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Identifying streamflow sources during spring snowmelt using water chemistry and isotopic composition in semi-arid mountain streams

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SUMMARY

Understanding streamflow generation using natural tracers in semi-arid, seasonally snow-covered mountain streams is essential for water resources management, water quality study and evaluation of impacts from climate change. This study reports temporal variations in stable isotopic ratios and concentrations of major dissolved ions of streamwater and precipitation between October, 2005 and May, 2007 in Red Canyon Creek and its tributary, Cherry Creek, draining carbonate-rich catchments on the southeastern flank of Wind River Range (Wyoming, USA). Although the isotopic ratios of oxygen and hydrogen in precipitation increased from approximately −33‰ to −13‰ and −260‰ to −110‰, respectively, during winters of 2006 and 2007, the oxygen and hydrogen isotopic compositions of streamwater at all sites remained unchanged throughout the year at −18.6 ± 0.3‰ (n = 88) and −142 ± 1.6‰ (n = 40) for $\delta^{18}O$ and $\delta^{2}H$, respectively. The isotopic values for the streamwater were identical to that found in groundwater, which had the values of −18.6 ± 0.2‰ (n = 26) and −142 ± 1.1‰ (n = 26) for $\delta^{18}O$ and $\delta^{2}H$, respectively. On the other hand, the temporal pattern of streamwater chemistry differed in space. In upper Red Canyon Creek, major dissolved ion concentrations in water varied little throughout the year. Nearly constant isotopic and chemical composition of streamwater at upper Red Canyon Creek indicated the dominance of the groundwater contribution throughout the year. In contrast, Cherry Creek had clear dilution of base metal and sulfate concentrations during increasing discharge at snowmelt, which is a clear indication of "new" water coming from fresh snowmelt. The contrasting behavior of stable isotopes and dissolved solutes during snowmelt at Cherry Creek suggests the isotopic tracers traditionally used in hydrograph separation failed to indicate different water sources at Cherry Creek. Combining isotopes and geochemical tracers indicates that streamwater at Cherry Creek during snowmelt is primarily a mixture of snowmelt and groundwater which have similar isotopic compositions but different chemical concentrations. The snowmelt is well mixed during temporary storage in a headwater wetland before reaching the sampling site. Such mixing plays an important role in reducing temporal variability of stable isotope values of fresh snowmelt water. We suggest that development of direct tracer experiments might help address the hydrodynamics of these kinds of watersheds in future research.

1. Introduction

Streamwater chemistry integrates the complicated ecological, hydrological and biogeochemical functions within an entire catchment (Bormann and Likens, 1967; Kendall and McDonnell, 1998; Likens and Bormann, 1995; Likens and Buso, 2006; Soulsby et al., 2002; Whitehead et al., 1986; Williams et al., 1993). Stable isotopic signatures ($\delta^{18}O$ and $\delta^{2}H$) of catchment waters together with mixing models have proved useful to identify hydrological sources and flowpaths under different flow conditions (Burns, 2002; Genereux and Hooper, 1998; Sklash, 1990; Sklash et al., 1976). Since Dinçer et al. (1970) first introduced the isotope separation technique to separate stream hydrographs in snowmelt-dominated watersheds into old water (or pre-event water, such as groundwater) and new water (event water), most studies using isotopes to study flow generation have been done in forested and humid and/or temperate areas (Burns, 2002; Buttle, 1994; Genereux et al., 2002; Gibson et al., 2000; Hooper et al., 1990; Hooper and Shoemaker, 1986; Shanley et al., 2002). New studies with different climatic and geographic settings are needed, especially in semi-arid and arid regions (Burns, 2002). In these regions, severe water scarcity is an issue and water supply largely relies on spring snowmelt. A recent study by Clark (2010) reported trends of decreasing streamflow and earlier snowmelt runoff from semi-arid to arid regions of the Western United States, which will potentially have a large effect

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on local and regional water resource management. Therefore, better understanding of how snowmelt recharges the watershed, generates streamflow and affects streamwater chemistry in these sensitive areas is crucial.

For high-elevation mountain streams, the largest portion of the annual streamflow occurs during melting of snow that accumulated during late autumn to early spring. The temporary storage of precipitation in snowpack, and its subsequent melting, controls the largest variability in solute and isotopic compositions of streamwater (Kendall and McDonnell, 1998). A snowmelt-driven water cycle presents unique challenges as well as opportunities to study hydrologic processes (Buttle and Sami, 1992; Huth et al., 2004; Jeelani et al., 2010; Laudon et al., 2002; Liu et al., 2004; Wels et al., 1991a). One challenge is characterizing the temporal and spatial heterogeneity of the isotopic compositions of event end-members.

In earlier studies, snow cores were used to characterize the event water during snowmelt runoff (Bottomley et al., 1986; Rodhe, 1981). However, recent work shows systematic variation in the isotopic composition of snowmelt caused by fractionation, which tends to produce melt water that is increasingly enriched over time, as it percolates through the snowpack (Feng et al., 2002; Taylor et al., 2001). In addition, when only two-component mixing (old and new waters) proved inadequate to explain the variation of streamwater chemistry, more sophisticated approaches emerged like three component mixing models (Hinton et al., 1994; Laudon et al., 2004; Liu et al., 2004). These studies have often been done in small, accessible, well-equipped watersheds and involved extensive sample collections of snow, snow pits, snowmelt, soil water, groundwater and streamwater. However, obtaining comparable data for mountain stream catchments, covering large areas and elevation changes, can be hindered by difficult access and infrequent sampling of snowmelt, soil water and streamwater during snow accumulation in winter and early spring. Nevertheless, even limited hydrological and geochemical data still may be useful to improve our understanding of source waters and flowpaths in these remote watersheds, and ultimately provide insights for watershed hydrologists and managers.

Red Canyon Creek offers a unique opportunity to investigate the hydrologic and geochemical dynamics of snowmelt and streamwater in a semi-arid region because it provides a contrasting climatic alternative to more humid watersheds that have been studied at similar scales in the eastern parts of the United States (e.g. Hubbard Brook, New Hampshire, and Coweeta, North Carolina). At Red Canyon Creek, variations in stream discharge at snowmelt should cause predictable changes in the chemical composition of many solutes in streamwater. For example, increased discharge commonly correlates to decreased total dissolved solids (Durum, 1953; Hem, 1948). But processes related to microorganisms and plants that affect concentrations of nutrients in humid region streams (Drever, 1994; Soulsby et al., 2002) and preferential leaching of strong acids from atmospheric acid deposition in snowpack (Driscoll et al., 2005; Hall et al., 2002; Siegel, 1979) should not be as prevalent at Red Canyon as in eastern watersheds because Red Canyon Creek does not have strong atmospheric acid deposition or humic soil development. Thus, studying the response of dissolved solids to changing hydrologic conditions of Red Canyon Creek affords the opportunity to address how isotopic and solute concentrations change without these confounding variables.

For this paper, we chose two mountain streams within the Red Canyon Creek watershed to investigate, upper Red Canyon Creek and Cherry Creek, a tributary to Red Canyon Creek. Both drain carbonate-rich catchments on the southeastern flank of the Wind River Range of Wyoming, but differ insofar as Cherry Creek is dominated by steep, narrow canyons with exposed bedrock at higher elevations and upper Red Canyon Creek includes watershed areas with more extensive glaciofluvial and alluvial deposits. Our main objectives are to understand how snowmelt affects the chemical composition of streamwater in semi-arid mountainous streams with different hydrodynamics and to characterize major sources of stream runoff by coupling stable isotope compositions and water chemistry.

2. Study area

The Red Canyon Creek watershed is in the transitional climate zone between the high elevations of the Wind River Range and the adjacent arid desert in Wyoming, USA (Fig. 1a and b). The main creek is over 10 km in length, flows in a north–northwest direction and discharges to the Little Popo Agie River (Fig. 1c and d). Three tributaries, Deep Creek, Barrett Creek and Cherry Creek, are located on the western side of the Red Canyon Creek valley (Fig. 1c). Deep Creek joins Red Canyon Creek close to its head waters, whereas Barrett and Cherry Creek join Red Canyon Creek near the base of the watershed. Red Canyon Creek water is mostly supported by the tributary discharges (Jin et al., 2010).

The two subwatersheds studied are Cherry Creek and upper Red Canyon Creek (Fig. 1c; Table 1). Cherry Creek, a 2nd order stream, drains a 31 km^2 watershed at elevations ranging from 1714 to 2767 m above sea level with a mean elevation of 2356 m. The mean slope is 13.4°. The 12 km creek flows to the northeast and discharges to Red Canyon Creek. An approximately 0.5–1 km^2 wetland is located in the headwaters of Cherry Creek (Fig. 1c) before it enters a narrow and steep mountainous channel (Jin et al., 2009). In the headwater of Cherry Creek, major geological formations include Bighorn dolomite and Mississippian-age Madison limestone (Fig. 2). There are also large areas of the Cherry Creek watershed underlain by the Tensleep and Amsden Formations in the middle part of the Cherry Creek subwatershed.

Upper Red Canyon Creek, a 9 km long 3rd order stream draining 50 km^2, includes two tributaries, Deep Creek and Barrett Creek. Its elevation ranges from 1708 to 2726 m with a mean elevation of 2108 m, which is 250 m lower than that of Cherry Creek subwatershed. The mean slope is 11.9°, lower than that of Cherry Creek. The most notable geomorphic features of the upper Red Canyon Creek subwatershed are the imposing dip slopes of the Permian-age carbonate, the Phosphoria Formation, Tensleep and Amsden Formations along its west side (Fig. 2). The Triassic Chugwater and Dinwoody Formations, consisting of red gypsiferous siliclastic rocks and glaciofluvial terraces underly the valley floor (Fig. 2). Mississippian-age Madison Limestone with headwater alluvium forms the crest of the watershed divide of the western side of the watershed (Fig. 2). Meadows adjacent to the creek, along the valley floodplain, are underlain by 6–7 m of unconsolidated alluvium. From the land surface, approximately 2 m thick silty sands are underlain by a high permeable layer of sand and gravel (Lautz and Siegel, 2006).

