## **KECK GEOLOGY CONSORTIUM**

## PROCEEDINGS OF THE TWENTY-FIFTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

April 2012 Amherst College, Amherst, MA

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## Keck Geology Consortium: Projects 2011-2012 Short Contributions—Front Range, CO Project

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### THE HYDROLOGY AND GEOCHEMISTRY OF TWO SNOWMELT-DOMINATED, ALPINE STREAMS IN THE BOULDER CREEK CRITICAL ZONE OBSERVATORY, FRONT RANGE, COLORADO JAMES N. WINKLER, University of Connecticut

Research Advisor: Will Ouimet

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## THE HYDROLOGY AND GEOCHEMISTRY OF TWO **SNOWMELT-DOMINATED, ALPINE STREAMS IN THE BOULDER CREEK CRITICAL ZONE OBSERVATORY, FRONT RANGE, COLORADO**

JAMES N. WINKLER, University of Connecticut Research Advisor: Will Ouimet

## **INTRODUCTION**

The chemistry of water in streams is influenced by climate and the chemical, physical, and biological processes active within the Critical Zone, which lies between the top of the vegetation canopy to the base of groundwater. In the critical zone, rock, water, air, soil, and biota interact to control the supply of nutrients, nature of habitats, quality of water, and evolution of the land surface. The suite of interactions that control rates of change in the critical zone, and how these relationships differ at multiple spatial and temporal scales, is not well understood (Anderson and Anderson 2010).

Spatial variations of stream solute concentrations reflect the hydrologic inputs and biogeochemical reactions occurring within a watershed (Asano et al 2009; Zimmer, 2010). Concentration patterns in space differ by solute, and are representative of water flowing over discrete geologic or biologic riparian features within the basin (Acuña and Dahm 2007). The Representative Elementary Area (REA) proposes that predictability of an average hydrochemical response for a catchment is controlled by its area (Wood et al 1988). Previous hydrologic research supports this concept; spatial variability of chemical constituents decreases with increasing catchment size as a result of hydrologic mixing (Wood et al 1988, Caine and Thurman, 1990). Convergent or asymptotic relationships of solute concentration as catchment size increases have been shown at the basin-scale and in catchments <0.01 km<sup>2</sup> (Asano et al 2009). Spatial changes in water quality may also reflect temporal changes in the varying contributions of soil and groundwater, biologic activity, or lithology (e.g., Caine and Thurman, 1990). Investigations of spatial variation in stream chemistry helps provide a greater understanding of

the influence of local conditions and the mixing of different hydrologic inputs, and how their importance varies by scale.

Temporal variation in stream solute concentrations reflects changes in flow pathways. In catchments with hydrologic cycles controlled by seasonal inputs, particularly high altitude catchments dominated by snowfall, water quality reflects patterns of snowmelt. Temporal trends of chemical concentrations in Rocky Mountain snowmelt display high values in late winter and spring that sharply decrease during the melting phase, and increase again during the late summer and fall (Caine and Thurman 1990). Small, snowmelt dominated alpine or mountain streams with large changes in discharge are particularly well suited to studying the sources and flow pathways of stream water (Campbell et. al. 1995).

This study examines water quality in two snowmeltdominated alpine sub-catchments with little macrovegetation to: (1) account for spatial variation and temporal trends of chemical constituents; and (2) correlate concentrations to physical and geochemical processes occurring within the Critical Zone.

## SETTING/LOCATION

Martinelli and Saddle are small, alpine catchments that support seasonal, late-lying snowfields situated on the south-facing slope of the lower Green Lakes Valley along Niwot Ridge, within the headwaters of North Boulder Creek (Fig. 1). Measured at the gages, these adjacent basins have nearly identical drainage areas of 0.25 km<sup>2</sup>, and extend from ~3420m to 3560 m elevation. Previous investigations of Martinelli have classified the small catchment as a nivation hollow (Thorn 1976), with thick accumulation of snow

