calcium concentrations were about 100 μeq L^{-1}, increasing to 220 μeq L^{-1} on the last sampling date in early September. Nitrate concentrations in the soil solution were always <5 μeq L^{-1}, except for a value of near 11 μeq L^{-1} on day 187. Ammonium concentrations were always at or below detection limits. The concentrations of DOC in the zero-tension soil lysimeters ranged from 10 to 40 mg L^{-1}, much greater than in the snow, snowpack meltwater, or surface waters. The amount of DON in the soil solution was also elevated relative to other water sources, ranging from 20 to 50 μmoles L^{-1}. In contrast to the snowpack, there was little DIN in the soil solution and the primary source of nitrogen was DON.

In an effort to understand source waters and flowpaths that might contribute to stream flow, we plot δ^{18}O versus sodium of stream waters along with potential end-members (Fig. 6). The binary plot of δ^{18}O versus sodium shows that stream waters generally plot on a mixing line between the snowpack values and baseflow. The snowpack value is from the sample collected at maximum accumulation (Table 1). Here we use the last sample collected at

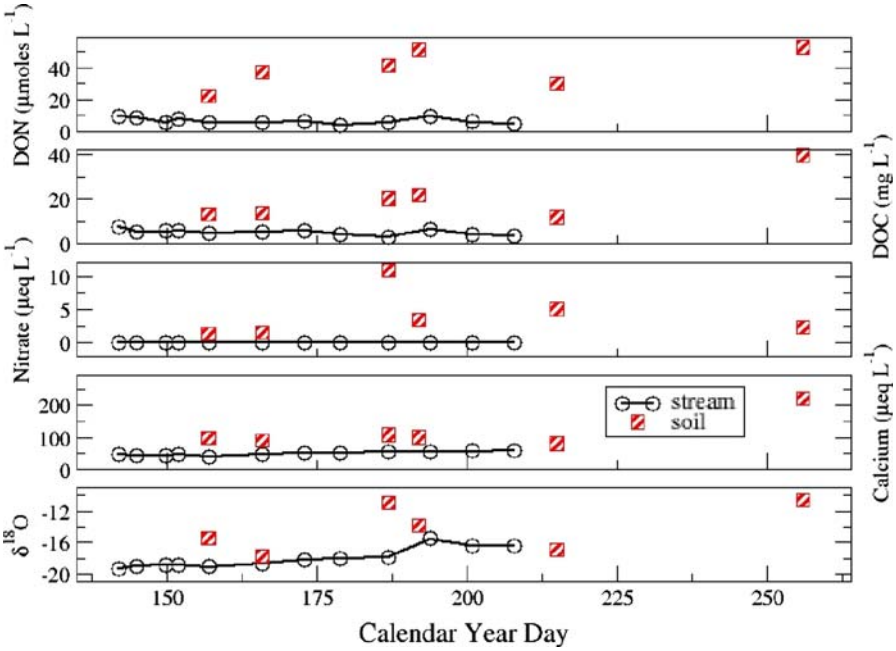

Fig. 5 Chemical, nutrient, and isotopic content of grab samples from the headwaters of Como Creek and from zero-tension soil lysimeters located adjacent to the array of snow lysimeters at the Soddie site on Niwot Ridge

the stream as representing baseflow, following the protocols developed by Liu et al. (2004) and Williams et al. (2006) for hydrologic mixing models in the alpine area of the NWT LTER site. Sodium concentrations in rainfall are relatively low; more than 20 years of summer precipitation measurements at the NADP site at the Saddle (1985–2007) show a median sodium concentration of 1.52 µeq L^{-1}. Splits of summer rain events collected at the NADP saddle site and analyzed for stable water isotopes had a mean δ^{18}O value of −5.72‰. Mean values and the standard deviation of δ^{18}O and sodium from snowmelt samples in 2006 ($n = 132$) plot on the same mixing line as snowpack values and baseflow. Sodium concentrations from the soil solution ($n = 6$) are similar to sodium concentrations in the stream, while δ^{18}O values for the soil solution are pulled towards more enriched rain values compared to snow and snowmelt. For example, the soil solution value from day 256 shows that the soil solution has about the same value of sodium as stream waters, but the δ^{18}O value in the soil solution of about −10‰ is much more enriched than stream waters. Thus, it appears that stream waters plot along a two component mixing line between snow and baseflow; however, later values are pulled somewhat toward the rain endmember by summer rain events.