A NOAA (National Oceanic and Atmospheric Administration) long-term meteorological station, located at 1760 m, is found at the Red Canyon Ranch within the watershed (Fig. 1d). The station records daily maximum, minimum and average air temperature, daily precipitation, wind speed and incoming solar radiation. On average, the watershed receives about 40 cm of precipitation per year (NOAA, 2008) mostly as snow. About 80% of the precipitation falls between October and May.

Hourly streamflow was recorded intermittently between 2005 and 2007 at a Parshall flume equipped with two pressure transducers at the mouth of the watershed (Fig. 1d). A USGS gage (USGS 06233000) is located in Little Popo Agie River, which is approximately 5 km downstream of the Red Canyon Creek confluence.

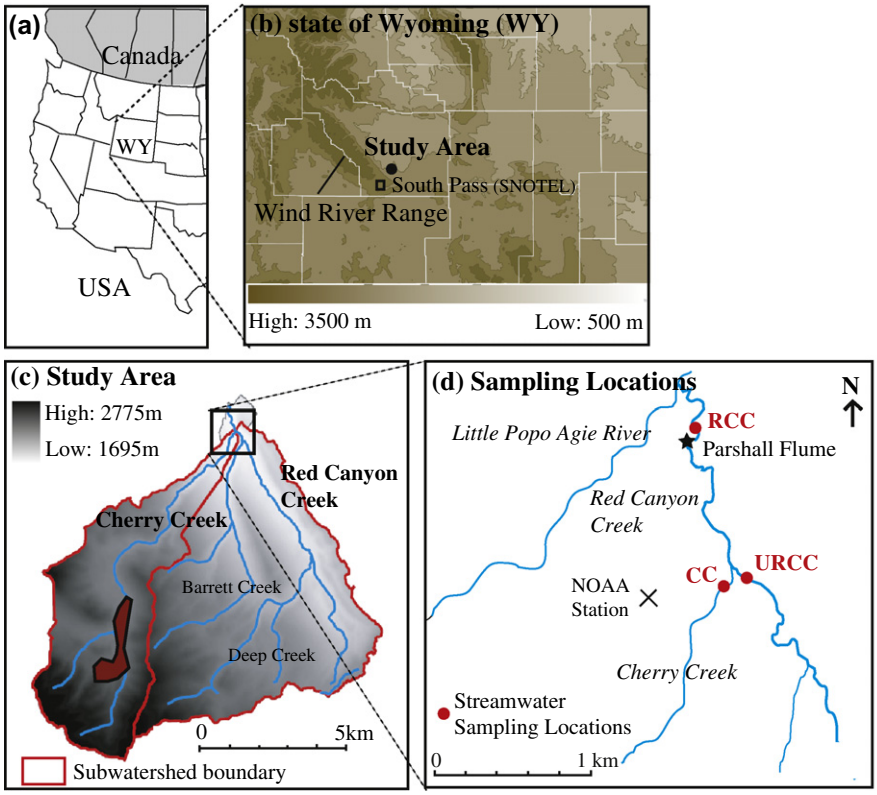

Fig. 1. The locations of (a) Wyoming in the United States; (b) the study area on the southeastern side of the Wind River Range on an elevation map of Wyoming (modified from http://www.geology.com/state-map/wyoming.shtml); (c) of the Red Canyon Creek watershed and two subwatersheds: Cherry Creek and upper Red Canyon Creek; and (d) three long-term sampling sites as well as a Parshall flume and NOAA CRN (climate reference network) station within the watershed.

Table 1
Comparison of Cherry Creek and upper Red Canyon Creek subwatershed basic characteristics.

	CC subwatershed	URCC subwatershed
Area (km^2)	31	50
Elevation (m)		
Min	1714	1708
Max	2767	2726
Mean	2356	2108
Std. dev.	216	221
Slope (°)		
Min	0	0
Max	46.9	45.9
Mean	13.4	11.9
Std. dev.	7.2	6.5

Daily average streamflow data can be readily accessed via http://www.nwis.waterdata.usgs.gov/nwis/.

A SNOTEL station, South Pass (latitude: 42.56°N; longitude: 108.85°W), has been operated by the Natural Resources Conservation Service (NRCS) since 1984, and is located approximately 15 km southwest of the Red Canyon Creek watershed (Fig. 1b). The elevation of the South Pass SNOTEL station is 2755 m. Snow surveys are done throughout the winter. Recorded parameters include daily precipitation, temperature, snow depth and snow water equivalent.

3. Methods

We collected streamwater at three locations weekly from October 2005 to May 2007 (Fig. 1d): (1) at the mouth of Cherry Creek subwatershed (CC); (2) in Red Canyon Creek immediately upgradient of the Cherry Creek confluence (URCC); and (3) near the gauge at the mouth of Red Canyon Creek (RCC). Streamflow at RCC consists of a mixture of CC and URCC waters (Fig. 1d), so the chemical composition of water at RCC was used to calculate the flow contribution from CC and URCC by using conservative tracers. Groundwater contributions to the stream between the Cherry Creek confluence and the RCC sampling site can be assumed negligible because the two sites have no significant differences in either flow rate or water chemistry (Jin et al., 2010).

We collected bulk precipitation (mostly snow) every 2–4 weeks, if present, from October 2005 to May 2007 with a polyethylene bottle attached to a 20 cm diameter funnel screened to exclude large particles from entering.

Jin et al. (2010) reported the stable isotopic compositions and major dissolved ion concentrations of shallow groundwater collected during a synoptic survey in 2006 from thirty-two monitoring wells and piezometers previously installed in a meadow of Red Canyon Creek. Wells and piezometers were constructed using 2-cm diameter PVC pipe casing to depths of between 2 and 6 m, with the bottom screen at an interval of 0.6–3.0 m (Lautz and Siegel, 2006). These data provide us with a measure of the isotopic and chemical composition of groundwater contributed to the stream as baseflow.

We filtered all samples through 0.45 μm hydrophilic polyvinylidene fluoride (PVDF) membrane filters and preserved aliquots collected for cation analysis by addition of HNO_3 to a pH < 3.0. The major cations, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and Sr^{2+} and Si, were analyzed using a Perkin–Elmer OPTIMA 3300DVICP-OES (inductively coupled plasma-optical emission spectrometry) at the State University of New York College of Environmental Sciences and Forestry (SUNY-ESF). Quality control (QC) samples were analyzed between every five to seven samples. Unless QC passed within 10% precision for all elements, recalibration was done to assure the quality of the

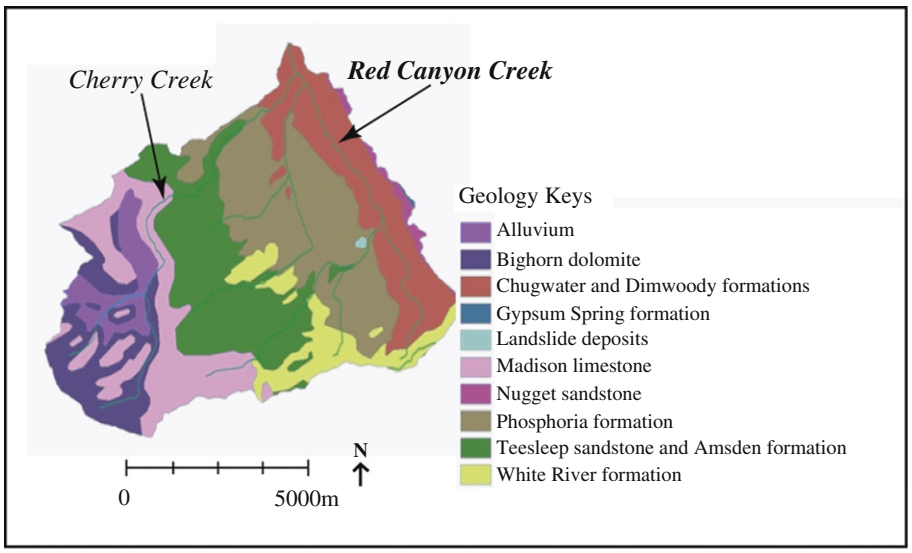

Fig. 2. Geologic map of the Red Canyon Creek watershed (Jin et al., 2010).

chemistry data. Samples analyzed for Cl^-, SO_4^{2-} and NO_3^- analysis were also passed through 0.45 μm filters and kept frozen before running on a Dionex ICS-2000 Ion Chromatograph at SUNY-ESF. Duplicates of samples were analyzed for every ten samples with precision <3%.

Precipitation and streamwater samples were measured for the stable isotopic ratios of $\delta^{18}O$ and δ^2H at the Stable Isotope Laboratory at the University of Calgary. We measured the stable isotopes of all streamwater samples collected during snowmelt. During baseflow, we only measured stable isotopes in streamwater samples on a monthly basis. The $\delta^{18}O$ values were measured using CO_2–H_2O equilibration interfaced with a Micromass IsoPrime-EA mass spectrometer. Generated H_2 gas was obtained using the zinc reduction method and δ^2H values were analyzed on a Micromass IsoPrime-EA mass spectrometer. The isotopic ratios for oxygen and hydrogen are reported in standard delta notation (δ relative to Vienna Standard Mean Ocean Water (VSMOW). Analytical precision is estimated at 0.3‰ and 1.0‰ for $\delta^{18}O$ and δ^2H, respectively.

Stream stage was recorded at 1-h intervals between October, 2005, and September, 2007, at the mouth of Red Canyon Creek (Fig. 1d) with pressure transducers installed in a Parshall Flume (Wanielista et al., 1997), which were used to calculate streamflow discharge. No data were obtained during the winter, when the temperature of streamwater remained below freezing, and between July and October, 2006, because of instrumental failure. Based on the flow information at the USGS station in Little Popo Agie, we assumed the Red Canyon Creek flow rates did not change dramatically when stream level data were not obtained during baseflow from July to October, 2006.