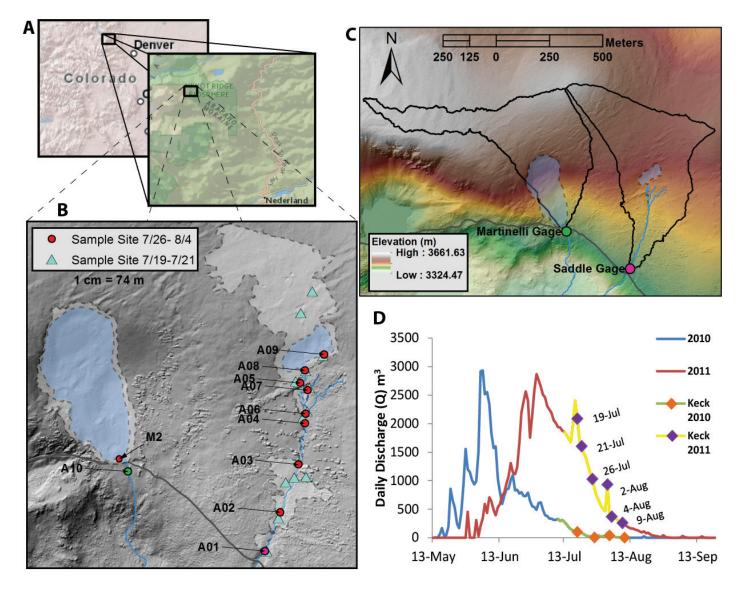


Figure 1. A. Regional location, B. Field area close-up for Martinelli and Saddle sub-catchments, displaying water sampling localities; C. Contributing drainage areas at stream gages derived from watershed modeling of 1-m LiDAR data (black lines represent drainage boundary). D. Comparison of daily discharge (m<sup>3</sup>) values at the Saddle Stream gage during the snowmelt season for the 2010 and 2011 years. Labeled data points (purple) are dates when water samples were collected.

by drifting; the snowfield does not always melt entirely between years (Caine and Thurman 1990). Average annual precipitation measured at a nearby weather station is ~130 cm (NADP meteorological station, CO02). Bedrock geology for both basins consists of intrusive rocks, namely a Precambrian granite, Tertiary quartz monzonite, and Tertiary syenite. These intrusions cross cut metasedimentary rocks (biotite schists and gneisses) of Precambrian age, which extend into the upper Green Lakes Valley, and may lie beneath portions of Martinelli that are mapped as covered by Quaternary alluvium and colluvium (Gable and Madole, 1976; Thorn 1976). The basins lie above the highest extent of recent glaciations in Green Lakes Valley. Soils are rocky, with many fines from dust input, and inactive patterned ground and solifluction lobes suggest that periglacial processes were active in Holocene time (Caine and Thurman 1990).

Seasonal streams that drain Martinelli and Saddle catchments result from melting snow in the warmer months, and are studied by the Niwot Ridge Long Term Ecological Research (NWTLTER) Project. The NWTLTER has collected discharge data at stream gages along Martinelli for 28 years; Nel Caine has gathered data in the same fashion for 18 years from a stream gage on Saddle (Fig. 1B).

## **METHODS**

Most of this study reflects field and lab work from summer and fall 2011. In addition, I add GPS and stream chemistry data from 2010 collected by Reese Lyerly (Keck student, 2010-2011), using similar methods to those discussed here. All data are discussed in the context of long-term water discharge and stream chemistry records collected and managed mainly by Nel Caine (UC Boulder) in association with the NWTLTER. The methods and techniques of NWTLTER's data collection and distribution can be found on their website (Niwot Ridge LTER, 2012).

## FIELD

A total of 42 water samples were collected at study locations between July 19 and August 9, 2011; the sites were visited twice per week during that time. I gathered 13 preliminary samples along the Saddle Stream on the first two sampling days, and chose 10 sites, including the stream gage locations, to collect water and measure discharge for the remainder of the field season. Only one site was continuously sampled for Martinelli, as the basin was predominantly snow covered for most of the field season. Sample localities were spread throughout the Saddle catchment to capture water representative of different drainage areas, varying influence of snowmelt and groundwater/ subsurface inputs, lithology, and wetland areas. Most water samples were hand filtered through a 0.4 micron filter within 24 hours of collection, and stored in a cool, dry location until transferred to the laboratory for further analysis.