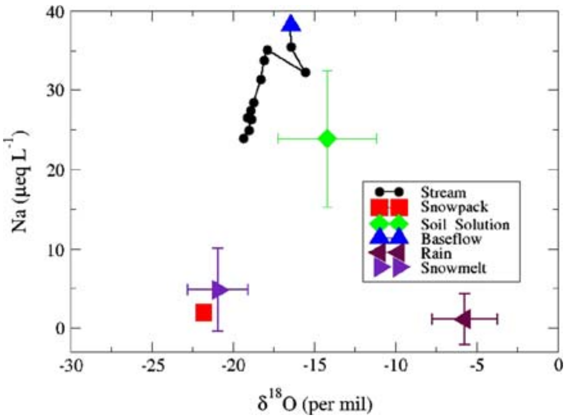

Fig. 6 A binary plot of δ^{18}O and sodium for surface waters from the headwaters of Como Creek in 2006, along with potential end-members (snow, snowmelt before contact with the ground, soil solution, summer rain, and baseflow). Means and standard deviation are plotted for snowmelt, soil solution, and summer rain. Snowpack values are from maximum accumulation

Based on the binary diagram, a simple two-component mixing model was used to characterize "reacted" and "unreacted" stream water and "new" and "old" stream water (Fig. 7). The two-component hydrograph separation followed the procedure of Sueker et al. (2000) and Liu et al. (2004), who used concentrations of sodium in snow and base flow for their flow path separation in stream waters of the Colorado Rocky Mountains. The mixing model indicates that on average reacted water provided 79% of the water in Como Creek and unreacted water contributed 21%. The contribution of reacted water to stream flow increased with time. New water was parameterized as the bulk δ^{18}O of the index snowpit (Table 1), following the protocol of Sueker et al. (2000). Old water was parameterized using the last soil solution collected in September, where δ^{18}O was −10 ‰. Results show that on average 73% of streamflow was new water and 27% was old water. The new water contribution was highest with the initial collection of water samples and decreased with time.

The binary diagram of δ^{18}O values and sodium concentrations suggests that streamflow samples are well-bounded by three potential end-members: snow (or snowmelt), baseflow, and rain (Fig. 6). We also ran a three-component mixing model using δ^{18}O and sodium values with these three end-members to further understand source waters and flowpaths that might contribute to water in Como Creek. Results show that stream waters were generally a simple mixture of snowmelt and baseflow, except near day 200 when rain contributed about 11% (data not shown).

Discussion

The concentration of inorganic N stored in the seasonal snowpack at the Soddie site is on the upper end of values reported for the northern hemisphere (Table 1). Concentrations of nitrate in 2006 and 2007 of around 11 µeq L^{-1} at NWT are greater than most areas of the Alps in Europe (Nickus et al. (1998) and similar to the value of about 10 µeq L^{-1} reported by Kuhn (2001) for an area in eastern Alps that is impacted by local air pollution. These nitrate values at NWT are much greater than the 0.2 µeq L^{-1} that Kang et al. (2004) report for the Himalaya range and about double the 5.7 µeq L^{-1} that they report for mountains in China. Barbaris and Betterton (1996) (Table 1) report nitrate values of 11.8 µeq L^{-1} for an area in Arizona near the Grand Canyon, very similar to our values in both 2006 and 2007.

Similarly, Rohrbough et al. (2003) report nitrate values of about 10 µeq L^{-1} from an alpine snowpack in Wyoming. Ammonium values at NWT are generally on the high end of reports from other seasonally snow-covered areas of the northern hemisphere (Table 1). These nitrate and ammonium values at the Soddie site are similar to those reported by Williams et al. (1996c, 2001) for the nearby Saddle site, an alpine area on Niwot Ridge about 1 km from