We calculated the annual flow of Red Canyon Creek and the Little Popo Agie River during the 2006 Water Year (October 1st, 2005–September 30th, 2006) and 2007 Water Year (October 1st, 2005–September 30th, 2007) by summing recorded mean daily streamflow and estimated daily streamflow during the winter and assuming simple linear recession of streamflow when no direct measurements of streamflow were obtained. We understand this regression approach introduces some uncertainty in the calculation. However, this small uncertainty compared to the large amount of discharge during snowmelt does not affect the main conclusions of this paper.

4. Results

4.1. Hydrology of the Red Canyon Creek

Mean daily stream discharge is shown in Fig. 3 with precipitation and temperature changes from October 1st, 2005 to September 30th, 2007. The maximum flow during the spring melt in 2006 was about 150 L/s in April, followed by a decrease to 100 L/s until the middle of June. In spring 2007, a sharp increase of flow occurred

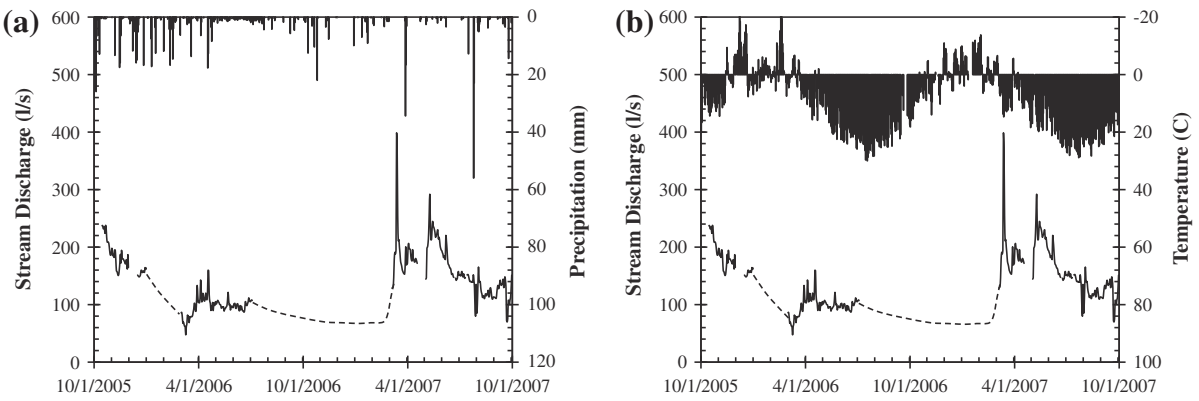

Fig. 3. (a) Daily stream discharge recorded at the Red Canyon Creek gauge and daily precipitation monitored at the NOAA station from October, 2005 to September, 2007; the dashed line indicates estimated values during winter baseflow periods and (b) daily stream discharge and recorded daily mean air temperature.

in early March when air temperature increased sharply from −5 °C to 15 °C in 2 weeks starting from the end of February. The streamflow dropped quickly when air temperatures fell below the freezing point. The second peak of snowmelt in 2007 occurred due to additional snowmelt within the watershed in May. The high streamflow in October, 2005, was because of autumn rainfall (Fig. 3).

During the 2006 Water Year (WY06), stream runoff was about 4×10^6 m^3, equivalent to 5.0 cm of water on the Red Canyon Creek watershed. The total precipitation that fell on the watershed was 4.5×10^7 m^3, equivalent to about 55 cm of water. The runoff constituted less than 10% of precipitation throughout the water year. During the 2007 Water Year (WY07), the ratio of annual runoff to precipitation was about 20%. The remainder of the precipitation was presumably lost to evapotranspiration or changes in wetland storage in the Cherry Creek watershed. The Little Popo Agie River, which Red Canyon Creek discharges to, had annual stream runoff rates of 4.9×10^7 m^3 and 4.8×10^7 m^3 for WY06 and WY07, respectively. The Red Canyon NOAA meteoric station data were used for calculating annual precipitation in the Little Popo Agie watershed. The calculated annual runoff to precipitation ratios were 27% and 44% for WY06 and WY07, respectively.

The 2 years of record for Red Canyon Creek and the Little Popo Agie River show that the ratios of runoff to precipitation are generally small, although we had to use the estimated data in winter, when flow gauging is not operational, to calculate the annual flow. Data from a single meteoric station can introduce some uncertain to the calculation. If accounting for the elevation change, the total annual precipitation may have been greater for both watersheds as the Red Canyon Ranch station is located at the bottom of the watersheds, which would lead to smaller runoff to precipitation ratios.

4.2. Temporal variation of stable isotopes of precipitation and streamwaters

From winter to early spring, the $\delta^{18}O$ and δ^2H isotopic compositions of precipitation increased in both years. The $\delta^{18}O$ values of precipitation ranged from −23.6‰ to −13.1‰ during winter 2006 and from −33.9‰ to −18.6‰ during winter 2007, respectively (Fig. 4; Appendix A). The $\delta^{18}O$ values in snow samples from 2007 were more depleted than that in the year of 2006. The volume-weighted mean $\delta^{18}O$ and δ^2H values for all precipitation were −20.8‰, −159‰ and −23.5 and −180‰ for 2006 and 2007, respectively (Table 2). A local meteoric water line (LMWL), $\delta^2H = 7.67 \times \delta^{18}O + 0.34$, is shown in Fig. 5.

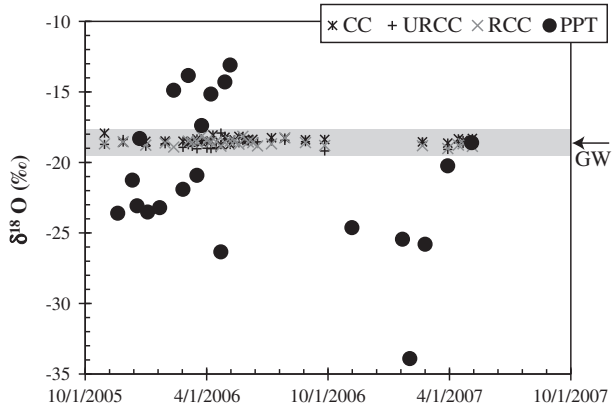

Fig. 4. The $\delta^{18}O$ temporal variations of the precipitation, which is mostly snow (PPT), and streamwater (CC, URCC and RCC) from October, 2005 to May, 2007. The arrow indicates the average groundwater (GW) $\delta^{18}O$ value of −18.6‰.

In marked contrast to precipitation inputs, the $\delta^{18}O$ and δ^2H isotopic compositions of streamwater at all sites remained remarkably uniform throughout the year (Fig. 4; Appendix A). At Cherry Creek (CC), upper Red Canyon Creek (URCC) and the lower Red Canyon Creek (RCC) sites, mean $\delta^{18}O$ values were −18.4 ± 0.3‰ (n = 29), −18.6 ± 0.3‰ (n = 29) and −18.6 ± 0.2‰ (n = 30), respectively (Table 2). The mean δ^2H values were −141 ± 1‰ (n = 14), −142 ± 1‰ (n = 12) and −144 ± 1‰ (n = 14), respectively. We saw no significant seasonal variation in the water isotopes of streamwater throughout the year, including when snowmelt presumably provided much of the streamwater (Fig. 4). All the streamwater samples fell on the LMWL as a small cluster (Fig. 5). The isotopic values for the streamwater were also identical to those found in groundwater, −18.6 ± 0.2‰ (n = 26) and −142 ± 1.1‰ (n = 26) for $\delta^{18}O$ and δ^2H, respectively (Fig. 5) (Jin et al., 2010).

4.3. Temporal variation for base cations and anions of precipitation and streamwater

The concentrations of major dissolved solutes in precipitation ranged from 0.3 to 3 mg/L, orders of magnitude smaller than that in either creek water or groundwater (Table 2; Fig. 6 and 7).

Concentrations of solutes varied temporally at CC site, particularly during snowmelt. The lowest concentration of Ca^{2+} in CC occurred during the spring snowmelt season in early April, 2006, concurrent with the maximum streamflow (Fig. 6). The concentration of Ca^{2+} was diluted from about 70 mg/L to about 20 mg/L. The Ca^{2+} concentration gradually increased from late April to June, 2006, to the same concentration found in baseflow when snowmelt ceased. During the rest of the year, concentrations of Ca^{2+} remained constant, at about 70 mg/L.

Streamwater SO_4^{2-} concentrations in CC decreased by half when the melting season started in March 2006 (Fig. 7), following the same pattern as the base cations. The SO_4^{2-} concentration gradually increased from April to June 2006 and showed slightly higher concentration than that of baseflow before the snowmelt. Streamwater Cl^- varied little and remained between 1 and 2 mg/L throughout the year and no considerable dilution was seen during the snowmelt (Fig. 7).

At URCC, in marked contrast to CC, streamwater Ca^{2+} concentrations varied little during snowmelt and the annual average concentration of Ca^{2+} of about 110 mg/L was much higher than in CC. Similarly, all other base cations (Mg^{2+}, K^+, Na^+, and Sr^{2+}), Si, and SO_4^{2-} varied little throughout the year in URCC, whereas these chemical constituents were clearly diluted by snowmelt in CC up to 80% (Fig. 6 and 7). Exceptions at URCC are streamwater Cl^- and NO_3^-, which show similar temporal patterns as observed at the CC site (Fig. 7).

The only solute with concentrations in precipitation higher than in streamwater was NO_3^- (Table 2). Streamwater NO_3^- concentrations varied seasonally at all sites with the lowest values observed during the summer months, followed by an increase in the late fall, remaining elevated through the winter months (November–March) (Fig. 7). The maximum concentration occurred in early March when the initial snowmelt started in the spring of 2006. Then NO_3^- decreased from a high of about 0.8 mg/L to about 0.1 mg/L in early April and remained at low concentrations during the summer and early fall before NO_3^- concentrations increased again in November of 2006.

At RCC, streamwater consists of a mixture of contributions from CC and URCC. All base cation and silica concentrations decreased during snowmelt at RCC, with the same timing as dilution of CC water. Solute concentrations generally remained constant for the remainder of the year (Fig. 6 and 7).