I traced the perimeter of snowfields lying within the basins (Fig. 2A), which was performed every day in the field with a Trimble GeoXT GPS. Wetlands (not shown here) also were traced to monitor the degree of soil saturation around the snowfields. Stream discharge was measured with the help of my Keck Colorado colleagues, using a tarp, calibrated bucket, and stopwatch. To increase accuracy, discharge was measured at least three times per site and averaged to obtain values; discharge localities are represented in Figure 2B. Discharge of the Martinelli stream was not measured because flow during the field season was too high to obtain accurate values with our methods. A Garmin Etrex handheld GPS was used to record all sampling sites and locations where discharge was measured.

## LABORATORY

Sample chemistry was measured at the Environmental Analysis Laboratory, Williams College, (Williamstown, MA) after the field season. I used automated colorimetry to measure concentrations of dissolved silica and ammonium using a Technicon AutoAnalyzer. Major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) were analyzed by atomic absorption spectrometry using a Perkin-Elmer AAnalyst 300. Ion chromatography was applied to examine concentrations of major anions ( $Cl^{-}$ ,  $SO_{4}^{2-}$ , and  $NO_{3}^{-}$ ). The acidity of samples was measured with a Fisher Accument pH meter 10 and Orion PerpHect Low Maintenance pH Electrode, which was recalibrated after every 10 samples. The acid neutralizing capacity (ANC), reported in mg/L of bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) was determined by titration, using a Hach digital titrator with 0.16N H<sub>2</sub>SO<sub>4</sub>.

## RESULTS

As the amount, source, and pathways of melting water change within alpine catchments during the year, stream discharge rates and solute concentrations are expected to change. The 2011 water year was well above average for precipitation and had late snowmelt, whereas 2010 was slightly below average. Water year precipitation totals, measured at the University Station (I-1) station, were 126.2 cm for 2011 and 79.5 cm for 2010. Annual flows at the Saddle stream gage for these two years reflect the precipitation pattern (Fig. 1D). The Saddle stream gage recorded a total of 52,230 m<sup>3</sup> over 95 days for 2010, and a total flow of 93,797 m<sup>3</sup> flow for 102 days during 2011. Average annual flow at Saddle from 1999- 2011 was ~60,000 m<sup>3</sup> over 106 days. Average annual flow for Martinelli (1982-2010) is ~77,000 m<sup>3</sup> over 119 days. Surprisingly, though, 1999-2010 saw approximately

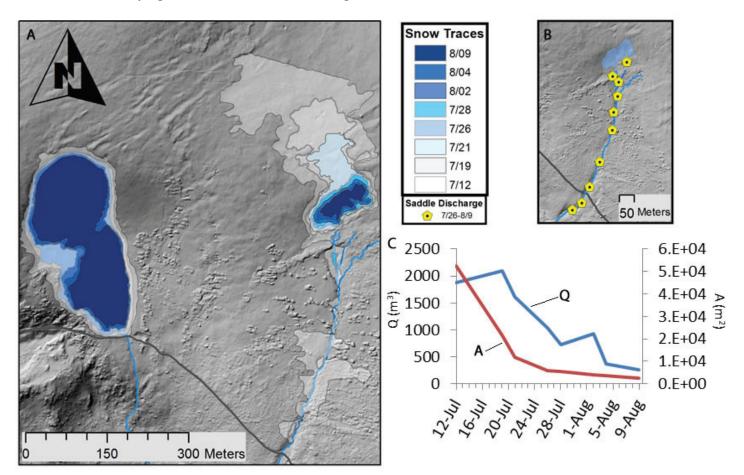


Figure 2. A. Evolution of snowfield areas of both Martinelli and Saddle Snowfields between July 12 and August 9, 2011. B. Discharge measurements sites with snowfield on July 26 shown for reference. C. Comparison of discharge (Q, m<sup>3</sup>) measurements at the stream gage with snowfield surface area  $(A, m^2)$  observed during the 2011 field season.

the same total run-off from these two catchments, with annual totals being within 30% of each other, and split half and half in terms of which catchment had greater runoff each year.