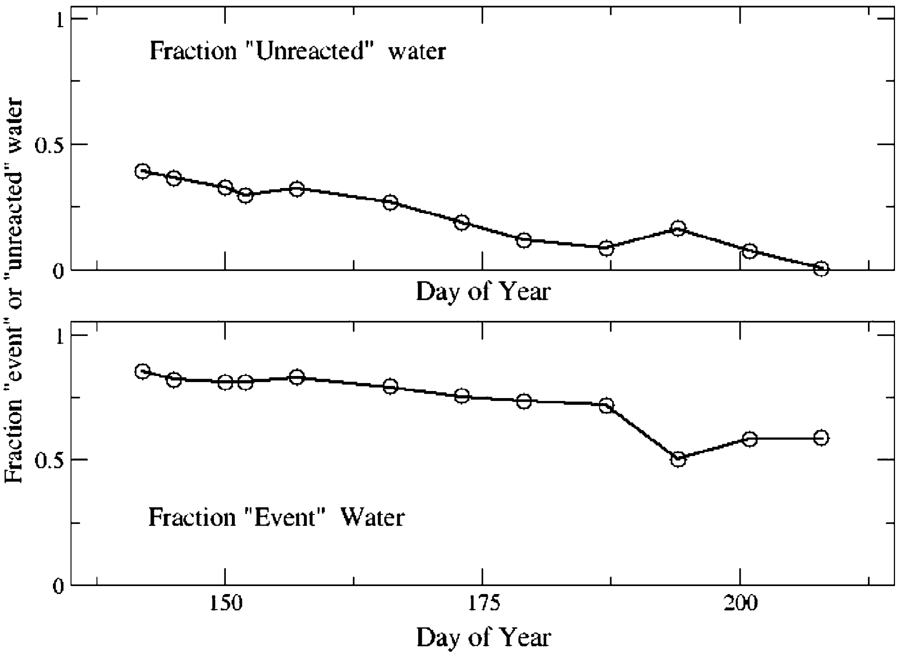

Fig. 7 Results of a two-component hydrologic mixing model applied to the headwaters of Como Creek. The *upper panel* is the fraction of "unreacted" water; "reacted" water that has undergone biological or geochemical reactions in the subsurface is the inverse. The *lower panel* is the fraction of stream flow that is "event" water or this year's snowmelt; the inverse is "old" water

the Soddie site. Thus, there does not appear to be a significant difference in the concentration of DIN between alpine sites and treeline sites on Niwot Ridge. This lack of spatial variation in the concentration of DIN and other solutes in snow is consistent with other studies at Niwot Ridge (Williams et al. 2001), the Sierra Nevada of California (Williams and Melack 1991b), and the Tien Shan of China (Williams et al. 1992). Evaluated levels of DIN in snowpacks of the western US appear to be elevated when compared to European and Asian snowpacks.

An ongoing question in snow-covered areas is whether the inorganic N deposited to the snowpack undergoes transformations, including immobilization and/or internal production. For example, photochemical reaction and product studies have shown that NO and NO_2 in the interstitial pore space of a snowpack can react with oxidants in the quasi-liquid layer or interstitial air to yield NO_2^- and NO_3^- (Jacobi and Hilker 2007). This source of internal production of nitrate could thus elevate concentrations of nitrate above that produced by wet deposition alone. In contrast, Rohrbough et al. (2003) suggest that DIN may be lost from the snowpack by volatilization processes. One method of evaluating the role of such transformations is to compare the nitrate concentration measured in the seasonal snowpack to alternate sources of nitrate. The VWM concentrations of nitrate for the winter and spring seasons at the Saddle NADP site were 14 μeq L^{-1} in 2006 and 16.5 μeq L^{-1} in 2007; almost exactly the same for the NADP site at C1. Thus, the nitrate concentrations in the seasonal snowpack were similar to or slightly lower than that recorded in wetfall for the same time period by nearby NADP stations, suggesting little loss or gain of nitrate from internal transformations or from dry deposition. These results are consistent with those reported by Williams et al. (1996a) for an alpine site at NWT near the Saddle NADP site. They evaluated potential transformations of DIN within a seasonal snowpack by adding isotopically labeled ammonium and nitrate to separate snowpack plots and reported no evidence for nitrification of ammonium or reduction of nitrate.

The high concentration of calcium in the snowpack for 2006 is noteworthy. The 35 μeq L^{-1} that we report for 2006 is much higher than the 10 μeq L^{-1} in 2007. The 35 μeq L^{-1} of calcium are also twice as high as the next highest report of calcium concentrations in seasonal snowpacks from the northern hemisphere in a comprehensive review by Edwards et al. (2007) (Table 1). The VWM seasonal concentrations of calcium in winter and spring of 2006 and 2007 for both NADP sites were always lower than 20 μeq L^{-1}. Thus, there appears to be an additional source of calcium to the snowpack in 2006 that was not recorded by the NADP wet deposition collector. Clow et al. (1997) used strontium isotopes to show that aeolian deposition of calcite contributed about 25% of the calcium content in outflow of the nearby and high-elevation Loch Vale catchment. Neff et al. (2008) have recently shown that mineral aerosols from dust are an important influence that can result in a more than fivefold increase in inputs of calcium to high-elevation ecosystems, with implications for surface-water alkalinity, aquatic productivity and terrestrial nutrient cycling. And much of this aeolian deposition occurs as dust on snow in high-elevation sites (Ley et al. 2004; Painter et al. 2007). In late February 2006, an unusual "red snow" event was reported by Losleben et al. (2006) that deposited a layer of red dust on the seasonal snowpack throughout the Front Range of Colorado. This "red snow" event appears analogous to episodic "Saharan desert deposition" to seasonal snowpacks in the Alps (Schwikowski et al. 1995). This "red snow" event may be responsible for the elevated calcium contents for the seasonal snowpack in 2006. The elevated concentrations of calcium that we report for the seasonal snowpack in 2006 are consistent with the soil analysis that suggests aeolian deposition at the Soddie site may be an important contributor to soil formation. The role that aeolian deposition may play in the biogeochemistry of seasonally snow-covered areas warrants more research.