We computed Pearson Correlations coefficients for all major elements for the three sites individually (Table 3). At CC, results

Table 2
The mean streamwater concentrations for all sites collected during the Water Year 2006 (October 2005–September 2006) and volume-weighted mean precipitation concentrations during the Water Year 2006 and 2007 (October 2006–September 2007).

Solutes (units)	CC site		URCC site		RCC site		Precipitation[a]
	Average	STD	Average	STD	Average	STD	Average
Calcium (mg/L)	63.33	12.87	111.14	9.78	86.89	10.57	2.77
Magnesium (mg/L)	27.12	5.76	32.58	2.10	31.09	1.75	0.31
Potassium (mg/L)	0.70	0.18	1.28	0.35	1.00	0.19	0.17
Sodium (mg/L)	2.83	0.72	6.18	0.52	4.59	0.65	1.04
Dissolved silicon (mg/L)	5.00	1.16	6.47	0.61	5.86	0.49	0.20
Strontium (mg/L)	0.28	0.07	0.87	0.08	0.57	0.11	0.01
Sulfate (mg/L)	46.57	10.57	173.51	18.34	115.31	15.92	1.03
Chloride (mg/L)	1.23	0.28	1.92	0.39	1.57	0.32	0.30
Nitrate (mg/L)	0.37	0.22	0.37	0.30	0.33	0.31	1.51
$\delta^{18}O$	−18.4	0.3	−18.6	0.3	−18.6	0.2	−20.8 (WY06) −23.5 (WY07)
$\delta^{2}H$	−141	1	−142	1	−144	1	−159 (WY06) −180 (WY07)

[a] Indicates volume-weighted mean concentration.

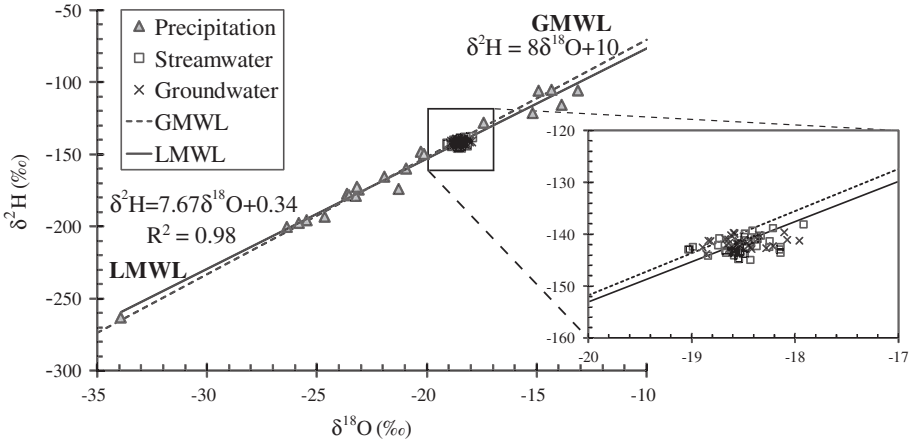

Fig. 5. The local meteoric water line (LMWL) of Red Canyon Creek and global meteoric water line (GMWL). The streamwater samples collected from October 2005 to May 2007 and groundwater samples collected in summer 2006 fell on the LMWL as a small cluster.

showed solutes such as all major cations, and SO_4^{2-} were positively correlated ($r > 0.5$, $p < 0.01$, $n = 54$). At URCC, the correlations between solutes were similar but not as strong as those at CC. At RCC, cations are positively correlated ($r > 0.5$, $p < 0.01$, $n = 57$).

4.4. Flow fraction from Cherry Creek and upper Red Canyon Creek

We used a simple two end-member mixing model using a conservative solute to calculate the approximate percentage contributions from Cherry Creek and upper Red Canyon Creek to lower Red Canyon Creek over time. Chloride and silica were not used for mixing models because they had similar concentrations among three sites, which could potentially introduce large uncertainties to the mixing model analysis. We assumed that Sr^{2+} and Na^{+} behaved most conservatively in the streamwater because Sr^{2+} and Na^{+} concentrations occurred below the solubility of $SrCO_3/SrSO_4$ and Na-associated minerals even during baseflow (Jin et al., 2010).

Despite some differences between results from the two tracers (Sr^{2+} and Na^{+}), the overall temporal trends throughout the year are similar (Fig. 8). Excluding the snowmelt period, Cherry Creek and upper Red Canyon Creek contributed approximately equal amounts of water throughout the year. At the onset of snowmelt (mid-March to early April), the proportion of flow from upper Red Canyon Creek increased to between 70% and 80%. Then, from mid-April to early June, the proportion of water derived from Cherry Creek increased dramatically to between 80% and 90% and the majority of the flow was from Cherry Creek (Fig. 8). Following the cessation of snowmelt, the percentage of water derived from the two catchments returned to approximately equal amounts.

5. Discussion

Changes in the stable oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) isotopic signatures of catchment waters are commonly used to identify hydrological source areas and flowpaths in watersheds (Burns, 2002; Rodgers et al., 2005; Sklash, 1990). In addition, the relationships between solute concentrations and streamflow change have also provided important formation on hydrological pathways. Different catchments may show different chemical and isotopic responses to hydrological events. Sometimes rainfall rapidly passes through catchments and provides the major portion of streamflow (Skartveit, 1981). However, in other watersheds, increasing discharge during storms and snowmelt comes from old or pre-event water because these catchments store large volumes of water and then release it to streams as storm water and snowmelt recharges the catchment from above (Neal et al., 1988; Neal and Rosier, 1990; Sklash et al., 1986; Wels et al., 1991b).

Remarkably, at Red Canyon Creek watershed, snowmelt did not affect the isotopic compositions of the streamwater draining either subwatershed. In contrast, water chemistry did respond to snowmelt in some and allowed for an estimate of contributions from different sources. We found striking the significant variations in

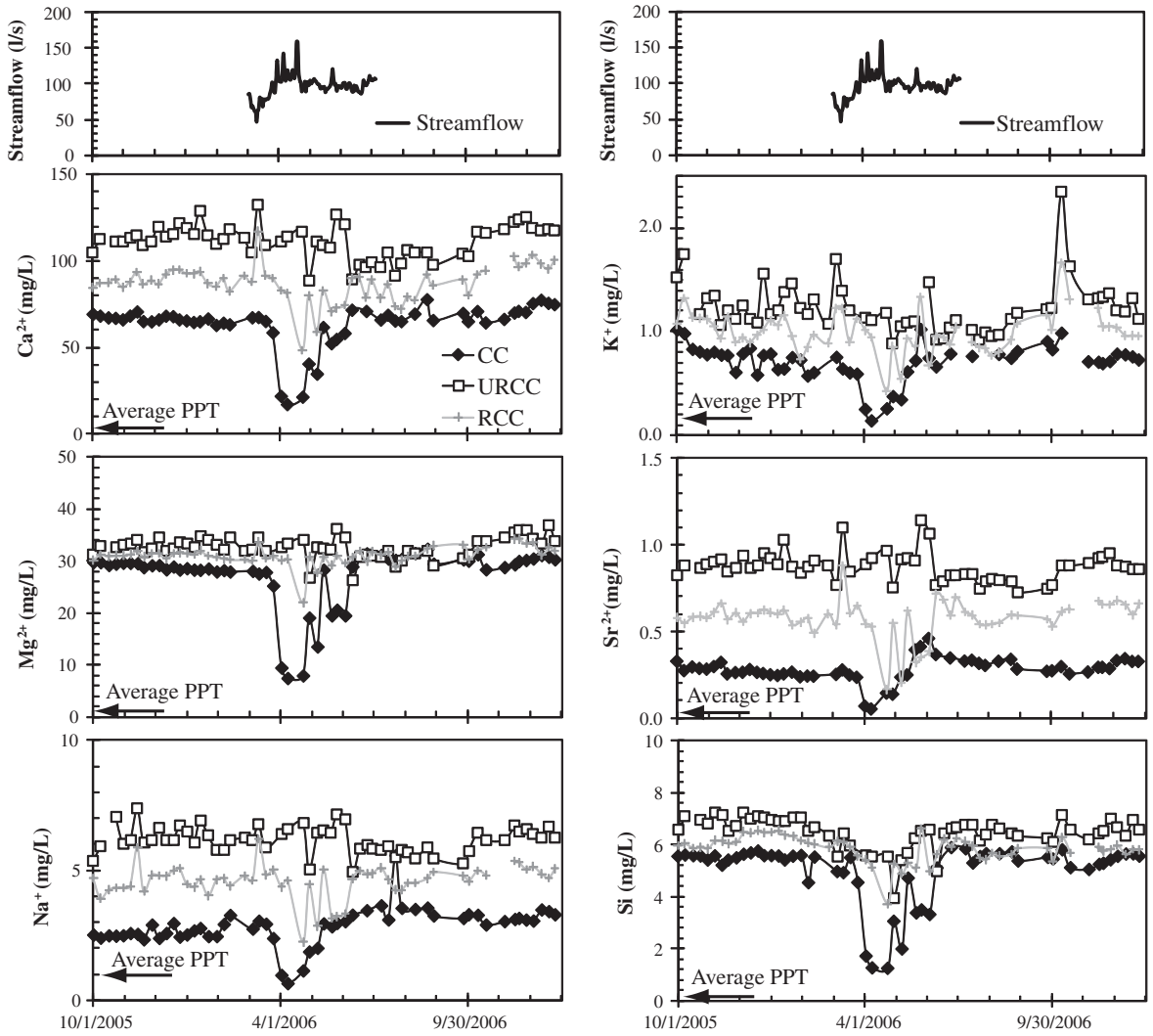

Fig. 6. Temporal variations of selected cations in streamwater from sites CC, URCC and RCC. Arrows indicate the solute concentrations in precipitation (PPT).

$\delta^{18}O$ values in rainfall coincident with essentially identical $\delta^{18}O$ values for the stream throughout the year. Moreover, the $\delta^{18}O$ values of streamwaters were essentially identical to the isotopic composition of groundwater.