Daily spikes in 2011 Saddle discharge values correlate to precipitation events and warmer temperatures (Fig. 1). Figure 2C shows that as the snowfield area of Saddle decreases over time, so does the total discharge (m<sup>3</sup>). Saddle snowfield decreased by 95% during this time, while the total reduction for Martinelli was 38% (Fig. 2). The persistence of the Martinelli snow highlights its thickness. Peak daily discharges at the Saddle gage (Fig. 1D) were nearly identical in the 2010 and 2011 melting seasons, but occurred at different times.

strength, and display near-neutral pH. For both Martinelli and Saddle, calcium (Ca<sup>+</sup>) is the dominant cation and bicarbonate  $(HCO_3^{-1})$  is the dominant anion. With the exception of ammonium  $(NH_{A}^{+})$  and nitrate  $(NO_3)$  ions, concentrations measured at the gages are approximately 2-3 times greater at Saddle (A01) than at Martinelli (A10). The 2010 concentrations were consistently higher ( $\sim 2x$ ) than all 2011 samples at analogous sample locations.

Variability of concentration with increasing drainage area generally decreases for Saddle stream (Figs. 3A, 3B and Table 1). In particular, cation concentrations (Fig 3A) are less variable with increasing catchment size than are anion concentrations (Fig 3B). The greatest variation in concentration is found between the two uppermost sampling sites in the Saddle subcatchment (A08 & A09). Site A08 sampled water

Overall, water samples (Table 1) are of low ionic

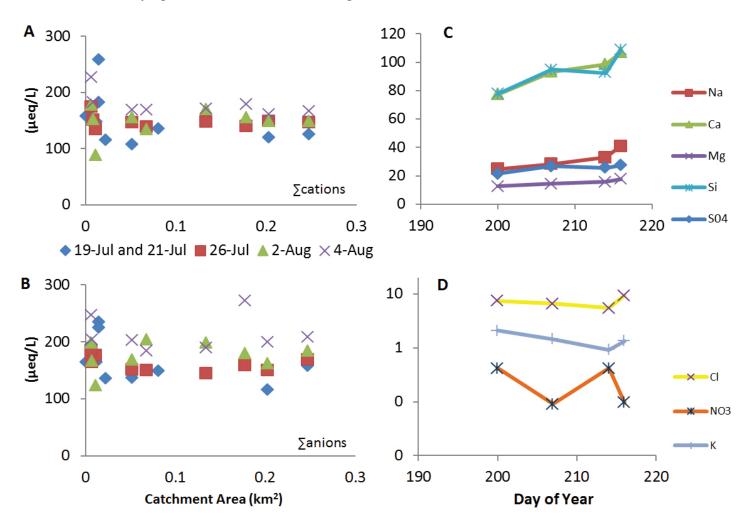


Figure 3. Spatial and temporal changes in solute concentration for Saddle Stream for the 2011 field season. (A)  $\sum$  anions ( $\mu$ eq/L) and contributing catchment area, (B)  $\sum$  cations ( $\mu$ eq/L) and contributing catchment area. (C) Weathering controlled and (D) Biologically controlled Saddle A01 solute concentrations with time for 2011 field season. Note y-axis of 3D is in a log scale ( $\mu$ eq/L). Data shown in Figures 3C and 3D are similar to patterns of concentration over time are observed for other sites.

flowing directly from snow into wetlands, while water at site A09 ran over colluvium and contributed to wetlands along the eastern edge of Saddle. Excluding K<sup>+</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, chemical concentrations at the Saddle stream gage are found within the range of concentration observed at sampling sites A08 and A09. Si, Ca<sup>+2</sup>, Mg<sup>+2</sup> and Na<sup>+</sup> concentrations generally increased with time over the sample period (Fig 3C), while K<sup>+</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> decreased and were more variable.

Most data points from 2011 and 2010 stream chemistry plot within a linear trend of Na and Si, well defined by long-term data of the NWLTER (Figure 4). Overall, concentrations of both dissolved silica and sodium in the 2011 year are lower than that of samples taken at nearly the same location and time of year during 2010.

### DISCUSSION

Temporal changes in solute yields of snowmelt-dominated stream waters reflect changes in input source and flow pathways as the availability of water within catchment declines over the melting season. The spatial variations of those same constituents indicate hydrologic mixing of source waters with distinct local conditions, and are influenced by some of the same seasonal variations that control stream flow.