The elevated concentrations of DOC and DON in snowpack meltwater towards the end of snowmelt compared to inorganic solutes (Figs. 2, 3, 4) are consistent with the snowpack acting as a trap or filter for organic debris transported by wind from nearby areas that are becoming snow-free. Williams et al. (2000) report that late-lying snowpacks in the Green Lakes valley are characterized by pockets of organic matter located on the snow surface at spatial distances of centimeter to meter. And Williams et al. (2001) have shown that in the alpine area of Niwot Ridge late-lying snowpacks capture organic debris transported by wind from nearby areas, resulting in the release of organic solutes in snowpack meltwater while concentrations of inorganic solutes are decreasing. At the Soddie site the ribbon forest appears to result in large spatial variations in the release of organic solutes from the seasonal snowpack (Fig. 4). Snow near the forest canopy may receive higher amounts of organic debris compared to open areas, resulting in higher concentrations of dissolved organic matter in meltwater. An outstanding question is whether the quality of the dissolved organic matter is labile or recalcitrant (e.g. Hood et al. 2003a, b).

The large amount of DIN stored in the seasonal snowpack (Table 2), together with evidence that N within the snow is preferentially eluted in the first portion of melt without undergoing significant transformations or immobilization in the snowpack (Fig. 3), suggest that much of the N-cycling in high-elevation catchments occurs during the snow-covered season. The recovery of isotopically labelled N in the soil under the snow cover of alpine areas (Williams et al. 1996a; Bilbrough et al. 2000), together with direct evidence of microbial N immobilization within the soil under seasonal snowpacks (Brooks and Williams 1999), suggests that heterotrophic immobilization of N in soil is an important control on the retention of N in the terrestrial environment. The amount of heterotrophic immobilization in turn, appears to be controlled by the development of the seasonal snow cover. Consistent and deep snowpacks insulate the soil from the cold air temperatures above the snow surface and allow soils to thaw before snowmelt (Sommerfeld et al. 1991, 1993; Brooks et al. 1996). The timing of snowpack development appears to determine how severely soils may freeze before being insulated by snow, and how long soils remain thawed before the initiation of snowmelt (Williams et al. 1998).

The two most important factors controlling the biogeochemical environment under high-elevation snowpacks appears to be the severity of soil frost and the duration of thawed soil (Brooks and Williams 1999). Freeze–thaw events are known to release labile, readily utilizable, organic carbon compounds that promote heterotrophic microbial activity (e.g. Schimel and Clein 1996; Lipson et al. 2000; Monson et al. 2006). Long-duration, early developing snowpacks may not result in a pulse of available carbon substrate (Brooks et al. 1997), but allow soil to remain thawed throughout the snow-covered season (Sommerfeld et al. 1993, 1996) providing an environment where lower levels of heterotrophic activity may occur throughout the snow covered season.

The observed control of snow cover on microbial activity appears to have two components. Insulation provided by snow cover with low-thermal conductivity allows soils to be warmer than the atmosphere and makes free water available which can support heterotrophic activity (Brooks et al. 1996). The second component is control over the amount of substrate available for heterotrophic activity in subnivial soils by the timing of snow cover early in the winter season. In the absence of early season snow cover, as soils freeze there is lysis of both plant and microbial cells. When soil subsequently thaws, either under winter snow cover or during melt, this freeze–thaw lysis of cells increases available, labile carbon sources for heterotrophic activity (Brooks et al. 1997, 1998). Thus, plant and microbial activity under the snowpack may be a crucial contribution to season-long nutrient demand, as well as facilitating rapid plant growth and development once the snow has melted (Bilbrough et al. 2000).

Much of the inorganic N released from the snowpack at the Soddie site appears to infiltrate the underlying substrate and undergo biogeochemical modifications. There was little DIN in the soil solution at any time (Fig. 5). Dissolved organic nitrogen was the dominant form of nitrogen in the soil solution, with concentrations as high as 50 μmoles L^{-1}. Concurrent with the elevated concentrations of DON in the soil solution were concentrations of DOC on the order of 20–40 mg L^{-1}. Thus, this subalpine soil appears to assimilate and convert inorganic N released from storage in the seasonal snowpack into organic matter.