The observed nearly constant $\delta^{18}O$ values in streamwater over time suggest that a homogenization process occurred either during the melting of snow or during the transport of meltwater to the stream. We examine three possibilities to account for the homogenization of the snow isotopic composition for each subwatershed: (1) rapid snowmelt and *in situ* mixing of meltwater; (2) groundwater "fill and spill", which is when groundwater is pushed out by recharge from more recent meltwater; and (3) homogenization of melt water during temporary surface or shallow storage.

First possibility is that when snow melts quickly and releases water with a homogenized isotopic value, regardless of stratification during the winter due to increasingly enriched snow fall, this meltwater would result in streamflow waters which have invariable isotope signal over time but variable chemistry due to dilution. Since upper Red Canyon Creek has unchanged chemical concentrations similar to groundwater showing no dilution directly from melting water, this hypothesis is unlike to take place at the upper Red Canyon Creek subwatershed. For Cherry Creek, this hypothesis is not likely either because melting lasts several weeks to over a month. Although getting direct measurements of snowmelt and snow depth change over time in the high country of Cherry Creek was not possible because of the remoteness of the highest elevation regions of the watershed where snow accumulation is greatest, a SNOTEL station at South Pass can be used as an analogous station. The South Pass station had about 20% more accumulative precipitation in WY06 (Fig. 9a) compared to the Red Canyon station, likely due to its higher elevation. Although South Pass (elevation = 2755 m) and Red Canyon (elevation = 1760 m) stations are not at the same elevation, the high elevation areas of Cherry Creek are coincident in elevation with the South Pass SNOTEL station. Thus, South Pass can be regarded as a first order approximation of the snow conditions in the high country of the Cherry Creek watershed. Fig. 9b shows that the melt at South Pass started in early April when air temperature was above freezing, which is about 1 month later than Red Canyon Creek. This is because upper Red Canyon Creek subwatershed is mostly located in lower elevation (Fig. 10 and Table 1) where melting season starts early. The change of the calculated flow proportion from upper Red Canyon Creek and Cherry Creek (Fig. 8) during snowmelt suggests different timing of melting in the two subwatersheds (Fig. 10). The greater proportion of water came from upper Red Canyon Creek during the onset of the snowmelt season likely due to its lower elevation and earlier snowmelt compared to Cherry Creek, which constituted more of streamflow in lower RCC during the later spring and early summer months (Fig. 8 and 10). The snowmelt in Cherry Creek likely persisted longer, with more

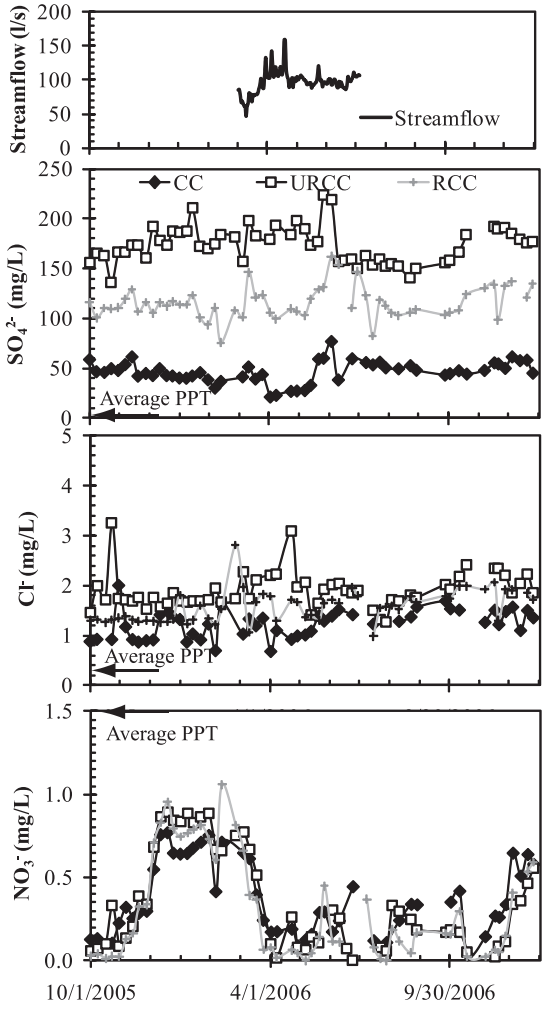

Fig. 7. Temporal variations of selected anions in streamwater from sites CC, URCC and RCC. Arrows indicate the solute concentrations in precipitation (PPT).

similar timing to the South Pass SNOTEL site. The analogous SNOTEL station (South Pass) shows the melt season lasts about 1.5 months suggesting rapid melting of snow with a homogenous isotopic value might not be realistic.

In addition, if rapid snowmelt and *in situ* mixing are taking places, using the winter volume-weighted precipitation isotope value as a surrogate for actual snowpack or snowmelt composition (−20.8‰ and −23.5‰ for 2006 and 2007, respectively), we would expect its value same as the isotopic composition in the streamwater during snowmelt. However, there were −2.2‰ and −4.9‰ differences in $\delta^{18}O$ between the volume-weighted mean of precipitation and streamwater for WY06 and WY07, respectively.

The second possibility to have unchanged $\delta^{18}O$ values in streamwater is groundwater "fill and spill", which is when groundwater is pushed out by recharge from more recent meltwater, resulting in homogenous isotopic and chemical values of streamwater as these in groundwater. At URCC, both stable isotopes and major dissolved solutes of streamwater showed nearly constant values throughout the year, although there was some enrichment of chemical elements, such as SO_4^{2-}, seen during baseflow. $\delta^{18}O$ values of streamwaters were also essentially identical to the isotopic composition of groundwater. Chemical and isotopic compositions of streamwater in URCC remained the same during both snowmelt and baseflow periods, which suggests that streamflow in upper Red Canyon Creek is derived from old water (pre-event groundwater) throughout the year. Others have observed that pre-event water supports streamflow during storm events and snowmelt

Table 3
Pearson correlation coefficients of streamwater samples from (a) Cherry Creek; (b) upper Red Canyon Creek (URCC); and (c) lower Red Canyon Creek (RCC). Only correlation significance at <0.01 level (2-tailed) were shown in the table.

	Ca	K	Mg	Na	Si	Sr	Cl	NO_3	SO_4
(a) At CC									
Ca	1								
K	.782	1							
Mg	.966	.743	1						
Na	.713	.527	.709	1					
Si	.936	.732	.977	.646	1				
Sr	.681	.728	.549	.678	.488	1			
Cl	.358			.453		.372	1		
NO_3					.400			1	
SO_4	.621	.696	.494	.578	.456	.865	.355		1
(b) At URCC									
Ca	1								
K	.468	1							
Mg	.909	.476	1						
Na	.783		.803	1					
Si	.443	.345	.513		1				
Sr	.835		.731	.810		1			
Cl							1		
NO_3	.405							1	
SO_4	.667		.525	.544		.786			1
(c) At RCC									
Ca	1								
K	.555	1							
Mg	.829	.605	1						
Na	.825	.395	.755	1					
Si	.615	.560	.619	.508	1				
Sr	.880	.483	.764	.912	.558	1			
Cl							1		
NO_3					.595			1	
SO_4									1

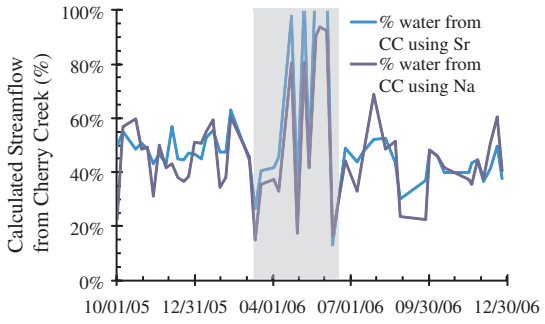

Fig. 8. Percentage of streamflow in Red Canyon Creek that is derived from Cherry Creek using Sr^{2+} and Na^+ as conservative tracers in two end-member mixing models. The shaded area indicates the snowmelt period, from mid-March to June.

(Kendall and McDonnell, 1998; Laudon et al., 2004; Wels et al., 1991a), but our finding that nearly all streamwater during snowmelt was derived from groundwater in a high-elevation mountainous stream is surprising.

The dominant old water contribution to streamflow may be due to the topography of the Red Canyon Creek watershed. The majority of upper Red Canyon Creek consists of gently dipping carbonate Phosphoria Formation. The valley floor of Red Canyon Creek is underlain by a sequence of glaciofluvial terraces. These glaciofluvial terraces are highly transmissive and can store large amounts of water (Jin et al., 2010). Snow falling on the upper Red Canyon Creek catchment may infiltrate, mix with deep fluvial groundwater, and displace stored water in the terraces to contribute to streamflow like shown the groundwater "fill and spill" concept in Fig. 11.

Due to the difference in topography and geological features, Cherry Creek does not fit in the groundwater "fill and spill" model.

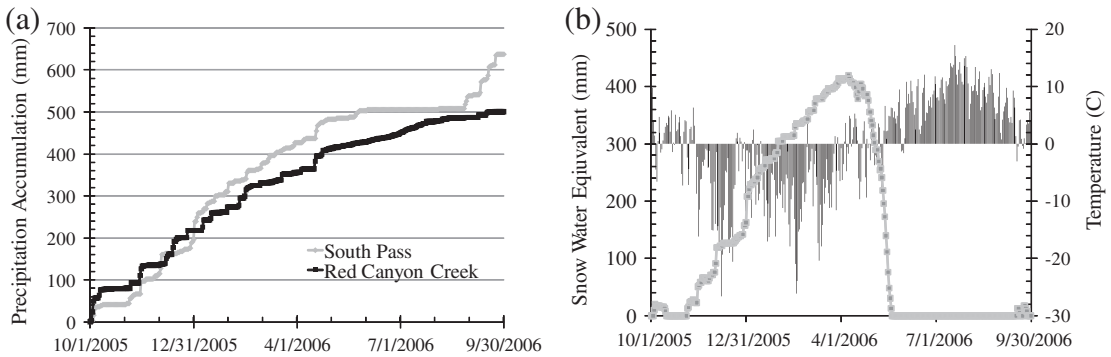

Fig. 9. a) Precipitation accumulation curves from the Red Canyon Creek NOAA meteorological station and South Pass SNOTEL site in WY06, respectively; b) Snow water equivalent (grey line with black markers) and temperature change (black columns) over time at South Pass SNOTEL site in WY06.