Most constituents along Saddle show a general de-175

crease of variability with increasing catchment area, similar to previous hydrochemical research (Asano et al 2009). Cations display decreasing variability with increasing catchment area at the scale of my study (0.25 km<sup>2</sup>) (Fig. 3A). In contrast, anions tend to be more variable both in space and longitudinally (Fig. 3B). Concentrations from samples representing similar areas are congruent; however, when values from my samples are compared to samples from catchments between 2 and 10 times greater, the patterns of convergence are less evident. Data collected by Caine and Thurman [1990] show a general increase of cation concentrations and decrease of anion concentrations downstream. Sulfate is an exception, as it tends to increase in the downstream direction, and balance the increasing cation concentrations.

The influence of snowmelt on stream chemistry decreases over time (Figs. 3C and 3D). Constituents that are predominantly independent of biologic uptake (3C) show a general increase over time, reflecting decreased dilution of ions by snowmelt and increased contact time with the subsurface. Conversely, constituents that probably are involved in soil reactions and biologic uptake (3D) vary more over time, which results from the greater contributions of groundwater to stream flow later in the season. Note that water sampled at the Saddle stream gage has a significantly greater travel distance from snow to gage in comparison to water sampled at the Martinelli gage. Uptake by ion exchange within the subsurface or biologic activity increases downstream (Caine and Thurman 1990), and may be the reason why  $NO_3^-$  is not present (or significant enough to be accurately measured) at the Saddle gage. Wetland vegetation found directly below Saddle snowfields may be significantly contributing to this uptake and removal of nitrate. Potassium (K<sup>+</sup>), another biologically mediated constituent, decreases along Saddle from the uppermost sample localities to the stream gage, and is supporting evidence for uptake of these solute species.

Solute concentrations from smaller sub-basins (<1km<sup>2</sup>) tend to be about twice as great compared to larger catchments. Higher concentrations reflect large accumulations of snow by drifting, and suggest a greater atmospheric and lesser biologic influence (Caine and Thurman 1990). Caine and Thurman (1990) found that, at all sites in the GLV, the relative importance of major cations was Calcium> Sodium> Potassium=Magnesium, with Sulfate and Bicarbonate as the dominant anions. My data show nearly the same relative importance, except magnesium is consistently higher by site, by day, for both catchments. A possible explanation for this finding would involve difference in bedrock geology. Two constituents, am-

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Site	Area	Q	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na⁺	$K^{+}$	${\sf NH_4}^+$	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub>	Cl⁻	NO <sub>3</sub>	Si	ъЦ
	km <sup>2</sup>	L/s	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L	µmol/L	рН
A01	0.25	8.0	99.6	16.0	34.1	1.2	3.0	153.3	26.7	7.2	0.0	98.7	6.8
A02	0.20	6.1	101.7	15.6	32.3	0.8	2.6	141.3	24.9	4.8	0.0	105.5	6.8
A03	0.18	5.5	102.9	15.0	34.1	1.1	5.2	175.3	24.2	3.6	0.0	103.4	6.9
A04	0.13	4.4	107.7	15.6	34.0	0.9	5.2	149.3	24.3	3.9	0.0	103.5	6.8
A05	0.07	1.9	96.9	13.6	30.4	1.0	5.2	154.7	17.8	6.0	1.0	94.5	6.9
A06	0.05	0.3	104.8	15.5	32.7	0.7	3.0	142.7	28.2	3.9	0.0	104.2	6.9
A07	0.01	0.7	107.1	14.8	34.5	0.8	4.1	137.3	36.0	4.7	0.0	100.0	6.6
A08	0.01	-	71.3	10.7	23.9	1.5	3.1	126.0	16.2	4.9	3.3	82.3	6.8
A09	0.01	0.8	133.0	17.5	35.2	2.6	4.1	166.7	37.9	3.6	1.9	108.9	6.7
A10	0.25	-	40.7	5.6	10.5	0.3	3.5	72.7	13.1	4.1	4.4	25.2	6.5

Table 1: Area, average field discharge, and average solute concentrations for stream locations sampled 3 or more days over the 2011 field season. Areas derived from watershed modeling of LiDAR data.