Concentrations of inorganic N in stream waters are consistent with the retention of DIN in these high-elevation soils. The lack of nitrate in surface waters at this treeline site is in sharp contrast to other high-elevation catchments in the Colorado Front Range (Williams et al. 1996c; Williams and Tonnessen 2000; Baron 2006) and to mountain catchments in north-eastern US (e.g. Rascher et al. 1987). Even though the storage and release of DIN from the seasonal snowpack each year was on the order of 2 kg-N ha^{-1}, essentially none of the DIN released from storage in the seasonal snowpack reached the nearby stream system. In contrast to several alpine watersheds in the Colorado Front Range where export of DIN in annual wet deposition at the catchment scale is about 70%

(e.g. Brooks et al. 1999; Williams et al. 2001), here retention of DIN is near 100%. Concentrations and fluxes of solutes from snow and forest floor during snowmelt in the west-central Adirondack region of New York showed that mineralization of nitrogen, followed by nitrification in the forest floor under the winter snowpack may be an important process contributing to elevated concentrations of nitrate in streams during the snowmelt period (Rascher et al. 1987). In contrast to alpine areas of the Colorado Front Range and mountain areas of NE US, this high-elevation, subalpine headwater system just below treeline may still be N-limited.

The main reason that this area at treeline is still N-limited may be that much of the snowmelt infiltrates into well-developed soils. There appears to be little difference in either concentrations or loading of DIN in the seasonal snowpack at this treeline site compared to the higher-elevation alpine areas of Green Lakes Valley. The main difference between the two sites is geomorphic. Sueker et al. (2000) used hydrologic mixing models in six catchments of the Colorado Front Range and report that areas with old debris were correlated with contributions from pre-event, reacted, and subsurface components, indicating that the debris provides storage capacity that delays flow, which increases residence times and sodium concentrations. Event water was correlated with steeper slopes, indicating that snowmelt is delivered rapidly to surface flow in high-gradient basins. Our mixing models are consistent with stream waters at the headwaters of Como Creek consisting primarily of “new” or “event” water that has infiltrated into the local subsurface environment and “reacted” with the subsurface environment. Thus, stream flow at the headwaters of Como Creek is primarily this year’s snowmelt runoff. However, the snowmelt has infiltrated into the subsurface environment, where DIN is assimilated and DON and DOC from the subsurface environment are transported to surface waters.

Conclusions

The concentration of inorganic N stored in the seasonal snowpack at the Soddie site of about 11 μeq L^{-1} is on the upper end of values reported for the northern hemisphere when compared to most areas of the Alps, Himalayas, and Tien Shan mountain ranges, but consistent with other reports of snowpacks in the Rocky Mountains. The storage of inorganic N in the snowpack at maximum accumulation averaged about 17 meq m^{-2}, or 170 eq ha^{-1} (on the order of 2 kg-N ha^{-1}). Solutes were released from storage in the form of an ionic pulse, with a maximum concentration factor of about four. The large proportion of annual N deposition stored in the seasonal snowpack, together with evidence that N within the snow is preferentially eluted in the first portion of melt without undergoing significant transformations or immobilization, suggest that much of the N-cycling in high-elevation catchments near treeline occurs during the snow-covered season. This subalpine soil appears to assimilate and convert inorganic N released from storage in the seasonal snowpack into organic matter. Stream flow at the headwaters of Como Creek is primarily this year’s snowmelt runoff. However, the snowmelt has infiltrated into the subsurface environment, where DIN is assimilated and DON and DOC from the subsurface environment are transported to surface waters. Thus, in contrast to nearby alpine areas, this subalpine site at treeline is still N-limited.

Acknowledgments Support for this research came from a National Science Foundation grant to the Niwot Ridge long-term ecological research program (Award DEB-0423662). Logistical support was provided by the Institute of Arctic and Alpine’s Mountain Research Station. Snowpit sampling was conducted in large part by undergraduate interns in Snow Hydrology (Geography 3912) under direction of the Niwot Ridge LTER field staff.

References

Bales RC, Davis RE, Williams MW (1993) Tracer release in melting snow: diurnal and seasonal patterns. Hydrol Process 7:389–401. doi:10.1002/hyp.3360070405

Barbaris B, Betterton EA (1996) Initial snow chemistry survey of the Mogollon Rim in Arizona. Atmos Environ 30:3093–3103. doi:10.1016/1352-2310(95)00293-6

Barbour MG, Billings WD (2000) North American terrestrial vegetation, 2nd edn. Cambridge University Press, Cambridge, pp 1–694

Baron JS (2006) Hindcasting nitrogen deposition to determine an ecological critical load. Ecol Appl 16(2):433. doi:10.1890/1051-0761(2006)016[0433:HNDTDA]2.0.CO;2