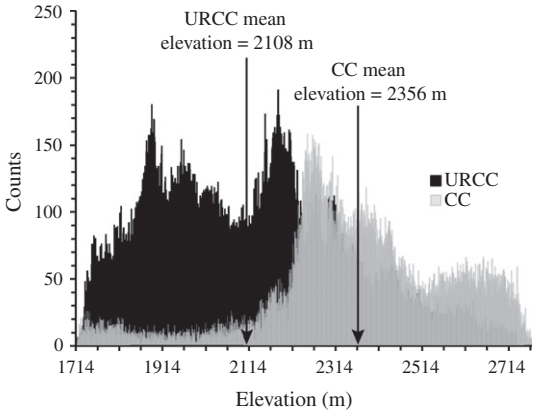

Fig. 10. A histogram showing the elevation distribution in the upper Red Canyon Creek and Cherry Creek subwatersheds.

The plausible explanation for the non-coincidence between isotopic and solute response to snowmelt at Cherry Creek is that the streamwater is a mixture of snowmelt and groundwater, which have similar isotopic compositions but different chemical concentrations. The snowmelt must be temporarily stored and well mixed before reaching our sampling site at CC, which could result in essentially the same isotopic composition. The difference in chemical composition may be due to the different residence time of melt water and groundwater. Mixing of varying ratios of snowmelt runoff and groundwater causes temporal variation of chemical concentrations in streamwater but not isotopic values. To reduce the temporal variation of stable isotopic values in snowmelt runoff, standing waters in lakes, ponds and wetlands may mix multiple waters and homogenize isotopic compositions. The headwaters of Cherry Creek contain a very large wetland complex, which could serve as a mixing reservoir (Fig. 1c). The uniform isotopic values of streamwater during snowmelt and baseflow may reflect the dampening of temporal variations of snow inputs when meltwater mixes in the wetland. When the wetland storage fills during snowmelt, stored dilute water in the wetland would be displaced to the stream channel. This process would mimic what was seen in streamwater chemistry because of surface storage in the Perch Lake watershed, Chalk River, Ontario (Buttle and Sami, 1992). Although we do not have direct temporal measurements of chemistry changes in the Cherry Creek wetland because it is remote and challenging to sample, our finding suggested temporary storage in the wetland complex plays an important role in this watershed (Fig. 11).

We fully recognize the degree of uncertainty with respect to the specific chemical and physical mechanisms that release old water during the storm events in catchments (Kirchner, 2003). The details on how meltwater recharges the alluvium/soils and displaces old waters to Red Canyon Creek still remain unclear. We do not have direct isotopic data or solute concentration data from soil profiles in the upper Cherry Creek watershed because the rugged and inaccessible topography there poses significant difficulties with respect to periodic access. Nevertheless, the constant isotopic composition of the creek water during snowmelt, coincident with dilution of major solutes, clearly shows that dilute water with identical isotopic composition as baseflow, dilutes baseflow at snowmelt. Different hydrological pathways during baseflow and

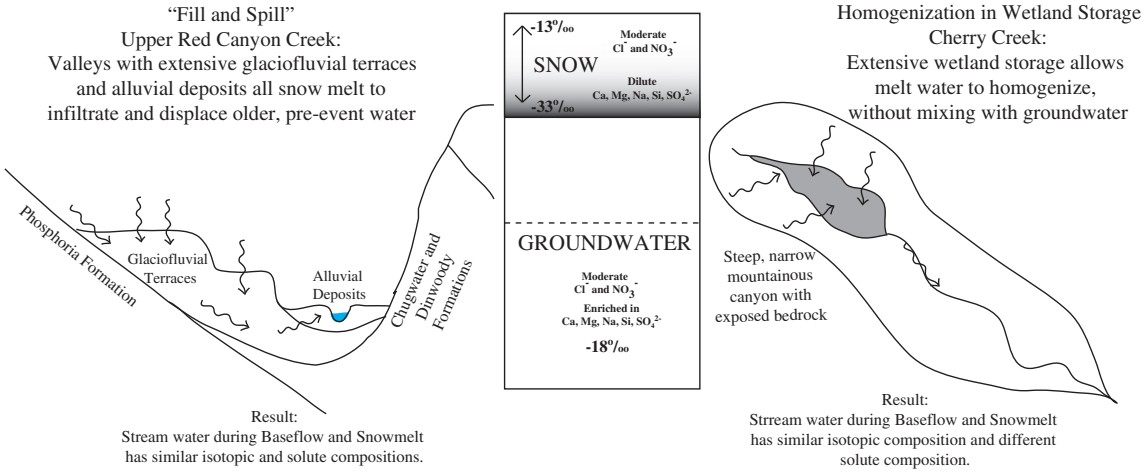

Fig. 11. A conceptual diagram illustrating the various hydrologic pathways controlling streamwater chemistry and isotopic composition during snowmelt in the two contrasting catchments.

snowmelt appear to provide different chemical compositions of water to the stream, while maintaining identical stable isotopes compositions.

Scientists and regulatory agencies both need to understand what controls streamflow in semi-arid and arid watersheds with higher elevation headwaters, and how snowmelt or rainfall recharge interacts with the groundwater systems that sustain baseflow. Our research at two adjacent subwatersheds suggests that the local topography and geomorphology features can be of particular importance to specific study. Our study also shows the conservative isotopes traditionally used in hydrograph separation failed to separate out different water sources or flowpaths. Using both isotopes and geochemical tracers is useful in determining source waters and possible flowpaths. For high elevation watersheds similar to Cherry Creek, carefully constructed direct tracer approaches may be needed, e.g. (Jin et al., 2009) to determine even the broad nature of the watershed hydrologic response to snowmelt and storms. Our study suggests that in these kinds of watersheds, when natural tracers, such as stable isotopes traditionally used may not be sufficient to resolve the major hydrologic questions, combining forces with other studies such as geochemical tracer and/or direct tracer tests might be proved to be extremely useful.

6. Conclusions

Isotopic and chemical compositions of streamwater in the Red Canyon Creek watershed were presented in this study. At upper Red Canyon Creek, nearly constant stable isotopes and solute compositions throughout multiple years indicated that streamflow was derived from groundwater and snowmelt mostly infiltrates into the glaciofluvial terraces and alluvium deposits, where it mixes with and displaces groundwater. Cherry Creek presented contrasting isotope and geochemistry patterns, which reflected streamwater was primarily a mixture of snowmelt and groundwater, which have similar isotopic compositions but different chemical concentrations. In Cherry Creek, the snowmelt is well mixed during temporary storage in a headwater wetland before mixing with baseflow and reaching our sampling site. Temporary wetland storage plays an important role in melt water homogenization and reducing temporal variability of stable isotope values in diluted snowmelt water. The local topography, geology and geomorphology features can be of particular importance to specific study.

The similar behaviors of stable isotopes and contrasting behaviors of major chemistry of streamwaters in Cherry Creek and upper Red Canyon Creek also suggest that using both isotopes and chemistry is a useful tool to understand water sources and flowpaths. Isotopes alone are not useful in the case of Cherry Creek to separate out the contributions of different end-members.

In addition, we suggest development of direct tracer experiments to address the hydrodynamics of these kinds of watersheds. When traditionally used natural tracers such as stable isotopes alone may not be sufficient to resolve major hydrologic questions, combining them with geochemical tracers or carefully constructed direct tracer tests may provide more information.

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Date	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	Sr (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	Date	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	Sr (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Cherry Creek (CC site)																							
10/01/05	69.25	1.01	29.65	2.51	5.56	0.33	0.88	0.13	58.82	n.a.	n.a.	05/21/06	52.16	0.72	19.38	2.83	3.38	0.39	1.39	0.29	59.23	−18.2	
10/08/05	68.20	0.98	29.63	2.39	5.62	0.28	0.92	0.13	46.71	n.a.	n.a.	05/26/06	54.68	1.02	20.48	2.96	3.50	0.41	1.29	0.29	60.13	−18.5	−141
10/16/05	67.20	0.83	29.08	2.48	5.59	0.30	n.a.	n.a.	n.a.	n.a.	n.a.	06/03/06	58.12	0.74	19.38	3.03	3.32	0.46	1.39	0.17	76.85	−18.4	
10/23/05	66.91	0.80	29.33	2.47	5.58	0.29	0.92	0.10	49.76	n.a.	n.a.	06/10/06	71.66	0.66	28.79	3.28	5.11	0.37	1.51	0.24	38.47	−18.4	−141
10/30/05	66.04	0.78	29.51	2.49	5.42	0.28	2.00	0.23	47.91	−17.9	n.a.	06/17/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11/06/05	68.22	0.80	29.49	2.57	5.58	0.30	1.17	0.32	53.79	n.a.	n.a.	06/24/06	70.94	0.78	31.32	3.45	5.90	0.35	1.41	0.45	59.63	n.a.	n.a.
11/13/05	70.65	0.77	29.42	2.54	5.22	0.32	0.92	0.25	61.48	n.a.	n.a.	06/29/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11/19/05	65.02	0.77	28.65	2.33	5.42	0.26	0.87	0.28	42.27	n.a.	n.a.	07/08/06	65.95	n.a.	31.02	3.64	5.85	0.33	n.a.	n.a.	n.a.	−18.2	−141
11/27/05	64.89	0.60	29.02	2.90	5.51	0.26	0.89	0.30	44.93	−18.6	−142	07/15/06	68.73	0.76	30.30	3.10	5.31	0.34	1.22	0.12	53.53	n.a.	n.a.
12/04/05	66.04	0.78	29.06	2.38	5.64	0.27	0.91	0.55	42.86	n.a.	n.a.	07/22/06	65.34	0.72	30.06	5.58	5.55	0.32	1.33	0.08	56.23	n.a.	n.a.
12/11/05	68.16	0.84	28.25	2.57	5.70	0.28	1.41	0.76	49.80	n.a.	n.a.	07/28/06	65.01	0.69	30.26	3.54	5.67	0.31	1.35	0.11	50.49	−18.3	n.a.
12/18/05	67.88	0.58	28.78	2.96	5.77	0.26	1.49	0.77	42.82	n.a.	n.a.	08/03/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
12/24/05	66.02	0.77	28.19	2.43	5.59	0.26	1.37	0.65	42.42	n.a.	n.a.	08/10/06	69.40	0.78	31.38	3.50	5.67	0.33	1.28	0.24	49.61	n.a.	n.a.
12/31/05	65.45	0.78	28.47	2.52	5.59	0.25	1.32	0.64	40.38	−18.5	n.a.	08/22/06	77.77	0.74	32.21	3.56	5.74	0.34	1.37	0.34	52.73	n.a.	n.a.
01/07/06	64.50	0.63	28.19	2.68	5.58	0.25	0.87	0.65	40.20	n.a.	n.a.	08/28/06	65.65	0.81	29.34	3.25	5.38	0.28	1.57	0.34	48.12	−18.4	−141
01/13/06	64.94	0.64	28.15	2.77	5.42	0.26	1.03	0.68	42.44	n.a.	n.a.	09/26/06	69.80	0.90	30.15	3.15	5.52	0.27	1.69	0.35	43.34	−18.4	n.a.
01/21/06	66.54	0.75	28.39	2.45	5.57	0.27	0.91	0.71	45.74	n.a.	n.a.	10/01/06	65.00	0.82	29.91	3.30	5.46	0.27	1.53	0.35	44.75	n.a.	n.a.