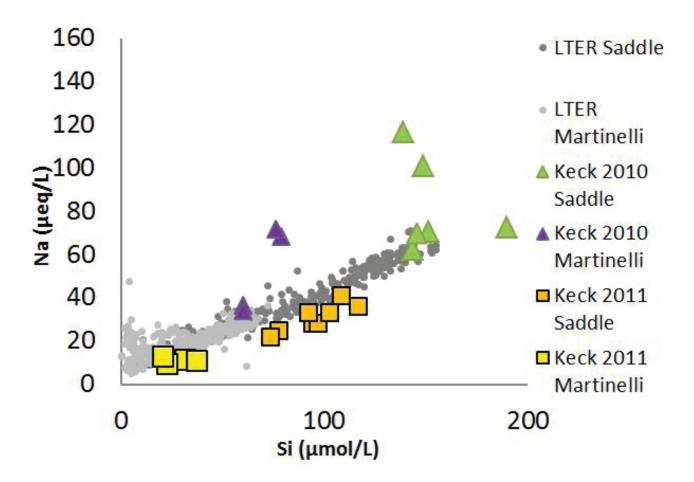


Figure 4. Sodium ion and dissolved silica concentrations in 2011 and 2010 for Martinelli and Saddle stream gages (A01, A10) plotted against long-term data of the NWLTER. Data for two Keck field seasons are generally consistent with trends in the long-term records of stream chemistry in Saddle and Martinelli measured by the NWLTER. Variation in 2010 Sodium ion concentrations may reflect differences in laboratory techniques.

monium  $(NH_4^+)$  and nitrate  $(NO_3^-)$ , show higher average values within the Martinelli water samples (Table 1). These constituents are significant contributors to concentrations found in wet deposition, and imply a greater atmospheric influence coupled with less biologic activity occurring in the Martinelli catchment.

The general pattern in Figure 4 indicates Saddle consistently has higher solute concentrations than Martinelli at the gage sites; specific concentrations and location along the trend vary throughout the season and annually. Figure 4 also shows clearly that 2010 had higher concentrations of both Na and Si than 2011, with 2011 concentrations from Saddle being similar to 2010 concentrations from Martinelli. The temporal Na and Si increases observed throughout the 2011 field season indicate movement up along the Na/Si trend toward the higher values of 2010. Samples were collected at roughly the same time of year, so differences likely represent lower discharge and less dilution in 2010. Less available water in the catchment decreases the degree of soil saturation and surface run-off and increases contact time with the subsurface within the groundwater. Sodium and silica are predominantly released into solution by chemical weathering of substrate (Dethier 1986); therefore, increased groundwater contact theoretically increases the concentrations of these solutes. The greater longitudinal distance for water to travel from snow to gage on Saddle helps explain the overall higher concentrations of sodium and silica, as water has longer groundwater contact times on Saddle, regardless of seasonal differences.

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The lower average ionic concentrations of from Martinelli indicate a greater snowmelt dilution signal when compared to water samples from the Saddle gage, and may also indicate lower annual solute yield for weathering related constituents such as Si, Na, Mg. and Ca. Current estimations of catchment area and average annual flows are similar for both basins, which imply that total solute removal is less from Martinelli than Saddle. However, the lack of detailed 2011 discharge data for Martinelli prevents further examination of this claim. Future analysis will investigate this comparison, taking into account annual totals of snow/precipitation (wet deposition), dust and associated water chemistry for each basin, and subtracting those values from the stream chemistry. If true, such analysis supports the idea that Martinelli not only displays differences flow pathways and contact time with groundwater contributing to stream chemistry than Saddle, but also may be chemically weathering more slowly.

## CONCLUSIONS

Temporal changes in solute yields of low order streams in alpine catchments reflect the changes in hydrologic input and flow pathway throughout the year. Spatial variations of those same constituents reflect hydrologic mixing of source waters with different local conditions; their influence on stream chemistry is controlled by climatologic differences by year. The Saddle catchment chemistry portrayed a greater influence groundwater contributions and biologic uptake. Contrastingly, Martinelli displayed a significantly greater dilution effect of snowmelt on stream chemistry.

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