Bilbrough CJ, Welker JM, Bowman WD (2000) Early spring nitrogen uptake by snow-covered plants: a comparison of arctic and alpine plant function under the snowpack. Arct Antarct Alp Res 31:191–195

Billings WD (1969) Vegetational pattern near alpine timberline as affected by fire-snowdrift interactions. Vegetatio 19:192–207. doi:10.1007/BF00259010

Brooks PD, Williams MW (1999) Snowpack controls on N cycling and export in seasonally snow-covered catchments. Hydrol Process 13:2177–2190. doi:10.1002/(SICI)1099-1085(199910)13:14/15<2177::AID-HYP850>3.0.CO;2-V

Brooks PD, Williams MW, Schmidt SK (1996) Microbial activity under alpine snowpacks, Niwot Ridge, Colorado. Biogeochemistry 32:93–113. doi:10.1007/BF00000354

Brooks PD, Schmidt SK, Williams MW (1997) Winter production of CO2 and N2O from alpine tundra; environmental controls and relationship to inter-system C and N fluxes. Oecologia 110:403–413

Brooks PD, Williams MW, Schmidt SK (1998) Inorganic nitrogen and microbial biomass dynamics before and during spring snowmelt. Biogeochemistry 43:1–15. doi:10.1023/A:1005947511910

Brooks PD, Campbell DH, Tonnessen KA, Heuer K (1999) Climate induced variability in surface water NO3-concentrations in headwater catchments. Hydrol Process 13:2191–2201. doi:10.1002/(SICI)1099-1085(199910)13:14/15<2191::AID-HYP849>3.0.CO;2-L

Buckner DL (1977) Ribbon forest development and maintenance in the central Rocky Mountains of Colorado. PhD dissertation, University of Colorado, Boulder

Burns DA (2004) The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming, USA—a critical review. Environ Pollut 127(22):257–269. doi:10.1016/S0269-7491(03)00264-1

Caine N (1996) Streamflow patterns in the alpine environment of North Boulder Creek, Colorado Front Range. Z Geomorphol 104:27–42

Clow DW, Mast MA, Bullen TD, Turk JT (1997) 87Sr/86Sr as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado. Water Resour Res 33(6):1335–1351. doi:10.1029/97WR00856

Colbeck SC (1981) A simulation of the enrichment of atmospheric pollutants in snow cover runoff. Water Resour Res 17(5):1383–1388. doi:10.1029/WR017i005p01383

Edwards AC, Scalenghe R, Freppaz M (2007) Changes in the seasonal snow cover of alpine regions and its effect on soil processes: a review. Quat Int 162–163:172–181. doi:10.1016/j.quaint.2006.10.027

Erickson TA (2004) Development and application of geostatistical methods to modeling spatial variation in snowpack properties, Front Range, Colorado. PhD dissertation, Department of Geography, University of Colorado

Erickson TA, Williams MW, Winstral A (2005) Persistence of topographic controls on the spatial distribution of snow depth in rugged mountain terrain, Colorado, USA. Water Resour Res 41(4):W04014. doi:10.1029/2003WR002973

Holtmeier FK (1982) “Ribbon-forest” and “Hecken”, streifenartige Verbreitungsmuster des Baumwuchses an der oberen Waldgrenze in den Rocky Mountains. Erdkunde 36:142–153. doi:10.3112/erdkunde.1982.03.02

Hood E, Williams MW, Caine N (2003a) Landscape controls on organic and inorganic nitrogen leaching across an alpine-subalpine ecotone, Green Lakes Valley, Colorado Front Range. Ecosystems 6:31–45. doi:10.1007/s10021-002-0175-8 (NY, print)

Hood E, McKnight D, Williams MW (2003b) Sources and chemical character of dissolved organic carbon (DOC) across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range, USA. Water Resour Res 39(7):1188. doi:10.1029/2002WR001738

Hooper RP, Shoemaker CA (1986) A comparison of chemical and isotopic hydrograph separation. Water Resour Res 22(10):1444–1454. doi:10.1029/WR022i010p01444

Jacobi HW, Hilker B (2007) A mechanism for the photochemical transformation of nitrate in snow. J Photochem Photobiol A Chem 185(2–3):371–382

Johannessen M, Henriksen A (1978) Chemistry of snow meltwater. Changes in concentration during melting. Water Resour Res 14:615–619. doi:10.1029/WR014i004p00615

Kang S, Mayewski PA, Qin D, Sneed SA, Ren J, Zhang D (2004) Seasonal differences in snow chemistry from the vicinity of Mt. Everest, central Himalayas. Atmos Environ 38:2819–2829. doi:10.1016/j.atmosenv.2004.02.043

Kuhn M (2001) The nutrient cycle through snow and ice, a review. Aquat Sci 63:150–167. doi:1015-1621/01/020150-18