(*continued*)

Date	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	Sr (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	Date	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	Sr (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
01/29/06	62.79	0.72	27.83	2.45	5.60	0.24	1.23	0.75	38.56	−18.5	−142	10/10/06	70.90	0.98	31.16	3.28	5.82	0.30	1.51	0.42	47.66	n.a.	n.a.
02/05/06	64.09	0.57	28.10	2.92	4.55	0.24	0.69	0.42	30.36	n.a.	n.a.	10/18/06	64.28	28.25	2.90	5.13	0.26	1.34	0.03	44.31	n.a.	n.a.	
02/11/06	63.18	0.60	27.82	3.27	5.54	0.24	1.66	0.71	37.01	n.a.	n.a.	11/05/06	66.29	0.71	28.67	3.03	5.06	0.27	1.26	0.14	47.94	n.a.	n.a.
02/25/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.5	n.a.	11/15/06	70.01	0.70	29.20	3.11	5.25	0.29	1.50	0.27	55.52	n.a.	n.a.
03/05/06	67.24	0.75	27.95	2.74	4.98	0.25	1.03	0.65	41.53	−18.6	−143	11/19/06	71.00	0.69	29.85	3.16	5.29	0.29	1.22	0.26	54.49	n.a.	n.a.
03/11/06	67.40	0.64	27.44	3.05	4.93	0.28	1.33	0.61	51.42	−18.5	n.a.	11/26/06	70.36	0.71	30.04	3.09	5.43	0.29	1.48	0.34	50.04	n.a.	n.a.
03/18/06	65.12	0.60	27.74	2.93	5.52	0.25	1.19	0.40	39.37	−18.3	−140	12/03/06	75.50	0.78	30.33	3.05	5.57	0.33	1.57	0.65	61.51	n.a.	n.a.
03/25/06	58.50	0.59	25.11	2.38	4.55	0.24	1.35	0.24	43.84	−18.6	−142	12/11/06	77.45	0.78	31.00	3.48	5.65	0.34	1.10	0.51	57.74	n.a.	n.a.
04/02/06	21.53	0.25	9.34	0.96	1.71	0.07	0.68	0.17	21.41	−18.5	−140	12/18/06	75.67	0.76	30.66	3.42	5.66	0.33	1.50	0.64	58.24	n.a.	n.a.
04/08/06	16.73	0.14	7.33	0.64	1.25	0.05	1.10	0.17	23.09	−18.5	−140	12/24/06	74.89	0.73	30.17	3.30	5.57	0.33	1.35	0.58	45.24	n.a.	n.a.
04/16/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.1	n.a.	02/20/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.5	n.a.
04/23/06	21.04	0.26	7.83	1.13	1.24	0.15	0.92	0.19	27.07	−18.7	−141	03/30/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.6	n.a.
04/29/06	40.31	0.37	18.96	1.86	3.06	0.14	0.99	0.09	27.43	−18.2	−139	04/15/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.3	n.a.
05/07/06	34.46	0.34	13.40	2.00	1.99	0.24	1.01	0.12	27.86	−18.7	n.a.	04/22/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.4	n.a.
05/13/06	61.61	0.61	28.19	2.94	4.72	0.25	1.08	0.16	33.09	−18.4	−139	05/06/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.3	n.a.
Upper Red Canyon Creek (URCC site)																							
10/01/05	105.05	1.53	31.23	5.34	6.59	0.83	1.45	0.06	156.37	n.a.	n.a.	05/21/06	107.89	1.09	32.13	6.45	6.25	0.91	1.64	0.11	177.25	−18.6	n.a.
10/08/05	112.61	1.75	32.96	5.92	7.08	0.88	1.99	0.07	165.22	n.a.	n.a.	05/26/06	127.03	n.a.	36.13	7.16	6.53	1.14	1.91	n.a.	223.68	−18.3	−142
10/16/05	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.70	0.10	163.06	n.a.	n.a.	06/03/06	120.93	1.48	34.45	6.94	6.57	1.06	2.03	0.30	219.27	−18.5	n.a.
10/23/05	110.98	1.17	32.68	7.06	6.94	0.87	3.25	0.33	136.00	n.a.	n.a.	06/10/06	88.98	0.92	26.26	4.94	5.00	0.77	2.05	0.25	157.65	n.a.	n.a.
10/30/05	111.10	1.32	33.05	6.03	6.84	0.88	1.74	0.09	166.89	−18.7	n.a.	06/17/06	98.04	0.93	30.82	5.81	6.45	0.79	1.90	0.07	158.33	−18.5	n.a.
11/06/05	113.57	1.35	33.32	6.14	7.24	0.90	1.70	0.14	166.19	n.a.	n.a.	06/24/06	96.40	1.05	31.17	5.98	6.62	0.83	1.86	n.a.	159.13	n.a.	n.a.
11/13/05	114.87	1.07	33.94	7.38	7.15	0.92	1.69	0.20	173.54	n.a.	n.a.	06/29/06	98.98	1.12	31.00	5.83	6.67	0.83	1.89	0.06	150.21	n.a.	n.a.
11/19/05	109.23	1.21	31.70	6.06	6.54	0.84	1.76	0.38	173.02	n.a.	n.a.	07/08/06	96.58	1.11	30.77	5.80	6.79	0.83	1.77	0.05	162.59	−18.5	−143
11/27/05	111.34	1.13	32.50	6.17	6.71	0.86	1.53	0.34	160.04	−18.4	−142	07/15/06	105.00	1.02	31.89	5.94	6.75	0.83	1.51	n.a.	153.71	n.a.	n.a.
12/04/05	119.78	1.25	34.59	6.63	7.22	0.93	1.76	0.68	191.91	n.a.	n.a.	07/22/06	91.70	0.92	28.75	5.52	6.17	0.75	1.32	0.08	159.17	n.a.	n.a.
12/11/05	114.34	1.13	31.88	6.13	7.00	0.87	1.58	0.86	177.93	n.a.	n.a.	07/28/06	98.54	0.99	30.03	5.79	6.40	0.79	1.27	0.06	152.21	−18.4	n.a.
12/18/05	115.48	1.09	32.33	6.18	7.08	0.88	1.64	0.89	173.42	n.a.	n.a.	08/03/06	106.50	0.96	31.94	5.67	6.77	0.80	1.71	0.34	154.37	n.a.	n.a.
12/24/05	121.76	1.56	33.47	6.71	7.04	0.95	1.86	0.84	188.00	n.a.	n.a.	08/10/06	104.90	0.97	31.40	5.47	6.62	0.79	1.69	0.30	152.33	n.a.	n.a.
12/31/05	118.95	1.17	33.43	6.48	6.94	0.92	1.70	0.84	186.81	−18.9	n.a.	08/22/06	104.90	1.13	32.03	5.86	6.43	0.79	1.81	0.25	141.26	n.a.	n.a.
01/07/06	115.19	1.20	32.69	6.08	6.91	0.89	1.67	0.89	187.81	n.a.	n.a.	08/28/06	97.62	1.18	29.17	5.45	6.34	0.72	1.76	0.19	149.85	−18.5	−143
01/13/06	128.58	1.39	34.63	6.92	6.89	1.03	1.69	0.83	210.96	n.a.	n.a.	09/26/06	104.30	1.22	30.57	5.24	6.26	0.75	2.01	0.17	155.81	−19.2	n.a.
01/21/06	114.94	1.47	34.15	6.33	7.07	0.87	1.69	0.87	172.13	n.a.	n.a.	10/01/06	102.80	1.23	31.18	5.75	6.12	0.77	1.92	0.18	158.67	n.a.	n.a.
01/29/06	109.53	1.23	33.00	5.78	7.04	0.83	1.70	0.88	170.40	−18.7	−144	10/10/06	116.60	2.35	33.87	6.44	7.15	0.88	2.18	0.17	166.96	n.a.	n.a.
02/05/06	112.91	1.16	32.17	5.76	6.56	0.87	1.94	0.67	175.19	n.a.	n.a.	10/18/06	116.40	1.63	33.86	6.16	6.58	0.88	2.41	0.05	184.34	n.a.	n.a.
02/11/06	118.39	1.31	34.53	6.14	6.68	0.91	1.66	0.66	184.05	n.a.	n.a.	11/05/06	118.50	1.31	34.43	6.16	6.21	0.89	n.a.	n.a.	n.a.	n.a.	n.a.
02/25/06	113.64	1.07	31.91	6.24	6.33	0.88	1.73	0.75	181.23	−18.9	n.a.	11/15/06	122.60	1.32	35.53	6.71	6.42	0.93	2.34	0.02	191.61	n.a.	n.a.
03/05/06	105.10	1.69	32.14	6.16	5.53	0.77	2.27	0.77	157.22	−18.7	−142	11/19/06	123.90	1.34	35.98	6.49	6.54	0.93	2.35	0.09	189.37	n.a.	n.a.
03/11/06	132.64	1.39	34.53	6.77	6.46	1.10	1.75	0.67	198.11	−18.9	n.a.	11/26/06	125.20	1.37	35.82	6.58	7.00	0.95	2.21	0.12	191.00	n.a.	n.a.
03/18/06	109.12	1.21	31.87	5.88	5.95	0.85	2.11	0.52	182.96	−19.0	−143	12/03/06	119.30	1.21	34.33	6.40	6.67	0.88	1.85	0.34	184.91	n.a.	n.a.
03/25/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.5	n.a.	12/11/06	117.30	1.19	33.38	6.27	6.36	0.87	2.05	0.36	178.75	n.a.	n.a.
04/02/06	111.29	1.14	32.64	6.38	5.62	0.88	2.19	0.10	178.78	−19.0	−142	12/18/06	118.60	1.33	36.90	6.66	6.96	0.86	2.23	0.46	175.39	n.a.	n.a.
04/08/06	113.86	1.11	33.43	6.56	5.54	0.92	2.22	0.02	193.77	−19.0	−143	12/24/06	117.80	1.13	33.85	6.25	6.59	0.86	1.86	0.56	176.50	n.a.	n.a.