Lepori F, Barbieri A, Ormerod SJ (2003) Causes of episodic acidification in alpine streams. Freshw Biol 48:175–189. doi:10.1046/j.1365-2427.2003.00972.x

Lewis WM Jr, Grant MC (1980) Relationships between snow cover and winter losses of dissolved substances from a mountain watershed. Arct Alp Res 12(1):11–17. doi:10.2307/1550586

Ley R, Williams MW, Schmidt S (2004) Microbial population dynamics in an extreme environment: controlling factors in talus soils at 3750m in the Colorado Rocky Mountains. Biogeochemistry 68(3):297–311. doi:10.1023/B:BIOG.0000031032.58611.d0

Lipson DA, Schmidt SK, Monson RK (2000) Carbon availability and temperature control the post-snowmelt decline in alpine soil microbial biomass. Soil Biol Biochem 32:441–448. doi:10.1016/S0038-0717(99)00068-1

Litaor MI (1993) The influence of soil insterstitial waters on the physicochemistry of major, minor and trace metals in stream waters of the Green Lakes Valley, Front Range, Colorado. Earth Surf Process Landf 18:489–504. doi:10.1002/esp.3290180603

Liu F, Williams MW, Caine N (2004) Source waters and flowpaths in a seasonally snow-covered catchment. Water Resour Res 40:W09401. doi:10.1029/2004WR003076

Losleben M, Williams M, Burns S, Helmig D, Hill K, Zukiweicz L (2006) Red dust layer surface effects on snowpack temperature gradients, subalpine forest, Niwot Ridge, Colorado. Poster presentation in MTNCLIM conference, Consortium for integrated climate research on western mountains

Marks D, Reba M, Pomeroy J, Link T, Winstral A, Flerchinger B, Elder K (2008) Comparing simulated and measured sensible and latent heat fluxes over snow under a pine canopy to improve an energy balance snowmelt model. J Hydrometeorol 9(6):1506–1522. doi:12450.1175/2008JHM874.1

Monson RK, Lipson DL, Burns SP, Turnipseed AA, Delany AC, Williams MW, Schmidt SK (2006) Winter forest soil respiration controlled by climate and microbial community composition. Nature 439(7077):711–714. doi:10.1038/nature04555

Neff JC, Ballantyne AP, Farmer GL, Mahowald NM, Conroy JL, Landry CC, Overpeck JT, Painter TH, Lawrence CR, Reynolds RL (2008) Increasing eolian dust deposition in the western United States linked to human activity. Nat geosci 1:189–195. doi:10.1038/ngeo133

Nickus U, Kuhn M, Novo A, Rossi GC (1998) Major element chemistry in alpine snow along a north–south transect in the eastern Alps. Atmos Environ 32:4053–4060. doi:10.1016/S1352-2310(98)00231-3

Painter TH, Barrett AP, Landry CC, Neff JC, Cassidy MP, Lawrence CR, McBride KE, Farmer GL (2007) Impact of disturbed desert soils on duration of mountain snow cover. Geophys Res Lett 34:L12502. doi:10.1029/2007GL030284

Rascher CM, Driscoll CT, Peters NE (1987) Concentration and flux of solutes from snow and forest floor during snowmelt in the west-central Adirondack region of New York. Biogeochemistry 3:209–224. doi:10.1007/BF02185193

Rohrbough JA, Davis DR, Bales RC (2003) Spatial variability of snow chemistry in an alpine snowpack, southern Wyoming. Water Resour Res 39:1190. doi:10.1029/2003WR002067

Schimel JP, Clein JS (1996) Microbial response to freeze–thaw cycles in tundra and taiga soils. Soil Biol Biochem 28:1061–1066. doi:10.1016/0038-0717(96)00083-1

Schwikowski M, Seibert P, Baltensperger U, Gäggeler HW (1995) A study of an outstanding Saharan dust event at the high-alpine site Jungfraujoch, Switzerland. Atmos Environ 29:1829–1842. doi:10.1016/1352-2310(95)00060-C

Shanley JB, Chalmers A (1999) The effect of frozen soil on snowmelt runoff at Sleepers River, Vermont. Hydrol Process 13:1843–1857. doi:10.1002/(SICI)1099-1085(199909)13:12/13<1843::AID-HYP879>3.0.CO;2-G

Sklash MG, Farvolden RN, Fritz P (1976) A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. Can J Earth Sci 13:271–283

Sommerfeld RA, Musselman RC, Wooldridge GL, Conrad MA (1991) The performance of a simple degree-day estimate of snow accumulation to an alpine watershed. In: Salm B (ed) Snow hydrology and forests in high alpine areas. IAHS Publ. 205, Wallingford, pp 221–228