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Date	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	Sr (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	Date	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	Sr (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
04/16/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.9	n.a.	02/20/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.6	n.a.
04/23/06	117.02	1.18	33.99	6.82	5.55	0.97	3.09	0.26	183.76	−17.9	−138	03/30/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−19.1	n.a.
04/29/06	88.81	0.89	26.65	5.01	3.97	0.75	1.97	0.08	198.18	−18.1	−142	04/15/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.6	n.a.
05/07/06	111.07	1.05	32.60	6.42	5.42	0.92	2.07	0.06	189.39	−18.4	n.a.	04/22/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.7	n.a.
05/13/06	109.13	1.09	32.46	6.53	5.71	0.92	1.40	0.15	173.79	−18.6	−143	05/06/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.7	n.a.
Red Canyon Creek (RCC site)																							
10/01/05	84.48	1.07	30.09	4.70	5.98	0.58	1.30	0.03	115.68	n.a.	n.a.	05/21/06	70.67	0.86	29.14	3.17	5.11	0.32	1.30	0.14	129.23	−18.7	n.a.
10/08/05	87.13	1.32	31.25	3.92	6.05	0.55	1.32	0.04	100.66	n.a.	n.a.	05/26/06	72.90	1.33	31.02	3.23	6.63	0.35	1.64	0.45	130.81	−18.1	−143
10/16/05	87.40	1.14	30.89	4.25	5.87	0.58	1.27	0.01	110.18	n.a.	n.a.	06/03/06	74.46	0.67	29.58	3.33	5.00	0.38	1.72	0.11	162.33	−18.6	n.a.
10/23/05	89.20	1.13	31.08	4.31	5.91	0.59	1.31	0.03	109.65	n.a.	n.a.	06/10/06	89.96	0.96	30.74	4.67	5.64	0.72	1.65	0.11	154.18	−18.6	n.a.
10/30/05	84.71	1.12	31.05	4.32	5.87	0.58	1.35	0.02	110.54	−18.7	n.a.	06/17/06	90.43	0.95	31.95	4.98	6.22	0.68	n.a.	n.a.	n.a.	−18.8	n.a.
11/06/05	87.71	1.06	31.27	4.38	6.17	0.61	1.38	0.13	119.22	n.a.	n.a.	06/24/06	78.97	0.88	29.92	4.86	5.93	0.59	1.96	0.09	110.26	n.a.	n.a.
11/13/05	93.63	0.94	31.92	5.87	6.14	0.66	1.31	0.16	128.92	n.a.	n.a.	06/29/06	89.13	1.04	31.80	4.87	6.26	0.70	1.80	0.05	147.03	n.a.	n.a.
11/19/05	86.80	1.14	30.84	4.19	6.05	0.57	1.28	0.32	106.70	n.a.	n.a.	07/08/06	78.41	0.98	31.15	5.09	6.12	0.61	1.22	0.37	122.67	−18.7	−143
11/27/05	88.81	0.91	31.47	4.81	6.11	0.61	1.30	0.34	116.30	−18.5	−144	07/15/06	86.54	0.90	31.66	4.63	5.95	0.59	0.98	0.08	82.32	n.a.	n.a.
12/04/05	86.66	0.94	31.45	4.79	6.50	0.55	1.28	0.71	105.22	n.a.	n.a.	07/22/06	73.81	0.85	28.84	4.24	5.51	0.54	1.55	0.01	118.40	n.a.	n.a.
12/11/05	92.45	0.90	30.46	4.78	6.46	0.60	1.26	0.83	115.84	n.a.	n.a.	07/28/06	72.23	0.84	30.10	4.24	5.44	0.54	1.57	0.00	112.94	−18.3	n.a.
12/18/05	94.83	0.97	31.46	5.00	6.55	0.60	1.27	0.96	112.32	n.a.	n.a.	08/03/06	79.20	0.77	30.83	4.50	5.68	0.54	1.60	0.19	105.44	n.a.	n.a.
12/24/05	94.97	1.02	31.62	5.07	6.47	0.62	1.34	0.79	117.16	n.a.	n.a.	08/10/06	77.33	0.80	31.01	4.51	5.57	0.55	1.52	0.12	103.13	n.a.	n.a.
12/31/05	92.83	1.11	31.45	4.46	6.50	0.61	1.81	0.75	113.86	−18.8	n.a.	08/22/06	92.16	0.92	32.33	4.68	5.64	0.59	1.77	0.05	106.23	n.a.	n.a.
01/07/06	92.60	1.06	31.23	4.36	6.55	0.60	1.23	0.77	113.66	n.a.	n.a.	08/28/06	86.09	1.08	32.90	4.93	5.88	0.59	1.67	0.17	108.94	−18.6	−142
01/13/06	93.83	1.15	31.96	4.63	6.38	0.62	1.31	0.79	123.38	n.a.	n.a.	09/26/06	89.12	1.16	33.11	4.78	5.86	0.57	1.79	0.16	103.55	−18.8	n.a.
01/21/06	86.86	0.96	31.00	4.02	6.33	0.54	1.60	0.81	100.66	n.a.	n.a.	10/01/06	80.21	1.02	30.29	4.57	5.38	0.53	1.74	0.16	105.99	n.a.	n.a.
01/29/06	85.38	0.74	30.75	4.64	6.16	0.55	1.33	0.73	93.56	−18.6	−143	10/10/06	92.18	1.66	32.12	4.98	6.28	0.61	1.99	0.30	108.51	n.a.	n.a.
02/05/06	90.09	0.85	30.42	4.68	6.09	0.58	1.22	0.61	110.69	n.a.	n.a.	10/18/06	94.46	1.31	32.62	4.80	5.68	0.63	1.99	0.02	124.14	n.a.	n.a.
02/11/06	82.55	0.97	30.23	4.40	6.03	0.49	1.52	1.06	75.75	−18.9	n.a.	11/05/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.93	0.02	130.49	n.a.	n.a.
02/25/06	91.50	0.89	30.24	4.78	5.91	0.60	2.81	0.81	107.94	n.a.	n.a.	11/15/06	102.40	1.23	34.22	5.36	5.90	0.67	2.06	0.07	134.14	n.a.	n.a.
03/05/06	87.88	1.23	30.03	4.60	6.14	0.54	1.96	0.66	101.22	−18.5	−144	11/19/06	96.50	1.05	34.20	5.30	5.77	0.65	1.30	0.05	98.11	n.a.	n.a.
03/11/06	117.15	1.22	33.66	6.21	6.11	0.88	1.06	0.39	146.35	−18.6	n.a.	11/26/06	98.77	1.05	33.33	5.03	5.82	0.65	1.92	0.15	132.47	n.a.	n.a.
03/18/06	91.77	0.90	30.54	4.83	5.92	0.60	1.67	0.37	121.30	−18.6	−145	12/03/06	103.40	1.04	33.53	5.14	5.99	0.68	1.91	0.41	136.68	n.a.	n.a.
03/25/06	90.04	1.12	30.93	5.01	5.57	0.65	1.83	0.07	123.61	−18.1	−144	12/11/06	98.20	0.96	31.16	4.86	5.64	0.65	n.a.	n.a.	n.a.	n.a.	n.a.
04/02/06	82.97	1.02	30.10	4.36	5.43	0.54	1.79	0.08	105.89	−18.4	−145	12/18/06	95.32	0.96	32.64	4.70	5.82	0.59	1.85	0.54	121.33	n.a.	n.a.
04/08/06	81.18	0.95	30.37	4.61	5.14	0.52	1.29	0.02	99.48	−18.5	−145	12/24/06	100.30	0.96	31.95	5.06	5.81	0.66	1.72	0.59	134.68	n.a.	n.a.
04/16/06	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.5	n.a.	02/20/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.8	n.a.
04/23/06	48.30	0.43	21.99	2.24	3.73	0.16	1.71	0.06	109.37	−18.8	−144	03/30/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−19.0	n.a.
04/29/06	79.84	0.85	30.84	4.45	5.26	0.55	1.67	0.04	107.07	−18.6	−144	04/15/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.8	n.a.
05/07/06	58.88	0.55	27.65	2.85	4.90	0.20	1.37	0.00	102.88	−18.5	n.a.	04/22/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.7	n.a.
05/13/06	82.79	0.93	30.66	5.03	5.29	0.62	1.41	0.05	119.15	−18.5	−144	05/06/07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−18.9	n.a.

Appendix A

A list of full chemistry data of streamwater samples collected at CC, URCC and RCC sites.

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