Sommerfeld RA, Mosier AR, Musselmann RC (1993) CO2, CH4 and N2O flux through a Wyoming snowpack, and implications for global budgets. Nature 361:140–143. doi:10.1038/361140a0

Sommerfeld RA, Massman WJ, Musselman RC (1996) Diffusional flux of CO2 through snow: spatial and temporal variability among alpine-subalpine sites. Global Biogeochem Cycles 10:473–482. doi:10.1029/96GB01610

Stottlemyer R (2001) Processes regulating watershed chemical export during snowmelt, Frasier Experimental Forest, Colorado. J Hydrol (Amst) 245:177–195. doi:10.1016/S0022-1694(01)00352-3

Stottlemyer R, Toczydlowski D (1996) Precipitation, snowpack, stream-water ion chemistry, and flux in a northern Michigan watershed, 1982–1991. Can J Fish Aquat Sci 53:2659–2672. doi:10.1139/cjfas-53-12-2659

Sueker J, Ryan JN, Kendall C, Jarrett RD (2000) Determination of hydrologic pathways during snowmelt for alpine/subalpine basins, Rocky Mountain National Park, Colorado. Water Resour Res 36(1):63–75. doi:10.1029/1999WR900296

Taylor S, Feng X, Williams MW, McNamara J (2002) How isotopic fractionation of snowmelt affects hydrograph separation. Hydrol Process 16:3683–3690. doi:10.1002/hyp.1232

Williams MW, Melack JM (1991a) Precipitation chemistry in and ionic loading to an alpine basin, Sierra Nevada. Water Resour Res 27:1563–1574. doi:10.1029/90WR02773

Williams MW, Melack JM (1991b) Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. Water Resour Res 27:1563–1574. doi:10.1029/90WR02773

Williams MW, Tonnessen KA (2000) Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. Ecol Appl 10(6):1648–1665. doi:10.1890/1051-0761(2000)010[1648:CLFIND]2.0.CO;2

Williams MW, Brown AD, Melack JM (1991) Biochemical modifications of snowmelt runoff in an alpine basin. In: Kienitz G, Milly PCD, Van Genuchten MT, Rosbjerg D, Shuttleworth WJ (eds) Hydrological interactions between atmosphere, soil and vegetation. IAHS-AIHS Publication 204, International Association of Hydrological Sciences, Wallingford, pp 457–465

Williams MW, Tonnessen K, Melack J, Yang DQ (1992) Sources and spatial variation of the solute content of snow in the Tien Shan, PR China. Ann Glaciol 16:25–32

Williams MW, Bales RC, Brown AD, Melack JM (1995) Fluxes and transformations of N in a high-elevation catchment, Sierra Nevada. Biogeochemistry 28:1–31. doi:10.1007/BF02178059

Williams MW, Brooks PD, Mosier A, Tonnessen KA (1996a) Mineral nitrogen transformations in and under seasonal snow in a high-elevation catchment, Rocky Mountains, USA. Water Resour Res 32(10):3161–3175. doi:10.1029/96WR02240

Williams MW, Baron J, Caine N, Sommerfeld R, Sanford R (1996b) Nitrogen saturation in the Colorado Front Range. Environ Sci Technol 30:640–646. doi:10.1021/es950383e

Williams MW, Losleben M, Caine N, Greenland D (1996c) Changes in climate and hydrochemical responses in a high-elevation catchment, Rocky Mountains. Limnol Oceanogr 41(5):939–946

Williams MW, Brooks PD, Seastedt T (1998) Nitrogen and carbon soil dynamics in response to climate change in a high-elevation ecosystem in the Rocky Mountains, USA. Arct Alp Res 30:26–30. doi:10.2307/1551742

Williams MW, Cline D, Hartmann M, Bardsley T (1999) Data for snowmelt model development, calibration, and verification at an alpine site, Colorado Front Range. Water Resour Res 35(10):3205–3209. doi:10.1029/1999WR900088

Williams MW, Rikkers MR, Pfeffer WT (2000) Ice columns and frozen rills in a warm snowpack, Green Lakes Valley, Colorado, USA. Nord Hydrol 31(3):169–186

Williams MW, Hood E, Caine N (2001) The role of organic nitrogen in the nitrogen cycle of a high elevation catchment, Colorado Front Range, USA. Water Resour Res 37(10):2569–2582. doi:10.1029/2001WR000485

Williams MW, Knauf M, Caine N, Liu F, Verplanck P (2006) Geochemistry and source waters of rock glacier outflow, Colorado Front Range. Permafrost Periglac Process 17(1):13–33. doi:10.1002.ppp535